The following publications on oil shale are available by writing directly to the Publications Department, Colorado School of Mines, Golden, Colorado 80401:

**Proceedings of the First Five Oil Shale Symposia**: 1964-68 (cloth), $12.00

**Synthetic Liquid Fuels From Oil Shale, Tar Sands, and Coal**: Proceedings of the Hydrocarbons Symposium, CSM Quarterly, v. 65, no. 4, 1970, $6.00

**Selected Topics of Recent Estonian-Russian Oil Shale Research and Development**, W. J. Cieslewicz, CSM Quarterly, v. 66, no. 1, 1971. $5.00

**Proceedings of the Seventh Oil Shale Symposium**, CSM Quarterly, v. 69, no. 2, 1974, $6.00

**Proceedings of the Eighth Oil Shale Symposium**, CSM Quarterly, v. 70, no. 3, 1975, $6.00

**Proceedings of the Environmental Oil Shale Symposium**, CSM Quarterly, v. 70, no. 4, 1975, $7.00

**Colorado Energy Resources Handbook**, v. 2, Oil Shale: Colorado Energy Research Institute, $5.50

**Recent Trends in Oil Shale, Part 1**: History, Nature, and Reserves, T. A. Sladek, Mineral Industries Bull., v. 17, no. 6, 1974, $2.00

**Recent Trends in Oil Shale, Part 2**: Mining and Shale Oil Extraction Processes, T. A. Sladek, Mineral Industries Bull., v. 18, no. 1, 1975, $2.00

**Recent Trends in Oil Shale, Part 3**: Shale Oil Refining and Some Shale Oil Problems, T. A. Sladek, Mineral Industries Bull., v. 18, no. 2, 1975, $2.00


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FOREWORD

The Tenth Oil Shale Symposium was held 13 years after the first of this series, and, at first glance, commercial production of oil from shale appears to be no closer to reality than it did in 1964. Even though the energy crisis is still with us--and during one month this year for the first time liquid petroleum imports comprised more than half of the total liquid fuels consumed by the United States--commercialization of shale oil is still an elusive goal. However, a deeper look shows that much has been accomplished.

Many man-years of work and many millions of dollars have been invested during this period to learn more about the processes and to minimize risks by obtaining data adequate for economic evaluation and design purposes. Many of the topics now under study were unimportant 13 years ago, especially in the areas of toxic substances, environmental pollution, and social planning. While in situ retorting was considered impractical then, today the trend is toward more emphasis on in situ operations to minimize solid materials handling problems and costs, and to reduce environmental and health effects to reasonable levels.

These trends are reflected in the topics covered by the speakers at the 1977 symposium and the range of interests of the attendees. As always, the success of the symposium is due to the authors and their employees who make the results of the work available by participating in the program. In addition, I am indebted to the session chairmen, and to John R. Reubens and Jon W. Raese who reviewed and prepared the papers for publication.
Introduction

This paper presents some of the highlights of the Phase II study effort conducted under U.S. Bureau of Mines Contract No. S0241073, and documented in the Final Report entitled, "Technical and Economic Study of the Modified In Situ Process for Oil Shale", available through NTIS.

A thorough understanding of the economic implications inherent in various factors in the design of a complex facility, as required for modified in situ production of oil shale, will be needed if sound, economical designs are to be achieved.

The Phase I effort, consisting of a technical analysis of the process from a mining standpoint, was reported briefly at the 9th Oil Shale Symposium (April 29-30, 1976).

This paper highlights the effect of variables in mining and processing of oil shale that have an impact on mine design and, ultimately, upon costs.

Background

The conclusions of the technical analysis were that two mining system designs were feasible for further study:

1. Room and pillar - vertical drill and blast concept,
2. Tunnel boring - horizontal ring drill and blast concept.

The room and pillar - vertical drill and blast system (fig. 1) was considered technically feasible in the current state of the art, because it employed only the techniques and equipment that are commonly used today. This system approximates the one used by Occidental Petroleum Corporation.

The tunnel boring - horizontal ring drill and blast system (fig. 2) was considered to be a second generation system in which as much excavation as possible was done by boring, and restabilization of burned-out retorts was used to increase

---

*Results of work conducted under Phase II of U.S. Bureau of Mines - Contract #S0241073
extraction ratio and resource recovery. Resource recovery, using the tunnel boring system, is increased by approximately 42 percent over recovery by conventional room and pillar mine.

Figure 2. - Tunnel boring - horizontal ring drill and blast concept.

Results

Technical analysis produced an appreciation for the complex nature of a modified in situ design. Because of the complexity of the calculations to meet contract requirements for cost benefit and cost trade-off studies, and the inherently large number of variables that must be considered in these calculations, we decided to develop a computer program to provide the answers. Using such a program would increase both efficiency and accuracy of the computations needed to improve the quality of the analysis. These goals were achieved. In the process, we developed a valuable tool for evaluating any combination of the many design factors with minimal effort; at the same time, a much better understanding was afforded of the complex and involved relationships inherent in the design.

The basic computer program is a mathematical model of the various elements of the design, including rock mechanics, retorting, blasting, ventilation, quantities, and costs. Sub-routines are interrelated so that a change in one is properly reflected in the others.

All costs are based on January 1975 figures. "Operating" costs are reported as "cost of sales" which includes the direct, indirect and fixed costs normally reported to an operations manager. "Capital" costs are reported as "initial capital costs", including pre-construction, plant and equipment and initial development costs. Tract bid payments were not included in the calculations because the study was made on a generic basis, not for a specific site. Reinvestment and expansion investment costs were not calculated for each case, but were calculated for a separate discounted cash flow return on investment (DCFROI) portion of the study of the two systems. Results of cost comparisons were reported both in terms of dollars-per-barrel and dollars-per-cubic meter of daily production.

The first comparison was between the two mining systems (table 1). Major design variables were held constant for both cases. Results show that the room and pillar method is more capital intensive but has a lower cost of sales than the tunnel boring method. The basic reason for the higher cost of sales for the tunnel boring method is the cost of stabilizing burned out retorts to obtain increased resource recovery.

To gain a better understanding of the effect of each of the many variables on cost, the following factors were selected as having a direct bearing on costs:

- Production rate (P)
- Grade (G)
- Retorting efficiency (RE)
- Entry size (ES)
- Burn rate (BR)
- Depth (D)
- Swell factor (SF)
- Retort height (RH)
- Equipment selection
- Permissible regulations
Table 1a and b - Comparison of base case computer runs for two mining methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Cost of Sales ($/BPD)</th>
<th>Initial Capital Cost (000$/BPD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 7 9 11 13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Room &amp; Pillar</td>
<td>8.77</td>
<td>6,946</td>
</tr>
<tr>
<td>Tunnel Boring</td>
<td>11.79</td>
<td>6,626</td>
</tr>
</tbody>
</table>

Design Constants
- P - 50,000 BPD
- BR - 0.5 in/hr
- G - 20 CFT
- SF - 25 percent
- D - 1,000 ft
- RE - 60 percent
- RH - 230 ft

Table 1b

<table>
<thead>
<tr>
<th>Method</th>
<th>Cost of Sales ($/CuMPD)</th>
<th>Initial Capital Cost ($/CuMPD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 45 65 75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Room &amp; Pillar</td>
<td>55.16</td>
<td>43,689</td>
</tr>
<tr>
<td>Tunnel Boring</td>
<td>74.16</td>
<td>-11,676</td>
</tr>
</tbody>
</table>

Design Constants
- P - 7949 Cubic Meters/Day
- BR - 1.27 Centimeters/ Hour
- G - 68.68 Liters/Tonne
- SF - 25 percent
- D - 304.8 Meters
- RE - 60 percent
- RH - 70.10 Meters

The basic technique for comparisons is to use a base case and change one variable at a time to establish relative change.

Hereafter, cost comparisons apply to the room and pillar method only, but the results would be similar for the tunnel boring method.

Comparison of Variables

Change-in-Production Rate - This change does not appear to have a large effect on cost. We did not have the opportunity to select the appropriate equipment size for the various production rates. Given proper data, there would probably be a larger change than shown in table 2. Optimum production for a single facility appears to be below 50,000 BPD (7949 CuMPD). It appears that the economics of scale of the operation have been exceeded at 50,000 BPD (7949 CuMPD). Costs reported for a 25,000 BPD (3975 CuMPD) production rate should not be considered entirely valid; they can be bettered by properly sizing the mining equipment.

Change of Grade - This change (table 3) has a dramatic effect on cost. The 25 gallons-per-ton (124.02 liters-per-tonne) line is not reported because it has too low a resource recovery for the base conditions. In this instance, a much more sophisticated rock mechanics design technique would probably yield a stable configuration. This technique would require a stability analysis of the pillar on an incremental basis (from top to bottom) with each major kerogen-rich zone being analyzed separately, but as a part of the whole, rather than the present technique of analyzing and designing only on the richest zone. Computer runs made for the tunnel boring system tend to confirm this trend.

Change of Burn Rate - This change (table 4) has a relatively large effect in the range of 0.5-2 in. per hour (1.27 cm-5.8 cm per hour), but does not have a significant impact between 2.0 and 4.0 in. per hour (5.8 cm-10.16 cm per hour). The effect of lower burn rates on cost can be attributed to satisfying the air requirements per retort but at levels not exceeding the capacities of the individual drifts. Higher
Table 3 a and b - Change in grade

<table>
<thead>
<tr>
<th>Grade Gallons per ton</th>
<th>Cost of Sales ($/BPD)</th>
<th>Initial Capital Cost (000$/BPD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>11.83</td>
<td>9,718</td>
</tr>
<tr>
<td>* 20</td>
<td>8.77</td>
<td>6,946</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Not Reported Due To Low Resource Recovery

500 foot depth only * Base Case

Table 4 a and b - Change in burn rate

<table>
<thead>
<tr>
<th>Burn Rate Inches per hour</th>
<th>Cost of Sales ($/BPD)</th>
<th>Initial Capital Cost (000$/BPD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>* 0.5</td>
<td>8.77</td>
<td>6,946</td>
</tr>
<tr>
<td>2.0</td>
<td>8.29</td>
<td>5,434</td>
</tr>
<tr>
<td>4.0</td>
<td>8.30</td>
<td>5,307</td>
</tr>
</tbody>
</table>

* Base Case

burn rates, not having an effect on cost, indicate the need to spread out the operation and enlarge the drift to meet ventilation requirements and each retort more rapidly. This, in turn, means that more mining areas are active and more equipment is required.

Change in Depth - This change (table 5) does not have a major effect on capital cost; only the cost of sales is affected to any degree. The 1500-ft (457.2 m) depth is not reported because of low resource recovery.

This depth could possibly be designed for adequate resource recovery by using an incremental pillar design, rather than a weakest point. The system design used, which minimizes the number of shafts required, is partially responsible for the small effect of depth on cost. Cost of constructing and operating shafts is quite small when compared to total capital and operating costs. Major items related to depth are shafts, hoisting, pumping, pipelines, electric feeder lines and ventilation.

Change of Swell Factor - This change (table 6) produces a definite improvement in cost, directly related to reduction of the swell factor. Overall costs of the process will be improved by reducing swell factor to the lowest practical value consistent with the pressure losses in the retort. This is an area in which field research will pay high dividends by developing the optimum drilling and blasting technique to produce the proper size of rubble. The goal of drilling and blasting should be to obtain uniform fragmentation of the oil shale while minimizing the fines generated in the blasting process. Reduction in swell factor tends to make the entire mining process more efficient as there is less swell room excavation per ton of material to be rubblized,
thus achieving a lower ton-ratio.

Table 6 a and b - Change in swell factor

<table>
<thead>
<tr>
<th>Swell Factor</th>
<th>Cost of Sales ($/BPD)</th>
<th>Initial Capital Cost ($/CuM/Day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent</td>
<td>$/BPD</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>7.96</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>8.38</td>
<td></td>
</tr>
<tr>
<td>* 25</td>
<td>8.77</td>
<td></td>
</tr>
</tbody>
</table>

* Base Case

Table 7 a and b - Change in retorting efficiency

<table>
<thead>
<tr>
<th>Retorting Efficiency</th>
<th>Cost of Sales ($/BPD)</th>
<th>Initial Capital Cost ($/CuM/Day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent</td>
<td>$/BPD</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>8.77</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>8.22</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>7.78</td>
<td></td>
</tr>
</tbody>
</table>

* Base Case

Table 8 a and b - Change in entry height

<table>
<thead>
<tr>
<th>Entry Height</th>
<th>Cost of Sales ($/BPD)</th>
<th>Initial Capital Cost ($/CuM/Day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feet</td>
<td>$/BPD</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>8.77</td>
<td></td>
</tr>
<tr>
<td>* 30</td>
<td>8.77</td>
<td></td>
</tr>
</tbody>
</table>

* Base Case

Change in Retorting Efficiency - This change (table 7) has an inverse effect on costs; as the efficiency rises, costs drop. This is a logical result and is to be expected. Research by chemical engineers should be continued at a high level with its objective being increased retorting efficiency as the grade of shale decreases. Greater retorting efficiency will increase resource recovery and make more of the reserves economically available for production. A better understanding of the retorting reaction is needed to make predictions as to the additional amount of kerogen obtainable from the walls and pillars of the retort.

Change in Entry Height - This change (table 8) produces a surprise: capital cost increases with a smaller entry. The unexpected effect was traced to an increase in the number of air and exhaust shafts needed because of the lower capacity of smaller tunnels and drifts to carry air for ventilation. In our final report to the Bureau of Mines, we investigated this variable further and found it affected many of the input values. In fact, of 90 values listed, 39 changed with reduction in drift height; of these 39 values, 21 decreased and 18 increased. This change produced a compensating reaction in cost of sales and increased initial capital investment. This exercise especially well demonstrates the value of having a computer design model. Such a model provides the designer with a valuable tool to test alternative ideas and determines economic feasibility before committing large sums of money to mine development.

Change in Retort Height - Table 9 is made up for 15 gallons-per-ton (51.5 liters/tonne) only, rather than the incomplete base case, because a full range of values is available for this grade. As would be
expected, table 9 shows that variation in retort height has a major effect on the costs. While costs decrease as the retort height increases, resource recovery also decreases as the retort height increases, conversely decreasing the life of the property. The decrease in resource recovery is traceable directly to the rock mechanics requirements for slender, stable pillars. These requirements are related to the L/R ratio of the pillars which, in turn, affects extraction ratio, a part of the resource recovery calculation.

Equipment Selection - This item (table 10) also has a significant effect on cost. The initial design base case visualized the use of large, front-end loaders and haul trucks for the load-and-haul cycle, with the rock being crushed before delivery onto a conveyor belt. However, a significant cost reduction is achieved when load-haul-dumps (LHD) are combined with feeder-breakers. The inherently more efficient operation of the LHD and feeder-breaker units, with resulting lower unit operating costs and fewer units required, reduces costs. The need to match equipment to specific portions of the work is apparent. Several other equipment categories, such as drilling and raise and tunnel boring, merit the same detailed study manner to effect further cost reductions.

Permissibility - A proposal to open a new mine in the deeper, central part of the Piceance Creek basin (Colorado), where gas is almost certain to be present, immediately raises questions of permissibility and the effect of "permissible" regulations. Table 11 represents the impact on cost of these regulations if all underground equipment is included. Related costs, as shown, reflect fire protection control, ventilation, equipment and explosives. Some of the proposed equipment cannot be certified at present because no large engine testing facility is available. No permissible explosives are currently in use in experimental oil shale mines and, if they are not required, their impact on cost may not be as great as shown.

Composite Runs - The effect of combining various good or positive parameters into a new set of operating conditions is partially demonstrated in table 12. The result is a domino effect: costs decrease more rapidly than would be expected by arithmetic progression. This process illustrates the complex interactions which occur in the design of a modified in situ facility. It also gives research and engineering some pre-
Table 11 a and b - Permissibility

<table>
<thead>
<tr>
<th></th>
<th>Cost of Sales ($)/BPD</th>
<th>Initial Capital Cost ($)/BPD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 7 9 11 13</td>
<td>3 5 7 9 11</td>
</tr>
<tr>
<td>* Nonperm</td>
<td>8.77</td>
<td>6,946</td>
</tr>
<tr>
<td>Permiss</td>
<td>11.70</td>
<td>8,712</td>
</tr>
</tbody>
</table>

* Base Case

Table 12 a and b - Composite runs

<table>
<thead>
<tr>
<th></th>
<th>Cost of Sales ($)/BPD</th>
<th>Initial Capital Cost ($)/BPD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 7 9 11 13</td>
<td>5 7 9 11</td>
</tr>
<tr>
<td>&quot;40</td>
<td>8.77</td>
<td>6,946</td>
</tr>
<tr>
<td>1,640</td>
<td>6.48</td>
<td>4,054</td>
</tr>
<tr>
<td>1,740</td>
<td>5.75</td>
<td>3,549</td>
</tr>
</tbody>
</table>

Const. | Variables | #40 | #1640 | #1740 |
--------|-----------|-----|-------|-------|
P - 50,000 BPD | BR | 0.5/hr | 2.0/hr | 4.0/hr |
G - 20 CFT | SF | 25% | 20% | 15% |
D - 1,000 ft | RE | 60% | 65% | 70% |
RH - 230 ft | DR | 30 feet | 20 feet | 20 feet |
Equip. | F-T | L-FB | L-FB |

Run Numbers | 40 | 1640 | 1740 |
------------|----|------|------|
P - 7949 Cu ft/hr | BR | 1.27 cm/hr | 5.08 cm/hr | 10.16 cm/hr |
G - 68.68 Liters/tonne | SF | 25% | 20% | 15% |
D - 364.8 Meters | RE | 60% | 65% | 70% |
RH - 70.10 Meters | DR | 9.14 Meters | 6.09 Meters | 6.09 Meters |
Equip. | FEL-TR-CRUSH | LHD-FB | LHD-FB |

* Base Case

liminary goals to achieve:
- Optimize burn rate
- Lower swell factor
- Increase retorting efficiency
- Select proper equipment
- Adjust mine opening size to be compatible with equipment size.

Other Investigations - During the course of this study, other investigations were conducted as a part of the total effort:

(1) Scheduling - Critical paths were constructed for both room and pillar and tunnel boring systems,
(2) Multi-level development - Improving resource recovery by shortening retort pillars and using multi-level mining. No significant improvement was found without restabilization.
(3) Combination in situ and surface retorting - A brief study of the combination system was conducted and, on the basis of information then available for surface retorting, the system showed significant improvement in both cost of sales and initial capital cost.
(4) Energy balance - The systems postulated will produce a positive energy ratio of from 5.25 to 13.95, depending upon the particular combination of variables and conditions.

The economic evaluation used consisted of a discounted cash flow. Return on investment calculation (fig. 3) shows rate of return plotted against selling price per barrel. The plot gives an indication of the economic feasibility of the process. This calculation does not include bonus bid payments. These are a front-end cost, reducing discounted cash flow return on investment by some unspecified amount, depending upon the tract bid price.
Selling Price of Shale Oil ($/bbl) and ($/CuM)

Figure 3. - Return on investment vs selling price.

Summary

1. We conceived and designed two mining systems.
2. We developed a computer program to model the systems.
3. We made studies of the effect of significant variables on cost.
4. We made an economic evaluation of the two mining systems.
ECONOMIC EVALUATION OF COMBINED IN SITU AND SURFACE RETORTING OF OIL SHALE

Allan P. Grossman
TRW, Inc.
One Space Park
Redondo Beach, California 90278

This study, completed in 1976, was made to provide Shell Oil Company's management with information that could affect their decision whether to continue the already substantial investment in the C-b project or not.

The successful bidders on federal lease Tract C-b in Colorado in 1974 were Tosco, Atlantic Richfield, Ashland and Shell. At the end of 1975, seeing that the project had no economic future and facing institutional obstacles, Tosco and Atlantic Richfield withdrew from this venture. At year's end, 1976, Shell also withdrew, citing many environmental and political obstacles, including the federal lease limitation of 5,000 acres per company (2,500 ha). These obstacles, in all, added non-technical risks the company felt were not commensurate with the potential return on a billion-dollar investment.

One of the reasons the project was not economically sound was its basic design. Mining was expected to take place in the Mahogany Zone, by room and pillar method, with surface retorting of the mined out shale. Due partly to lower quality rock strength, total resource recovery was lower than anticipated. Shell therefore made a study of alternate methods of developing Tract C-b. Aimed primarily at increasing recovery, one of the most interesting possibilities the study discovered was in situ retorting, using a process similar to that proposed by Occidental Petroleum Company.

Mining problems related to in situ retorting can be very complex. It is difficult to make a realistic evaluation of in situ retorting or the combination of in situ and surface retorting without a good, detailed mining study. Pressed for time, Shell arranged with the Bureau of Mines to use the Fenix & Scisson study data (before final publication) for a study of the mine design and associated costs as they might be related to the C-b tract.

The basic Fenix & Scisson design utilized for this evaluation was the room and pillar, vertical drill and blast method to create an upper level drill station and a lower level room that provides, in combination with the drill station, a void volume of 25 percent. Figure 1 shows a cross section of the retort used in this evaluation.

For Tract C-b, with an overburden of over 300 meters, the maximum retort height considered feasible in the Fenix & Scisson studies was about 70 meters (230 ft). Core data from Tract C-b indicate a maximum Mahogany Zone mining height of 24 meters. The preferred, richer mining section is 11 meters high with an average assay of about 42 gallons of oil a ton. In order to create the desired void volume for in situ retorting, it is preferable to mine out as much as possible from the rich Mahogany Zone for two reasons:

1. For this study, we assumed that mined out shale would be retorted on
Figure 1. - In situ mine design, by Fenix and Scisson, Inc.

the surface in Tosco-II type units whose liquid yield is over 95 percent of Fisher assay, compared to an estimated 60 percent yield by in situ retorting. Clearly, overall yield is improved by surface retorting of as much of the rich shale as possible.

(2) Richer shales are more susceptible to plastic deformation than lean shale. In situ retorting of these richer shales could cause non-uniform gas distribution and/or excessive pressure drop.

With these considerations in mind, the mining plan was modified for use on Tract C-b as shown in figure 2. Although it would be preferable to extend the retort downward from the identified mining zone to cover the desired depth, rock quality below the mining zone was poorer than that above it. This is not expected to be a limiting factor for in situ retorting. As a conservative approach for a screening evaluation, Shell's study assumed development only in the higher quality rock above the Mahogany Zone.

The overall processing concept for a combination of in situ and surface retorting is shown in figure 3. The liquid product from in situ retorting comes to the surface as an oil and water emulsion. It must be separated and the water treated for further plant use. This minimizes the requirement for external supplies of clean water. In the Fenix & Scisson study, the low Btu gas exiting from the in situ retorts was flared, probably not an acceptable disposition for both economic and environmental reasons. Although this gas has a low heating value, it represents about 25 percent additional liquid yield on an equivalent Btu basis. So it is necessary to use that heat value within the plant either for power generation or as fuel for the surface processing facilities.

Figure 2. - Tract C-b in situ retort development.
Design and cost estimates from the Colony Project were used for most of the surface retorting facilities. Oil product from both the in situ and surface retorts goes to a common fractionation system which strips out the gas components and separates the $480^\circ\text{C}$+ residual fraction. The latter is processed in delayed cokers so that the final oil product will have an end point of about $500^\circ\text{C}$. The viscosity and pour point of the residue-free shale oil are also reduced, thereby making a product that can be shipped to distant markets in conventional pipeline facilities. The residual material which is fed to the cokers contains appreciable mineral matter as very fine particles. This must be removed by high temperature centrifuges or other means before coking in order to produce a saleable coke product.

Earlier evaluations of the Colony and C-b Projects have shown that severe, high pressure hydrotreating of the shale oil to very low nitrogen levels increases product cost by $4-5$ a barrel. This adds a strong
incentive to eliminate the additional capital and operating costs for this process, at least for the first prototype plants. Considering the high risks of such plants, using as yet commercially unproven technology, added on-site investment for denitrification unnecessarily compounds the risks involved. Prototype or modular demonstration plants should, therefore, be designed to produce no more than transportable and saleable synthetic fuel. Any additional processing should be done in existing refineries. In fact, some limited direct blending of high nitrogen shale oil fuel fractions with low nitrogen fuels may be feasible in certain applications.

Storage stability of raw shale oil can, however, be a problem. To correct this, we assume that the diolefins in the raw shale oil would be selectively saturated by hydrostabilization at low temperature over conventional hydrotreating catalysts. We estimate the hydrogen consumption for this to be about a hundred standard cubic feet per barrel of feed, compared to approximately 1,800 standard cubic feet per barrel for severe hydrodenitrification.

In this design, the high Btu product gas from the Tosco retorts would be treated with DEA to remove essentially all hydrogen sulfide and carbon dioxide. High purity hydrogen from the Tosco retorts can then be recovered by cryogenic separation technology. We also note that proprietary processes can be used in conjunction with hydrostabilization to remove arsenic from the shale oil.

Capital investment and operating costs for this combined in situ and surface retort system are shown in figure 4. The initial capital expenditure required to reach full production of 54,000 barrels per stream day, is over 600 million dollars. This does not include 71 million dollars in lease bonus payments for Tract C-b. It also does not include any sunk costs for environmental background monitoring, engineering studies and preparation of the detailed development plan.

<table>
<thead>
<tr>
<th>Capital Investment ($MM,1976)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-situ Retorting:</td>
</tr>
<tr>
<td>Surface plants</td>
</tr>
<tr>
<td>Shafts, tunnels, drifts</td>
</tr>
<tr>
<td>Retort development and</td>
</tr>
<tr>
<td>operation</td>
</tr>
<tr>
<td>Crushing, ore handling, spent</td>
</tr>
<tr>
<td>shale disposal</td>
</tr>
<tr>
<td>Surface pyrolysis</td>
</tr>
<tr>
<td>Process facilities</td>
</tr>
<tr>
<td>Utilities and general</td>
</tr>
<tr>
<td>facilities</td>
</tr>
<tr>
<td>Predevelopment, community</td>
</tr>
<tr>
<td>assistance and miscellaneous</td>
</tr>
<tr>
<td>Deferred mining equipment</td>
</tr>
<tr>
<td>($7.7MM/year average)</td>
</tr>
<tr>
<td>Operating costs ($MM,1976)</td>
</tr>
<tr>
<td>Annual cost, at full</td>
</tr>
<tr>
<td>capacity</td>
</tr>
<tr>
<td>Initial in-situ demonstration</td>
</tr>
</tbody>
</table>

Figure 4. - Capital investment and operating cost for combined in situ and surface retorting.

Low Btu gas exiting from in situ retorts is both a problem and an opportunity. It could be used to generate over 300 megawatts of power on either a combined cycle system or a conventional steam power plant. For purposes of this study, we assumed that retort gas had zero value but no capital or operating costs were included for gas compression, selective low pressure H$_2$S removal, or power generation from the gas. A later study of this portion of the system indicates that compression and treating costs would be less than $1.00 per million Btu, assuming compression only to a level sufficient to fire a conventional steam boiler.

This combination of in situ and surface retorting would yield 54,000 barrels a day of oil plus propane. Total oil production over a 30-year plant life would be on the order of 500 million barrels. This represents a 55 percent increase in resource recovery, as compared to the estimated 330 million barrels that could be produced solely by room and pillar mining in the Mahogany Zone with all surface retorting.
Discounted cash flow calculations were made at several oil price levels to obtain a curve depicting the annual rate of return as a function of the value of the shale oil product. All calculations are based on constant 1976 dollars. The oil price can, therefore, be related to the 1976 cost of imported oil and the controlled price of domestic oil. As a first approximation, the rate of return will be close to the true return on investment if product prices continue to rise at the same rate as the inflation of construction and operating costs. Of course, if we have an abnormal inflation in construction and operating costs and prices remain controlled by the government, then these return on investment figures would not apply, since they are based on constant dollars.

The results of this evaluation are shown in figure 5. We estimate the value of this low end point shale oil, not hydrotreated, at $12.50 per barrel at the plant site relative to 1976 prices. At this price, the annual rate of return is about 12 percent. By comparison, in situ retorting alone would yield less than 9 percent return on investment; surface retorting alone, only slightly better than 9 percent return. The combined operation offers economic advantages.

At this time, we should consider the differences between the modified in situ process as described in this study, and the process described by Occidental in the latest detailed development plan submitted by the new partners in the C-b project, Ashland and Occidental. One difference is that Occidental rubblizes the shale to a "bulked full" retort. They claim that the rubble provides sufficient support to the barrier pillars and roof to permit areal extraction efficiencies of 60-70 percent. This concept also permits retorting of shale to a greater depth without subsidence, and, consequently, greater use of the resource vertically. The second major difference is the use of super-heated steam as a diluent for combustion air rather than recycled gas from the retorts.

Figure 5. - Return on investment.

The Occidental design for use of their modified in situ process on the C-b tract is based upon a retorting interval of 95 meters, starting just below the top of the Mahogany Zone and ending just above the bottom of the R-6 Zone, as shown in figure 6. Individual retorts are 61 meters square but lack a central support pillar.

By operating "bulked full" and with steam diluent, Occidental anticipates a resource recovery from Tract C-b of 1.2 billion barrels by in situ alone or over 1.6 billion barrels with the combination of in situ and surface retorting. Compare this to only 330 million barrels by the original room and pillar mine design with surface retorting alone. Given that high a resource recovery, we estimate the return on investment for combined in situ and surface retorting at over 15 percent, basis 100 percent equity investment. Such a rate
of return appears to justify proceeding with the development of Tract C-b, as Occidental and Ashland now seem prepared to do.

Although a 15 percent rate of return would appear to justify proceeding with even a high risk project such as the C-b shale venture, major political obstacles pose a significant threat to the success of the venture. For example, pending divestiture legislation against the major oil companies, adding severely restrictive, non-degradation amendments to the Clean Air Act, and continuation of crude oil price controls. If shale oil is produced in commercial quantities, will Congress then include it under controlled prices at a level that prohibits a return on investment commensurate with the risks involved? Will it prohibit the major oil companies from participating in shale oil projects under the misguided concept that oil companies are not competitive? Will Congress continue to limit the federal shale leases to 5,000 acres per company, thus preventing them from fully using the technology that they have developed at great risk and expense? Considerations such as these weighed very heavily in Shell's decision to abandon its interest in Tract C-b, rather than continue a high risk investment in the face of these potential federal restrictions.

In conclusion, we offer two suggestions to speed up development of oil shale as a supplemental source of liquid fuels: First - directed to ERDA, whose directors are seeking the most effective ways of spending their share of the tax pie - It appears that Occidental and Ashland are the only companies ready to proceed with a commercial shale oil venture at the present time. They will use Occidental's modified in situ process on Tract C-b, but the detailed development plan, submitted in March, indicates they have deferred any decision to use mined out shale in surface retorts. On the other hand, ERDA and Congressional committees have been considering proposals to finance full-scale surface retort modules. It appears logical to install one or two such demonstration modules on Tract C-b since no additional mining costs would be involved, utilities and roads will be available, and the product could be treated and shipped to markets at a nominal incremental cost. Occidental may not welcome such activities in the midst of their in situ development, but this would lead more rapidly to the combination retorting which this analysis indicates will increase resource recovery and reduce overall unit product costs.

Second - related to the non-technical, institutional and legal obstacles to both conservation and the commercialization of alternative energy sources such as shale oil and coal conversion to gaseous fuel - Technical solutions to these problems are being resolved by industry, but attempts to commercialize the new technologies are thwarted by institutional barriers. The net result is delay and added costs and hardships to the consumers. A report by the Office of
Technological Assessment over a year ago recommended that ERDA devote a substantial effort to resolving the non-technical barriers to development of alternate energy sources. Regardless of whether this or another agency takes on the job, it is clear that Congress must take the lead in reducing the obstacles that they themselves have imposed on energy development.
As the costs of individual projects continue to increase, and the ability of energy companies to generate capital decreases, energy investment alternatives must be analyzed more carefully than ever to determine where to invest the limited funds available. First generation shale oil plants will have major economic risks associated with the construction and operation of new technology at commercial scale. Industry has historically taken this type of risk, but shale oil plants have substantial added risks in the form of major future product price uncertainties and uncertainties related to future government policies regarding energy pricing and environmental regulations. In order to justify the allocation of capital to synthetic fuels plants, it appears essential that government share these risks with industry.

Federal support for modular demonstration of oil shale technology has been proposed as one means of risk sharing by the government. Current proposals call for the construction of modular facilities at federal expense. A modular plant is one containing a single retort producing 6,000 to 10,000 barrels of shale oil per day. By comparison, a commercial plant would produce about 50,000 or more barrels of shale oil per day and would incorporate several parallel retort trains operating in concert with mining, upgrading, and support facilities. Extent of the reserves, project life, and many other factors are considered when sizing a commercial plant.

An engineering contractor's estimate, prepared in September 1975, indicated that total capital cost for a commercial plant producing 48,000 barrels of upgraded shale oil per stream day would be about $829 million. Annual operating costs were estimated to be $75 million per year. Since then, no additional estimates have been undertaken; however, monitoring of equipment and manpower cost escalation since then indicate that these costs would be about 11 percent higher now. In contrast, a one-train modular plant producing 8,000 to 10,000 barrels per day at the same location might cost $250 million with annual operating costs of $20 million. A breakdown of these capital costs is given in table 1.

Considering these economies of scale, it is reasonable to ask why an oil shale developer might choose to undertake a modular demonstration program before full scale commercial plant construction and operation. There are both advantages and disadvantages to modular development, and we believe that a federal government synthetic fuels program should provide incentives for both modular plants and first-generation multiple retort commercial plants. Selection between these alternatives should be based on the specific next step requirements of the developer and the state of the technology to be employed in the project.

Modular Alternatives

If a modular oil shale demonstration plant is to be built, the developer has some
significant alternatives to consider. Will he produce raw shale oil or will he upgrade on site? Will the module be designed for expansion to a full scale commercial plant at some future date, or will it be a "one-shot" plant to be shut down and possibly dismantled once the modular demonstration is completed? Other decisions, such as plant location, water supply, product transportation mode, and product testing depend heavily on the upgrading alternative selected and the intended long-term disposition of the module.

Scope

Table 2 enumerates some of the factors to be considered in establishing the scope of a modular demonstration program. How soon does the developer want to begin, when will the results be needed? What are the technology questions to be answered, what information is needed on environmental and socioeconomic impacts? How large must the demonstration project be to satisfy these information needs? What constitutes a successful demonstration? How and when will the program terminate?

Questions concerning technology demon-

Table 1 - Comparison of commercial and modular plant costs.

<table>
<thead>
<tr>
<th></th>
<th>Commercial</th>
<th>Modular</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product Oil, BPSD</td>
<td>48,000</td>
<td>8,000</td>
</tr>
<tr>
<td>Capital, $ Million</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mining, Crushing, Disposal Equipment</td>
<td>118</td>
<td>28</td>
</tr>
<tr>
<td>Pyrolysis, Oil Recovery</td>
<td>244</td>
<td>50</td>
</tr>
<tr>
<td>Upgrading</td>
<td>103</td>
<td>41</td>
</tr>
<tr>
<td>By-product Recovery</td>
<td>54</td>
<td>13</td>
</tr>
<tr>
<td>Utilities, General Facilities</td>
<td>159</td>
<td>50</td>
</tr>
<tr>
<td>Mine Pre-development Costs</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>Catalysts, Chemicals, Spare Parts</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>Project Management, Plant Staffing</td>
<td>25</td>
<td>12</td>
</tr>
<tr>
<td>Community Assistance Expenses</td>
<td>28</td>
<td>10</td>
</tr>
<tr>
<td>Other Miscellaneous Capital Costs</td>
<td>74</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>829</td>
<td>250</td>
</tr>
<tr>
<td>Operating Costs, $ Million/Year (excluding by-product credits)</td>
<td>75</td>
<td>20</td>
</tr>
</tbody>
</table>

Note: Above numbers exclude any cost for reserves.
Table 3. - Planning and implementation of a modular demonstration program.

Factors influencing the selection of technology to be demonstrated

- Applicability of process to general industry use
- Degree of present technical development
- Scale-up limitations
- Probability of success
- Downstream processing or end use testing requirements

demonstration project, the technology to be demonstrated should be that which can be used by a maximum number of developers, has already had some development work, and has a reasonable chance of successful operation at commercial scale.

Mining - In mining, the most well-developed technology is the room and pillar technique which has been tested by the federal government, Mobil Oil Corporation and others at Anvil Points, and by Colony Development Operation at its Parachute Creek facilities. Colony Development Operation has mined at rates up to 2,500 tons per day and removed over 1.3 million tons of oil shale from its mine since it was opened in 1965. Today, Colony is continuing a modest rock mechanics program in the mine to determine long-term pillar load-carrying capabilities, and stress distribution in the mine. We have found that there is much more to be learned about optimizing pillar size and orientation for increased resource recovery and improved mine safety.

Even though room and pillar mining is generally accepted as well-developed technology, uncertainties concerning underground haulage and ventilation would be removed by operation of a large-scale underground mine.

Modified in situ, in situ, mechanical miner, retreat chamber, and other oil shale mining techniques are in various stages of research and development or subcommercial scale demonstration. Based on published information on the mining aspects of in situ and modified in situ recovery techniques, it appears that schemes developed by Occidental Petroleum, Shell Oil Company, Equity Oil Company are the most advanced oil shale recovery technologies other than room and pillar mining. These techniques appear to us to be promising complementary recovery schemes to be used in conjunction with room and pillar mining and surface retorting for increased recovery of the overall oil shale reserve.

Retorting - No two potential commercial oil shale retorts are at the same state of development and there are significant differences in scale-up limitations for the various retorts. Table 4 lists some, but not all, oil shale retorting processes receiving some current interest. None of these retorts has been built and operated on oil shale at a commercial scale. Benefits would result from modular scale demonstration of any of these retorts.

From a process design standpoint, there are two general categories into which the previously mentioned retorting techniques fall. For discussion purposes, we shall call them "segmented" and "combined"; in both cases, the retorting sequence is the same: preheating, retorting, product recovery, and waste cooling. The difference is in the degree of independence or physical separation between individual steps during the retorting process.

Retorting processes, such as TOSCO II, Lurgi-Ruhrgas, Superior, and the Galoter process, fall into the segmented category. As illustrated in figure 1, each stage of retorting is performed in an individually controlled system within the overall process. These processes are generally complex from a mechanical standpoint, but are more amenable to modification if actual operating conditions fail to match design conditions. Conservate design can be used to guarantee operation more readily in segmented processes, and scale-up is not too difficult in the 10:1 size ratio range. Too conservative an approach, however, can lead to high capital costs.

Combined processes, on the other hand, perform the necessary unit operations in as
Table 4. - Oil shale retorting schemes.

<table>
<thead>
<tr>
<th>Process Developer</th>
<th>Process</th>
<th>Demonstrated Throughput, T/D</th>
<th>Announced Consideration of Its Use by U.S. Oil Shale Developers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petrobras and Cameron Engineers</td>
<td>Petrosix</td>
<td>2,000</td>
<td>None</td>
</tr>
<tr>
<td>Development Engineering, Inc.</td>
<td>Paraho</td>
<td>280</td>
<td>White River Shale Project</td>
</tr>
<tr>
<td>Lurgi</td>
<td>L-R</td>
<td>15</td>
<td>Rio Blanco Oil Shale Project</td>
</tr>
<tr>
<td>Occidental Petroleum Corporation</td>
<td>Oxy Modified In Situ</td>
<td>(500 B/D)</td>
<td>C-b Shale Oil Project</td>
</tr>
<tr>
<td>Superior Oil Company</td>
<td>Superior Multi-Mineral Process</td>
<td>100</td>
<td>Superior Oil Company</td>
</tr>
<tr>
<td>Tosco Corporation</td>
<td>TOSCO II</td>
<td>1,000</td>
<td>Rio Blanco Oil Shale Project Colony Development Operation</td>
</tr>
<tr>
<td>Union Oil Company of California</td>
<td>Union A</td>
<td>1,200</td>
<td>C-b Shale Oil Project</td>
</tr>
<tr>
<td></td>
<td>Union B</td>
<td>5</td>
<td>Union Oil Company of California</td>
</tr>
<tr>
<td>U.S.S.R.</td>
<td>Galoter</td>
<td>550</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>Kiviter</td>
<td>275</td>
<td>None</td>
</tr>
</tbody>
</table>

few vessels as possible. Usually one vessel is sufficient for all operations. Examples of what we call combined processes are the Paraho, Union, Petrosix, and Kiviter retorts. Figure 2 presents a simplified concept of combined processing. A combined process is characterized by continuous flow of shale through a single vessel in which preheat, retorting, and product recovery are achieved in adjacent zones. The integrity of these zones is maintained through injection of combustibles, air and inert gases, by controlling shale feed rate, and maintaining a specific feed particle size range. In situ and modified in situ retorts also fit the combined process category. In these processes, as in the old NTU oil shale retort, the shale does not move but the preheat and retorting zones progress through the bed. Integrity of the moving zones is maintained by injection of combustibles, air and inert gas, or other fluids to control the rate of combustion underground.

Combined processes are mechanically simpler and should be cheaper to build than a segmented unit of equivalent capacity. They do not have as much "fix-up" flexibility and the operator has fewer independent variables to use in controlling the retorting process. Successful operation is therefore more dependent on the correlation between design assumptions and actual operating conditions and scale-up is probably more difficult than for segmented processes.
processing plants or used for large scale end-product tests. If raw shale oil is produced, however, the processing alternatives are severely reduced and may not reflect the markets which a commercial shale oil product might serve.

Considering the long-term projections for energy consumption in the U.S., it appears obvious that shale oil's long-term contribution to this country's energy demand will be to augment the supply of middle distillate fuels such as diesel, jet, and No. 2 fuel oil. The need to demonstrate the technology for upgrading shale oil to a level from which such fuels may be readily produced is just as great as the need to demonstrate retorting technology.

Information to be Obtained

In establishing the scope of his program and selecting technology, a developer must look at the effect a modular demonstration project might have on commercial scale economics. Can the module provide information which will allow reductions in overall plant cost? Will it provide the information necessary to make certain process decisions? The cost of undertaking modular development before proceeding with full scale commercial development will likely be greater than building the commercial plant initially and modifying it as necessary during the start-up phase of operation. Each oil shale developer must weigh this cost against the possible benefits of increased chance of technical success.

Another factor to be considered is the extent to which a modular plant can be used to provide information for a better understanding of environmental and socioeconomic impacts of a full scale plant. Can air and water quality predictions be confirmed? Can effects on wildlife, vegetation, and humans be measured and extrapolated to a full scale plant? What levels of employment are required? Will new community services be needed?

What is to be done with the products from a modular plant? Oil production would
probably range from 5,000 to 10,000 barrels per day. Depending on the facilities installed, there may also be significant quantities of sulfur and ammonia by-products. At this scale, it would be possible to conduct product transportation and performance tests previously impossible because of an insufficient supply of sample.

What data can a developer expect to obtain from a modular program?

One obvious advantage of a modular program is demonstration of retorting technology on a commercial scale. Since a commercial retorting facility is by definition a combination of modules, design uncertainty is minimized. In theory, a developer would need only to duplicate the demonstrated design several times over when building a commercial plant.

Beyond this, the usefulness of data obtained from a modular demonstration facility becomes a function of the scope of the program.

Several questions concerning the impact of oil shale development will be only partially answered or left unanswered by operation of a modular facility of limited scope. Data can be collected on ambient air quality, but the degree, location, and duration of construction activity may not represent full scale commercial construction. Good data can be obtained from mining and waste disposal activities, but water supplies and consumption patterns will not necessarily be the same as those for the commercial plant. A small modular program might use local wells as water supply rather than piping river water to the plan.

Socioeconomic impacts of a modular demonstration program could be far different than those from construction and operation of a commercial facility. The demand for housing and other services would last only as long as the demonstration project continued. This would inhibit development of major capital items such as sewer and water systems, communications, and other utilities. It could also place a heavy burden on remaining residents if such services are not paid for before tax sources related to the modular program are depleted.

Colony's proposed commercial plant, on the other hand, would employ about 1,100 permanent employees. Total direct and indirect employment generated by Colony would be about 2,500 jobs. A population increase resulting from this number of jobs does require socioeconomic impact mitigation such as that proposed by Colony Development Operation. Rio Blanco oil shale project, C-b shale oil project, White River shale project, and others have similar plans. Conclusions drawn by the BLM in Colony's draft environmental impact statement are that the long-term socioeconomic impact of a commercial plant is positive. A stable community is established, an adequate tax base provides long-term income to pay for the cost of sewer, water, school, and other permanent facilities.

Logistics

Table 5 presents some logistic factors a developer must consider. There are a large number of permits required, environmental and socioeconomic baseline data needs to be met before development can begin. At last count, Colony had more than sixty permits, licenses, or approvals to obtain before work could begin on the plant, staging area, and community development. Starting from scratch, a delay of several years or more will occur before actual construction of commercial facilities can begin.

Plant water supply is critical. The developer can obtain water supplies by purchasing water from storage, diverting surface runoff under the Colorado water-right priority system, or developing groundwater supplies. Each of these alternatives is a time-consuming task and none is without its own peculiar problems.

How is disposition of the modular plant products to be handled? Pipeline, truck, and rail transportation are all possible. The selection depends upon the size of the demonstration plant and resultant quantity of product. Again, planning and implementing
Table 5. - Planning and implementation of a modular demonstration program.

Logistics factors
- Permit requirements
- Water supply
- Disposition of plant products
- Availability of support facilities
- Taxes or other funds available to local governments
- Disposition of modular facilities following a demonstration program

The product transportation system would add significantly to lead time and cost of a modular demonstration program.

Power must be available. If existing distribution lines with adequate capacity are not located nearby, the developer is faced with the cost and permitting process delays of bringing adequate electricity to the modular plant site.

If the project is to be located on federal land, how will local governments obtain money equivalent to property taxes that would be paid if the project were located on private lands? Are there other impact mitigation funds available?

The best way to evaluate these and similar questions is to look at decisions by developers of projects already underway. This strongly suggests that a developer take full advantage of work which has been done already by meshing his plans with those of a project where these questions have already been addressed.

Conclusion

In conclusion, we believe that modular demonstration of oil shale technology is useful and that it is appropriate for the federal government to undertake a risk-sharing program with industry. We believe, however, that the scope of a demonstration program must be large enough to provide the necessary information on all aspects of commercial oil shale technology, including mining, retorting, upgrading, and end-use tests, and to provide the scale and detail of information needed for adequate assessment of environmental impacts.
PREPARATION OF SHALE-OIL GASOLINE

Philip L. Cottingham
Laramie Energy Research Center
U.S. Energy Research & Development Administration
Laramie, Wyoming 82071

Abstract
Shale oil, produced from oil shale of the Rocky Mountain region by many of the usual retorting processes, consists mainly of high boiling compounds of nitrogen, sulfur, and oxygen; less than half is hydrocarbons. Gasoline boiling-range naphtha has been produced in a yield of 49.6 percent by volume by recycle thermal cracking of the crude. The raw naphtha, of poor quality, was upgraded by dilute acid and caustic treatment followed by concentrated sulfuric acid treatment. Hydrofining thermally cracked naphtha at 400 and 800 psig produced better yields of stable gasoline with slightly lower clear octane numbers but higher leaded octane numbers. Recycle hydrocracking of crude shale oil at 3,000 psig produced over 100 percent by volume of stable, low-sulfur, low-nitrogen gasoline with low octane numbers. Hydrotreating of a naphtha from hydrocracking crude shale oil, to reduce its nitrogen content to 7 ppm, followed by catalytic reforming raised its octane numbers to 89, clear, and 99 with 3 ml of TEL.

Introduction
Oil shale of the Green River Formation in the Rocky Mountain region of the United States is one of the largest potential sources for alternate liquid fuels to supplement our supply of natural petroleum. In considering how shale oil can contribute to our liquid fuel supply, it is normal to consider its possible use in preparing motor gasoline. This paper reviews some of the methods that have been investigated in former U.S. Bureau of Mines research and more recent Energy Research and Development Administration efforts in preparing motor gasolines from shale oil.

Crude Shale Oils
Crude shale oils produced from Green River shale by several types of aboveground retorts have remarkably similar properties when the retorts are operated under conditions intended to maximize the yield of oil (Dineen and others 1952; Dineen 1954; Thorne and Ball 1954). Table 1 shows properties of shale oil produced by the N-T-U and gas-combustion retorts. The oil contains less than 5 percent by volume of naphtha distilling in the gasoline range; approximately half of the oil is nondistillable at a temperature of 807°F (corrected to 760 mm) by the Bureau of Mines analytical distillation method (Stevens and others 1952). Such oils have high specific gravities, high pour points, and high viscosities; they usually contain about 0.7 to 0.8 percent by weight of sulfur, about 2 percent nitrogen, and over 1 percent oxygen. The hydrogen/carbon atomic ratio is about 1.6. This ratio is considerably less than the ratio of 2.0 for monoolefins and the 2.0 or greater for saturated hydrocarbons.

In one extensive analysis (Cady and Seeleg 1952), of a shale oil with properties similar to those shown in table 1, it was found that less than 40 percent by weight of the oil consisted of hydro-
Table 1. - Properties of crude shale oils

<table>
<thead>
<tr>
<th>Type of retort</th>
<th>N-T-U</th>
<th>Gas-combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity, °API</td>
<td>20.3</td>
<td>18.6</td>
</tr>
<tr>
<td>Specific gravity, 60/60°F</td>
<td>0.932</td>
<td>0.943</td>
</tr>
<tr>
<td>Pour point, °F</td>
<td>90</td>
<td>85</td>
</tr>
<tr>
<td>Viscosity at 100°F, cs</td>
<td>60.3</td>
<td>66.8</td>
</tr>
<tr>
<td>Viscosity at 100°F, SUS</td>
<td>280</td>
<td>310</td>
</tr>
<tr>
<td>Sulfur, wt%</td>
<td>0.79</td>
<td>0.69</td>
</tr>
<tr>
<td>Nitrogen, wt%</td>
<td>2.10</td>
<td>2.13</td>
</tr>
<tr>
<td>Oxygen (by difference), wt%</td>
<td>1.10</td>
<td>1.01</td>
</tr>
<tr>
<td>Carbon, wt%</td>
<td>84.61</td>
<td>84.87</td>
</tr>
<tr>
<td>Hydrogen, wt%</td>
<td>11.40</td>
<td>11.30</td>
</tr>
<tr>
<td>C/H wt ratio</td>
<td>7.42</td>
<td>7.50</td>
</tr>
<tr>
<td>H/C atom ratio</td>
<td>1.60</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Distillation, BuMines Distillation Method (4), corrected to 760 mm, vol%:

- Naphtha, up to 392°F: 2.7  4.4
- Light distillate, 392°F to 595°F: 16.5  14.6
- Heavy distillate, 595°F to 807°F: 31.2  31.3
- Residuum, + 807°F: 49.6  49.7

Recycle Thermal Cracking

The preparation of motor gasoline from shale oil requires a reduction of the boiling range by some method. The simplest method for accomplishing this is thermal processing. Between 1949 and 1954, thermal cracking, delayed coking, and various other thermal processes were studied with the 300-barrel per day unit operated by the U.S. Bureau of Mines near Rifle, Colorado. Of these methods, recycle thermal cracking produced the best yields of gasoline-range product within the limits of the operations studied (BuMines RI 4866-1952). Figure 1 is a flow diagram of the equipment used for recycle thermal cracking.

Table 2 shows operating conditions and yields for a recycle thermal cracking operation using this equipment, which produced 49.6 percent by volume of 405°F end-point naphtha. The naphtha had ASTM distillation temperatures of 89°F initial, 143°F at 10 percent, 295°F at 50 percent, and 396°F at 90 percent. It contained 0.72 percent by weight of sulfur and 1.10 percent by weight of nitrogen; the hydrocarbons consisted of 36 percent by volume of paraffins plus naphthenes, 46 percent olefins, and 18 percent aromatics. Motor-method octane numbers of the naphtha were 71.0 clear and 76.5 with 3 ml of tetraethyllead per gallon, while research octane numbers were 79.0 clear and 87.3 with 3 ml of tetraethyllead.

Acid Treating of Naphtha - Because of the poor stability of raw naphthas derived from thermal processing, they were treated at the small Rifle refinery with counter-current acid treating equipment. (Flow diagram, fig. 2, BuMines, RI 4943-1953). The tar acids were first removed with dilute sodium hydroxide solution, and then the tar bases were removed with dilute sulfuric acid. The naphtha was next treated with two stages of sulfuric acid sludge and then with fresh concentrated sulfuric acid. Finally, the naphtha was washed with water and treated with dilute sodium hydroxide solution to neutralize any acid left in it. The treated naphtha was distilled in a rerun distillation
Figure 1. - Recycle cracking of crude shale oil.

Table 2. - Recycle cracking crude shale oil

<table>
<thead>
<tr>
<th></th>
<th>Heater outlet</th>
<th>Reaction chamber</th>
<th>Flash chamber</th>
<th>Top</th>
<th>Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °F</td>
<td>920</td>
<td>848</td>
<td>762</td>
<td>386</td>
<td>621</td>
</tr>
<tr>
<td>Pressure, psig</td>
<td>200</td>
<td>200</td>
<td>64</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Vol%</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>49.6</td>
<td>40.1</td>
</tr>
<tr>
<td>Residuum</td>
<td>45.9</td>
<td>51.9</td>
</tr>
<tr>
<td>Gas</td>
<td></td>
<td>7.7</td>
</tr>
<tr>
<td>Loss</td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>95.5</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Figure 2. - Tar-acid and tar-base removal and acid treating of distillates.

unit to remove any polymer formed during the treatment.

Table 3 gives details for a typical acid treatment of naphtha from recycle thermal cracking, and table 4 shows yields and properties of the raw naphtha, treated naphtha, and redistilled polymer-free gasoline. The yield of stable, essentially nitrogen-free gasoline from this treatment was 80.7 percent by volume of the raw naphtha; the gasoline had research-method octane numbers of 73.0, clear, and 82.0 with 3 ml of tetra-ethyllead (BuMines RI 4866-1952). Some loss in octane numbers occurred during the treatment, but the rerun distillation usually restored most of the loss.

Catalytic Hydrofining of Naphtha - Another method of stabilizing raw naphtha from thermal cracking of shale oil involves hydrofining the naphtha over a sulfur-resistant or sulfaactive catalyst. The Laramie Energy Research Center laboratory studied catalytic hydrofining of thermally cracked shale-oil naphthas, using the hydrogenation equipment whose simplified flow diagram is shown in figure 3.

The hydrogenation unit consisted of a downflow reactor containing 50 cc of catalyst in a stationary bed near the center of the reactor. Oil and hydrogen were mixed at the top of the reactor, passed downward through the catalyst, out of the reactor through an air-cooled section of tubing and a back-pressure regulator, and into a low-pressure separator vessel. Excess hydrogen and light hydrocarbons, including most of the butane and lighter gases, were separated from the liquid product at that point. Most of the water, ammonia, and hydrogen sulfide formed during the reaction were collected with the liquid product and later removed by a water wash.
Table 3. - Acid treating recycle cracked naphtha (at 45° to 55°F)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Tar acid removal</td>
<td>2.9 vol% of 15% NaOH</td>
</tr>
<tr>
<td>Tar base removal</td>
<td>16.2 vol% of 14.4% H₂SO₄</td>
</tr>
<tr>
<td>Fresh acid treatment</td>
<td>15.4 lb 66° acid per bbl</td>
</tr>
<tr>
<td>Neutralization</td>
<td>1.5 vol% of 15% NaOH</td>
</tr>
</tbody>
</table>

Tables 5 and 6 show results obtained in hydrofining raw thermally-cracked naphtha over a commercial cobalt-molybdate-alumina catalyst (Cottingham and others 1956). Hydrofining temperatures in this work were kept high (961° to 979°F in the experiments shown) to prevent loss in octane numbers of the naphtha. Consequently, yields of hydrofined naphtha were lower than would have been obtained at lower operating temperatures. Nevertheless, yields were better than those obtained by acid treating.

Clear octane numbers were lower, but leaded octane numbers were higher than those of gasolines produced by acid treating of cracked naphtha. This result was probably due to the highly paraffinic nature of the

Table 4. - Acid treated recycle cracked gasoline

<table>
<thead>
<tr>
<th></th>
<th>Raw</th>
<th>Treated</th>
<th>Redistilled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery, vol%</td>
<td>100.0</td>
<td>87.7</td>
<td>80.7</td>
</tr>
<tr>
<td>Gum, ASTM, mg/100 ml</td>
<td>351</td>
<td>ND</td>
<td>2.0</td>
</tr>
<tr>
<td>Sulfur, wt%</td>
<td>0.62</td>
<td>0.51</td>
<td>0.22</td>
</tr>
<tr>
<td>Nitrogen, wt%</td>
<td>0.93</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>Octanes:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Motor, clear</td>
<td>68.8</td>
<td>64.7</td>
<td>65.4</td>
</tr>
<tr>
<td>+ 3 ml TEL</td>
<td>75.4</td>
<td>63.2</td>
<td>74.8</td>
</tr>
<tr>
<td>Research, clear</td>
<td>76.7</td>
<td>70.9</td>
<td>73.0</td>
</tr>
<tr>
<td>+ 3 ml TEL</td>
<td>84.3</td>
<td>70.0</td>
<td>82.0</td>
</tr>
<tr>
<td>Distillation,°F:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP</td>
<td>94</td>
<td>107</td>
<td>111</td>
</tr>
<tr>
<td>50%</td>
<td>287</td>
<td>291</td>
<td>255</td>
</tr>
<tr>
<td>EP</td>
<td>403</td>
<td>494</td>
<td>393</td>
</tr>
</tbody>
</table>

Figure 3. - Simplified flow diagram of hydrogenation unit.
Table 5. - Hydrofining recycle cracked naphtha over cobalt molybdate catalyst.

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °F</td>
<td>961</td>
<td>979</td>
<td>958</td>
</tr>
<tr>
<td>Pressure, psig</td>
<td>400</td>
<td>400</td>
<td>800</td>
</tr>
<tr>
<td>( \text{H}_2 ) feed rate, scf/bbl</td>
<td>2,000</td>
<td>2,000</td>
<td>2,000</td>
</tr>
<tr>
<td>( \text{H}_2 ) consumed, scf/bbl</td>
<td>760</td>
<td>780</td>
<td>910</td>
</tr>
<tr>
<td>Space velocity, ( V_o/V_c ) /hr</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Throughput, ( V_o/V_c )</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>400°F gasoline, vol%</td>
<td>89.7</td>
<td>86.7</td>
<td>87.0</td>
</tr>
<tr>
<td>+400°F polymer, vol%</td>
<td>2.6</td>
<td>1.9</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Table 6. - Hydrofining recycle cracked naphtha.

<table>
<thead>
<tr>
<th>Naphtha properties:</th>
<th>Feed</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur, wt%</td>
<td>0.71</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Nitrogen, wt%</td>
<td>0.99</td>
<td>0.38</td>
<td>0.35</td>
<td>0.27</td>
</tr>
<tr>
<td>Gum, Cu dish, mg/100 ml</td>
<td>1,500</td>
<td>25.5</td>
<td>23.8</td>
<td>16.8</td>
</tr>
<tr>
<td>Induction period, hrs</td>
<td>0.3</td>
<td>24+</td>
<td>24+</td>
<td>24+</td>
</tr>
<tr>
<td>Hydrocarbons, vol%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paraffins</td>
<td>29</td>
<td>64</td>
<td>65</td>
<td>71</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>6</td>
<td>3</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Olefins</td>
<td>47</td>
<td>8</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Aromatics</td>
<td>18</td>
<td>25</td>
<td>29</td>
<td>22</td>
</tr>
<tr>
<td>Octane numbers:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Motor, clear</td>
<td>65</td>
<td>62</td>
<td>65</td>
<td>60</td>
</tr>
<tr>
<td>Motor, + 3 ml TEL</td>
<td>73</td>
<td>78</td>
<td>81</td>
<td>80</td>
</tr>
<tr>
<td>Research, clear</td>
<td>75</td>
<td>68</td>
<td>70</td>
<td>65</td>
</tr>
<tr>
<td>Research, + 3 ml TEL</td>
<td>81</td>
<td>84</td>
<td>86</td>
<td>83</td>
</tr>
</tbody>
</table>

hydrofined products. Nitrogen removal from the naphtha was not as good as was obtained with concentrated acid treatment, but sulfur removal was much better. The copper-dish gum values and the induction periods of over 24 hours in the oxidation-stability test showed the hydrofined naphthas to have acceptable stability.

Hydrogenation of Crude Shale Oil

Catalytic hydrogenation of crude shale oil offers a method for removing the sulfur and nitrogen from the oil and, at the same time, eliminating the nondistillable heavy residuum fraction by converting it to lower-boiling distillate. This method has distinct advantages over thermal processing, which removes only part of the sulfur and nitrogen and converts part of the oil to residuum or coke.

Catalytic hydrogenation studies have been made in the laboratory with the apparatus whose flow diagram was shown in figure 3. Table 7 shows results from recycle hydrogenation of crude shale oil over cobalt molybdate catalyst at 3,000 psig and 889°F. Yield of \( \text{C}_5^+ \) gasoline fraction was 99.3 percent by volume and yield of \( \text{C}_4^+ \) gasoline, 106.8 percent by volume. The 1.7 percent by volume of recycle oil at the end of the experiment was accumulated as pump holdup material and samples removed for analysis during the run. Conversion of the recycle oil would have increased gasoline yields.

Table 8 shows properties of the gasoline fraction obtained during the recycle run. Sulfur in the gasoline was only 0.05 percent and nitrogen percentage was so low it

Table 7. - Recycle hydrogenation of gas combustion crude at 3,000 psig over cobalt molybdate catalyst.

<table>
<thead>
<tr>
<th>Conditions:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Average temp., °F</td>
<td>889</td>
</tr>
<tr>
<td>Pressure, psig</td>
<td>3,000</td>
</tr>
<tr>
<td>( \text{H}_2 ) feed rate, scf/bbl</td>
<td>6,000</td>
</tr>
<tr>
<td>( \text{H}_2 ) consumed, scf/bbl of fresh feed</td>
<td>2,040</td>
</tr>
<tr>
<td>Space velocity, ( V_o/V_c ) /hr</td>
<td>0.98</td>
</tr>
<tr>
<td>Throughput, ( V_o/V_c )</td>
<td>82.2</td>
</tr>
<tr>
<td>Recycle/fresh feed vol ratio</td>
<td>1.03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Yields:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline, vol%</td>
<td>99.3</td>
</tr>
<tr>
<td>( \text{C}_4^+ ) in gas, vol%</td>
<td>7.5</td>
</tr>
<tr>
<td>Gasoline, ( \text{C}_4^+ ), vol%</td>
<td>106.8</td>
</tr>
<tr>
<td>Recycle oil, vol%</td>
<td>1.7</td>
</tr>
<tr>
<td>Catalyst deposit, wt%</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Table 8. - Gasoline from recycle hydrogenation of gas combustion crude at 3,000 psig.

<table>
<thead>
<tr>
<th>Gravity, °API</th>
<th>57.7</th>
<th>Nitrogen, wt%</th>
<th>nil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity, 60/60°F</td>
<td>0.748</td>
<td>Gum, ASTM, mg/100 ml</td>
<td>1.8</td>
</tr>
<tr>
<td>Hydrocarbons, vol%</td>
<td></td>
<td>Reid vapor pressure, psig</td>
<td>11.0</td>
</tr>
<tr>
<td>Paraffins + naphthenes</td>
<td>80</td>
<td>ASTM distillation, corrected</td>
<td></td>
</tr>
<tr>
<td>Olefins</td>
<td>7</td>
<td>to 760 mm, °F:</td>
<td></td>
</tr>
<tr>
<td>Aromatics</td>
<td>13</td>
<td>IBP</td>
<td>103</td>
</tr>
<tr>
<td>Octane numbers:</td>
<td></td>
<td>10% recovered</td>
<td>159</td>
</tr>
<tr>
<td>Motor, clear</td>
<td>48</td>
<td>50% recovered</td>
<td>272</td>
</tr>
<tr>
<td>Motor, + 3 ml TEL</td>
<td>73</td>
<td>90% recovered</td>
<td>374</td>
</tr>
<tr>
<td>Research, clear</td>
<td>51</td>
<td>EP</td>
<td>404</td>
</tr>
<tr>
<td>Research, + 3 ml TEL</td>
<td>76</td>
<td>Recovery, vol%</td>
<td>95.0</td>
</tr>
<tr>
<td>Sulfur, wt%</td>
<td>0.05</td>
<td>Loss, vol%</td>
<td>4.2</td>
</tr>
</tbody>
</table>

could not be detected by the Kjeldahl analytical procedure. Gum content of the gasoline was only 1.8 milligrams per 100 ml.

Catalytic Reforming Hydrogenated Naphtha - Gasoline fractions obtained from hydrogenation of gas combustion crude shale oil at any but extremely high temperatures usually have octane numbers too low to permit use of the fractions directly as automobile fuel. Catalytic reforming to increase octane numbers may require an additional hydrotreating step to reduce the nitrogen content even further before the naphthas are fed to a reforming unit. An investigation of such a process was made with a naphtha having properties very much like those shown in Table 8, and produced by hydrogenation of gas combustion crude at 1,000 psig (Barker and Cottingham 1972, 1973). The naphtha was further hydrotreated over a commercial nickel tungsten catalyst at 700°F, space velocity of 1.0 Vg/Vc/hr, with hydrogen rate of 5,000 scf/bbl. This reduced its nitrogen content to 7 ppm and its sulfur content to below 10 ppm. Light naphtha was removed by distillation up to a cut temperature of 160°F, and the heavier portion was used as feed to a catalytic reforming unit. Table 9 shows operating conditions for three different reforming runs at 200 psig over a commercial platinum-containing catalyst. Table 10 shows properties of the hydrotreated feed and the reformates.

The highest octane product, obtained at the highest temperature investigated (917°F), was obtained in a yield of 79.9 percent by volume of the feed. The Research Method octane numbers were 89, clear, and 99 with 3 ml TEL. The unleaded octane number of 89 shows that the reformate could be used in a
refinery gasoline pool to produce lead-free gasoline.

Summary

Shale oil produced from oil shale of the Rocky Mountain region by many of the usual retorting processes consists mainly of high-boiling compounds of nitrogen, sulfur, and oxygen; less than half of the oil consists of hydrocarbons. Gasoline boiling range naphtha has been produced in a yield of 49.6 percent by volume by recycle thermal cracking of the crude. This poor quality naphtha was upgraded by hydrofining and by chemical extraction processes. A higher yield of better-quality naphtha was produced by hydrogenating the crude at 3,000 psig. Hydrogenated naphtha was catalytically reformed to a high-octane product.

References


Table 9. - Catalytic reforming hydrogenated naphtha (operating conditions).

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °F</td>
<td>860</td>
<td>886</td>
<td>917</td>
</tr>
<tr>
<td>Pressure, psig</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>V_o/V_c/hr</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Throughput, V_o/V_c</td>
<td>68</td>
<td>71</td>
<td>70</td>
</tr>
<tr>
<td>L_feed, scf/bbl</td>
<td>3,000</td>
<td>3,000</td>
<td>3,000</td>
</tr>
<tr>
<td>Liquid yield, vol%</td>
<td>87.8</td>
<td>84.3</td>
<td>79.9</td>
</tr>
<tr>
<td>Liquid yield, wt%</td>
<td>91.0</td>
<td>87.9</td>
<td>84.4</td>
</tr>
</tbody>
</table>

Table 10. - Catalytic reforming hydrogenated naphtha (properties).

<table>
<thead>
<tr>
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Early improved the quality of naphtha by thermal cracking and by chemical extraction processes. A higher yield of better-quality naphtha was produced by hydrogenating the crude at 3,000 psig. Hydrogenated naphtha was catalytically reformed to a high-octane product.
THE OUTLOOK FOR OIL SHALE

Harry Pforzheimer
Vice President
Sohio Petroleum Company
300 Enterprise Bldg.
Grand Junction, Colorado 81501

With the grip the federal government has on all forms of energy produced in this country, what our President says or does not say, or does or does not do, about energy is most important. As most of us know, he said nothing about oil shale in his energy message to the nation on April 20, 1977. This is not surprising since very few people, outside of those in the industry, know anything about oil shale and its promise as a source of energy.

At this particular moment, the production of crude shale oil from the rich oil shale deposits of Colorado, Utah and Wyoming is commercially feasible at current world oil prices. This is not only my opinion, finally arrived at after many years of searching for a viable process; others are saying so too.

Occidental Petroleum Company and Superior Oil Company, as well as the Paraho Development Corporation, following its conduct of the oil shale demonstration at Anvil Points, near Rifle, Colorado - a program in which I served as director - have all made encouraging, independent public statements about oil shale's current economic attractiveness. I believe Union Oil Company agrees but is a little more conservative in approach. This, in spite of our industry's many problems.

So far, the major obstacles to launching a shale oil industry in the United States include:

(1) Unrealistic environmental standards that the bare ground in oil shale country cannot meet.

(2) U.S. price controls on domestic oil, including a legislative price rollback at the end of 1975: a rollback imposed two years after the Arab embargo when incentives rather than restraints were badly needed.

(3) Lack of a national energy plan containing proper incentives. Such a plan may now begin to unfold.

(4) Need for a land exchange with the federal government to block-up private land holdings for development.

I have no reason to doubt any of the recent statements by others that oil production from oil shale is commercially feasible. These statements are consistent with the conclusions reached at the completion of the three-year, privately-funded, $10 million Paraho oil shale demonstration and the current Paraho operations under Navy contracts. These tests of the Paraho process and hardware have been and are being carried out in the presence of government observers. They have been conducted in full public view and will continue to be so. We are proud of what is being accomplished: making oil from rock.

I have been involved in oil shale since 1963, when Sohio, in association with Cleveland-Cliffs Iron Company and Tosco, began Colony Development. We also began acquiring oil shale reserves and water rights for future development when the technology was ready and the economics justified.
Over the earlier years, gradual technical progress was made in spite of any disappointments. We would move ahead one step and back two. During the last few years, however, significant and very real technical breakthroughs have occurred. These have been made in many areas by a number of developers, witness the recent record.

Paraho itself has achieved many breakthroughs. It is significant that on April 20, 1977, Paraho completed the current run on its semi-works retort after 105 days of continuous operation. Not only has Paraho equipment operated 24 hours a day, seven days per week, at essentially 100 percent service factor, since being re-lit on January 5, 1977, it has survived a number of power outages, courtesy of Colorado Public Service Company.

Other Paraho breakthroughs include:

1. A significant reduction in water requirements. Like Superior and Oxy, the Paraho retort makes water. We have uses for that water and a little more. But, to produce crude shale oil commercially, our water use will be only 20 percent of what earlier work indicated would be necessary. Most of this will be returned to the atmosphere by evaporation. It will not be locked up in the retorted shale. To go all the way to a high quality synthetic shale oil will take only one-third as much water as we once thought.

2. The major reduction in water requirements from the improved characteristics of Paraho's retorted shale. Because of these same characteristics, we have been able to develop improved methods for disposing of it.

3. High thermal efficiencies, which result from burning the residual carbon on the retorted shale, and high net yields of oil are obtained day in and day out. Net liquid recovery of C5+ oil is 94 to 96 percent of Fischer Assay. In addition, a net yield of low Btu gas equivalent to about 5 gallons of fuel oil per ton of rock is obtained. These figures are all net yields. They are over and above the fuel consumed in the process.

4. Pour point depressants have been identified by others which make Paraho crude shale oil and probably most other crude shale oils transportable by pipeline. This should transfer the refining problem, including its investment, its refinery people and its refinery water requirements, to existing refineries where these requirements are already available. These existing plants, some of which are already running below capacity, can be modified at much lower cost than building new pre-refineries out here. Moreover, these existing plants are able to produce products where the people and markets already are.

Paraho has reported the results of its latest commercial evaluation study. The final report of the Paraho oil shale demonstration projected production of crude shale oil of pipeline quality in a nominal 100,000 barrel per day plant for $11.50 a barrel. This compares to $13 to $15 per barrel for imported crude. Paraho's price is projected to yield a 15 percent investor's discounted cash flow rate of return on an estimated investment of $1.2 billion (100 percent equity - 1976 dollars). All the engineering design standards used in this commercial evaluation have been equalled or exceeded during the initial 105 day Navy run.

Superior and Occidental are reporting similar and sometimes lower prices. I believe their results and their processes complement ours. This is another important breakthrough for oil shale. If the underground areas we mine out for above-ground retorting were subjected to a follow-up, using in situ retorting of some type, overall economics would be improved, even if
there were a relatively low yield of secondary recovery of shale oil. Or, alternatively, rock mined out by others before in situ retorting could be run through a Paraho retort, thus improving the economics and conservation aspects of a purely in situ operation.

In those areas that have appreciable quantities of nahcolite or dawsonite in the oil shale deposits (most do not), Superior has developed promising processes for recovering these materials. Their recovery would also improve the economics of shale oil production.

I have always been an optimist, believing that "right is might" and will succeed. It begins to look as if I was correct in my beliefs - the outlook for oil shale in this country has never been better. We finally seem to have succeeded in developing a number of technologies that work and are environmentally acceptable. Their developers claim that each method, by itself, offers a way to produce shale oil at a profit. I think a combination of methods would prove even more attractive. But, very few people outside our industry know anything about these advances and their promise of success.

We are going to have to overcome this lack of public and governmental knowledge. After hearing President Carter's message, I am even more convinced we must get together and work harder to get our message across. Unfortunately, we have not done so in the past and, need I remind anyone, we have suffered accordingly.

An encouraging sign, however, is the federal government's shift toward a more enlightened position. So far, the U.S. Navy has been the leader in this move. This is evidenced by the Navy's involvement with Paraho and its planning for the Navy's shale oil reserves. I believe the new Energy Department is preparing to continue along the lines initiated.

I quite agree with President Carter that we are running out of natural crude oil in the world. Certainly, we cannot expect to find crude oil in large enough quantities to sustain the current growing world consumption. Conservation is a must. I also agree whole-heartedly with the tenth point in Mr. Carter's plan: the need to develop unconventional sources of energy. I consider oil shale such an unconventional source. Keep in mind that the recoverable oil in the oil shale deposits of Colorado, Utah and Wyoming is estimated at 600 billion barrels. This exceeds the known natural crude oil reserves of the entire world. It is a resource we cannot allow our government to overlook.

To accomplish this, we must start working together on the next two logical steps in commercialization of oil shale.

First, we must proceed with a series of crude shale oil refinery runs. These have been initiated by the Navy with a recent request for proposals to run up to 100,000 barrels of Paraho crude shale oil.

Second, a development planned by many of us, is the construction and operation of full-size retorting modules of both the above ground and in situ type.

Concurrently with these steps, we should make every effort to correct the present unrealistic environmental standards. Where the terrain itself, bare ground, fails to meet environmental standards, to construct commercial plants would be ludicrous. We also must try to obtain more investor confidence if we are to keep shale oil production in the hands of private enterprise, not government. The key to gaining such investor confidence is successful refinery runs and successful full-size module operations, all properly publicized. And, given success with both, we may be able to make a case for lowering environmental standards to a more realistic level.
Abstract

The physical availability of the water needed for the development of oil shale resources in Western Colorado has been extensively studied during the past few years, both by government and industry researchers. Relatively little attention, however, has been given to recent changes and developments in the law and their impact upon the legal availability of this water. This paper discusses some of the more significant recent developments as they affect the oil shale development.

The most significant developments have been in Federal Law. The Federal Water Pollution Control Act Amendments of 1972; the National Environmental Policy Act; the Safe Drinking Water Act; the Colorado River Basin Salinity Control Act; the Colorado River Basin Project Act and Minute 242 of the International Boundary and Water Commission have all applied significant new constraints on the use of the Colorado River for supplying water to, and receiving waste water from, the oil shale region.

Developments within Colorado have also had a significant impact. The passage of Senate Bill 213, concerning the pumping of non-tributary water, the changed adjudication and administration procedures, under the Water Right Determination and Administration Act of 1969, and key court decisions may be expected to exert great influences. Key among those court decisions are those regarding the adjudication of federal reserved rights in Colorado. One highly significant development in Colorado may be the minimum streamflow appropriations under Senate Bill 97.

Finally, political developments, based upon relatively recent legislation, may be expected to influence the availability of water for oil shale. Designation of the Eagle's Nest Wilderness Area under the Wilderness Act has recently served as a non-water forum for those opposed to water development plans of the City of Denver. Similar pressures may be expected in the oil shale region, as may pressures based on the Wild and Scenic Rivers Act, particularly in the White River Basin. Environmental challenges to the design of the West Divide Project also provides an important case in point for study by oil shale developers.

The oil shale developer should be familiar with all of these developments and their possible impacts upon the legal availability of water for oil shale.

Introduction

The fact that development of the oil shale resources of western Colorado will require vast quantities of water is not news. Nor is the fact that these vast quantities are not readily available. This subject has been written about and discussed at great length, particularly at previous meetings of the School of Mines Oil Shale Symposium.

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1See Appendix A for all footnotes in this paper.
Several excellent analyses of the physical supply side of the problem have appeared in recent years, and several development companies have undertaken ambitious and imaginative programs to secure a supply of this precious commodity.

So much has been written and said about water for oil shale development, in fact, that a previous contributor to the Symposium suggested that the subject be omitted from the program in future meetings, a suggestion that obviously has not borne much fruit.

We do not propose to plow this ground again, nor do we presume to add another rehash to the already voluminous literature. Our purpose in this Symposium is to offer an update of the legal fraternity's impact on the subject, hoping to draw together for the Symposium's consideration some developments of the past few years which have heaped complexity upon complexity in the legal search for adequate supplies of water for development of oil shale. Understanding these developments, we hope, will lead to a better understanding between the technical departments and the legal departments, and will result, ultimately, in making the lawyer's task an easier one.

The developments, like the problem itself, are both federal and state concerns. The water lawyer cannot approach the problem without considering both sides. Because of the multi-state impacts of development, the federal government's environmental concerns and the heavy involvement of federal lands and finances, a large body of federal law affects the directions the use of water will take. But because water is a state resource (at least for the time being), and state law governs distribution of water, the states also help to determine the direction of this development. And because, as is so often the case, each state's system of distribution is different from the others, some degree of specialization or emphasis is needed. Since the major oil shale deposits, and the Symposium, are found in Colorado, it is appropriate here to focus on Colorado's laws.

Recent Federal Developments

It once could be said that the most significant impact on western Colorado water use was the "law of the river". This unique body of specialized statutes, compact, treaties and judicial decisions was viewed as the main interstate determinant of the use of Colorado River water. More recently, however, two new influences are being felt: federal claims, including the claims of the Indian tribes, and water pollution controls.

The long-awaited quantification of federal and Indian water claims in Colorado is now underway. Filings during three recent months (Dec. 1976-Feb. 1977) in just one of the Colorado River sub-basins in Colorado demonstrate the seriousness of these claims. Essentially, the entire San Juan River basin has been claimed, and the claimed priority dates are sufficiently senior to most projected private projects to create a real problem.

Committing all or most of the water of the San Juan River basin to uses other than energy development does not, of course, directly affect the physical supply of water for oil shale development; the oil shale is in the White River and Colorado River mainstem basins. But the law of the river apportions all of the water of the basin, and withdrawals from the San Juan are charged against Colorado's share just as surely as are withdrawals from the mainstem or the White.

Sidestepping the question of whether federal reserved rights may exist in Colorado at all, and assuming that such rights may be asserted and will be affirmed by the courts, the reserved right doctrine might prove to be beneficial to oil shale development. Large areas of oil shale deposits are located within the naval oil reserves, on federally-owned land, administered by the Bureau of Land Management. At least two developers have already attempted to assert claims based upon the federal reserved rights doctrine, as lessees of federal tracts in Colorado.
Whichever direction the federal reserved rights litigation takes, it will certainly be lengthy. Ultimate resolution will certainly come from the Supreme Court, unless Congress intervenes. There is no reason to assume early development of these reserved rights once decreed, but rather we should expect the final word on the shape and size of these rights to be coming many years down the road. The important question, then, is whether anyone can afford to let these claims cloud development of Colorado River waters during this period. Without advocating any particular approach, it does seem that the country can ill-afford to let development of oil shale remain in limbo during this period. Congress can act to remove this obstacle; the question is whether it will do so.

The more serious problem in the short term, and from a technical viewpoint, is water quality. In the past five years, all branches of the federal government have taken firm stands for improving the quality of the country's rivers and ground water. Both the Colorado River and oil shale development present significant and unique water quality problems, chiefly salinity. The Federal Water Pollution Control Act Amendments of 1972, Public Law 92-500, contains a flat prohibition against discharging any pollutant into any water anywhere in the United States, unless a permit is first obtained from the federal or state government. Specific standards have been, or will be, set for various pollutants, including salinity (total dissolved solids), and for various activities. Mining and processing of oil shale are covered, as are the expected associated municipal and domestic developments. Unless a technology can be developed which will enable oil shale development to dispose of all saline waters that might be expected to result from development on the site, with no discharge to the streams, developers of oil shale are going to have to deal with P. L. 92-500. Underground disposal by well injection is no answer either, because of the Safe Drinking Water Act. Colorado River salinity has become something of a cause celebre, particularly on the federal level. Totally apart from the significant financial loss experienced in the lower basin, and the mandates of P. L. 92-500, salinity is now an international concern, and has become the subject of a federal program all by itself. The Colorado River Water Quality Improvement Program provides for both the control of several notorious point and diffuse sources of salinity in the Upper Basin and the desalting of return flows from the Wellton-Mohawk Valley Project in Arizona. The CRWQIP is significant for the development of oil shale through the demand for federal funding and the requirements of NEPA.

Of course, federal funding demands entail a whole body of legal restrictions in any sphere, not just where water or energy is involved. NEPA, the National Environmental Policy Act of 1969, has already been mentioned, and is certainly already familiar to this Symposium. The context in which NEPA is particularly significant here is in the Council on Environmental Quality's demand that NEPA impact statements clearly spell out the impact of a project on other federal projects, whether directly related or not. Clearly, any federally-funded water project for oil shale development will have to deal with the downstream effects of Colorado River salinity, and the effects on the CRWQIP. The broad range of NEPA impacts upon oil shale development, is beyond the scope of this paper, and is treated elsewhere in these Proceedings.

Federal funding for water for oil shale development involves a large body of federal law, even in addition to the law of the river. As mentioned earlier, the law of the river has a great impact upon the availability of Federal funds for water projects. In particular, the Colorado River Basin Projects Act has a tremendous potential impact. The Upper Basin states’
**quid pro quo** for supporting the Central Arizona Project was section 501 of the act, which purports to require work on certain Upper Basin projects to proceed at the same time, and at the same pace, as the CAP. Among the Upper Basin projects expressly authorized and mentioned in the act is the West Divide Project, somewhat related to oil shale development.

So far, at least, section 501 has not impeded the progress of the CAP while West Divide is being held up. Whether the Upper Basin states will take any action to bring about the parity the act seems to demand, and what form that action might take, are both unknown.

Those already familiar with federal water development are familiar with the Bureau of Reclamation and the Corps of Engineers. And, of course, those who read the papers are familiar with the current furor over the new administration's reassessment of many western water projects. Forecasting political winds is beyond the scope of this paper, and the expertise of its authors. One conclusion does seem to be clear: the reclamation laws and water resources laws that have been on the books for many years are going to get more than the lip service and passing interest given to them in the review of existing projects. It is conceivable at least that legal challenges to projects, based upon their whole costs and benefits, will become a central part of future taxpayer action, rather than continue to be the handmaiden or make-weight to NEPA challenges.

Whether adequate authority exists for Bureau of Reclamation construction of water projects for oil shale development is another question to be answered separately, economic and political factors aside. So far, at least, the Bureau and its clientele have not admitted to going into the "water-for-energy" business except as a sideline to its irrigation of arid lands function, so the courts haven't had the opportunity to rule on the question. It does merit further study, however, from an impartial quarter.

**Recent Colorado Developments**

Those returning to this Symposium after having attended earlier meetings are familiar with the basic tenets of water law in the western states. For those who find the field "arcane and often baffling," as does the Denver Post, several excellent articles and books are available. For the purposes of this paper, only three simple ideas need be kept in mind:

1. Water is a publicly-owned resource, subject to state laws of distribution and use.

2. In Colorado, the water of every natural stream is available for appropriation and use by private individuals, and that right of appropriation may never be denied.

3. In times of scarcity, priority of right (seniority) governs distribution among the several water users from the same source.

Unfortunately, or perhaps fortunately, depending on whether one is a water lawyer or not, these three principles only raise a multitude of questions, and answer few. The key recent Colorado developments discussed here, however, raise fairly basic questions related to the three principles, and an extensive knowledge of water law is not absolutely essential to an understanding of the difficulties.

It was mentioned earlier that federal and Indian reserved rights claims are a significant threat today, and that their quantification is seemingly underway. Recent decisions have established that the quantification process can proceed in state courts, at least in Colorado. But it is not at all clear that the entire set of rules established by Colorado law are going to be applied, and so the oil shale developer may be playing in a game where some of the players, at least, are using a different set of rules.

For those of us less fortunate than Uncle Sam, the Water Right Determination and Administration Act of 1969 will control our securing the right to use water out of
natural streams. The most fundamental changes wrought by that act have tremendous impact upon the oil shale developer's securing a supply of water.

Under earlier statutes, adjudication of water rights was a very sometimes thing. Adjudications were held only when someone or another got fed up enough to bother to go to the court and start the action. There was, in fact, considerable incentive for not doing so, for the petitioner was generally obligated to pay the costs of notifying everyone else on the stream that an adjudication was underway. Generally the only incentive to commencing an adjudication was the fear that if it weren't done sooner or later valuable evidence would be lost, and valuable seniority lost with it.

Since Colorado long has had a rule that the seniority or priority of a water right is measured by the date the appropriation was commenced, subject only to previously adjudicated rights, there was an incentive to enter an adjudication proceeding once someone else began it. But there was no incentive beyond that mentioned earlier for beginning one. Under the 1969 Act, however, that is no longer true. Now the date of appropriation still governs seniority, subject to earlier adjudicated rights, but each calendar year is taken to be a separate previous adjudication. A water user concerned about his seniority, as all should be, dares wait no longer than the next December 31 to file his claim after commencing his appropriation. The resulting need for prompt completion of plans is great.

An area of great uncertainty under the 1969 Act is the question of standing, or who is allowed to challenge a claim in the adjudicating court. Under the previous statutes, only those capable of showing injury to their own water rights were permitted to object, a provision that essentially meant that a water user merely seeking to retain a recent date against the challenges of those who might come along later was free from challenge. Some very large and ambitious projects received decrees under this provision, decrees which have since proved to be invaluable.

But no longer. The 1969 Act says that "any person" can object to the awarding of a decree, and "person" is defined extremely broadly. So far the Colorado Supreme Court has indicated only that someone totally uninterested, perhaps from New York or some other distant point, might be barred under the act, but nothing more. Where the line may ultimately be drawn is anyone's guess.

A third feature of the 1969 Act bears discussion here. It is by no means the only remaining interesting problem raised by the act, but since volumes could be written about the act a halt must be called somewhere. This provision is the one calling for tabulation of existing rights on basin-wide priority lists, an administrative tool that has heretofore been handled somewhat haphazardly by the Division Engineers. Two distinct problems are raised by this part of the act:

First, the amalgamation of the priorities into division-wide lists may be expected to generate nearly endless confirmatory litigation. Each water user can be expected to argue for the highest possible place on the list for his rights, on any basis he can find. This, of course, means that all the other water users will have to take care that their rights are not passed up in the process. If this part of the act hasn't yet been criticized as a "lawyer's full employment act", it probably should be.

Second, and probably more important, the tabulation provisions require the identification of all abandoned water rights, and ten years nonuse is considered prima facie evidence of abandonment. The final impact of this provision upon water matters, and even the law of the river, can only be speculated on.

Colorado, unlike most western states, has left the determination of water rights entirely in the hands of the court system. This vestige of the old frontier spirit has also kept Colorado from adopting any for-
feiture laws, so prevalent in the west. As a result, up to now, the only thing preventing someone from resurrecting a long-abandoned water right, or enlarging upon the historic use of a largely-unused right, was the threat of a private lawsuit by a neighboring water user. Imagine the scramble when all the owners of partially or totally unused water rights come into court to justify lack of use on pain of being wiped off the books! Another lawyers full employment act? Perhaps.

The significance of the abandonment tabulation provision for the oil shale developer is this: existing rights, whether originally appropriated for oil shale purposes or bought and transferred to oil shale purposes, cannot be kept "in the bank," so to speak; they must be used or lost.

Whether the courts will adopt strict or lenient standards to judge abandonment is unknown. Some comfort, perhaps, may be taken from the lenient standards used to judge diligent completion of conditional appropriations. Perhaps not, for the parallel is not complete, and there are signs that the diligence standard is becoming stricter.

So much for the first principle. As to the second, the undeniable right to appropriate water, two significant problems bear discussing: what water is open to appropriation, and how undeniable is undeniable? At present, these are problems mainly for the ground water community.

Colorado law has never really defined the term "natural streams". Where surface waters are concerned, it is not too difficult to tell the difference between natural streams and everything else, although one pending case may even call that statement into question. Similarly, insofar as some ground waters are concerned, the distinction is fairly easily made. Obviously, water pumped from the stream alluvium is directly connected to the natural stream and, if rationality is to prevail, must be considered part of a natural stream. But what about an underground stream that actually flows, and always has, but has no apparent hydraulic connection to a surface natural stream; does that qualify? And what about a long-range connection, with the impact felt only 100 years later, or more, or a connection only in the sense that water to recharge the aquifer was once surface water on its way to a stream? The answers have not yet been given.

A great part of the problem itself comes from Colorado water law. Technically-minded people rightly think of water as just one thing, one category: water. Maybe there are two categories: surface water and ground water. Colorado, however, has at least four: surface water, tributary ground water, non-tributary ground water, and "designated" ground water. At present, the law treats them all differently.

Because the oil shale country of Western Colorado contains large ground water supplies, supplies that appear to be in large part non-tributary, this category merits discussion. The discussion has to be somewhat truncated, however, because nobody is really sure what legal rules apply.

A fifteen-year old case, Whitten v. Coit, established that under the old laws non-tributary ground water was not subject to appropriation, adjudication and administration like surface water. But that case did not say what rules do apply. If the right fact situation had presented itself, the court could have chosen a modified appropriation system, the common law rules, or some kind of correlative rights doctrine. Shortly thereafter, the General Assembly expanded the state's involvement, but it was still unclear what rules applied to non-tributary ground water.

Whitten v. Coit and the 1965 ground water statutes did not stop owners of non-tributary wells from having their wells adjudicated; under the 1969 Act the practice has grown greatly. The rationale is simply that if one can obtain a decree from the proper water court, saying that one's water is not subject to the act, one has
some assurance that the Division Engineer\textsuperscript{118} is not going to be able to shut down the well,\textsuperscript{119} at least not now. Unfortunately, however, since the law doesn't deal specifically with this water, as yet, such a decree may offer no protection or assurances against future interference.

The General Assembly did make an attempt, of sorts, to deal with this type of water in 1973, in what is generally known as Senate Bill 213.\textsuperscript{120} Having created "designated" ground water in 1965,\textsuperscript{121} and having at the same time given the State Engineer the power to deny the privilege of drilling any well if doing so would interfere with someone else's \textit{bona fide} appropriation of water,\textsuperscript{122} the legislature in S.B. 213 sought to bring the last remaining water supply in Colorado, non-tributary ground water, under control. It is still an open question whether it succeeded or not.

S.B. 213 simply provides that in ruling on an application for a non-tributary well, the State Engineer shall consider the water under the well owner's own land as unappropriated and shall consider the life of the aquifer to be 100 years.\textsuperscript{123} Does that provision conclusively establish the appropriation doctrine for this water?\textsuperscript{124} Does it allow the withdrawal of only 1 percent of the water per year? Does it prohibit withdrawal of a neighbor's water? Does it affect the Water Courts' jurisdiction or powers in any way?\textsuperscript{125} These questions have yet to be answered.

The upshot of all this is that the oil shale developer (or anyone else for that matter) when dealing with ground water that is apparently non-tributary, is operating somewhat in the dark and at some risk. The risk is not great, to be sure, but it exists, and the time for the right test case to appear is ripe.

In fact, the issue of whether a given aquifer is tributary or non-tributary is an extremely difficult one to settle. Colorado law presumes that all water in the state is tributary to a natural stream;\textsuperscript{126} any one claiming his source is non-tributary must demonstrate that fact to the court by a preponderance of the evidence. This applies to both surface and ground water.\textsuperscript{127} One result is that the claimant must bear the burden of overcoming not only the legal presumption, but also the weaknesses of the science of ground water hydrology and the pitiful lack of hard data.\textsuperscript{128} Unless the claimant overcomes these burdens, his appropriation will be subject to administration by the Division Engineer, in accordance with the priority system.\textsuperscript{129} If ground water is involved, priority administration becomes exceedingly difficult, and it often occurs that wells are regulated as a class, without discriminating among them by their actual priorities.\textsuperscript{130} As water use in the Colorado River basin in Colorado becomes more intensive, regulatory pressures leading to significant restrictions on the use of ground water should be expected.\textsuperscript{131}

It is worth noting, parenthetically, that the law of the river is not clear where ground water is concerned.\textsuperscript{132} Some view the use of ground water as the salvation for the Upper Basin states from the inequities\textsuperscript{133} of the 1922 compact,\textsuperscript{134} maintaining that the compact does not limit ground water use.\textsuperscript{135} While this may be true in the literal sense, consumption of tributary ground water which diminishes the flow of the river to the Lower Basin would certainly be governed by the compact,\textsuperscript{136} although the problem of apportioning that use among the Upper Basin states still remains an open question.\textsuperscript{137}

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Just to further confuse the picture, consider the priority of the federal and Indian reserved rights claims. The previous adjudication doctrine, referred to earlier, apparently does not apply to these claims, although Colorado water users defending against these claims have certainly not conceded this point. The situation derives from the fact that the United States was not involved in adjudications until very recently, at least insofar as the reserved claims are involved. The argument is that since the government was not a party to these adjudications, the adverse effects of the adjudications cannot be applied against the government's rights.

The result then is that until these rights are deduced to definite quantities, and begin to be exercised to some extent, nobody knows how junior or senior his own rights may be, in relation to the amount of water actually physically present in the river. Rights that now appear to be quite senior and valuable may be wiped out in a short time.

The point that we hope to have made by this discussion is that water law is severely hampered by the infirmities of the sciences. The basic principles are simple, but new problems tend to present themselves faster than their solutions; new ideas and technologies for withdrawing water are generated and implemented long before the ideas and technologies needed to integrate them into the system. Thought and research and investment must be directed toward this integration now, while sufficient slack still exists, before the system becomes overloaded. We, like most water lawyers, are confident that it can be done, but we face tremendous
some assurance that the Division Engineer is not going to be able to shut down the well, at least not now. Unfortunately, however, since the law doesn't deal specifically with this water, as yet, such a decree may offer no protection or assurances against future interference.

The General Assembly did make an attempt, of sorts, to deal with this type of water in 1973, in what is generally known as Senate Bill 213. Having created "designated" ground water in 1965, and having at the same time given the State Engineer the power to deny the privilege of drilling any well if doing so would interfere with someone else's bona fide appropriation of water, the legislature in S.B. 213 sought to bring the last remaining water supply in Colorado, non-tributary ground water, under control. It is still an open question whether it succeeded or not.

S.B. 213 simply provides that in ruling on an application for a non-tributary well, the State Engineer shall consider the water under the well owner's own land as unappropriated and shall consider the life of the aquifer to be 100 years. Does that provision conclusively establish the appropriation doctrine for this water? Does it allow the withdrawal of only 1 percent of the water per year? Does it prohibit withdrawal of a neighbor's water? Does it affect the Water Courts' jurisdiction or powers in any way? These questions have yet to be answered.

The upshot of all this is that the oil shale developer (or anyone else for that matter) when dealing with ground water that is apparently non-tributary, is operating somewhat in the dark and at some risk. The risk is not great, to be sure, but it exists, and the time for the right test case to appear is ripe.

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The point that we hope to have made by this discussion is that water law is severely hampered by the infirmities of the sciences. The basic principles are simple, but new problems tend to present themselves faster than their solutions; new ideas and technologies for withdrawing water are generated and implemented long before the ideas and technologies needed to integrate them into the system. Thought and research and investment must be directed toward this integration now, while sufficient slack still exists, before the system becomes overloaded. We, like most water lawyers, are confident that it can be done, but we face tremendous
obstacles in obtaining rights to use the water generated by the new ideas and technologies as long as the information to support that investigation is not forthcoming.

Recent Political Developments

The final area of concern to those interested in securing water supplies for oil shale development in Western Colorado is political, an area that is really beyond our own expertise and, perhaps, beyond the scope of this Symposium. Nevertheless, a brief discussion of some recent developments seems appropriate, if only to aid in our understanding of those irrational forces that often shunt aside and negate rational processes. Two recent case histories adequately present the picture:

Long ago, the Denver Water Board\textsuperscript{178} adopted an energetic and far-reaching water acquisition policy. As early as the 1920s (and before) Denver began investigations of the upper tributaries of the Colorado River as potential sources of water for that city. Diversions began years ago through the Moffat, Roberts and Vasquez Tunnels. Opposition to Denver's plans was always strong, and time and again Denver overcame the opposition and forged ahead - without Federal aid, it should be noted - on the basis of Colorado water law.\textsuperscript{179}

Denver has recently, however, seemingly been tripped up. Not by anything in water law, not by anything related to federal funding, but by legislation that has nothing to do with water law: the Wilderness Act.\textsuperscript{180} Denver's planned expansion of its Roberts Tunnel/Dillon Reservoir system into the Eagle-Piney area has been thwarted, for the time being, by designation of the Eagle's Nest Wilderness Area, whose boundaries, as drawn, include the points at which Denver proposed to divert water. Denver has thus been forced to move its diversion points downstream, beyond the boundaries of the wilderness area. If Denver is to divert this water now, it must pump the water up to Dillon Reservoir, rather than rely on gravity to deliver the water. The resulting increases in construction and operating costs may do the project in altogether.\textsuperscript{181}

We neither applaud nor decry this development, but merely to point out that the same kind of thing can happen in oil shale country as well as in the headwaters area. Potential wilderness areas can be found where water for oil shale would come from.\textsuperscript{182} Wild and Scenic Rivers designation\textsuperscript{183} for portions of the White River basin\textsuperscript{184} has been proposed and is being studied.\textsuperscript{185} Other potential stretches have been proposed elsewhere in the Colorado River basin,\textsuperscript{186} and could also affect oil shale water development. Rare species of fauna and flora exist in oil shale country,\textsuperscript{187} and so the Endangered Species Act\textsuperscript{188} must be considered an obstacle to oil shale water development, just as it has become in other parts of the country.\textsuperscript{189} Other such potential obstacles surely exist; in time, resourceful and imaginative foes can be expected to discover and raise them.

The West Divide Project is an authorized water development project under the Colorado River Basin Project Act.\textsuperscript{190} It is one of the Upper Basin projects, supposed to proceed alongside the Central Arizona Project.\textsuperscript{191} Water rights have been acquired, and some fairly detailed planning completed.\textsuperscript{192} The West Divide Project would furnish some quantity of water for oil shale development in Western Colorado,\textsuperscript{193} if it is built.

That "if" looms large today. The residents of the area where the West Divide Project is proposed to be built, and their local governments,\textsuperscript{194} are having serious second thoughts about the whole idea, and it is suddenly doubtful that any variation of the project will ever be built, let alone the original project.\textsuperscript{195}

Conclusion

In this paper, we have tried to create an awareness of the kinds of hurdles faced by lawyers and engineers who are trying to secure firm and dependable supplies of water for the western Colorado oil shale industry. The need for water is great, the physical
availability restricted and even uncertain, and the legal and political obstacles complex and difficult. No single discipline can master the problems; rather, this is an area where the need for cooperation and interdisciplinary effort is most strongly felt. Above all, the scientist, the engineer, the technician, must understand the lawyer's role in securing a water supply, and must conduct investigations and research generating the hard information which the lawyer needs to do his end of the job. To that end, all those involved should be aware of developments in the law which point out the paths which must be followed.
EXPLOSION AND FIRE PROPERTIES OF OIL SHALE

J. K. Richmond and L. F. Miller
U.S. Department of the Interior
Bureau of Mines - Pittsburgh Mining and Safety Research Center
4800 Forbes Avenue
Pittsburgh, Pennsylvania 15213

Abstract
Because experience in the mining of oil shale is limited, the possible fire and explosion hazards of mining and processing have not been assessed in detail. The U.S. Bureau of Mines has recently conducted extensive dust explosion tests in its Experimental Mine. Using dust of a fineness comparable to pulverized coal dust, we found that dust explosions, initiated by natural gas-air explosions, would propagate through clouds of oil shale dust whose assay was equal to or greater than 25 gallons per ton (94 kg/tonne). Nominal explosive dust concentrations ranged from 0.2 to 0.6 ounce per cubic foot of air (0.2 - 0.6 gm/liter), depending on organic content. Explosions occurred when the nominal concentrations of volatiles exceeded 0.05 oz/ft³ (0.05 gm/liter). Rock dust, when premixed with the oil shale dust, was effective in suppressing explosions. Results of laboratory tests of spontaneous ignition of oil shale dust (the richer shales compare with coal dust) and a laboratory-scale fire test, in a gallery lined with oil shale bricks, are reported. After a considerable ignition period, flame propagated through the gallery in the presence of ventilating flow.

Introduction
Although oil shale has been mined and processed for many decades in this and other countries, such as Scotland and Estonia, there have been few accidents due to fires or explosions of the raw material. Most of the mining in this country has been by room-and-pillar method, using conventional explosives. At this date, operations are governed only by safety regulations for metal and non-metal mines, even though the raw material is combustible under certain conditions. Officials of the Mining Enforcement and Safety Administration (MESA) and Nagy and Grant (1976) have reviewed problems of permissibility (ignition hazards, etc.). These reviews discussed the explosive potential of oil shale dust, the fire hazards which might eventually occur as the oil shale mining industry grows, especially if methane is encountered, and also called for more data to define these hazards, so that safety standards can be developed in advance. Thus, disasters can be prevented and operators can predict the impact of safety standards on costs of operations.

In the Soviet Union, Bykov and Tereshchenko (1968), suggested wetting the shale dust with water to prevent dust explosions. They reported that the lower limit of their combustible shale dust was 6 g/m³, and that the dust is easily wetted by water sprays without addition of wetting agent.

The potential hazards of methane gas in oil shale mines were reviewed by Kissel (1975). Results indicated measurable amounts of methane, especially at considerable distances from the outcrops. This work continues.

Even before any commercial production
of shale oil was attempted, the U.S. Bureau of Mines (Allison and Bauer, 1926) evaluated the explosive potential of oil shale dust. Shale dust explosion tests were conducted in a laboratory steel dust gallery and in the Experimental Mine normally used to produce coal dust explosions. Dust samples from eastern and western United States and from Australia were tested, with assays given in some cases. The ignition source was usually a charge of black powder. In one test in the Experimental Mine, shale dust was distributed on the mine surfaces at a rate of 0.9 pound per linear foot (1340 gm/m) for about 300 feet (92 m) in each of the two entries. The flame was carried for at least 275 feet (84 m) in both entries. Explosion pressures developed were not reported. Allison and Bauer concluded that the oil shale dusts they tested are explosive and that explosiveness increases with combustible content; that some formation of dust in mining and handling is unavoidable; and that the same precautions against dust explosions should be taken in the oil shale industry as in the coal mining industry. It had been reported that dust produced in Scottish shale-mining operations was non-inflammable and non-explosive.

The Pittsburgh Technical Support Center of MESA (Kawenski 1974) conducted laboratory tests of explosive potential on five oil shale dust samples supplied by the Laramie Energy Research Center. These samples were taken from the Bureau of Mines' oil shale mine near Rifle, Colorado, from the Mahogany Ledge (zone) of the Green River Formation. The Fischer assay of the samples ranged from 14 to 65 gallons of oil per ton (53 - 244 kg/tonne). The raw material was pulverized so that all particles passed through a 200 mesh screen (74 micrometers). Kawenski did proximate and ultimate analyses and determined ignition temperature of dust clouds and dust layers, minimum ignition energy of dust clouds, minimum explosive concentration of dust clouds, and maximum pressure and rate of rise of pressure developed in a closed bomb. This report also concluded that oil shale dust is explosive, with its explosive potential increasing with organic content. The calculated, empirical Index of Explosibility is less than 0.1, compared with 1.0 for Pittsburgh seam coal dust.

The above is not intended to be a complete review of information to date on the fire and explosive properties of oil shale, but is representative enough to indicate the lack of quantitative data available, especially in respect to large-scale phenomena. The following is a progress report on recent research done on this subject at the U.S. Bureau of Mines.

Recent Research on Fire and Explosive Properties of Oil Shale

Source and Preparation of Dust Samples - All of the material used in tests described hereafter came from the Anvil Points Mine near Rifle, Colorado, now owned by the Energy Research and Development Administration (ERDA). The mine was operated under contract by the Cleveland-Cliffs Iron Co., and the material was mined and initially sorted by representatives of the above organizations. The oil shale was mined from the Mahogany Zone of the Green River deposit. Coarse material from the mine was crushed to 3/4 inch x 0 (1.9 cm x 0) size and assayed by the Laramie Energy Research Center, ERDA. The material was then pulverized by the Donaldson Co., Majac Division, Tulsa, Oklahoma* to approximate the size of pulverized coal dust, where about 80 percent by weight will pass through a 200 mesh screen. Two tons (1818 kg) each of four different grades were obtained in this manner. Intermediate grades were obtained by mixing. Samples of the pulverized dust were sent again to Laramie, where it was determined that the pulverizing did not change the assay (table 1a).

Some samples were also picked up from the Experimental Mine after an explosion

*Manufacturer's name for reference only, does not imply approval or disapproval by the Bureau of Mines.
Table 1a. - Raw and pulverized oil shale - assay and size distribution.

<table>
<thead>
<tr>
<th>Lot No.</th>
<th>Assay RP5 kg/T</th>
<th>Weight % Gas + Oil Loss</th>
<th>Size Distribution % Passing</th>
</tr>
</thead>
<tbody>
<tr>
<td>500T Test Batch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. 3/4&quot; x 0</td>
<td>46.0 173</td>
<td>17.6</td>
<td>4.4</td>
</tr>
<tr>
<td>(1.9cm x 0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b. Pulverized</td>
<td>46.0 173</td>
<td>17.6</td>
<td>4.5</td>
</tr>
<tr>
<td>MAJAC 5082</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. 3/4&quot; x 0</td>
<td>19.8 74</td>
<td>7.5</td>
<td>1.8</td>
</tr>
<tr>
<td>(1.9cm x 0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b. Pulverized</td>
<td>18.7 70</td>
<td>7.1</td>
<td>1.8</td>
</tr>
<tr>
<td>MAJAC 5083</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>a. 3/4&quot; x 0</td>
<td>24.5 92</td>
<td>9.3</td>
<td>2.4</td>
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<tr>
<td>(1.9cm x 0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b. Pulverized</td>
<td>26.52 98</td>
<td>9.9</td>
<td>2.5</td>
</tr>
<tr>
<td>MAJAC 5084</td>
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<td></td>
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<tr>
<td>a. 3/4&quot; x 0</td>
<td>50.7 190</td>
<td>19.3</td>
<td>4.3</td>
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<tr>
<td>(1.9cm x 0)</td>
<td></td>
<td></td>
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<tr>
<td>b. Pulverized</td>
<td>50.5 189</td>
<td>19.1</td>
<td>4.6</td>
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<tr>
<td>MAJAC 5154</td>
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</tr>
<tr>
<td>a. 3/4&quot; x 0</td>
<td>40.0 152</td>
<td>15.2</td>
<td>3.6</td>
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<tr>
<td>(1.9cm x 0)</td>
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<td></td>
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</tr>
<tr>
<td>b. Pulverized</td>
<td>42.3 159</td>
<td>16.0</td>
<td>5.7</td>
</tr>
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</table>

*Net microslice, with ultrasonic shaking.

test, to try to determine what happened to the mineral matter as well as to the organic matter during an explosion. Samples of dust were scraped from the ribs of the Anvil Points Mine, and other samples were taken from the crusher area; all of these were classified by screens and assayed by classification (Table 1b). Analyses of oil shale/rock dust mixtures are listed in table 1c.

Late in 1976, mining was resumed in the Anvil Points Mine, and a large (9 lbs - 4 kg) sample of dust was taken from surfaces near the mining operation. This dust was classified into 6 samples, and each sample assayed, with the results shown in table 1d and in figure 1a. In this case, the trend of increasing richness with increasing particle size is clear.

A graph of the average correlation between Fischer assay (in gallons per ton) and weight percent total organic, oil, organic gas, and carbonaceous residue is shown in figure 1b. The information for this graph was obtained, partly by interpolation, from Stanfield and others (1951), and is consistent with the data in table 1a.

In the past, some workers have analyzed oil shale samples, using the standard ASTM proximate analysis intended for coal, where-in the temperature is maintained at 900°C for some time to drive off the volatiles.

Table 1b. - Mine site dust size and assay evaluation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size Range</th>
<th>Assay pet kg/T</th>
<th>Oil + Gas wt % Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mine dust</td>
<td>+500μm</td>
<td>21.5</td>
<td>81</td>
</tr>
<tr>
<td>-500μm/+74μm</td>
<td>20.9</td>
<td>78</td>
<td>7.9</td>
</tr>
<tr>
<td>-74μm</td>
<td>14.5</td>
<td>54</td>
<td>5.5</td>
</tr>
<tr>
<td>Grinding House area</td>
<td>-500μm/+250μm</td>
<td>25.8</td>
<td>97</td>
</tr>
<tr>
<td>-250μm/+105μm</td>
<td>25.4</td>
<td>95</td>
<td>9.6</td>
</tr>
<tr>
<td>-105μm/+74μm</td>
<td>19.5</td>
<td>73</td>
<td>7.4</td>
</tr>
<tr>
<td>-74μm/+44μm</td>
<td>20.5</td>
<td>77</td>
<td>7.7</td>
</tr>
<tr>
<td>-44μm</td>
<td>17.5</td>
<td>66</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Table 1c. - Oil shale/rock dust mixture assays.

<table>
<thead>
<tr>
<th>Mine Shot No.</th>
<th>Stock Oil Shale Assay pet kg/T</th>
<th>5 R.D. Added</th>
<th>Desired Assay pet kg/T</th>
<th>Actual Assay pet</th>
<th>Oil + Gas wt % Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>EM5710</td>
<td>50.5</td>
<td>189</td>
<td>62</td>
<td>19.5</td>
<td>73</td>
</tr>
<tr>
<td>EM5711</td>
<td>50.5</td>
<td>189</td>
<td>43</td>
<td>29.5</td>
<td>111</td>
</tr>
<tr>
<td>EM5712</td>
<td>42.4</td>
<td>159</td>
<td>14</td>
<td>36.3</td>
<td>136</td>
</tr>
<tr>
<td>EM5713</td>
<td>42.4</td>
<td>159</td>
<td>51</td>
<td>25.3</td>
<td>119</td>
</tr>
<tr>
<td>EM5714</td>
<td>42.4</td>
<td>159</td>
<td>43</td>
<td>25.0</td>
<td>94</td>
</tr>
<tr>
<td>EM5715</td>
<td>42.4</td>
<td>159</td>
<td>43</td>
<td>25.0</td>
<td>94</td>
</tr>
</tbody>
</table>

Table 1d. - Analysis of samples taken from Anvil Points Mine during active mining.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Size Range Micrometers</th>
<th>Pct of Total Sample</th>
<th>Assay pet kg/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+500μm</td>
<td>21</td>
<td>31.5</td>
</tr>
<tr>
<td>2</td>
<td>-500μm/+250μm</td>
<td>7</td>
<td>30.1</td>
</tr>
<tr>
<td>3</td>
<td>-250μm/+105μm</td>
<td>15</td>
<td>28.0</td>
</tr>
<tr>
<td>4</td>
<td>-105μm/+74μm</td>
<td>6</td>
<td>26.2</td>
</tr>
<tr>
<td>5</td>
<td>-74μm/+44μm</td>
<td>14</td>
<td>21.4</td>
</tr>
<tr>
<td>6</td>
<td>-44μm</td>
<td>37</td>
<td>10.8</td>
</tr>
</tbody>
</table>

It appears to us that this test is entirely inappropriate for oil shale, because a considerable portion of the dolomite is also decomposed at 900°C; results would be misleading. So, in this paper, reference is made only to the modified Fischer assay designed for oil shale at the Laramie Energy Research Center (Stanfield and Frost 1949). In this analysis, maximum temperature is 500°C.

Tests in the Experimental Mine - All dust explosion tests described below were performed in the Main Entry of the Experimental Mine of the U.S. Bureau of Mines at Bruceton, Pa. (see map, fig. 2).

This entry is essentially a concrete tunnel in the Pittsburgh coal seam, about 1300 feet (397 m) long, with average height of about 6 feet (1.8 m), and average width of about 9 feet (2.8 m), closed at one end,
Figure 1a. - Oil shale dust from active mine.

Figure 1b. - Fischer assay of oil shale from Mahogany Ledge (Zone), Green River Formation.

Figure 2. - Map of experimental mine.
and open to the atmosphere at the other, almost horizontal. Dust explosions are normally initiated by the explosion of a mixture of natural gas and air confined at the closed end by a plastic diaphragm. Dust mixtures are distributed toward the entry from the initiation zone on the floor, on shelves along the walls, and on transverse shelves near the roof. The intensity of the gas explosion is adjusted so it will disperse and ignite dust in its vicinity. A propagating dust explosion is defined as one which will propagate flame past the end of the initial dust test zone, while maintaining flame speed and pressure. A marginal explosion is defined as one which will propagate flame to the end of the dust test zone, while the accompanying flame speed and pressure are decaying continuously. It is assumed in the latter case, that, had the test zone been longer, such an explosion would have been labeled non-propagating. A non-propagating explosion is therefore defined as one in which the flame does not reach the end of the test zone, regardless of flame speed and pressure. Nominal dust concentration is defined as the total weight of dust deposited in the test zone, divided by the volume of air included in the same zone.

The entry is instrumented for half its length with pressure transducers and phototransistors in the wall, and with probes to measure dynamic pressure and dust concentration during explosions. The pressure transducers measure static pressure, and the phototransistors measure flame radiation and time of arrival of leading edge of flame, from which flame speeds can be calculated. From many tests in the single entry, it has been found (Richmond and Liebman 1974) that the static pressure rise is proportional to flame speed for steady or accelerating flames. From dynamic pressure data, air velocities in advance of flame may be calculated. Dust concentration probes are optical devices which can measure local concentrations of dust as a function of time. The effect of change of air density due to pressure rise is accounted for by an adiabatic pressure correction, and the instantaneous mass ratio of dust to air is calculated.

Occasionally, during the testing, a high-speed movie camera was placed in the entry, looking at the face, to record the progress of the dust explosions. Movies of these oil shale dust explosions (in color) are indistinguishable from ones taken of coal dust explosions.

Signals from instruments in the Experimental Mine are transmitted through long, shielded cables to a control room on the surface, where they are recorded redundantly by analog light-beam oscillographs and by a process control computer. The latter machine digitizes the data in real time, processes the data, and plots the data in suitable units shortly afterwards. The effective bandwidth of the oscillograph galvanometers is about 600 hertz, and that of the computer (which can scan 60 channels of data every 2 milliseconds) is about 250 hertz.

Results of Dust Explosion Tests and Discussion - The results of 17 oil shale dust explosion tests in the Experimental Mine are listed in tables 2 and 3, using material collected and prepared as described previously. All assays were carefully verified, and nominal concentration and propagation were defined in the previous section. The volatile material is defined as oil plus gas, obtained from figure 1. It is tentatively assumed that the carbonaceous residue, being of low volatility, does not contribute to the propagation of explosion. This assumption is similar to that verified with regard to coal dust explosions (Richmond and others 1975a). The incombustible in these tables is defined as the inorganic component of the oil shale. The carbonaceous residue (which is only a few percent of the total) is actually combustible, but is assumed to burn so slowly that it does not contribute to the propagation of explosion. These assumptions will be further discussed later. Table 3 lists
Table 2. - Explosibility tests with oil shale dust.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Ignition Source</th>
<th>Oil Shale Dust Test Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length of Zone, % ft meters</td>
<td>Length of Zone, ft meters</td>
</tr>
<tr>
<td>3651</td>
<td>7 15 4.6</td>
<td>300 92 46 173 20 74</td>
</tr>
<tr>
<td>3652</td>
<td>7 15 4.6</td>
<td>180 55 46 173 20 74</td>
</tr>
<tr>
<td>3693</td>
<td>7 15 4.6</td>
<td>300 92 25 94 11 86</td>
</tr>
<tr>
<td>3700</td>
<td>7 30 9.2</td>
<td>300 92 25 94 11 86</td>
</tr>
<tr>
<td>3701</td>
<td>9 30 9.2</td>
<td>300 92 50 188 22 71</td>
</tr>
<tr>
<td>3702</td>
<td>7 20 6.1</td>
<td>300 92 34 128 15 81</td>
</tr>
<tr>
<td>3706</td>
<td>7 15 4.6</td>
<td>300 92 34 128 15 81</td>
</tr>
<tr>
<td>3707</td>
<td>7 20 6.1</td>
<td>300 92 50 188 22 71</td>
</tr>
<tr>
<td>3708</td>
<td>7 30 9.2</td>
<td>300 92 19 71 8 89</td>
</tr>
<tr>
<td>3709</td>
<td>9 30 9.2</td>
<td>300 92 19 71 8 89</td>
</tr>
</tbody>
</table>

Table 3. - Explosibility tests with oil shale dust-rock dust mixtures.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Ignition Source</th>
<th>Dust Test Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>3710</td>
<td>9 30 9.2</td>
<td>300 92 62 19 71 83</td>
</tr>
<tr>
<td>3711</td>
<td>7 30 9.2</td>
<td>300 92 41 30 113 13</td>
</tr>
<tr>
<td>3712</td>
<td>7 20 6.1</td>
<td>300 92 14 36 135 16</td>
</tr>
<tr>
<td>3713</td>
<td>7 30 9.2</td>
<td>300 92 31 29 109 13</td>
</tr>
<tr>
<td>3714</td>
<td>7 30 9.2</td>
<td>300 92 43 24 90 11</td>
</tr>
<tr>
<td>3715</td>
<td>9 30 9.2</td>
<td>300 92 43 24 90 11</td>
</tr>
</tbody>
</table>

the results of six tests in which some of the richer oil shale dusts were inhibited by mixing with ordinary rock dust, whose particle size distribution is similar to that of the oil shale dust.

Significant results listed in tables 2 and 3 are described graphically in figures 3 and 4, as limits of explosibility of the oil shale dust tested. Figure 3 is plotted in a manner similar to that used in R.I. 8077 (Richmond and others, 1975a), and in a subsequent paper (Richmond and others, 1975b) for coal dust, where nominal dust concentration for propagation or non-propagation is a function of incombustible content. In the case of the coal dust data, the incombustible content was changed by adding rock dust, and each rank of coal has a unique function.

Figure 3 shows that the concentration limit: for rock dust mixed with oil shale are slightly higher than those for pure oil shale, indicating the rock dust is slightly more effective in inhibiting explosions that is the inorganic matter in the oil shale.

At this point, we assume that this effect is due to the fact that the mineral matter of oil shale is only about one half carbonates, which have a higher heat capacity (including decomposition) than do the other components. The rock dust is almost entirely calcium carbonate. It was not possible in these tests to obtain explosions with
incombustible content greater than 86 percent (or less than 25 gallons per ton (94 kg/tonne)). Also shown, for comparison, on figure 3 is the explosibility limit curve for Pittsburgh pulverized coal dust/rock dust mixtures, taken from Richmond and others (1975a,b). It will be seen immediately that the oil shale dust will propagate explosions at much greater incombustible content than will the coal dust/rock dust mixtures. Of course, the rest of the data for coal dust shows that pure coal dust has a much lower explosion limit than any obtainable oil shale material. A tentative explanation for the explosive behavior of oil shale dust is that the kerogen pyrolyzes at a considerably lower temperature than does the coal, and, possibly, the pyrolysis products contain more hydrogen.

Some of the points discussed in the previous paragraphs can be seen better in figure 4, where the nominal concentration of volatiles is plotted as a function of incombustible matter (volatiles were defined above). It will be seen here that the minimum concentration of volatiles for propagation is almost independent of incombustible over the explosive range tested. Volatiles appear to be the normalizing factor. The critical concentration shown, 0.05 oz/ft³ (or 50 mg/liter) happen to be about the lean explosive limit for most hydrocarbons. The agreement may be only fortuitous; the actual amount of volatiles being pyrolyzed during the explosion is unknown but may be assumed to be proportional to the value obtained by assay.
The trend in the data for the rock dust mixture is less clear. Also shown on figure 4 are the data for Pittsburgh coal dust/rock mixtures, which have an upper limit of 70-75 percent incombustible. The lean limit of volatiles for Pittsburgh coal is around 0.03 oz/ft$^3$ (30 mg/liter), as determined in mine tests. These comparisons between coal dust and oil shale dust do not signify much since they are quantitatively different. It may also be noted that the minimum volatile content (about 10 percent) of oil shale dust for propagation happens to be the same as for coal dust, since it has been established that anthracite coal dust will not propagate explosions (Hartman 1957). But, in each case, volatile content is based on different standard heating tests, not necessarily descriptive of the rapid heating in explosions.

The fluid dynamics of the oil shale dust explosions in the single entry of the Experimental Mine may be understood by examination of figures 5 and 6, which contain static pressure histories at various stations for a lean and a rich oil shale dust explosion, respectively. Also shown are the arrival of the leading edge of flame, the effective end of flame radiation, and some of the resulting compression and expansion waves. Generally, the flame from the gas explosions alone does not travel past 100 feet (31 m) from the face, but the resulting shock wave may be seen to form the beginning of the complex pressure wave (called the "pioneer wave"), which is transmitted through the length of the mine. The length of the mine also determines the period of the pressure pulse, as indicated by the arrival of the expansion wave from the open end. The static pressures at flame arrival in these tests in a single entry are also proportional to and related to flame speed by the acoustic approximation as mentioned earlier (Richmond and Liebman 1974).
Figure 5. - Static pressures and wave diagrams for EM Test 3701.
Assay = 25 gpt (94 kg/tonne); C = 0.60 oz/ft³ (0.6 g/l).

Figure 6. - Static pressures and wave diagrams for EM Test 3707.
Assay = 50 gpt (188 kg/tonne); C = 0.225 oz/ft³ (0.225 g/l).
Fluctuations in pressure are caused by momentary deceleration of flame, due to a difficult ignition or to compression and expansion waves reflected from recesses in the walls. Movies verified that the flame always filled the entry soon after initiation.

Some of the complex relationships between flame speed, air speed, static pressure rise, and concentrations of dust picked up by the air in advance of flame may be seen in figure 7, which represents the same test as figure 6. The dust concentrations in this case were measured by optical dust probes at midheight, about 30 inches (76 cm) from a rib, and are corrected for air density increase due to pressure rise. Air velocities at the 100-, 200- and 300-foot stations were calculated from static pressure and drag probe data, while velocities at the 400-foot locations were calculated from data from a pitot probe located there. Distributions of dust across the entry are not known at this stage, so only relative changes can be reported. At the dust probe located at 100 feet (30.5 m), the concentration was quite small before the flame arrived. There seems to be some critical air velocity (and flame velocity) of about 200 ft/sec (61 m/s) before dust begins to appear at the probe location, but, on film, dust can be seen to come off the surfaces at a velocity of about 100 ft/sec (31 m/s). Some time is required for the dust to fill the cross-section (Hwang 1974). It has also been observed that the minimum velocity that dust explosions can maintain is about 150 ft/sec (46 m/s).

A summary of available data from all tests, relating nominal dust concentration to flame travel, maximum concentration of dust at the probes before flame arrival, and maximum flame speed and pressure is given in table 4. An attempt to relate nominal dust concentration to the maximum measured concentration at the different locations is shown in figure 8. Unfortunately, there are not enough data for the oil shale dust tests at the 100-foot station to provide a correlation, but the data at the 200- and 300-foot stations (and other data for coal dust) do indicate that the maximum concentration of dust at a given point is proportional to the nominal loading.

It may be possible to generalize the concentration of dust at a given point in time and space within the dusted zone (while dust remains upstream), as follows: 

$$ C \propto C_0 \int (V - V_o)dt $$

where $C$ = instantaneous dust concentration 

$C_0$ = nominal dust concentration 

$V$ = instantaneous air velocity 

$V_o$ = threshold air velocity for dust pick up

When the dust concentration, due to the above factors, drops below the critical value over most of the cross section, the flame will go out. Nominal concentrations in figure 8 are given in lb dust/lb air, where, at normal mine ambient pressure and temperature, 1 oz/ft$^3$ = 0.833 lb/lb (1g/l = .833 g/g). In this manner, it is possible to account for increase in air density due to pressure rise. Nominal concentrations were used in tables 2 and 3 and in figures 3 and 4, since these represent the initial conditions to be found in a mine whose hazard potential is to be evaluated. But, the critical stage for propagation is always found near the beginning of the dust zone, such as at the 100-foot location, where maximum dust concentration in advance of flame is about equal to nominal value. If the flame is able to make it to this point, with sufficient speed to continue to disperse dust, dust concentrations further toward the entry will be greater due to the greater velocity impulse given by equation (1), and the flame will accelerate.

Coking was sometimes observed in the Experimental Mine after a vigorous explosion particularly after Test 3701 (see figure 5) which involved a heavy loading of shale assaying at 25 gpt (84 kg/tonne). This material is usually reported to be non-coking, but heavy deposits of coke were found, mostly on trailing edges of probes and shelves, and granules were found on the
Figure 7. - Relation between flame speed, air speed, static pressure and dust concentration in an oil shale dust explosion.
Table 4. - Dust concentration measurements.

<table>
<thead>
<tr>
<th>Test</th>
<th>Nominal dust concentration</th>
<th>Flame travel, ft meters</th>
<th>Maximum Concentration of Dust at Station Before Flame Arrival</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cu ft (g/l)</td>
<td>lbs dust (gm/gm)</td>
<td>E100</td>
</tr>
<tr>
<td>3651</td>
<td>0.15</td>
<td>0.13</td>
<td>300</td>
</tr>
<tr>
<td>3652</td>
<td>0.30</td>
<td>0.25</td>
<td>350</td>
</tr>
<tr>
<td>3693</td>
<td>0.30</td>
<td>0.25</td>
<td>150</td>
</tr>
<tr>
<td>3700</td>
<td>0.30</td>
<td>0.25</td>
<td>250</td>
</tr>
<tr>
<td>3702</td>
<td>0.30</td>
<td>0.25</td>
<td>550</td>
</tr>
<tr>
<td>3705</td>
<td>0.15</td>
<td>0.13</td>
<td>100</td>
</tr>
<tr>
<td>3706</td>
<td>0.15</td>
<td>0.13</td>
<td>250</td>
</tr>
<tr>
<td>3707</td>
<td>0.225</td>
<td>0.19</td>
<td>550</td>
</tr>
<tr>
<td>3708</td>
<td>0.40</td>
<td>0.33</td>
<td>200</td>
</tr>
<tr>
<td>3709</td>
<td>0.60</td>
<td>0.50</td>
<td>250</td>
</tr>
</tbody>
</table>

**OIL SHALE & ROCK DUST**

| Test | 3710 | 0.600 | 0.50 | 75 | 23 | - | - | - | - | - | - | - | - | - |
|      | 3711 | 0.384 | 0.32 | 500 | 122 | - | - | - | - | - | - | - | - | - |
|      | 3712 | 0.314 | 0.26 | 550 | 168 | - | - | - | - | - | - | - | - | - |
|      | 3713 | 0.391 | 0.33 | 450 | 137 | - | 0.84 | - | - | - | - | - | - | - |
|      | 3714 | 0.470 | 0.39 | 300 | 92 | - | 0.42 | - | - | - | - | - | - | - |
|      | 3715 | 0.600 | 0.50 | 550 | 168 | - | 0.68 | - | - | - | - | - | - | - |

*No dust maximum; dust flame speed and pressure decaying from ignition source values.

floor. Analysis of the coke indicated the disappearance of most of the organic material, as well as decomposition of the analcime and dolomite.

Dust in Mine and Grinding House - Malcolm Smith of ERDA made an attempt to sample dust from the walls of the Anvil Points Mine and in the grinding house. During shutdown periods, very little dust could be removed from the walls of the mine, but much more was obtained at the Paraho grinding house with the results listed in table 1c. It will be seen that coarser dust is slightly richer than fine dust, a result to be expected based on the greater friability of the leaner oil shale. But not enough samples are available at the present writing for us to be able to modify the results of figures 3 and 4. Therefore, if one assumes that the average assay in the Anvil Points Mine is 30 gpt (113 kg/tonne), then the lower explosive limit is 0.3 oz/ft³ (0.3 g/l). For a typical room size of 50 by 60 by 70 feet (15 by 18 by 21 meters), the volume is 210,000 ft³ (5670 m³), and 4,000 pounds (1818 kg) of pulverized dust would be required to fill a room with an explosive mixture. The average dust layer density on six surfaces would have to be about 0.2 lb/ft² (0.098 gm/cm²), or a layer thickness of about 0.038 inch (0.097 cm), for a dust bulk specific gravity of 1.0. Large amounts of dust are raised by the detonation of non-permissible explosives, but ignitions are not reported, apparently because sufficient concentrations of fine dust are not present when the explosive flame exists. Accidental ignition would obviously be easier if methane were present, but the effect of methane on the dust concentration limits has not been determined yet.

Spontaneous Ignition of Oil Shale Dust - Comparative measurements of the ignition temperature of 25 gm samples of 46-gpt and 25-gpt (173 and 84 kg/tonne) oil shale dust were made in a laboratory furnace, in addition to samples of Pittsburgh seam pulverizer dust. 

*Private communication, C.D. Litton, May 197
coal dust and sand as a control. At an oven setting of 350°C, both coal and 46-gpt (173 kg/tonne) oil shale ignited, corresponding to an inert temperature of 130°C. At an oven setting of 300°C, corresponding to 110°C inert temperature, no ignition was observed for either oil shale or coal. No ignition of 25 gpt (84 kg/tonne) oil shale occurred at inert temperatures up to 160°C, but ignition did occur at 180°C. No claim was made that the above measurements are absolute, but they do indicate that richer oil shale is similar to coal in this respect. The ignition temperatures quoted here are slightly less than those reported by Kawenski (1974), who reported 180°C for a 34-gpt (128 kg/tonne) sample in a different furnace.

Oil Shale Fire Test - One oil shale fire test was conducted in the fire research laboratory of the Bureau of Mines, using oil shale bricks 4-1/2 x 6-1/2 x 2 inches (11.4 x 16.5 x 5.1 cm), cut from material from the Anvil Points Mine.* The average assay of the bricks was 44-gpt (165 kg/tonne). The bricks lined a rectangular tunnel with an air space 10 inches square and 20 feet long (25.4 cm x 6.1 m), with a ventilation flow of 3 to 10 ft/sec (0.9 to 3.1 m/s). The oil shale was ignited with considerable difficulty with a methane-oxygen blowtorch, and the propagation of flame observed was for the entire length. Temperatures were measured and gas samples taken during the test, which lasted several hours. At maximum intensity, the maximum surface temperature was about 970°C, and fuel-rich combustion occurred after 0.6 hour of fire propagation.

At this point, gas sampling and analysis showed the following values:

- CO - 2%
- CO₂ - 17%
- O₂ - 0.5 - 2%
- CH₄ - 1.8% (maximum)
- N₂ - balance

The maximum gas temperature in the exhaust rose to 1070°C at 2 hours after ignition. The flame spread rate was estimated to be about 0.08 cm/sec along the surface. The fire was sealed after four hours and extinguished with the help of added nitrogen. A detailed report of temperatures, gas analysis, and assay of the spent shale will be published later.

Future Work

Future work should definitely include a study of the effect of particle size and added methane as well as ignition source strength on the explosive potential of oil shale dust. Fire tests need to be conducted with leaner bulk material in large slabs, to

determine the effect of ignition source temperature, size, and duration determined.

Summary and Conclusions

The explosive potential of pulverized oil shale dust of material from the Anvil Points Mine was determined, as a function of nominal dust concentration, added rock dust, and oil assay. This oil shale is in the Mahogany Zone of the Green River deposit. The dust particle size was similar to that of pulverized coal dust, i.e., about 80 percent through 200 mesh (74 micrometers). In the Bruceton Experimental Mine, explosions were not possible with dust which assayed less than 25 gpt per ton (94 kg/tonne). The minimum nominal explosive concentration varied between 0.2 and 0.6 oz/ft$^3$ (0.2 and 0.6 g/$l$) for 50 gpt and 25 gpt (188 and 94 kg/tonne), respectively, while the minimum concentration of volatiles was 0.05 oz/ft$^3$ (0.05 g/$l$) for all propagating explosions. Volatiles are defined as oil plus gas by the modified Fischer assay. The corresponding upper limit for incombustible material was 86 percent for propagation. Rock dust was slightly more effective than the inorganic part of the oil shale for preventing propagation. Explosion flame speeds as high as 1500 ft/sec (458 m/s), with corresponding overpressures of 30 psi (207 kPa), were observed. For propagation to occur, initiation source strength had to be such that the minimum nominal concentration of dust lifted from surfaces was maintained for the first 100 feet (31 m) of the dusted zone. For a typical room in the Anvil Points Mine, 4,000 lbs (1818 kg) of pulverized dust would be required to fill the room with an explosive mixture. The coarser fraction of the dust formed naturally in the mine and crusher tends to be richer in kerogen.

Spontaneous ignition tests of dust samples indicate that richer oil shale (46 gpt (173 kg/tonne)) has an ignition temperature similar to that of Pittsburgh pulverized coal dust, with the leaner shale having a somewhat higher temperature.

A preliminary test with bulk oil shale (bricks) in a fire tunnel indicated fire propagation was possible in a ventilating flow from 3 to 10 ft/sec (0.9 to 3.1 m/s), after a difficult start. Surface temperatures up to 970°C were observed. The oil shale fire was similar to coal fires under the same conditions; however, maximum temperature and net enthalpy were lower for oil shale.

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ELECTRICAL AND THERMAL TRANSPORT PROPERTIES OF GREEN RIVER OIL SHALE HEATED IN NITROGEN

J. DuBow, R. Nottenburg, K. Rajeshwar, R. Rosenvold
Department of Electrical Engineering
Colorado State University
Fort Collins, Colorado 80523

Abstract

The electrical and thermal transport properties of selected grades of Green River oil shale were characterized by simultaneous parameter measurement techniques. Data were obtained on thermal conductivity, thermal diffusivity, dielectric constant, dielectric loss tangent and differential thermal analysis of Green River oil shale heated in a nitrogen environment.

Thermal conductivity varies from 0.2 to 1.0 BTU/ft-hr-°F and tends to decrease with increasing temperature. The thermal diffusivity varies from 0.2 to 0.45 ft²/day and also tends to decrease with increasing temperature. Both thermal conductivity and thermal diffusivity decrease with increasing kerogen content.

Dielectric constant, which measures electrical energy stored in the material, decreases with increasing frequency. As temperature increases, dielectric constant initially decreases; then increases again, attaining values close to room temperature value. Loss tangent, a measure of electrical energy absorbed by the material, decreases with increasing frequency and increases with increasing temperature. At temperatures approaching the retorting temperature, a secondary peak appears in the loss tangent. This peak correlates with the onset of kerogen decomposition, as indicated by DTA. These data are indicative of potential applications as retort diagnostics and electrical heating and fracture processes.

Introduction

Although oil shale retorting is a thermal process, the thermal transport properties of oil shale are incompletely known (Cameron Engrs. 1974). Thermal conductivity is a measure of the static thermal response of the material. However, dynamic thermal response, or temperature-time distribution in the material, is determined by thermal diffusivity. Thus, both thermal conductivity and thermal diffusivity are needed to calculate heat flow through a material since they constitute the thermal transport properties of the material. Previous studies employed transient line probe techniques that do not suitably average over the structural heterogeneities created by the varve structure in oil shale (Tiien and others 1968; Prats and O'Brien 1975). Both of these parameters have not been directly measured on similar samples, but, instead, have been inferred from data published by different authors.

The electrical properties of minerals have been used in geophysical prospecting applications for many years (Keller and Frischnecht 1967). Recently, electrical techniques have been studied as possible ore bed heating and fracture tools (DuBow, ed. 19). The electrical transport properties consist of dielectric constant, a measure of the fraction of energy in an electric field stored inside the material, and loss tangent, a measure of the fraction of the energy in an electric field dissipated by
material (Parkhomenko 1967). Other sets of parameters may equivalently describe these properties. These electrical transport properties vary as a function of applied frequency of excitation, as a function of temperature, and also as a function of the grade of oil shale. Evaluation of potential applications of electrical properties requires these data to be available. Moreover, the electrical and thermal properties of many materials are interrelated (Smith and others 1967). The simultaneous measurement of both parameters, using techniques described below, can help elucidate the origins of variations in the electrical and thermal properties of the material.

Our approach has been to measure thermal and electrical properties simultaneously, as a function of temperature and potential oil yield. Specifically, thermal conductivity and a.c. electrical impedance were measured simultaneously, as a function of temperature and potential oil yield. A.c. electrical impedance and differential thermal analysis were measured simultaneously, as a function of temperature and potential oil yield. In addition, thermal diffusivity was measured as a function of temperature and potential oil yield.

Measuring thermal and electrical properties simultaneously tends to eliminate intersample artifacts and highlight interparameter relationships. In addition, these techniques yield certain derived parameters, such as dipole activation energies, structural transition temperatures and temperature coefficients of expansion and resistance (DuBow and Nottenburg 1976). In order to improve the resolution and repeatability of the experiments, experimental techniques have been automated, using an HP 2100 minicomputer and an 8080 microprocessor system. The digital control and data acquisition system allows data storage for future studies and results in a larger quantity of data being obtained in a shorter time than manual techniques allow.

Although measurements were made simultaneously, results will be presented sequentially in order to unify the thermal and electrical characteristics. Experimental technique and data reduction will be discussed in the sections describing individual properties.

Thermal Conductivity

Thermal conductivity was obtained simultaneously with a.c. electrical impedance. The electrical impedance portion of this measurement and simultaneous DTA/electrical impedance measurement are described in the electrical impedance section.

Thermal conductivity data were obtained, using the comparative technique (Tye 1967). Figure 1 shows an outline of the test stack. The weight on top of the stack corresponds to an applied uniaxial load. A temperature gradient is impressed across the test stack via the upper and lower stack heaters. This temperature gradient divides among the upper and lower pyrex discs and the oil shale sample under test. Copper electrodes make electrical contact with the shale for impedance measurements and help improve thermal contact between the oil shale and the pyrex reference discs.

From the temperature drops across each of the test stack elements, thermal conductivity may be obtained from the following equation (Tye 1967)

\[ K_S = \frac{L_S}{2AT_S} \left[ \frac{\Delta T_T}{L_T} K_T + \frac{\Delta T_B}{L_B} K_B \right] \]

where \( S, T, \) and \( B \) refer to the oil shale, top reference and bottom reference, respectively. \( L \) is the thickness, \( \Delta T \) the temperature drop, and \( K \) the thermal conductivity. Three zone guard heating was used to minimize lateral heat flow and to maintain one-dimensional heat flow. The gaseous environment has a significant effect upon the thermal properties of oil shale. Even small amounts of air in the test stack volume results in an exothermic decomposition that dominates thermal conductivity (Smith and others 1967). Therefore, all measurements were carried out in a rapidly-flowing, nitrogen atmosphere. Samples were two in. (5 cm) in diameter and 3/4 in. (19 mm) thick.
Figure 1. - Thermal conductivity test stack.
In figure 2, thermal conductivity for five different grades of oil shale is plotted as a function of temperature. The thermal conductivity exhibits a gradual decrease with temperature and with increasing oil yield.

The samples appear to cool down rapidly during the reaction, indicating occurrence of endothermic behavior. This agrees closely with the DTA data, discussed in subsequent sections. Measurements are difficult during endothermic decomposition of kerogen, due to inability to obtain thermal equilibrium. Samples heated at low nitrogen flow rates develop a white, ashy aureole, adjacent to their external surfaces, indicating oxidation of residual carbon from decomposition of organic matter. This behavior is even more pronounced for samples with high oil-yield (40 gpt (0.18 m³) or greater); these samples undergo such strong exothermic reactions that temperatures cannot be controlled accurately. The "richer" samples also lose structural integrity at temperatures greater than 400°C.

A marked change in thermal conductivity is also seen, in all cases, after decomposition of organic matter, except for samples with very low oil-yield. This would seem to suggest that samples with low organic content exhibit a smaller temperature variation of thermal conductivity than those with high organic content; the fall-off in thermal conductivity values is quite appreciable; final values in some cases approaching 50 percent of original value. The initial sharp decrease in thermal conductivity with temperature, observed for some samples, is correlated with loss of capillary water. This observation is corroborated by thermal behavior of these samples, as shown by DTA; a sharp change in the slope of the baseline and a gradual endothermic behavior (starting around 170°C), preceding the main decomposi-

![Figure 2. - Thermal conductivity for five different grades of oil shale.](image-url)
tion endotherm due to organic matter, are interpreted as arising from the same effect. We made no attempt in our experiments to control the amount of moisture initially present in the samples.

Thermal Diffusivity

We measured thermal diffusivity with the laser-flash technique (Lindroth 1974). The experimental setup is shown in figure 3. The laser is a high power, carbon dioxide laser, chosen because 10.6 micron radiation is strongly absorbed in most rocks. The laser beam, expanded by a 3:1 beam expander, illuminates the oil shale sample which is enclosed in a cylindrical tube, oven-heated to a preset temperature. The temperature-time history of the sample's rear surface is obtained with a thermocouple whose signal is amplified by a high-gain, low-noise amplifier and recorded in a transient digitizer for subsequent transmission to a computer or an oscilloscope.

From the temperature-time history of this surface, the thermal diffusivity may be obtained according to

\[ \alpha_S = \frac{1.37 \ L_S^2}{t_{1/2}} \]

where, \( \alpha_S \) is the thermal diffusivity of the oil shale, \( L_S \) is the thickness of the oil shale disc, and \( t_{1/2} \) is the time it takes for the oil shale sample to attain one-half the maximum change in temperature obtained upon heating with the laser. Samples are approximately 7/8 in. (22.2 mm) in diameter; thickness is approximately 3/16 in. (4.77 mm). Temperature gradients across the sample are typically 2 to 5°C. It is worth noting that only relative, not absolute, measurements of temperature are required.

The results of measurements of thermal diffusivity of Green River oil shale are summarized in figure 4. Thermal diffusivity is seen to decrease with increasing temperature and oil yield. Trends in variation of this parameter, significantly enough, closely parallel changes observed in thermal conductivity of the material. No corrections for heat losses have been attempted in

Figure 3. - Thermal diffusivity block diagram.
the present data since temperatures employed are below the range where radiative heat losses become significant. The small, surface area-to-thickness ratio of oil shale test samples also serves to minimize radiative heat loss and satisfies the requirement of one-dimensional heat flow, essential for application of the "flash-technique." Thermal diffusivity values, found in the present investigation, are somewhat lower than values calculated by Prats and O'Brien (1975) from thermal conductivity data.

Dielectric Analysis/Differential Thermal Analysis (DA/DTA)

In order to estimate the effect of chemical reactions and changes of phase upon electrical and thermal impedance, we developed a technique consisting of simultaneous measurement of a.c. electrical impedance and differential thermal analysis. We modified a DTA apparatus, including electrodes for measuring electrical impedance at selected temperature intervals.
Figure 5. - Sample vessel for DA/DTA.

Figure 5 depicts the sample vessel for DA/DTA. The sample and reference discs are 7/8 in. (22.2 mm) diameter and 1/4 in. (6.4 mm) thick. The experiments were run, using intact cores of oil shale, in contrast to most previous DTA investigations in which DTA is run on powdered samples. Pulverization of the sample could alter its thermal and electrical properties. As indicated in figure 5, the sample is held, under pressure exerted by two stainless steel springs, between two silver electrodes. Nitrogen is flushed through the sample chamber in order to suppress exothermic reactions.

Figure 6 is a representative DTA curve on a 40 gpt (0.18 m³) oil shale sample. Thermal decomposition of organic matter in the shale is seen to be endothermic in nature and takes place in the range, 400-500°C. Note that decomposition temperatures are markedly dependent on source and type of oil shale. Considerable variations have been observed in temperatures corresponding to the decomposition of the organic matter -- peak temperatures, in some cases, being as low as 350°C. The thermal and depositional history of any sample is therefore of extreme importance to its useful characterization by DTA. Splitting of the endothermic peak (fig. 6) could result from multi-step decomposition of the organic matter, or from decomposition of minerals, such as pyrite or magnesium siderite (Smith 1977). Using selected temperatures (typically 20° intervals), we measured a.c. electrical impedance over the frequency range, 10 Hz to 10⁶ Hz, thus obtaining dynamic a.c. impedance measurements during the course of the chemical reactions.

A.C. Electrical Impedance Measurements

A simplified block diagram of the a.c. electrical impedance set-up is given in figure 7. The measurement sequence is cyclic;
a.c. impedance is obtained over the frequency range $10 \text{ Hz}$ to $10^6 \text{ Hz}$. Upon a signal from the microprocessor, the frequency synthesizer applies a sine wave signal simultaneously to the oil shale and to the reference channel of the gain phase meter. The gain phase meter determines relative attenuation and phase shift of the signal as it passes through the shale. Time needed to perform this measurement depends upon frequency, being considerably shorter at higher frequencies. After an appropriate settling time, the microprocessor transmits attenuation and phase shift to the minicomputer which, in turn, stores the data on magnetic tape for subsequent processing. The computer then sends a signal to the microprocessor, indicating the data acquisition cycle is completed, and the measurement cycle repeats.

From attenuation and phase, equivalent electrical resistance and capacitance of the sample are computed. System response is automatically subtracted from the raw data during analysis. From the sample's geometry, resistance and capacitance, dielectric constant and loss tangent are calculated. These material-dependent, "constitutive" parameters are more general than the geometry-dependent, electrical impedance parameters (von Hippel 1954). Dielectric constant is a measure of the fraction of energy in the electric field energy stored in the material, while loss tangent is a measure of the fraction of energy in the electrical field.

Figure 7. - Electrical impedance block diagram.
Figure 8. - Low temperature dielectric constant of 66.7 gpt (0.302 m$^3$) oil shale.

dissipated by the material. These two parameters commonly characterize the dielectric properties of a material, although numerous other equivalent parameter sets could also be used (von Hippel 1954).

Figures 8 and 9 depict the behavior of dielectric constant of 66.7 gpt (0.302 m$^3$) shale as a function of temperature and frequency. Similar behavior was observed for other grades. Dielectric constant is seen to decrease from a relatively high value at low frequencies (412 Hz) to a lower value at high frequencies. In addition, dielectric constant is seen to decrease initially with increasing temperature. However, at about 250°C, dielectric constant is seen to begin increasing again, especially at lower frequencies. At temperatures where significant amounts of organic decomposition occur, dielectric constant attains values approaching low temperature values. However, falloff with frequency is more rapid. The origins of this effect are as yet not well understood. Pore pressure effects and capillary water in the shale could possibly play a role in this effect. This possibility is indicated by the shift in baseline slope on the DTA at about 250°C.

Typical data, showing variation of dielectric parameters with frequency, are shown in table 1 for a 37 gpt (0.17 m$^3$) oil shale sample. The dielectric constant, $\varepsilon'$, shows the frequency dependence, characteristic of water-bearing sedimentary rocks and minerals (Parkhomenko 1967): a sharp decrease in dielectric constant at low frequencies, and relative insensitivity to frequency at higher values, typical for all samples studied. The high values of dielectric constant found for the oil shale samples may be explained in terms of the Maxwell-Wagner theory for interfacial polarization (Cole 1961). The presence of semi-conducting clay particles, giving rise to a membrane effect, might also account for the large values of dielectric constant (Keller and Licastro 1959). The data, shown in table 1, also reveal a sharp increase in a.c. conductivity with increasing frequency. This behavior is consistent with Parkhomenko's published work on the electrical properties of limestone, marl and dolomite (1967). This shows that the less the water-content, and/or the higher the resistivity of the material, the greater the decrease in resistivity with increasing frequency. Water content of oil shale is variable; it seldom exceeds 6-10 percent, however, a figure well within the limits observed for sedimentary rocks exhibiting similar dielectric behavior.
The nature of dispersion observed in oil shale for the loss tangent, $\tan \delta$, is shown by a typical curve (Fig. 10) for a 26 gpt (0.12 m$^3$) sample. Presence of a broad peak, at low frequencies (<1000 Hz), is interpreted in terms of interfacial polarization effects. Occurrence of secondary maxima in $\tan \delta$, at higher frequencies, observed only at higher temperatures, is also significant. The peak maxima show a pronounced dependence on temperature, shifting to higher frequencies with increasing temperature. It is possible to extract activation energies for dipole relaxation processes from such temperature dependent behavior. In materials as heterogeneous and complex as oil shale, the wide range of relaxation times significantly complicates the interpretation of these data. Dependence of the magnitude of $\tan \delta$ on temperature also indicates that at high temperatures, where $\tan \delta$ shows values of less than 1, conduction is primarily ohmic; whereas, at low temperatures ($\tan \delta < 1$), conduction is by displacement mechanisms. This behavior is consistent with observed changes in resistivity of oil shale with temperatures; changes in resistivity, of over five orders of magnitude, are commonly observed for oil shale samples.

Figure 11 shows loss tangent versus frequency for a 29.8 gpt (0.14 m$^3$) shale. The same major features are observed as for the 26 gpt (0.12 m$^3$) sample. A secondary peak in the loss tangent appears at temperatures where organic decomposition begins to occur, as indicated by the DTA curve. However, temperatures at which this secondary peak begins to occur are lower for higher grade shale.

Figure 12 shows the temperature dependence of dielectric constant of oil shale for different grades, ranging from 7.5 to 60 gpt (0.034-0.302 m$^3$). Sharp changes in $\varepsilon'$ values, at temperatures in the range 100-150°C, are possibly correlated with loss of capillary water and change in pore structure of samples. The pronounced increase in dielectric constant, at temperatures above 270°C, probably arises from the onset of decomposition of organic matter. Thermal behavior of samples, as shown by their DTA carried out simultaneously under the same conditions, exhibits remarkably similar trends and points towards a common origin for observed effects.

**Conclusion**

In these experiments, we observed a significant, close similarity, with temperature variation, in trends of different thermal and dielectric parameters of oil shale. Results indicate that interpretations, based on a combined use of thermal and dielectric
12.0  
10.8  
9.6  
8.4  
7.2  
6.0  
4.8  
3.6  
2.4  
1.2  
10  
100  
1000  
10,000  
100,000  
1,000,000  
10,000,000  
100,000,000  

TAN DELTA

Figure 10. - Temperature dependent loss tangent versus frequency for 26.0 gpt (0.12 m³) oil shale.

measurements, yield valuable information required for a complete characterization of thermophysical behavior, especially for complex, heterogeneous materials like oil shale. Further work, aimed at accounting for observed trends in terms of a unified model, is in progress. Application of electrical prospecting methods to oil shale, particularly induction and radio wave methods, requires knowledge of frequency dependence of its electrical resistivity and dielectric constant. A detailed investigation of the relationships observed in the present work should be useful in explaining mechanisms of polarization and providing a basis for a theory on the behavior of oil shale in a.c. fields.

Results of this investigation show that when oil shale is heated in nitrogen:

1) Thermal conductivity decreases with increasing temperature and increasing grade and attains values ranging from 0.2 to 1.0 BTU/ft-hr °F;

2) Thermal diffusivity decreases with increasing temperature and increasing grade and attains values from 0.2 to 0.6 ft²/day;

3) Dielectric constant decreases with increasing frequency and attains relatively high low frequency values of over 400;

4) Dielectric constant initially decreases with increasing temperature and then increases. At temperatures where significant organic mat
Figure 11. - Temperature dependent loss tangent for 29.8 gpt (0.14 m³) oil shale.

- Organic matter decomposition occurs, the low frequency dielectric constant attains its low temperature values;
- Loss tangent decreases with increasing frequency and increases with increasing temperature;
- At temperatures where significant organic matter decomposition occurs, the loss tangent begins to exhibit secondary peaks at frequencies around 10⁵ Hz;
- DTA data and changes in dielectric property data correlate well.

The thermal and electrical data developed can be used to develop sensors for retort diagnostics and to investigate the feasibility of novel electrical processing and prospecting options for oil shale.

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Figure 12. - Low frequency dielectric constant versus temperature for various grades of oil shale.

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Abstract

This paper presents a computer-based pillar design method to calculate the proper size pillar to achieve a pre-selected factor of safety. Systematic oil shale pillar design is needed to accomplish rapid evaluation of multiple mining plans. Equivalent stability for different mining methods will require different pillar sizes and yield different extraction ratios. Equivalent extraction, using different mining methods, will result in different relative stability.

The computer program calculates the size of barrier and chain pillar design with a pre-selected factor of safety which can be computed provided the needed input data is provided. If the depth, mining height, Fischer assay, rock mass cohesion, entry and (or) room configuration and the pre-selected safety factor are given; barrier pillar dimensions can be selected rapidly.

Introduction

This paper reviews some of the pillar design techniques applicable to oil shale mining. Traditionally, the design of underground mine pillars has been based upon trial and error. The difficulty in precisely quantifying the physical properties of rocks, determining pre-mining stress state and its role in the design; and the knowledge that these factors vary from location to location, have necessitated this approach. No commercial oil shale mine is in operation in U.S. to date, and so far all of the mining experience is based on limited data from experimental mines. Information is limited to certain outcrops of the Green River Formation and shallow depths at the edge of the Piceance Basin.

Rock mass response within the central basin could be quite different from that observed near outcrops. This paper presents a confined core chain and barrier pillar design approach, which takes into account certain mechanical properties of intact rock mass, namely: angle of internal friction and cohesion. This pillar design approach is being applied successfully at National Coal Board mines in England, and, at present, it is being used as a means of design for new underground oil shale, coal, salt and hard rock mines.

Scope

The design of pillars depends on the strengths and weaknesses of the oil shale rock mass. Understanding of the structural geology, orientation of structural features, joint set characteristics, hydrology, rock substance and rock mass properties and the in situ stresses could be essential in the optimum design of underground oil shale mines. The distribution of stresses within a pillar and assumptions of loading must also be defined.

This paper presents a chain and barrier pillar design procedure, based on confined core concept, adapted from Wilson's (1972) studies in England. In addition, a summary of the physical properties of oil shale from previous investigators is presented as
a nomograph, relating barrier pillar width to thickness of overburden.

Engineering Geology of Colorado Oil Shale

The Green River Formation in the Parachute Creek basin, Colorado, is a large structural downwarp that has undergone minimal tectonic activity. The formation is composed of the Douglas Creek, Garden Gulch, and Parachute Creek members. The younger Parachute Creek member is economically the most important, as it contains virtually all the shale oil, nahcolite (soda ash), and dawsonite (alumina) resources. All proposed mining is in this member.

The Parachute Creek member is a kerogen-rich marlstone, composed of thin laminations of alternately rich and lean oil shale. In addition, this member is subdivided into rich and lean oil shale zones that vary from less than 10 to greater than 40 gallons per ton (gpt) and vary in thickness from 20 to greater than 200 feet. The Mahogany Zone comprises the upper and most consistently rich zone. Bedding dips range from 27 degrees on the northern rim to less than three degrees on the southern margin. Bedding in the central portion of the basin has a relatively flat dip. The total thickness ranges from 400 to 2,000 feet with up to 1,200 feet of overburden.

Stratigraphic marker beds in the Green River Formation extend over large areals, frequently the entire basin. Only minor normal faulting is found near the center of the basin. The principal mineral constituents are calcite, dolomite, illite and yellow organic material. Minor constituents are quartz, orthoclase feldspar, plagioclase feldspar, pyrite, marcasite, analcite, opal, black opaque organic material and small wood fragments. Silica is present and represents approximately 30 percent. The thin alternating beds of rich and lean shale tend to weaken the rock substance.

Rock Mass Properties

Review of Literature - To design an underground oil shale mine it is essential to have data about mechanical as well as geological properties of the marlstone. Our review of published literature on the Parachute Creek basin revealed considerable published data on the mechanical properties of oil shale. But, additional site specific rock mass properties from testing core samples are needed to design any oil shale mine. The rock mass properties essential for the preliminary design of these underground openings follow.

Knowledge of the rock mass behavior provides information about the disturbance of natural stresses resulting from underground excavation. In addition, excavation-induced stress changes are affected by the geological discontinuities present in the mass. Rock mass classifications have been proposed by Deere (1975), Laubsher (1975), Bieniawski (1973), Denkhaus (1973), Barton (1975), Terzaghi (1964), Lauffer (1958) and
Hansagi's Kiruna (K) factor of classification is similar to Deere's RQD and was developed as the result of long-term investigations at Swedish iron mines. Hansagi's K factor takes into account the strength distribution of rock cores and the compressive strength of the strata. The K factor estimates the support requirements for tunnels.

Bieniawski's (1973) proposed classification of rock masses is more comprehensive than the aforementioned classifications. It provides a sound basis for classification of rock masses into groups. These groups are state of weathering; uniaxial compressive strength of intact rock; spacing of joints or bedding surfaces; strike and dip orientations; separation of joint surfaces; continuity of joints and groundwater inflow. For swelling rocks, such as clay-shales, Bieniawski recommends the durability and slackability tests or the weatherability test.

Bieniawski's classification is more comprehensive because the rocks are divided into five classes and further subdivided on the basis of eight parameters given above. The five classes are very good, good, fair, poor and very poor. In each class, the eight parameters are rated and the total rating of a rock mass makes it possible to predict an overall ranking.

Table 1 presents reported uniaxial compressive strengths of oil shale specimens with respect to Bieniawski's rock mass classification for oil shale with an oil content from 10 to 60 gpt. Note that oil content increase corresponds with decrease in the compressive strength.

Rock Mass Weaknesses - The major rock mass weaknesses present in the Green River Formation are limited to the joints and fractures encountered at shallow depths and near outcrops. Sufficient mining has not been done to expose their frequency and magnitude at central basin depths. A well-defined system of northwest- and northeast-trending joints has been delineated on surface exposures of the Green River Formation in the Piceance Creek basin. These roughly horizontal rock units are characteristic-ally cross-bedding jointed. The individual joint sets may persist vertically for a few tens of feet and across several beds, but then terminate at the boundary of a unit.
Table 1. - Classifications for strength of intact rock: uniaxial compressive strength, Mpa.
been observed in outcrops and on aerial photographs. These master cross-bedding joints are widely spaced, and also appear to terminate against bedding plane weaknesses.

Additional rock mass weaknesses in the Green River Formation are bedding-plane partings. Bedding-plane partings occur only occasionally and between beds with pronounced elastic property differences. These elastic differences appear to correlate with Fisher assay and color differences.

**Engineering Properties of Oil Shale**

The unconfined compressive strength perpendicular to the bedding of oil shale specimen has been measured by several investigators.

Abel and Hoskins (1976) reported a parabolic relationship between unconfined compressive strength and Fisher assay determinations reported by researchers (fig. 1). Sellers and others (1972) correlated density to Fisher assay making it possible to relate engineering properties to Fisher assay through density. Figure 2 presents Sellers' relationship of specific gravity to Fisher assay.

**Strength Properties.** Figure 1, which presents the unconfined compressive strength perpendicular to the bedding of oil shale specimens versus Fisher assay indicates that compressive strength reaches a minimum at about 50 gpt. These and similar Fisher assay-related physical properties were presented at the 9th Oil Shale Symposium by Hoskins and others.

**Creep Characteristics.** Sellers studied long-term creep characteristics of oil shale and reported that no creep was observed below 2000 psi uniaxial compression.

Sellers reported that the Fisher assay becomes critical above 30 gpt, where the specimens underwent permanent deformation, when subjected to uniaxial compression of above 2000 psi. At stress levels from 2000 to 6000 psi, plastic deformation followed a logarithmic relationship with time, rapidly decaying to zero in a few days. At compressive stress levels above 8000 psi, 30 gpt and higher oil contents specimens undergo continuing, permanent deformation to failure.

Hoskins and others (1976) reported that massive plastic deformation of oil shale occurs under triaxial compression tests. Confining pressures of 1,500 psi permit at least 25 percent shortening to occur without brittle failure. The load carrying capacity of a triaxially confined oil shale specimen decreases progressively as plastic deformation proceeds. This phenomenon is important to the response of the confined central core of any overloaded pillar. Such an overloaded pillar would be expected to undergo measurable progressive deformation until it transfers its overload to adjacent pillars or fails.

**Design Considerations**

**Design of Oil Shale Pillars - Review of Literature.** Review of published work on oil shale mine pillar design is limited to research involved with design and development of relatively recent experimental mines. Merrill (1954) reported results of the extensive USBM-supported physical testing program performed for the Anvil Points oil shale experimental mine. Comprehensive testing at three separate laboratories of unconfined compressive strength, Young's modulus, Poisson's ratio, modulus of rigidity and
sonic velocities found that the oil shale could be classified as a moderately strong rock depending on the oil content. As oil content increased, the rock became more plastic and generally weaker.

Tesch (1961) performed experiments on oil shales from Anvil Points to investigate the relationship of oil content (5 to 60 gpt) with Young's modulus, unconfined compressive strength, Poisson's ratio and modulus of rupture, both parallel with and perpendicular to the bedding planes. He concluded that oil content affects sample strength and that compressive strength was higher parallel to bedding. Raju (1961) also investigated the effects of bedding on the elastic, static, and dynamic behavior of oil shale. His tests indicated that compressive and tensile strengths are higher for loads applied parallel to the bedding planes.

Sellers reported physical testing results with respect to Fisher assay. He determined the direction of the in situ stress field. He concluded that the maximum principal stress was in the horizontal plane at Anvil Points.

Agapito (1974, 1972) reported the results of physical testing and displacement measurements at Colony Development Company's experimental mine near Rifle, Colorado, and presented a design for large oil shale pillars based on loads and modes of failure. Agapito's data was used as input to a finite element program to predict stability and failure.

A review of the pillar design literature potentially applicable to oil shale mine design is briefly presented below:

Greenspan (1945), Terzaghi and others (1952), presented geometric elastic stress concentrations around single and multiple openings in tabular and graphical form. Experimental stress analysis was employed by Duval (1948), Panek (1951) and Caudle and Clark (1955) to estimate boundary stresses for a limited set of opening geometries.

Obert and others (1960) presented a pillar design technique for competent rock based on testing of rock samples having the same shape as the ultimate pillar. Holland (1962) derived a formula based on testing specimens and indicated that the probable strength of a coal pillar is related to the least width of the pillar, thickness of the pillar and a coefficient depending upon the particular coal comprising the pillar. Bieniawski (1969) and Bieniawski and Van Heerden (1975) presented a formula based on the results obtained from large-scale in situ tests conducted on coal specimens. They concluded that the relationship between strength and least width to height ratio of the pillar is linear.

Salamon and Munro (1967), and Salamon (1967) studied failed and stable pillars in South African coal mines and developed an empirical formula based on statistical interpretation.

Pariseau (1975) presented a stress analysis pillar design technique based on flow and fracture mechanics. He used two-dimensional finite element analysis to compute the stability of mine pillars for flat layered deposits. He concluded that mine pillar design based on one-dimensional analysis is over-simplified. More realistic, two-dimensional analyses can include parameters such as stratigraphy, structure, groundwater, rock properties, progressive failure, varying loads, roof, rib and floor interactions, caving, mining sequence, and so forth.

Wilson (1972) reported on laboratory studies and underground pillar evaluation in English coal mines. Wilson divided the pillar into two zones: a central inner core, subjected to a triaxial stress condition, and a yielded and/or yielding zone which surrounds and constrains the inner core. According to Wilson's concept, the pillar is confined at the roof and floor by in situ horizontal stress field. The in situ confining stresses, acting on the core of pillars, is approximated by triaxially loaded coal specimens, which represent the pillar core. Wilson's approach permits an estimate of the load-carrying capacity of any given size and shape coal pillar. To apply
Wilson's approach to oil shale, knowing the angle of internal friction and cohesion of oil shale are essential.

**Confined Core Approach** - The confined core approach, introduced by Wilson (1972), estimates the load-carrying capacity of pillars. Figure 3 shows the cross-section of a wide pillar and the vertical stress distribution through the pillar. The vertical stress at the ribs of the pillar is less than the pre-mining vertical overburden stress. The distribution of vertical stresses is the same on both sides of the pillar. The low vertical rib stress is due to the fact that the rock exposed at the sides of the pillar is not confined and is probably fractured. However, toward the center of the pillar the vertical stress increases as a result of increasing effectiveness of roof and floor confinement.

According to Abel and Hoskins (1976), the horizontal stress is zero at the mid-height of a pillar ribs, and, at some distance from the edge of the pillar, the horizontal stress reaches the in situ horizontal stress. The actual distance between the pillar edge and the peak vertical stress location is related to the shear strength of the pillar rock. The stronger the rock, the shorter the distance between the edge of pillar and the peak vertical stress location.

At some distance in from the edge of the pillar, the peak, or maximum sustainable vertical stress under the in situ horizontal confining stress, is reached. The rock between this peak stress and the edge of pillar is called the "yield zone" by Wilson. Within the yield zone, the rock has failed or is failing; it has passed the yield point. On the other side of the abutment peak, the rock has not yielded, is relatively undisturbed and will obey the laws of elasticity. This area is called "pillar core". The pillar core, surrounded by yielded zones, and constrained by them and the in situ horizontal stress, will be considerably stronger as the result of its confinement. The effect of confining pressure on the strength of rock was studied experimentally by Price (1963) and Hobbs (1970, 1964). The relation between confining pressure and failure stress is somewhat non-linear, particularly at higher confining stresses.

According to Wilson, vertical stress decreases toward the center of the pillar from the peak vertical stress in the case of a wide pillar loaded below its strength. However, the peak vertical stress is always located at the center of a narrow pillar.

Wilson studied the maximum stress that could be carried by the confined pillar core and concluded that the maximum stress is related to triaxial confined strength of the pillar rock. The in situ (virgin) horizontal stress is the maximum confining stress available in the rock before mining. The hydrostatic case is considered to be a close approximation for the virgin horizontal and vertical stress conditions in sedimentary terrain. Shepherd and Kellet (1969) found, through field investigation, that the vertical stress was generally very nearly equal to overburden load.

**Design Parameters** - To design oil shale pillars, using the confined core approach, the cohesion of the rock and the internal angle of friction or the passive pressure coefficient are required. The passive pressure coefficient limits the peak vertical stress the pillar can carry under the local horizontal in situ stress confinement. These parameters are generally determined from triaxial compression testing of rocks.
Design Procedure for Coal Pillars - Wilson approximated the non-linear relationship between confining pressure and stress at failure from the work of Price and Hobbs, for British coal measures and derived a straight line approximation of the Coulomb equation. According to the Coulomb equation, the stress required to cause failure is a function of failure stress in the unconfined condition, confining stress and the passive pressure coefficient.

Obert and Duvall (1967) present the mathematical relationship between passive pressure coefficient to angle of internal friction for rocks. To compute the Coulomb equation coefficients, the numerical values of failure stress for uniaxial and triaxial tests are plotted versus confining stress, and the slope of the "best-fit" straight line is the passive pressure coefficient.

Maximum stable vertical pillar stress is a function of depth below surface, density of overburden rock, average bolting (support) stress and cohesion of rock mass. Peak pillar stress location is a function of seam height, passive pressure coefficient, maximum stable vertical pillar stress, rock mass cohesion, and average bolting (support) stress.

When additional load is applied to the pillar, the stress in the confined central core reaches the peak stress. The pillar must start to fail if more load is applied to the pillar. Pillar failure proceeds either from the edge or from the weakest part of the pillar. Wilson hypothesized that the maximum load that could be carried by the confined core of a pillar was the confined triaxial strength of the rock at the assumed hydrostatic horizontal in situ stress.

Citing the vertical stress distribution ahead of advancing longwalls, Abel and Hoskins concluded that, if the pillar is large enough, the peak stress decreases to the pre-mining vertical stress at some distance ahead of the advancing face and the abutment or peak stress location. Excava-

tion of ground during mining disturbs the natural stress state within a limited zone of influence, sometimes referred to as the arch distance. These zones of influence must be taken into account when designing barrier pillars.

Barrientos and Parker (1974) applied the pressure arch concept at the White Pine copper mine and improved roof conditions in room and pillar mining. By limiting panel widths to less than the influence zone, panel pillars were shielded from tributary area-loads. Wardell and Eynon (1968) concluded that the pressure arch approach improves the potential extraction ratio at great depth, provided panels are limited in width.

Evans (1941), describing British coal mine experience, recognized the existence of arches in underground coal mines and concluded that, when using "yield pillar" techniques, after pillars yielded for a critical width, roof conditions improved. Abel and Hoskins combined British investigations of arch distance, figure 4, and introduced a formula, which relates the influence zone, or arch distance, to depth.

A non-yielding (stable) design for underground mine pillars, must assume that pillars are wide, i.e., a confined core develops. The strength of rectangular chain pillars is defined as a function of maximum stable vertical pillar stress, pillar width, pillar length, and distance into pillar at the location of maximum stable pillar stress. The strength of barrier pillars (long pillars) is defined as a function of maximum stable vertical pillar stress, distance into pillar at location of maximum stable pillar stress and barrier pillar width. The total load-carrying capacity of an entry pillar configuration is defined as a function of number of entries and chain pillars, maximum stable vertical pillar stress, pillar widths, pillar lengths, distance into pillars at the location of maximum stable pillar stress and width of entries. The maximum potential load imposed on the entry pillars plus the barrier
Design of Chain Pillars for Oil Shale

This oil shale pillar design is based upon Wilson's pillar loading and design procedure. Wilson's approach requires knowing two engineering properties of oil shale: cohesion and angle of internal friction. The required oil shale data was compiled by Abel and Hoskins. A typical stress at failure versus confining pressure plot for one Fisher assay oil shale is presented in Figure 5. The linear relationship between confining pressure and stress at failure permits a "best fit" calculation of Coulomb's equation.
Figure 5. - Triaxial test results for 0.125 m$^3$/metric ton (33 gpt) Fischer assay oil shale.
The cohesions employed in this pillar design were 66 psi and 2180 psi (0.46 - 15.0 Mpa) and angle of internal friction was 30.7°. An overburden rock density of 134 lbs/ft³ was employed and an average exterior bolting or backfill pillar confining stress of zero was then assumed.

Pillar strengths and tributary loadings were calculated by computer at 100-foot (30.5 m) depth increments from 200- to 3200-foot (61 - 976 m) depths. The computer program generated the barrier pillar width necessary to carry predicted tributary area loads. Chain pillar and entry configurations were determined by previous equipment selection and were limited in number. A chain pillar and entry configuration and the variable barrier pillar required for stability are presented in figure 6.

During the course of computer analysis, two design alternatives were employed; one extremely conservative, the other, liberal (more realistic). Conservative design procedure is based on the assumption that the oil shale pillars are semi-granular in nature: a pile of fragments that have a cohesion of only 66 psi. (Note: Cohesion equal to zero makes Wilson's approach mathematically invalid.) Such a conservative assumption results in wider barrier pillar and longer life for barrier pillars, as indicated on figure 7. The liberal design procedure employs a cohesion of 2180 psi, computed from back analysis of the pillar failure and stress results reported by Agapito (1974).

The narrower barrier pillars determined with this higher cohesion assumption should have a shorter stable life. The deterioration of any pillar is controlled by geological processes over which engineers can exert little control. If time-dependent pillar deterioration could be halted, short-life pillars would be stable forever.

Figure 6. - Room and pillar oil shale mining with pillar extraction.
Figure 7. - Barrier pillar design nomograph for oil shale.

Evaluation of 3- and 5-entry systems, figure 7, indicates that, generally at shallow depths, there is no pillar loading requirement for barrier pillars and the loads transferred from adjacent fully extracted and caved areas onto the chain pillars can be supported by the chain pillars alone. Barrier pillars are required in this case only for ventilation control, in order to isolate the caved areas from main entries and to prevent contamination of intake air.

Investigation of conservative 3- and 5-entry systems indicates that when the tributary area load on the chain pillars is greater than their strength, the barrier pillars will carry part of individual chain pillar tributary area loads. To accomplish this, the central chain pillars must be within an arch distance of the barrier pillars. The barrier pillars can then pick up part of each chain pillar's tributary load. For the conservative design case, the barrier pillar width required for the 5-entry system is greater than for the 3-entry system. The barrier pillars must carry that portion of the chain pillar tributary loads which the chain pillars cannot support. For the liberal design case, the barrier pillar width for the 3-entry system is greater than for the 5-entry system for depths less than about 3,000 feet (915 m). In this case, the strength of individual chain pillars exceeds the tributary load on the chain pillar and chain pillars carry part of the load normally tributary to the barrier pillar. At greater than 3,000 feet (915 m) depth, the liberal design, chain pillar strength does not equal their tributary load and the barrier pillars must carry the excess.

Computerizing Wilson's approach made selection of barrier pillar width for any given depth and for varied entry and chain pillar dimensions faster and easier. One objective of the preliminary rock mechanics study was to design barrier pillars that would create stable and safe conditions and yet allow the greatest resource recovery through full extraction. In designing an oil shale mine, Wilson's pillar design approach provides an indication of the barrier pillar width required with respect to depth. Thus, modification of the mine layout during the detailed mine design and during early stages of mine development would be possible under reasonably safe conditions.

Conclusions

The rational design of oil shale mine pillars, in general, and barrier and chain pillars, in particular, requires knowing or assuming the following basic information:

1. In situ stress field prior to mining.
2. Load deformation behavior of pillars in both pre-failure and post-failure states.
3. Mine stiffness distribution throughout the mine structure.
4. Rock mass behavior and orientation of openings.

This information should encourage more accurate approach to oil shale mine design.
The confined core method is the most realistic preliminary method for oil shale pillar design. It permits design of any size and shape pillar.

Optimum design of barrier and chain pillars to protect main entries can permit recovery of significant amounts of oil shale which could otherwise be lost in rule-of-thumb barrier pillars.

Improvement in pillar design could result in significant improvements in extraction ratios. At present, no information is available about the strength of barrier pillars from pilot oil shale mines. When pilot mines grow to sufficient size that barrier pillars are required; loading, arch distance and strength data should be collected. This information would be useful in the evaluation and refinement of barrier and chain pillar design procedures presented here.

At present, due to insufficient and localized pillar design experience, the development of effective, empirical pillar design is not possible. In addition, the dependency of strength of oil shale on Fisher assay makes the development of any empirical pillar design formula much more complicated.

Acknowledgments

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List of Symbols and Abbreviations

- \( \gamma \) = Density (lb/ft\(^3\))
- \( \sigma_h \) = Horizontal stress (psi)
- \( \sigma_o \) = Compression strength at edge of pillar. Estimate of rock mass cohesion (psi)
- \( \sigma_o' \) = Pillar edge strength (psi)
- \( \sigma_v \) = Vertical stress at seam level (psi)
- \( \sigma_v' \) = Maximum stable vertical pillar stress (psi)
- \( \sigma_B \) = Average bolting (support) stress applied to pillar edge (psi)
- \( \phi \) = Angle of internal friction (degrees)
- \( C_o \) = Uniaxial compressive strength (psi)
- \( H \) = Depth below surface (ft)
- \( L \) = Load carrying capacity of pillar (short tons)
- \( L' \) = Pillar edge load addition (psi)
- \( L \) = Pillar length (ft)
- \( m \) = Pillar (seam) height (ft)
- \( P \) = Pillar width (ft)
- psi = Pounds per square inch
- \( R \) = Extraction ratio
- SF = Safety factor

\[
\tan\beta = \frac{(1 + \sin\phi)}{(1 - \sin\phi)} = \text{passive pressure coefficient}
\]

\[
\gamma = \text{Distance into pillar (ft)}
\]

\[
\Delta \gamma = \text{Distance into pillar at location of maximum stable pillar stress (ft) and edge of confined core}
\]

\[
n = \text{Number of chain pillars}
\]

\[
n + 1 = \text{Number of entries}
\]

\[
W = \text{Entry width (ft)}
\]

\[
BP = \text{Barrier pillar width (ft)}
\]

\[
AD = \text{Arch distance (ft)}
\]

\[
LR = \text{Strength of rectangular pillars (tons)}
\]

\[
LB = \text{Strength of barrier (long) pillars (tons/running ft)}
\]

\[
LP = \text{Load-carrying capacity of pillars (tons/running ft)}
\]

\[
LD = \text{The maximum potential load imposed on the chain (entry) and barrier pillars (tons/running ft)}
\]

Pillar Loading Analysis

The maximum stable vertical pillar stress:

\[
\Delta = \frac{(6.94 \times 10^{-3}\gamma' H + \sigma_B \tan\beta + \sigma_o)}{(\sigma_v + \sigma_B)} \quad (\text{psi})
\]

The peak pillar stress location:

\[
\Delta \gamma = \frac{m}{\sqrt{\tan\beta (\tan\beta - 1)}} - \frac{\Delta \gamma}{\sigma_v + \sigma_o} \quad (\text{ft})
\]

The arch distance:

\[
AD = 0.154 (H) + 70 \quad (\text{ft})
\]

The strength of wide (rectangular) entry pillars for non-yielding (stable) case:

\[
LR = \frac{\gamma}{2000} \sigma_v (P - \sigma_v - \Delta \gamma + \frac{A}{4} \frac{A^2}{2}) \quad (\text{tons})
\]

The strength of the two barrier pillars
(long pillars) at both sides of the entries:

\[ LB = 2 \times \frac{Y}{2000} \frac{A}{v} (BP-Y) \] (tons/running foot)

The total load carrying capacity of all the chain pillars is:

\[ LP = n \times \frac{Y}{2000} \frac{A}{v} \left( \frac{\Delta}{\Delta} + \frac{\Delta}{\Delta} + \frac{\Delta}{\Delta} \right) \] (tons/running foot)

The maximum potential load imposed on the entry pillars plus the barrier pillars is defined by:

\[ LD = \frac{Y}{2000} H[nP+(n+1)W+2BP+2AD] \] (tons/running foot)

The safety factor (S.F.) is defined as the ratio of load carrying capacity of chain pillars to the tributary area load:

\[ SF = \frac{LP + LB}{LD} \] (a)

for a safety factor of unity, all the terms at (a) are known except depth (H) and barrier pillar width (BP); for a given depth, the barrier pillar width can be computed easily.

References


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Introduction

The use of longwall methods for the mining of coal has a long history in Europe. In the United States, however, the first "modern" longwall system was installed as recently as 1960. Since then, its use has been increasing. At present, there are approximately eighty operating longwalls and many more are planned. In addition to coal, longwall methods have also been used for mining other bedded deposits, notably, rock salt, potash, hematite and trona. These non-coal operations use the same type of equipment as for mining coal except that individual elements of the system (cutting machine, face conveyor and face supports) are much more robust to cope with the harder materials.

This paper conceptualizes two systems, using longwall mining methods, to develop horizontal in-situ retorts for the exploitation of oil shale. As background, however, we have included a brief description of the longwall system as currently practiced in coal.

Description of the Longwall Method

Panel Development - Development of a conventional longwall panel is illustrated in figure 1. The panel is developed with two sets of flank entries, A and B, connected by a starter entry C. A typical panel will have a length of 762 m to 1525 m and a width of 122 m to 213 m. On completion of development, which is usually done by drum-type continuous miners, the longwall equipment is installed (fig. 2) in the starter entry and mining retreats back to the main entry barrier pillars (fig. 3).
Figure 2. - Typical longwall panel prepared for mining.

Figure 3. - Typical longwall panel during mining.
Longwall Equipment Components

The longwall method employs a combination of three basic equipment components (fig. 4).

- A cutting machine
- A face conveyor
- A support system

Cutting Machine - The most accepted method for cutting coal or ore is the ranging drum shearer, which can be equipped with single or double drums (fig. 5). The units used in non-coal deposits are generally double-drum, heavy duty types. At present, machines capable of extracting 4.9 m in one pass are commercially available; units designed to handle 6.1 m in a single pass are in the planning stage. A variety of drum diameters and web widths are available to cover a wide range of conditions.

Face Conveyor - Transport of coal or ore along the face is accomplished with an armored face conveyor (fig. 6). Although there are many arrangements of chains and flights, the single center strand seems to be the most effective. This unit is presently the major source of downtime on longwall faces and, depending upon the hardness of the material being mined, wear can be a serious problem. In addition to conveying mineral, the armored conveyor also provides the traveling track for the shearer which is mounted upon it.

Support Systems - The roof support system is the key to success on any longwall face. Available today are four types of roof supports:

- Frames
- Chocks
- Shields
- Chock-Shields

Each of these supports has the common element of hydraulic legs, attached to a base and to some type of roof-supporting structure. Their function is to maintain a safe working environment in the face area, and to supply sufficient resistance to effectively cave the immediate roof strata behind the longwall as the face retreats.

Frames. Frame-type supports represented an early attempt at developing a self-
advancing support. Mainly because of inherent instability, they have now been largely replaced by chocks and shield types.

Chock Type Supports. A typical chock-type support is shown in figure 7. A range of designs of four and six leg units exists to suit a wide variety of conditions. An important aspect of chock selection is the nature of the immediate roof and floor. In the U.K., a support resistance of .10 meganewtons per square meter is adequate to cave the normally soft roof rocks. Under massive sandstone roof, however, support resistances as high as .575 to 1.15 meganewtons per square meter may be necessary to ensure caving.

Shield Supports. Figure 8 shows a typical shield-type support. This unit is currently enjoying a measure of instant success in the United States. Its primary advantage over the chock is its continuous one-piece canopy and a caving shield that combine to provide excellent roof support, simultaneously providing superior protection of the working area from the caving waste. These units are particularly effective under friable roof conditions. Full discussion of the relative merits of chocks and shields is beyond the scope of this paper, but it should be pointed out that shields should not be regarded as a universal panacea for all roof control.

Chock Shields. A chock-shield type support is shown in figure 9. This is the most recent evolution in roof-support design and combines many of the advantages of chocks and shields.

Longwall Sub-Level Caving

The conventional range of longwall systems for one pass extraction is limited to a mining height of 4.6 m to 5.5 m. In order
to extend the use of the system to the mining of thicker seams, a wide variety of methods has been developed, one of which (sub-level caving) seems applicable to the development of in-situ retorting. A brief description follows:

Basically, this method consists of mining out a face in the conventional way at the base of the seam. Figure 10 shows a typical section during mining. A wire mesh panel is installed over the supports during the working of the face. At the rear of the specially-designed "banana-type" support (fig. 10a), "windows" are cut in the mesh and the caved coal is drawn onto a rear conveyor. When waste appears at the flow point, the hole in the wire mesh is repaired and the support is moved forward.
Special Considerations for the Longwall Development of an In-Situ Retort

In addition to the normal design parameters for a longwall panel, five important items must be considered for longwall development of an in-situ retort:

- Cave Height
- Percent Extraction
- Compaction Time of the Caved Material
- Panel Drainage
- Size of the Caved Oil Shale

Caved Height - An estimate of caved height can be made by considering the volumes occupied by broken and unbroken material. Fragmented rock occupies a volume about one-and-a-half times that of solid rock; hence, if the degree of fragmentation is adequate, a thickness of roof strata equal to twice the seam thickness will provide sufficient material to fill the void space. The strata above this zone will undoubtedly fracture to some extent, but will remain in place, supported by the fragmented material below. Measurements have shown that the zone of roof strata affected by mining can be as much as 45-50 times mining height (Dahl and Von Schonfeldt 1976). It would be necessary, therefore, when evaluating a deposit for longwall development of an in-situ retort, to carry out a thorough rock mechanics investigation in order to define the geometry of the probable caving zone. In some instances, it may be necessary to limit the height of the caved zone developed above a panel by restricting panel width.

Percentage Extraction - To obtain the required amount of extraction to develop a retort (approximately twenty percent), it is possible to use a single pass longwall
for zones up to 30 m in thickness. For zones greater than 30 m, it will be necessary to use the sublevel caving method.

Reconsolidation of the Caved Material
The time required for consolidation of gob (waste) material may be as little as six months or as much as two years. These figures are based on experience in thick-seam coal where the gob must consolidate before mining can begin immediately below the gob. The time required for consolidation is a function of the material characteristics of the overburden, panel geometry, particle size and time. Further research is needed to adequately define the effect of these parameters in relation to oil shale.

Panel Drainage - Drainage of products during the retorting phase can be accomplished by providing an adequate grade and conduits in the retort floor. As shown in figure 11, it is possible to provide a crown along the center of the panel, with perforated conduits on the floor. The conduits can be connected to a collector system in the outer entries of the panel. The outer entries and cross-cuts can also provide access to introduce air and fuel into the retort for proper burning.

Size of the Caved Material - To obtain proper sizing of caved oil shale, it may be necessary to prefractionate the immediate roof of the extraction zone ahead of the longwall face advance. Two methods of prefractionating are shown in figures 12 and 13. Both methods would use existing off-the-shelf equipment with conventional explosives.

Conceptual Applications of the Development of In-Situ Retort by Longwall Methods
The following concepts are based on the use of equipment and design parameters previously outlined:

Concept A - As shown in figure 14, this panel would be developed with two entries on each side of the panel and a starter entry connecting the entries across the end. Crosscuts between each set of entries would provide adequate ventilation during development with the outer road providing access to the panel during the retort phase. During the mining phase, the overlying oil shale can be drilled and blasted from the inside entries on each side of the panel ahead of face advance as shown in figures 12 and 13. Assuming the zone to be mined is 30 m thick and twenty-percent extraction ratio is required, a panel 91 m wide and 762 m long, as in figure 14, would yield the following:

<table>
<thead>
<tr>
<th>Tonnage</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Development Tons</td>
<td>87,828</td>
</tr>
<tr>
<td>Longwall Tons</td>
<td>975,000</td>
</tr>
<tr>
<td>Total Tons Mined</td>
<td>1,062,828</td>
</tr>
<tr>
<td>Oil Shale Tons Broken For In-Situ</td>
<td>4,420,000</td>
</tr>
<tr>
<td>Total Gross Tons</td>
<td>5,482,828</td>
</tr>
</tbody>
</table>

Direct and Indirect In-Panel Cost

<table>
<thead>
<tr>
<th>Cost</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Development Entry Cost</td>
<td>$343,847</td>
</tr>
<tr>
<td>Longwall Cost</td>
<td>2,550,787</td>
</tr>
<tr>
<td>Total In-Panel Cost</td>
<td>$2,894,634</td>
</tr>
</tbody>
</table>
Figure 12. - Method of prefracturing, using head and tailgates.

Figure 13. - Method of prefracturing, using an overhead entry.

Direct and Indirect In-Panel Cost
for Tons Mined and Caved $ 0.528/Ton

Assumed grade of oil shale to be 40 gal/ton.

Direct and Indirect In-Panel Cost
per Inplace bbl $ 0.554/bbl

These costs are direct and indirect in-panel costs, and are 1.5 times the cost of longwall mining under similar conditions. Not included is the cost for development of main entries, shafts or capital equipment depreciation. These out-of-panel costs should be no greater and, in most cases, less than for the other mining methods. Development of the panels would be with continuous miners, similar to the Jeffrey 120 HR, which has been proved capable of cutting oil shale in the trona operations near Green River, Wyoming. Outbye equipment would be
Figure 14. - Concept A and Concept B.
shuttle cars and conveyor belts. As shown in figure 14, the head and tailgate entries would be 6 m wide and 3 m high. The collector entries would be 3 m wide and 2.4 m high. Crosscuts would also be 3 m wide and 2.4 m high. The outer entry on the headgate side would also serve as a tailgate collector entry for the next adjacent panel. We estimate that time to develop this type panel would be 30 days, operating three shifts per day, with one continuous miner on each side of the panel. Time to longwall mine the panel would be 166 days, working three shifts per day.

**Concept B** - This concept (fig. 14) uses the sublevel caving method and is designed for seams greater than 30 m thick. As a basis for comparison, assume the zone being mined by this concept is 76 m thick. Panel development will be the same as for Concept A, except that face length will increase from 91 m to 152 m and the longwall face to be cut will be 3 m high rather than 5.5 m. The results would be:

**Tonnage**

- Development Tons: 90,428
- Longwall Tons: 812,500
- Cave Tons: 3,250,000
- Total Tons Mined: 4,152,928
- Oil Shale Tons Broken: 21,702,928
- Total Panel Tons Mined and Broken: 25,855,856

**Direct and Indirect In-Panel Cost**

- Development Entries: $354,025
- Longwall Face Cut: 2,925,000
- Longwall Cave: 6,500,000
- Total In-Panel Cost: $9,779,025

**Direct and Indirect In-Panel Cost per Tons Mined, Caved and Broken**: $0.378/Ton

Assume grade of oil shale to be 40 gal/ton.

**Direct and Indirect In-Panel Cost per Inplace bbl**: $0.397/bbl

For this case, the cost of continuous miner development was 1.5 times that experienced under similar conditions. Longwall face costs were 2.0 times those for slower face advance. Cost of pulling the caved material was estimated at $2.00 per ton.

Estimated time to develop this type panel is 32 days, operating three shifts per day, with a continuous miner unit in each set of entries. Time to longwall mine and pull the caved material would be approximately 322 days. The time to mine and pull the cave is based on thick-seam coal operations in France. The development of improved supports and pulling methods should reduce the time required but the caving characteristics of the oil shale could cause the time to increase.

**Conclusion**

In addition to the apparent advantages in development to production ratio and cost, longwall has proved to be the safest of any method used for the extraction of underground coal, salt, potash, hematite or trona. Longwall methods also require only a minimum of permanent support during development. Another advantage is that by proper spacing of crosscuts, it will be possible to have better control of the burn front and recovery of products.

It is our opinion that the use of longwall mining methods offers the safest and most economical method to develop and mine oil shale, either for in-situ retorting, as presented here, or for total recovery, as with thick-seam coal operations. As with any method, it must be evaluated on a site-specific basis and compared with other methods. Further research is also needed to evaluate many of the unknown areas mentioned.

**References**

DESIGN CONSIDERATIONS OF MECHANICAL FRAGMENTATION SYSTEMS
FOR ENTRY DEVELOPMENT IN OIL SHALE

D. A. Larson and R. C. Olson
Twin Cities Mining Research Center
Bureau of Mines
P.O. Box 1660
Twin Cities, Minnesota 55111

Abstract
The Underground Mining Division, Twin Cities Mining Research Center, U.S. Bureau of Mines has conducted research to evaluate bits and cutters of continuous fragmentation machines for oil shale. Laboratory experiments were performed to (1) define fundamental differences in performance of the various bits and cutters and (2) relate inherent advantages of the different cutting tools to entry development in oil shale. In addition, mechanical excavation machines that have potential in oil shale mining are presented.

The bit and cutter experiments were performed on oil shale samples from the Mahogany Zone, Parachute Creek Member of the Green River Formation, in the Piceance Creek Basin (Colo.). A linear cutting apparatus was used to load and traverse a bit or cutter across a smooth shale surface; a rotary drill was used for tests with drag bit cutterheads. Graphs of specific energy, chip weight, groove width, and cutting coefficient versus depth; cutting force and depth of cut versus normal force; and specific energy versus penetration rate of drag bit cutterheads are presented.

The experiments demonstrated that (1) specific energy decreases with increasing depth of penetration, rapidly at first, then approaching a constant; (2) drag bits are more efficient, and (3) the specific energy for steady fragmentation is about 40 percent of that required for independent groove fragmentation. The benefit of drag bit fragmentation efficiency was demonstrated by comparison calculations for drag bit and disk cutter machines. These comparisons were made using a disk cutter tunnel boring machine, a drag bit tunnel boring machine, and a continuous drum miner. At the same production rate, the drag bit tunnel boring machine required only 12 percent of the thrust and 45 percent of the torque needed by the disk cutter machine. Even though the production rate of the drum miner was 60 percent of that of the other machines, it required only 10 percent of the torque and 20 percent of the thrust needed by the disk cutter tunnel boring machines.

Introduction
The use of tunnel and raise boring machines; shaft drills; drum, boom-type and boring-type miners for mechanically excavating shafts, raises, and tunnels has increased significantly in the last 25 years. The many advantages of continuous mechanical excavation, such as, increased advance rates, opening stability, safety, and minimum overbreak, have led to its use in many civil and mining applications (Morrell and Larson 1974). Before these machines are used for oil shale, basic fragmentation studies of the bit and cutter are required to determine the best machine type.

This paper summarizes the application of these machines to entry development in oil shale. The Bureau's Twin Cities Mining Research Center initiated a research program as the first step in scientifically predict-
ing future machine performance in oil shale. This bit and cutter evaluation examined the fragmentation efficiencies of various bit and cutters. This work is an extension of research started several years ago on diamond and percussive drilling characteristics and tunneling machine research. Some publications that apply directly to mechanical fragmentation of oil shale, although not cited in the text, are included under references: Bruce 1969; Rad, Rad and Olson 1974.

The bit and cutter evaluation study for oil shale used a Bureau-designed linear cutting apparatus and a horizontal rotary drill. Several types of drag bits and disk cutters were used in the experiments. This report includes the results obtained from a 60-degree disk cutter, large and small point attack drag bits, and cutter-type drag bits, and includes relative comparisons for 90-degree and gear-type disk cutters and finger-type drag bits. At least 30 tons (27 metric tons) of oil shale were obtained from the Colony Development Operation near Rifle, Colo. Test block sizes ranged from 3 x 3 x 1-1/2 ft (0.9 x 0.9 x 0.5 m) to 4 ft (1.2 m) cubes and had compressive strength range of 6,000 to 18,000 psi (41 to 126 MN/m²) and grade range of 21 to 67 gallons (0.095-0.301 m³) per ton.

Bit and Cutter Evaluation Study for Oil Shale

The Bureau's Twin Cities Mining Research Center initiated a research program to define preliminary machine requirements and the technical feasibility of fragmenting oil shale with various bits and cutters. The objective of this research was to develop bit and cutter design requirements for tunnel boring and continuous mining machines and to estimate their overall performance.

Experimental Equipment and Test Procedures - Bits and cutters were evaluated on two experimental test fixtures: a linear cutting apparatus, named the rock cutting device (RCD) and a large rotary drill, named a horizontal underground borer (HUB). The RCD was used for independent cutting tests with disk cutter and drag bits, as shown in figure 1.

From left to right, the top row shows a disk and gear tooth cutter; the bottom row shows a small point attack drag bit, a large point attack drag bit, and a cutter-type drag bit. The disk cutters used were 1 in. (2.5 cm) thick and 7 in. (18 cm) in diameter with a cutting edge of 90° and 60°. The gear tooth cutter was constructed with 60° cutting tips. The small point attack drag bit was 5 in. (13 cm) long and 1 in. (2.5 cm) diameter with a tip angle of 75°. The large point attack drag bit was 5.5 in. (14 cm) long and 1.5 in. (3.8 cm) diameter with a tip angle of 75°. The cutter drag bit was 3 in. (7.6 cm) long and 0.5 in. (1.3 cm) thick with a negative 10° rake.

Single bits and cutters were tested on the Bureau-designed RCD (fig. 2). This apparatus is designed to load and traverse a bit or cutter across rock surface and to measure the forces, speed, and depth of cut.

Figure 1. - Bits and cutters used in the linear cutting tests.
(Rad and Schmidt 1973). Normal load and horizontal motion for the bits and cutters are provided by two hydraulic cylinders. Hydraulic systems are designed to provide a maximum of 30,000 lb (135,000 N) normal force; 15,000 lb (68,000 N) horizontal force, and cutting speed up to 70 in./sec (177 cm/sec). The linear cutting experiments reported were primarily designed to define the fundamental differences of the bits and cutters in fragmenting oil shale. They were performed under a narrow range of experimental conditions, including, linear motion, single groove studies, absence of indexing effects, and smooth rock surfaces. The samples were oriented to simulate a vertical direction of cut within horizontally bedded oil shale deposits. Data for each bit and cutter were developed through several tests on a few oil shale samples.

Since linear cutting does not duplicate the field conditions of the continuous fragmentation machines, a large drill was modified to test steady-state conditions with various cutterheads like the one shown in figure 3. This cutterhead is 2 ft (0.6 m) in diameter and uses the large point attack drag bit shown in figure 1. The bit spacing can be varied from 1 to 3 in. (2.5 to 7.6 cm). The test fixture is shown in figure 4. The HUB, a small raise borer mounted horizontally, is designed to provide a maximum rpm of 80, thrust of 162,000 lb (721,000 N) and torque of 31,000 ft-lb (43,000 Nm) (Schmidt and others 1975). Rpm, thrust, and torque were recorded during tests. Cutter-
head advance was parallel to the bedding to simulate horizontal entry development.

Experimental Results - Specific Energy. Relative efficiency of a fragmentation process can be measured by the energy (cutting force times length of cut) required to break out a unit volume of rock; i.e., specific energy. Fragmentation efficiency increases as specific energy decreases (Morrell and Larson 1974; Gaye 1972). As found in previous mechanical fragmentation experiments with disk cutters (Morrell and Larson 1974; Rad 1974), figure 5 shows that as groove depth increases, specific energy decreases; rapidly at first, then approaching a constant value.

Figure 3. - Two-foot rotary cutterhead used for steady-state tests.
Figure 5. - Specific energy as a function of groove depth in oil shale for independent linear grooves.

The curves in figure 5 represent the results of independent linear cutting tests with a 60° disk cutter, cutter drag bit, and large and small point attack drag bits. The figure shows the relative fragmentation efficiency of the different tools. Specific energy differences, at any depth, demonstrate that the overall efficiency of the small point attack and cutter type drag bits is better than the disk cutter and the large point attack drag bit.

Tests also indicated that as the depth of groove increases, the magnitude of the lateral forces and vibrations increased. In designing an ideal machine for oil shale, specific energy, and magnitude of the lateral forces and vibration should be minimized. From the standpoint of fragmentation efficiency, the depth of cut need not exceed 0.3 to 0.4 in. (0.8 to 1 cm) because specific energy does not decrease significantly. In addition, 90° disk and gear tooth cutters were also tested. The 90° disk induced very little damage to the rock and the gear tooth did not improve the fragmentation efficiency of the disk cutter.

Cutting Forces. Figure 6 shows an inherent disadvantage of the disk cutter. The curves represent the results of linear, independent cutting tests. The thrust, or normal force, required to penetrate the oil shale is six times greater for the disk than the drag bits. At the same normal force, drag bits are able to penetrate at least eight times deeper than the disk cutter. The figure illustrates why drag bit machines can react to the thrust forces with their weight, while tunnel boring machines require large-capacity rib jacks.

Figure 7 shows how cutting force is related to normal force in linear, independent cutting tests. Cutting force is the force required to pull the tool through the shale and is the force that determines the torque required to rotate a cutterhead. The figure shows that the drag bit cutting force is much greater than that required for the disk. This cutting force difference is caused by the plowing action of drag bits through rock versus the rolling action of disk cutters.

The ratio of cutting force to normal force, cutting coefficient, when plotted against groove depth, allows comparison of the force applications necessary to fragment shale. This comparison can be used to illustrate the advantages and disadvantages of various continuous fragmentation machines. Cutting force, normal force, and depth are proportional to the respective torque, thrust, and rate of penetration of these machines. As shown in figure 8, for independent linear cutting tests, the coefficient increases linearly with depth, with the drag bits having a higher coefficient (as much as four times higher) than that of the disk cutters. Any increase in this ratio indicates that cutting force increases more than normal force. This, in turn, increases fragmentation energy input but decreases specific energy (see fig. 5). However, in a mining situation, both forces have to be realistically reacted. The force reactions are provided through the machine's thrust and rotary system, weight, and auxiliary hold-downs. In the case where cutter forces can be easily reacted and wear is not a problem, drag bits are advisable; however,
when high drag bit forces cannot be reacted, or wear is excessive, disk cutters are used.

Groove Characteristics. Weight of chips per unit length was chosen as a measure of groove size since it is proportional to volume and normalizes the length of different grooves. Figure 9 shows chip weight per unit length as a function of the groove depth for independent linear cutting tests. In practical terms, the curves indicate fragmentation is increased by depth. The figure indicates that disk cutters fragment the shale easily, but they are limited to shallow depths because of the normal force requirements. The cutter and small point attack bit fragmented the most shale for any given depth.

Groove width can serve as a first approximation for optimum tool spacing. In figure 10, width is plotted as a function of groove depth. For oil shale, width to depth ratio is about 9 for the disk cutter, and ranges from 5 to 7 for drag bits. The ratio indicates that disks would have a greater optimum spacing than the drag bits at the same depth of cut. However, the large normal force requirements of disks limit their penetration to shallow depths.

Steady State Testing. Unfortunately, well-controlled, independent linear cutting tests do not duplicate the fragmentation process of boring or mining machines. Therefore, steady-state conditions were evaluated with a disk cutter and drag bit to
better understand this fragmentation process. The steady-state condition is reached when fragmentation efficiency is not increased by removing more layers of rock. A rotary drill (fig. 4) was used for the drag bit steady-state tests. One of the cutterheads (fig. 3) was mounted with large point attack drag bits. Since the capability of the rotary drill test fixture and sample size was limited, the steady-state disk cutter test was performed on the RCD (fig. 2). The test involved removing six layers of oil shale with interacting groove tests. Interacting grooves means the oil shale was broken out between the grooves and a layer is the average groove depth.

Figure 11 compares steady-state drag bit drilling with independent linear cutting drag bit tests, where specific energy is plotted as a function of drilling rate. The figure shows specific energy decreases, with depth, for both linear cutting and rotary drilling. The large point attack drag bit was used for the linear cutting and 2-ft-diam (0.6-m) rotary tests. The difference between the 2-ft (0.6-m) rotary and the linear cutting shows the benefit of steady-state fragmentation by the reduction of...
Figure 8. - Cutting coefficient as a function of groove depth in oil shale for independent linear grooves.

specific energy between the two curves. At the minimum specific energy level, the steady-state condition required only 30 percent of the specific energy requirements of independent linear cutting tests. The other curve on the figure is the test result from a 1-ft (0.3-m) cutterhead, using small finger cutter bits. With this type of bit, fragmentation efficiency, lowest specific energy, was best; however, it easily deviated from the hole axis and was not capable of high drilling rates.

The steady-state disk cutter test only represents one data point and can only be compared to an independent linear cutting test on the same oil shale sample. Making this comparison at the same depth of groove, the steady state required only 45 percent of the specific energy required by independent groove tests.

The rotary tests also emphasized the importance of optimizing the specific energy, considering the lateral loading and vibrations. An increase in depth increased the shock loads to the drill. From the standpoint of fragmentation efficiency, figure 11 shows there is very little gained by increasing the drilling rate more than 0.4 in. (1 cm) per revolution for the 2-ft (0.6-m) cutterhead.

Application of Results - Even though the bit and cutter experiments were performed under a narrow range of experimental conditions, the results can be used to approximate mechanical fragmentation machine performance. Disk cutter and drag bit machine requirements can be directly compared, assuming their use on a large rotary cutterhead, such as a tunnel-boring machine. For simplicity, this comparison was made, using linear cutting test results at lower specific energy levels. The calculation was
restricted to fragmentation characteristic of the 7-in. (18-cm) 60° disk cutter and the small point attack bit. For equal tunnel sizes (11.3-ft-diam [3.4-m]), it was assumed that both cutterheads rotated at 5 rpm and penetrated 0.28 in. (0.71 cm) per revolution. This yields a production rate of 37 tons (33 metric tons) per hour, at an advance rate of 6 ft (1.8 m) per hour, considering cycle time. The experiment data dictated a 2.5-in. (6.4-cm) disk cutter spacing and a 2-in. (5-cm) drag bit spacing. Comparison calculations, using 33 disk cutters and 40 drag bits, showed that the disk cutter machine would require a thrust of 990,000 lb (4.4 MN) and a torque of 560,000 ft-lb (760,000 Nm). The drag bit machine would require a thrust of 120,000 lb (530,000 N) and a torque of 240,000 ft-lb (320,000 Nm).

Calculations also indicated that the torque requirement for the disk cutter machine could not be significantly reduced by decreasing cutter spacing.

Another interesting comparison is the capability of a continuous drum miner. In this case, production rate is limited by the specifications of one of the most powerful miners manufactured. Its capabilities are limited by 120,000-ft-lb (160,000-Nm) torque; 83,000-lb (370,000-N) forward thrust; and 60,000-lb (270,000-N) shearing force.

The assumptions were as follows: 10- by 10-ft (3.1 by 3.1 m) face (the same face area as the tunnel boring examples); 1-in (2.5-cm) bit spacing, for a total of 132 small point attack drag bits; 44.5-in (113-cm) drum diameter; 25 rpm, and 6-in. (15-cm) sumping depth.
Figure 10. - Groove width as a function of groove depth in oil shale for independent linear grooves.

From experimental results of the small point attack drag bit, equations were defined for torque, thrust, and shearing force, as a function of depth, for the sumping and shearing cycle. Depth of cut per revolution and time delays determine cycle time. Calculated depth of penetration per revolution was 0.2 and 0.7 in. (0.5 and 1.5 cm) for the sump and shear, respectively. Therefore, one cycle produces 3.4 tons (3.06 metric tons) in 8.3 min. This yields a production rate of 24 tons (21.6 metric tons) per hour and an advance rate of 3.6 ft (1.0 m) per hour. Production rate could be increased with auxiliary jacks.

These examples are used only to illustrate the difference between a drag bit and disk cutter machines; production rates should only be considered as first approximations. For example, predictions could have been improved, using the steady-state test results and the 7-in. (18 cm) disk cutter which is approximately one-half the size used on the tunnel boring machines. However, at the same production rate, the drag bit tunnel boring machine required only 12 percent of the thrust and 43 percent of the torque needed by the disk cutter machine. Even though production rate of the drum miner was 60 percent of that of the
other machines, it required only 10 percent of the torque and 20 percent of the thrust needed by the disk cutter tunnel boring machine.

Summary

The important results of the bit and cutter evaluation are as follows:

(1) Fragmentation efficiency - Specific energy varies inversely with groove depth. As depth approaches zero, specific energy increases rapidly; and, as depth increases, specific energy decreases and approaches a constant value. Drag bits are more efficient than disk cutters. Specific energy for steady-state fragmentation is about 30 percent for drag bits and 45 percent for disk cutters of that required for independent groove fragmentation. Future improvements in mechanical fragmentation, such as water jet assisted bits (Morrell and others 1970) show some promise for increasing the fragmentation efficiency.

(2) Cutting forces - Depth of penetration is approximately a linear function of normal force for any bit or cutter. Drag bits required only one-sixth the normal force needed for disk cutters for the same depth of penetration. Drag bit cutting force is nearly four times greater than that required for the disk cutter at the same normal force. However, at equal depths of penetration, drag bits require a smaller cutting force than the disk cutter.

(3) Groove characteristics - Width varies directly with groove depth for all
cutting tools. The results demonstrate that optimum spacing for the disk could be as much as 1.7 times the optimum spacing for drag bits.

(4) Machine requirements - The machine requirements for drag bits are less than for disk cutters. This was illustrated by the comparison of two tunnel boring machines. The drag bit machine required only 12 percent of the thrust and 43 percent of the torque required by the disk cutter machine to obtain the same production rate.

Candidate Mechanical Driving Systems for Oil Shale

To determine the best machine for entry development in oil shale, machine experience must be considered. Basically, entry driving requires successful completion of three principal activities:

(1) Break the rock free from the face.
(2) Muck and transport the broken rock.
(3) Support the surrounding rock mass (Schenck 1974).

Explosives can excavate tunnels in all rock types with daily advance rates of 40 to 60 ft (12 to 18 m). Although versatile, the conventional drill-and-blast system has the disadvantage of accomplishing the three basic activities cyclically. This precludes any dramatic increases in excavation rates. Furthermore, excavation costs increase when tunnel diameter is below 11 ft (3.4 m) because of restricted working space (Muirhead and Gossip 1968).

By contrast, today's fully mechanized miners, roadheaders, and boring machines execute the first two principal activities simultaneously and continuously. The main advantages of continuous entry systems are:

- Break the rock continuously.
- Muck and transport continuously, at the rate material is produced.
- Provide a roof and/or wall requiring less support than the fractured rock left by blasting. The amount of overbreak rarely exceeds 5 percent, whereas, it often exceeds 25 percent in conventionally driven openings.

- Provide an inherently safer working environment since the excessive noise, fumes, and vibration of blasting are eliminated (Schenck 1974; Bruner 1974).

The disadvantages vary with machine type.

Continuous entry driving systems that could be used in oil shale can be divided into two categories:

(1) Continuous miners - Highly mobile machines, usually track mounted, which include the fixed drum miner, roadheader, and boring-type miner.

(2) Boring machines - These include tunnel and undercutting type boring machines.

Continuous Miners - Drum Miners. The first continuous mining machines were chain-type ripper miners, introduced in the late 1940s to the coal industry. These machines were replaced by drum-type continuous miners (fig. 12), such as the Jeffery Heliminer, Joy 11-CM and 14-CM, and the Marietta Drum Miner (Schenck 1974). Most are crawler mounted, with four basic structural components, consisting of main frame, gathering head, intermediate and discharge conveyor, and cutter drum.

The drum miner excavates a rectangular cross-section, the width of the cutter drum, cyclically. The cycle starts with the sump, where the bits are forced into the face at the roof line, then forced to the floor by hydraulic cylinders during the shear down. Next, the cusp is removed during the cut out. Finally, the machine is repositioned for the next cutting cycle (Fife 1974).

Main advantages of drum-type continuous miners are:

- High production rates - Trevorrow (1975) cites an example of cutting hard bottom rock of a coal mine (compressive strength: 21,000 and 30,000 psi [140 and 210 MN/m^2]), at 2.1 and 1.4 tons (1.9 and 1.3 metric tons) per minute. This production converts to advance rates of 16 and 11 ft (4.9 and 3.4 m) per hour for a 10- by 10-ft (3.1 by 3.1 m) heading. At these
high production rates, the continuous drum miner would require only a few hours of cutting time to outperform a conventional system.
- Relatively low investment cost.
- Crawler mounting gives the flexibility and maneuverability necessary for most mining systems, including 90° cross cuts.
- Easy bit changing and inspection - With these machines, the face is accessible.
- Roof support installation capability close to the face.
- Ready availability of spare parts.

The main disadvantages of the drum miner are:
- Lack of cutting force - Cutting forces are distributed over many bits and are solely reacted by the machine's weight since most machines are not braced against the roof or walls.
- High dust generation - Cutterheads, laced with many bits, create fines
Roadheaders. Roadheaders, or boom-type continuous miners, have been in use since the 1950s. The first one, an Alpine, ripper-type miner (fig. 13) was introduced into the United States in 1969. The milling type, Dosco Mark 2A, was introduced into North America in 1973. Roadheaders are similar to drum miners, except for the articulated boom. In addition, they are lighter and require less horsepower (Schenck 1974), and are capable of cutting harder rock (Kogelmann 1974).

The main advantages of the roadheader are:

- Ability to cut harder rock than drum or boring-type continuous miner since machine weight can be concentrated on one bit at a time.

Figure 13. - Boom-type continuous miner. (Courtesy, Alpine Equipment Corporation.)
Relatively low capital cost.
Generates less dust than drum miner.
Can negotiate steep grades and tight crosscuts (Schenck 1974).
Ability to excavate various cross-section shapes.
Roof support installation capability at the face.
Greater utilization than a drum miner. Kogelman (1974) cites an example where a roadheader outperformed a drum miner in an iron ore mine. However, Schenck (1974) states that roadheaders have lower production rates.
The disadvantages of the roadheader are:
- Productivity generally lower than drum and boring type miner.
- Milling type cutterhead throws fragmented rock sideways and requires a separate mucking cycle.
- Careful maintenance required.
The ripper-type roadheader has been used to excavate rock up to 18,000 psi (120 MN/m²).

Boring-Type Miners. Boring-type continuous miners (fig. 14), such as the Joy, Goodman, and Marietta, were first introduced for coal mining; however, they have obtained their greatest success in potash, salt, and trona mining. Such miners, equipped with two to four cutterheads and up to 1,500 hp, have achieved production rates up to 15 tons (13.5 metric tons) per minute (Schenck 1974). A kerf-core cutting principle produces larger cuttings than other continuous miners by cutting deep kerfs and breaking the core. The main advantages of the boring-type continuous miners are:
- High production rates.
- Crawler mounting gives flexibility and maneuverability necessary for curves and crosscuts.
- Easy inspection and replacement of bits.
- Ready availability of spare parts.
The disadvantages of the boring-type continuous miners are:
- Cutting reaction force is only the machine weight.
- Can only operate on moderate grade since they are heavy.
- Difficult to control dust on second pass.
- Limited excavation shapes.

Boring Machines - Tunnel Boring Machine. The tunnel boring machine or mole (fig. 15) evolved over the last century, beginning in England in 1856; however, the 1950s saw their first extensive use (Weber 1970; Bruce and Morrell 1970). During the past 15 years, techniques have improved enough to give this machine the economic edge over conventional methods for single entry development. Today's machines range in size from 6 to 40 ft (1.8 to 12 m) in diameter. The tunnel borer performs best on projects of several miles with few setups.
The machine can be visualized as a self-advancing, rotary drill, capable of cutting the circular face in a semicontinuous fashion. The machines are made up of an inner and outer frame. The inner frame carries the cutterhead that rotates and advances. The outer frame is held stationary by hydraulic rib jacks during the cutting cycle (Bruce and Morrell 1970). Thrust and torque capabilities are up to $2 \times 10^6$ lb (8.8 MN) and $1.5 \times 10^6$ ft-lb (2.1 x 10⁶ Nm), respectively. All U.S. hard-rock machines use some type of rolling cutters. The most popular are single or multiple disks, or roller-shaped bits with carbide inserts. The single or multiple disk cutters yield the best penetration, if there is effective fragmentation between adjacent disks.
The main advantages of the tunnel boring machine are:
- Continuous fragmentation.
- Continuous mucking at cutting rate.
- Machine availability of about 50 percent (Hamilton 1972).
- Smooth roof with little overbreak, which allows less costly roof support.
- Easy dust control.
- High penetration rates in competent and uniform rock (Barendsen 1972).
The disadvantages of the tunnel boring machine are:
Figure 14. - Boring-type continuous miner. (Courtesy, National Mine Service Co.)

- High capital cost - To offset the $1,300 per horsepower cost with power requirements up to 1,500 hp, the machine must be capable of boring 6 to 12 miles (10.8-21.6 km).
- High cutter costs - According to Weber (1970), they range from $0.04 to $0.70 per ft$^3$ ($1.40$ to $25$ per m$^3$).
- Much labor for setup and disassembly - This restricts the machine to developments of more than 1 mile.
- A large turning radius, generally 300 to 400 ft (91 to 120 m).
- Tunnel geometry only circular.

Undercutting Boring Machine. A new concept in tunnel boring, using the undercutting principle, was patented in 1951, originally tested in the early 1960s, and, since 1968, undercutting boring machines have been manufactured by Atlas Copco (fig. 16). The typical undercutting boring machine breaks the rock by inducing stresses that exceed its compressive/shear strength through a thrust force applied parallel to the tunnel axis.

The undercutting principle, as shown in figure 17, undercuts the rock with drag bits mounted on a rotating swinging cutterhead. The undercut ridge is easily broken and
Figure 15. - Eighteen-foot-diameter tunnel boring machine (3). (Courtesy, The Robbins Co.) creates 70 to 85 percent of the excavated volume. The forces required to oppose the cutting forces are provided by rib jacks. This undercutting method is adaptable to several different tunnel cross sections, as shown in figure 18. Figure 16 shows the smallest version, the minifullfacer, of the Atlas-Copco machines.

Atlas Copco machines have driven tunnels through homogeneous rock with compressive strengths up to 30,000 psi (210 MN/m²). Test tunnels have been driven in 55,000-psi (380-MN/m²) rock. The minifullfacer has obtained advance rates up to 8.2 ft (2.5 m) per hour.

The advantages of the undercutting boring machine are:

- Low cutter cost since only part of the excavated volume is cut. Case histories list cutter costs from $0.05 to 0.16 per ft³ ($1.80 to $5.60 per m³) for 15,000- to 28,000-psi (100- to 190-MN/m²) shale.
- Undercutting boring machines require less than 30 percent of the thrust required by tunnel boring machines.
- Undercutting produces less fines. Less than 10 percent of muck is below
Figure 16. - Minifullfacer tunnel boring machine. (Courtesy, Atlas Copco, Inc.)

3/8-inch (9.53 mm) size.
- Easy bit changing.
- Variability of tunnel geometries with different machine designs.

The disadvantages of the undercutting boring machine are:
- Low maneuverability since the machines are propelled by rib jacks. However, the machines can be designed to turn in a 40-ft (12 m) radius which is better than that of the tunnel boring machines (Barendsen 1972; Brodbeck 1974; Talvensaari 1974).
- Less flexible than the continuous miners.

Figure 17. - Drag bit cutterhead used for undercutting principle. (Courtesy, Atlas Copco, Inc.)
machines; however, they can be used to predict trends for the fragmentation efficiency of the various bit and cutters. The important criteria for choosing an entry development machine for a field trial should be:

1. the machine should require no, or slight, modification -- this dictates hard rock experience;
2. the fragmentation process should be as efficient as possible;
3. the systems should be as flexible as possible.

For vertical development, machine selection is limited to the shaft drill and the raise boring machine. The separation of cutterhead and machine, limits their performance to the capability of the drill steel to react the dynamic forces generated by the fragmentation process. Because of this system limitation, there are only minor variations of the roller cutter fragmentation process. However, our experiments indicated oil shale fragmented more efficiently when cut to simulate vertical entry development.

Several machines have been used in non-coal formation for horizontal development, making the choice of machine more difficult. One can, however, make up a decision matrix, emphasizing the important criteria for the future job. Using our test results and information we prepared a simplified matrix (Table 1) to illustrate the possible selection process of a machine for a field trial. Table 1 is oversimplified and very subjective. Its primary purpose is to stimulate thought. Each category of machine characteristics was ranked, from 1 to 3, and category ranks for each machine were added. The undercutting boring machine received the highest ranking because it incorporates many of the advantages of both a disk cutter and drag bit machines. If there is a use for a small size entry, the minifullfacer or the midifullfacer would be a logical choice to develop cost and performance data on mechanical fragmentation systems for oil shale.

Recommendations and Conclusions

The next step in introducing mechanical fragmentation systems to oil shale mining should be a field trial to develop some cost and performance data. In mechanical excavation, bit and cutter wear is an important cost consideration. Even though we did not examine wear qualitatively, none of the bits or cutters used in our experiments, showed any appreciable wear. In fact, the large point attack drag bits showed no wear after cutting up to 1,500 linear feet (460 m) for the steady-state tests. The experimental results cannot be applied directly to predict the performance of any of the candidate machines; however, they can be used to predict trends for the fragmentation efficiency of the various bit and cutters. The important criteria for choosing an entry development machine for a field trial should be:

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1. the machine should require no, or slight, modification -- this dictates hard rock experience;
2. the fragmentation process should be as efficient as possible;
3. the systems should be as flexible as possible.

For vertical development, machine selection is limited to the shaft drill and the raise boring machine. The separation of cutterhead and machine, limits their performance to the capability of the drill steel to react the dynamic forces generated by the fragmentation process. Because of this system limitation, there are only minor variations of the roller cutter fragmentation process. However, our experiments indicated oil shale fragmented more efficiently when cut to simulate vertical entry development.

Several machines have been used in non-coal formation for horizontal development, making the choice of machine more difficult. One can, however, make up a decision matrix, emphasizing the important criteria for the future job. Using our test results and information we prepared a simplified matrix (Table 1) to illustrate the possible selection process of a machine for a field trial. Table 1 is oversimplified and very subjective. Its primary purpose is to stimulate thought. Each category of machine characteristics was ranked, from 1 to 3, and category ranks for each machine were added. The undercutting boring machine received the highest ranking because it incorporates many of the advantages of both a disk cutter and drag bit machines. If there is a use for a small size entry, the minifullfacer or the midifullfacer would be a logical choice to develop cost and performance data on mechanical fragmentation systems for oil shale.
Table 1. - Simplified decision matrix to select a candidate machine for oil shale entry development.

<table>
<thead>
<tr>
<th>Desirable machine characteristic for oil shale entry development</th>
<th>Fixed drum miner</th>
<th>Road-header</th>
<th>Boring-type miner</th>
<th>Tunnel boring machine</th>
<th>Undercutting boring machine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low specific energy .........</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Low normal force ...........</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Large cutter spacing .........</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Stable machine structure ...</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>High maneuverability and low mobilization ..........</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Hard rock experience .........</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Total .............</td>
<td>13</td>
<td>13</td>
<td>14</td>
<td>11</td>
<td>15</td>
</tr>
</tbody>
</table>

1Space between undercuts.
2High lateral force generated by disk cutter.

Acknowledgments

The Bureau acknowledges the continuing advice, information, and assistance from various mining and tunneling machines and cutting element manufacturers. Special thanks are due to the Colony Development Operation for furnishing oil shale samples.

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EVALUATION OF ROCK SPRINGS SITE 9 IN SITU OIL SHALE RETORTING EXPERIMENT

A. Long, Jr., N. W. Merriam, and C. G. Mones
U.S. Energy Research and Development Administration
Laramie Energy Research Center
Laramie, Wyoming 82071

Abstract

Results of the first 150 days of operation of an in situ oil shale retorting experiment near Rock Springs, Wyo., are presented. A zone of oil shale located in the Tipton Member of the Green River Formation was retorted. The target zone was 137 feet (41.8 m) deep, 40 feet (12.2 m) thick, and assayed 21.3 gallons of oil per ton (.097 m³/metric ton) of shale. A section 70-feet square (21.4 x 21.4 m) with eight peripheral production wells was hydraulically fractured to produce three horizontal fractures. Slurry-type explosive was forced into the fractures and detonated to produce a bed of oil shale rubble.

The oil shale bed was ignited on April 5, 1976, using an electrical resistance heater to heat air, which was then supplemented with propane in the central injection well. The advance of the combustion front was monitored with a computer-based data acquisition system, reporting temperatures, pressures, flows, and gas compositions each hour. The air injection was moved to well 10 in the northeast section of the pattern on the 60th day of operation to increase oxygen utilization, which averaged 65 percent.

The effects of in situ retorting upon air, ground surface temperature, and ground water were followed during the course of the test. A broad-ranging biochemical study of the effects of retort water on the environment has been initiated.

Material balance calculations indicated that 3,260 tons (2.934 metric tons*) of oil shale were retorted, representing 21 percent of the oil shale in the target zone. Oil migration beyond the pattern was evidenced and only 2,483 gallons (11.3 m³) or 1 percent of the shale oil resource was recovered. Nitrogen balances showed an average recovery of 93 percent of injected air. A total calorific value of 1,515 million Btu's of gas, averaging 38 Btu/scf, was produced.

A complete evaluation of the experiment is planned after core samples are taken.

Introduction

Most of the western oil shale resource is either too low grade to make conventional mining economically feasible, or exists in deposits too thin to make modified in situ recovery workable. The Laramie Energy Research Center has pioneered research into in situ retorting processes which have the potential to recover the vast shale oil resource from these less attractive deposits in an environmentally sound and economically feasible manner.

One of the most encouraging early tests (Burwell and others 1970) was conducted at Rock Springs site 4 in the spring of 1969. A 20-foot (6.1 m) thick by 25-foot (7.6 m) square block of oil shale, 65 feet (19.8 m) below the surface was hydraulically and explosively fractured and was then retorted in situ. The combustion phase was sustained

*Ed. note: ASTM metric practice followed.
for 42 days, and terminated when the objectives of the experiment were met. Injection pressures were generally 100-150 psig (710.6 Kgscm), which were higher than desired, contributing to the low (less than 40 percent) recovery of injected air. Over 190 barrels (36.5 m³) of shale oil were recovered.

The experiment at Rock Springs site 9 was a scaled-up version of the experiment at site 4. The shale zone used was larger, deeper, and fractured, using a technique similar to that used at site 4. Explosive fracturing was modified to permit operation at lower injection pressure and to improve gas recovery. A computer-based, data acquisition system was included at site 9 to monitor the progress of the experiment and summarize results.

This paper presents results of site 9 in situ retorting, from the sustained ignition on April 5, 1976, through the first 150 days of operation. At the time of writing, the air injection phase has been curtailed, the retorting zone is still hot, and liquid recovery continues. A complete postburn evaluation, including core sample analysis of the site, is planned for mid-1977.

Site Preparation

The target shale zone is located in the Tipton Member of the Green River Formation oil shale between 137 and 177 feet (42 and 54 m) below surface level. A core evaluation showed an average 21.3 gallons of oil per ton (89 liters per m ton) and 2.3 weight by percent water by Fischer assay in the target zone. Oil shale assays from core evaluation are shown in Table 1.

The well pattern, shown in figure 1, was a square section 70 feet (21.4 m) on a side, with production wells set at each corner of the square and at the midpoints of each side. An injection well was drilled in the center of the square, and temperature

<table>
<thead>
<tr>
<th>Depth in feet</th>
<th>Gal per ton</th>
<th>S.G. oil, Oil Water</th>
<th>Depth in feet</th>
<th>Gal per ton</th>
<th>S.G. oil, Oil Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>134.4-135.5</td>
<td>17.2</td>
<td>4.1</td>
<td>0.914</td>
<td>155.0-156.2</td>
<td>25.3</td>
</tr>
<tr>
<td>135.5-136.5</td>
<td>19.6</td>
<td>4.3</td>
<td>.905</td>
<td>156.2-157.3</td>
<td>25.9</td>
</tr>
<tr>
<td>136.5-137.4</td>
<td>34.0</td>
<td>5.9</td>
<td>.923</td>
<td>157.3-158.5</td>
<td>21.1</td>
</tr>
<tr>
<td>137.4-138.2</td>
<td>32.4</td>
<td>5.5</td>
<td>.924</td>
<td>158.5-159.6</td>
<td>20.3</td>
</tr>
<tr>
<td>138.2-139.3</td>
<td>27.6</td>
<td>5.9</td>
<td>.925</td>
<td>159.6-161.2</td>
<td>16.5</td>
</tr>
<tr>
<td>139.3-140.2</td>
<td>31.2</td>
<td>5.5</td>
<td>.914</td>
<td>161.2-162.2</td>
<td>32.2</td>
</tr>
<tr>
<td>140.2-141.1</td>
<td>25.9</td>
<td>5.3</td>
<td>.912</td>
<td>162.2-163.5</td>
<td>26.5</td>
</tr>
<tr>
<td>141.1-142.0</td>
<td>25.8</td>
<td>4.1</td>
<td>.916</td>
<td>163.5-164.7</td>
<td>32.4</td>
</tr>
<tr>
<td>142.0-142.5</td>
<td>15.1</td>
<td>2.9</td>
<td>.912</td>
<td>164.7-165.9</td>
<td>31.5</td>
</tr>
<tr>
<td>142.5-143.5</td>
<td>18.9</td>
<td>4.1</td>
<td>.913</td>
<td>165.9-166.9</td>
<td>18.8</td>
</tr>
<tr>
<td>143.5-144.7</td>
<td>11.8</td>
<td>3.7</td>
<td>.900</td>
<td>166.9-167.9</td>
<td>25.0</td>
</tr>
<tr>
<td>144.7-146.0</td>
<td>18.5</td>
<td>5.8</td>
<td>.903</td>
<td>167.9-169.0</td>
<td>16.4</td>
</tr>
<tr>
<td>146.0-147.0</td>
<td>14.3</td>
<td>6.5</td>
<td>.905</td>
<td>169.0-170.1</td>
<td>16.5</td>
</tr>
<tr>
<td>147.0-148.1</td>
<td>11.8</td>
<td>5.0</td>
<td>.904</td>
<td>170.1-171.1</td>
<td>28.0</td>
</tr>
<tr>
<td>148.1-149.2</td>
<td>18.9</td>
<td>6.2</td>
<td>.913</td>
<td>171.1-171.5</td>
<td>28.8</td>
</tr>
<tr>
<td>149.2-150.5</td>
<td>20.8</td>
<td>7.0</td>
<td>.921</td>
<td>171.5-172.1</td>
<td>31.1</td>
</tr>
<tr>
<td>150.5-151.5</td>
<td>17.7</td>
<td>6.7</td>
<td>.925</td>
<td>172.1-173.4</td>
<td>12.5</td>
</tr>
<tr>
<td>151.5-152.8</td>
<td>17.8</td>
<td>5.5</td>
<td>.931</td>
<td>173.4-174.7</td>
<td>25.2</td>
</tr>
<tr>
<td>152.8-154.0</td>
<td>15.9</td>
<td>4.3</td>
<td>.931</td>
<td>174.7-175.9</td>
<td>18.8</td>
</tr>
<tr>
<td>154.0-155.0</td>
<td>18.4</td>
<td>7.2</td>
<td>.928</td>
<td>175.9-177.1</td>
<td>10.9</td>
</tr>
</tbody>
</table>

*From site 9 well No. 1, drilled in the NW 1/4 SW 1/4 NW 1/4 of Sec. 15, T. 18 N., R. 106 W., Sweetwater County, Wyo. Surface elevation 6,339.74 feet.
monitoring wells were located midway between the center well and the wells in the side of the square. Three wells were later drilled northeast of the basic pattern to verify suspected oil migration into that area.

The 8.6-inch (21.9 cm) central well and the eight 7-inch (17.8 cm) production wells were drilled to 136 feet (41.5 m), cased, and cemented. Open holes were then drilled to 191 feet (58.3 m) in each of these wells.

Tests run on oriented core samples from wells 7 and 8 (Pasini and others 1972) showed minimum tensile strength and sonic velocity in the N 30-60 W direction, so any vertical fractures opened by heating or induced stresses would be expected to run N 30-60 E.

The oil shale formation was hydraulically fractured in three horizontal planes, using a straddle packer to control fracture locations. Fracture locations are shown in figure 2. The fractures were propped with a viscous gel carrying 10/20 mesh sand, followed by 6/8 mesh sand. All three fractures intersected all eight production wells, which was verified by impression packer surveys, air flow tests, and hot film flow logging. Natural fractures, evaluated by sonar scan, caliper log, seismic wave velocity, and downhole TV before explosive fracturing, were generally not significant (Stevens and others 1975).

The central well was stemmed with sand
The fracture frequency analysis of cores from those wells showed most fractures near the upper hydraulic fracture, and few fractures between the middle and lower hydraulic fractures. These data indicate that the detonation took place in the upper hydraulic fracture.

When it became apparent that a second shot was necessary to achieve substantial fracturing, well 10 (fig. 1) was drilled and cased to 151 feet (46 m), sealing off the top hydraulic fracture. The well was then completed to 191 feet (58.3 m), intersecting the middle and lower hydraulic fractures. Then, 2,500 pounds (1,138 kg) of explosive were injected into the middle and lower fractures and promptly detonated. All wells were cleaned, increasing depths by several feet. Downhole photographs, air flow tests, and well logs showed significant fracturing resulted from the second shot.

Before ignition, air flow tests were run to evaluate flow distribution and capacity. Air was injected into well 1 and flowed from all eight production wells. Then, wells 2, 3, 4, and 5 and wells 6, 7, 8, and 9 were alternately opened and closed in sets. Air flowed evenly to all four quadrants with all three flow configurations. The results of these tests, shown in table 2, show that resistance to flow within the shale bed was very uniform, or more likely, flow resistance of the shale bed was small compared to the flow resistance of the symmetrical piping system. Air recovery averaged 93 percent during the cold flow test.

Monitoring System

The shale bed was divided into four quadrants for data collection purposes. Each quadrant included a temperature monitoring well and two production wells (fig. 3). The temperature measurement well contained five thermocouples spaced vertically at 10-foot (3 m) intervals within the shale bed. Thermocouples were also mounted in all eight production wells at 190 feet (58 m) to measure bottom hole temperature and at 140 feet

to a level above the middle fracture and the upper fracture was sealed off with cement. The cement was then drilled out of the wellbore and 7,000 pounds (3,185 kg) of slurried explosive were charged to the well with the intention of forcing the explosive into the center fracture for detonation, while using the upper and lower fractures to reflect shock waves and limit extension of vertical fractures. Following placement of the explosive, all wells were stemmed with sand to confine the explosion.

Problems with the detonating system resulted in a delay between placement of the explosive and detonation. Evaluation of the stress wave data, logging of wellbores, and post-shot core samples indicated that significant fracturing did not result from the explosion. Calculations indicated that only about 1,000 pounds (454 kg) of the explosive detonated. Maximum propagation of the detonation was 20 feet (6.1 m) from the well. Examination of the post-shot, wash water failed to locate any of the explosive.

Four new temperature monitoring wells (02-05) were drilled midway between the central well and the four inner production wells.

FIGURE 2 - CROSS SECTION LOOKING NE, SITE 9, ROCK SPRINGS.
FIGURE 3. - FLOW DIAGRAM - SITE 9.
pumps metered. Gas from 300 scfm (8.49 cu mpm) 525 scfm (14.86 cu mpm) to measure average gas temperature from each well.

Gas-flows from each pair of wells were combined into a single stream which was metered. Gas flows from wells 2 and 7, 3 and 8, 4 and 9, and 5 and 6 were measured and sampled separately, generating data for four separate sets of energy and material balances.

Injected air flow and gas production were measured with orifice meters and subsequently corrected for temperature and pressure. Ambient humidity was also measured and used in calculating air flows. Gas-flow was sampled downstream from demist towers and analyzed by gas chromatography. Gas properties were recalculated each time a new sample was analyzed and these properties used in flow calculations.

Retorting progress was followed with a computer data acquisition system that printed out hourly reports of flows, temperatures, pressures, analyses, material balance, and gas properties. Gas recovery was based on a nitrogen balance, with typical recovery in the 90 to 95 percent range.

Recovery System
Primary liquid recovery was by lift pumps set at approximately 188 feet (57.3 m) in each of the production wells. The pumps were set above the bottom of the wells to provide space for debris accumulation while remaining well below the lower hydraulic fracture to keep the shale bed drained during retorting. The system was designed to use gas flow to sweep liquid into the well, with gas rising to the surface and liquid falling, to be pumped out. Locating the pumps significantly below the lower hydraulic fracture also served to keep the least temperature-resistant parts of the pumps out of the flow of the potentially hot gas stream. Liquid flow from each pump was piped to the holding tank in the quadrant in which the well was located.

A packed-bed, demist tower was installed in each quadrant to recover entrained liquid from the combined gas flow from each well pair. Liquid from each demist tower was drained to the holding tank in that quadrant and combined with liquid pumped to the surface. When it became apparent that liquid was passing through the demisters, a second-stage, mist eliminator was installed in the composite gas line upstream from the flare.

Liquid collected in the quadrant holding tanks was periodically pumped to the common storage tank where water was separated. The storage tank was equipped with a steam coil and a recirculation pump used to aid in the phase separation and to mix the separated oil phase for sampling. Liquid recovery data was collected by gauging the mix tank.

Liquid Recovery
Table 3 is a summary of oil and water recovered from site 9. All liquid produced at the site was combined in a holding tank, the water layer decanted, the oil-water layer mixed and an aliquot withdrawn. The aliquot was then distilled to dryness and the oil content of the tank calculated on a water-free basis.

Properties of shale oil recovered from site 9 are summarized in table 4.

There is considerable evidence that much of the oil retorted from the oil shale was not recovered. On the 80th day of operation, the pump was removed from well 6; the check valves were found plugged by debris. The well had a large quantity of oil and water in it. After the repaired pump was reinstalled, well 6 produced over 17 barrels (3.2 m³) of liquid in an 18-hour period, indicating that area of the shale bed was flooded with liquid. A similar situation was observed at well 2 on the 83rd day of operation. High levels of liquid were also observed in observation wells 02 and 05. These wells were cleared with a bailer and jet pump, collecting 18 barrels (3.3 m³) of

<table>
<thead>
<tr>
<th>Air Injected (cu ft/min)</th>
<th>Injection pressure (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>230 scfm (6.51 cu mpm)</td>
<td>2.8-2.9 psig (0.2 Kgs/cm)</td>
</tr>
<tr>
<td>300 scfm (8.49 cu mpm)</td>
<td>4.0-4.2 psig (0.29 Kgs/cm)</td>
</tr>
<tr>
<td>525 scfm (14.86 cu mpm)</td>
<td>5.2-5.4 psig (0.37 Kgs/cm)</td>
</tr>
</tbody>
</table>

Table 2. - Cold flow summary.
Table 3. - Liquid recovery for site 9.

<table>
<thead>
<tr>
<th>No. of days</th>
<th>Oil</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Barrels</td>
<td>Avg bbls/day</td>
</tr>
<tr>
<td>0-31</td>
<td>15.2</td>
<td>0.49</td>
</tr>
<tr>
<td>31-44</td>
<td>4.6</td>
<td>.35</td>
</tr>
<tr>
<td>44-59</td>
<td>1.4</td>
<td>.09</td>
</tr>
<tr>
<td>59-65</td>
<td>3.3</td>
<td>.55</td>
</tr>
<tr>
<td>65-87</td>
<td>3.0</td>
<td>.14</td>
</tr>
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<td>87-100</td>
<td>5.5</td>
<td>.42</td>
</tr>
<tr>
<td>100-116</td>
<td>10.3</td>
<td>.64</td>
</tr>
<tr>
<td>116-141</td>
<td>15.8</td>
<td>.63</td>
</tr>
<tr>
<td>Total</td>
<td>59.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. - Properties of shale oils.

<table>
<thead>
<tr>
<th></th>
<th>Rock Springs site 9&lt;sup&gt;1&lt;/sup&gt;</th>
<th>LERC&lt;sup&gt;2&lt;/sup&gt;</th>
<th>TOSCO II surface retort&lt;sup&gt;3&lt;/sup&gt;</th>
<th>Rock Springs site 4&lt;sup&gt;4&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spec. Gr. 16/16° C</td>
<td>0.893</td>
<td>0.911</td>
<td>0.899</td>
<td>0.970</td>
</tr>
<tr>
<td>Viscosity, Cp @ 38° C</td>
<td>7.0</td>
<td>13.0</td>
<td>18.5</td>
<td>34</td>
</tr>
<tr>
<td>Pour point, ° C</td>
<td>9</td>
<td>16</td>
<td>16</td>
<td>-1</td>
</tr>
<tr>
<td>Heating value, Kcal/Kg</td>
<td>10,312</td>
<td>10,201</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carbon, wt-pct</td>
<td>84.1</td>
<td>84.3</td>
<td>85.1</td>
<td>-</td>
</tr>
<tr>
<td>Hydrogen, wt-pct</td>
<td>11.7</td>
<td>11.8</td>
<td>11.6</td>
<td>-</td>
</tr>
<tr>
<td>Nitrogen, wt-pct</td>
<td>1.4</td>
<td>2.1</td>
<td>1.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Sulfur, wt-pct</td>
<td>1.5</td>
<td>.6</td>
<td>.9</td>
<td>.5</td>
</tr>
<tr>
<td>Distillation, vol-pct:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1BP-204° C</td>
<td>8.0</td>
<td>7.2</td>
<td>-</td>
<td>10.5</td>
</tr>
<tr>
<td>204°-315° C</td>
<td>38.4</td>
<td>22.8</td>
<td>-</td>
<td>60.5</td>
</tr>
<tr>
<td>315°-426° C</td>
<td>37.4</td>
<td>41.1</td>
<td>-</td>
<td>28.9</td>
</tr>
<tr>
<td>426° C +</td>
<td>16.2</td>
<td>28.9</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>1</sup>Average of eight analyses collected during 150 days of in situ retorting.
<sup>2</sup>Average of twelve analyses for LERC 10- and 150-ton retort runs.
<sup>3</sup>Frost and Cottingham 1974.
<sup>4</sup>Burwell and others 1969.

Liquid in 2 days. As a result of reworking the pumps, total site liquid production went from only 19 barrels (3.3 m³) per week to 112 barrels (21.5 m³) the week after repairs were made.

Removal of liquid from the shale bed dramatically changed the gas analyses, particularly oxygen concentration. As shown in table 5, the combustion reactions increased after pumps were reworked and liquid was removed from the shale bed.

During the period, starting on the 90th day of operation and afterwards, there were numerous instances of wells which stopped producing. In nearly all instances, when pumps were removed they were found to have worn leather sealing rings, plugged check valves, or were covered by propping sand or shale chips. Usually the well was found to have a liquid level well above the pump.

We postulated that pressure in the retorting zone could force oil outward from the pattern along fractures. Since liquid would accumulate in the lower voids first, with oil floating on top of the water, the oil would flow preferentially into fractures as liquid level rose. This postulation was tested by drilling wells 11, 12, and 13,
northeast of wells 2 and 7, where fracturing adjacent to the pattern was thought to be most significant. On day 102, while drilling well 11, a sample of cuttings at 144 feet (43.9 m) showed oil on its surface. A Fischer assay showed 10 gallons per ton (41.8 liters per m ton) above the background oil content in that sample. When the drill reached 167 feet (50.9 m) a flow of gas burst from the well, followed by about 10 barrels of liquid. Liquid had definitely migrated beyond the pattern.

Wells 12 and 13 were drilled the 122nd day of operation and no blowouts were observed. Also, free liquid was not apparent at either of these wells at the time of completion. Gas flow was detectable when the wells were completed. After these new wells were piped into recovery equipment and the shale bed was pressured, 7 barrels of liquid were recovered from entrainment in the gas flow from each well.

Environmental

Before the start of retorting, extensive studies were begun to measure the effects of in situ oil shale retorting upon subsurface, surface, and atmospheric environments. Background water quality data were measured (Pasini and others 1972) and continued study is underway to quantify effects on ground water during and after retorting. A 333-barrel (65.3 m³) sample of water, recovered from the shale bed during the retorting phase, is being tested for biochemical properties. Composition of water recovered from the retort bed is shown in table 6. Analyses of water samples taken from individual production wells are shown in table 7.

Aerial infrared photography measured ground surface temperatures. On the 164th day of operation, no difference could be detected between surface temperature above the retorting site and surface temperature of the surrounding area. Resistance-type temperature measuring elements have been installed in shallow wells above and adjacent to the retorting area. No temperature changes were detected after 200 days in this continuing study.

Effluent gases, before combustion in the flare, were analyzed for minor components by mass spectrometry. Results are summarized in table 8.
Table 6. - Characteristics of retort water from Rock Springs site 9.*

<table>
<thead>
<tr>
<th>Component</th>
<th>High</th>
<th>Low</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>5,100</td>
<td>2,600</td>
<td>3,925</td>
</tr>
<tr>
<td>Carbonates</td>
<td>2,000</td>
<td>0</td>
<td>662</td>
</tr>
<tr>
<td>Bicarbonates</td>
<td>25,000</td>
<td>1,000</td>
<td>12,040</td>
</tr>
<tr>
<td>Sulfate</td>
<td>4,700</td>
<td>1,200</td>
<td>2,300</td>
</tr>
<tr>
<td>Chloride</td>
<td>5,200</td>
<td>1,400</td>
<td>3,090</td>
</tr>
<tr>
<td>Total organic carbon</td>
<td>6,300</td>
<td>780</td>
<td>2,310</td>
</tr>
<tr>
<td>Boron</td>
<td>32</td>
<td>20</td>
<td>24</td>
</tr>
<tr>
<td>Fluoride</td>
<td>100</td>
<td>35</td>
<td>68</td>
</tr>
<tr>
<td>Chemical oxygen demand</td>
<td>22,000</td>
<td>5,000</td>
<td>11,640</td>
</tr>
<tr>
<td>Ammonium</td>
<td>6,700</td>
<td>0</td>
<td>3,120</td>
</tr>
</tbody>
</table>

*Average of eight samples from mix tank. All in mg/l.

Table 7. - Water analyses from individual production wells from Rock Springs site 9.

<table>
<thead>
<tr>
<th>Well</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids, gm/l.</td>
<td>21.2</td>
<td>12.6</td>
<td>23.0</td>
<td>16.0</td>
<td>11.6</td>
<td>2.4</td>
</tr>
<tr>
<td>Total dissolved solids, gm/l.</td>
<td>8.6</td>
<td>10.8</td>
<td>11.9</td>
<td>14.2</td>
<td>10.8</td>
<td>2.2</td>
</tr>
<tr>
<td>Fixed solids, gm/l.</td>
<td>6.7</td>
<td>8.5</td>
<td>2.9</td>
<td>11.5</td>
<td>8.0</td>
<td>1.7</td>
</tr>
<tr>
<td>Carbonates, ppm</td>
<td>1948</td>
<td>2273</td>
<td>3345</td>
<td>1786</td>
<td>2111</td>
<td>-</td>
</tr>
<tr>
<td>Bicarbonates, ppm</td>
<td>2312</td>
<td>2642</td>
<td>6672</td>
<td>5120</td>
<td>3236</td>
<td>1651</td>
</tr>
<tr>
<td>Carbon, TOC, ppm</td>
<td>749</td>
<td>421</td>
<td>1042</td>
<td>435</td>
<td>489</td>
<td>Nil</td>
</tr>
<tr>
<td>NH₃ nitrogen, pct</td>
<td>.03</td>
<td>.005</td>
<td>.016</td>
<td>.043</td>
<td>.031</td>
<td>Nil</td>
</tr>
<tr>
<td>Kjeldahl nitrogen, pct</td>
<td>.05</td>
<td>.013</td>
<td>.029</td>
<td>.062</td>
<td>.046</td>
<td>.002</td>
</tr>
<tr>
<td>Chromium, ppm</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Cobalt, ppm</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Copper, ppm</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Manganese, ppm</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Magnesium, ppm</td>
<td>7.2</td>
<td>8.8</td>
<td>22.6</td>
<td>9.5</td>
<td>8.7</td>
<td>3.0</td>
</tr>
<tr>
<td>Nickel, ppm</td>
<td>Nil</td>
<td>Trace</td>
<td>Trace</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Zinc, ppm</td>
<td>.3</td>
<td>.3</td>
<td>.3</td>
<td>.2</td>
<td>.3</td>
<td>.6</td>
</tr>
<tr>
<td>Calcium, ppm</td>
<td>9.2</td>
<td>9.1</td>
<td>9.1</td>
<td>2.0</td>
<td>1.0</td>
<td>14.5</td>
</tr>
</tbody>
</table>

Table 8. - Effluent gas prior to combustion, Rock Springs site 9.

<table>
<thead>
<tr>
<th>Component</th>
<th>High</th>
<th>Low</th>
<th>Average concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>285 ppm</td>
<td>0 ppm</td>
<td>34.8 ppm</td>
</tr>
<tr>
<td>NO</td>
<td>178 ppm</td>
<td>0 ppm</td>
<td>83.3 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>47 ppm</td>
<td>0 ppm</td>
<td>3.0 ppm</td>
</tr>
<tr>
<td>H₂S</td>
<td>189 ppm</td>
<td>0.05 ppm</td>
<td>50.2 ppm</td>
</tr>
<tr>
<td>COS</td>
<td>.02 pct</td>
<td>.02 pct</td>
<td>.02 pct</td>
</tr>
<tr>
<td>NH₃</td>
<td>.12 pct</td>
<td>.01 pct</td>
<td>.01 pct</td>
</tr>
</tbody>
</table>

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Retorting

Sustained ignition was achieved on April 5, 1976. An electrical resistance heater, suspended in the injection well opposite the lower fracture, was used to preheat air to ignition temperatures. Propane was fed into the injection well and mixed with air at the outlet of the heater. Propane flow was controlled at a rate to hold the concentration in the final propane-air mixture below the lower flammable limit. The low concentration of propane limited the possibility of flashing to a small mixing area at the injection point. The low propane concentration also required fuel to be freed from the oil shale to bring the mixture above the lower flammable limit. Propane injection continued for the first 17 days of operation, was discontinued, resumed on the 32nd day, and finally terminated on the 79th day of operation.

During the first phase of operation, air was injected into the central well at an initial rate of 90 scfm (2.5 m³ pm) at 30 psig (2.1 Kgscm) with almost total utilization of oxygen. Air flow was steadily increased to 250 scfm (7.07 m³ pm) at a peak injection pressure of 110 psig (7.7 Kgscm) on the 25th day of operation. Gas production was equally distributed among the four quadrants during this period. Progress of the combustion zone was seen when the temperatures in 03 observation well rose as shown in figure 4.

From the 25th to 35th days of operation, injection pressure declined to 40 psig (2.8 Kgscm), flow distribution shifted to 60 percent into the 2-7 quadrant, and oxygen utilization declined to about 50 percent. Air injection was reduced to 150 scfm (4.25 m³ pm) to increase oxygen utilization. Combustion temperatures were observed in well 10 on the 26th day of operation as shown in figure 5. The flame front passed through well 10 along the upper fracture.

Days 35 to 60 were characterized by a divergence of oxygen utilization among the individual quadrants. At the extreme divergence, the oxygen utilization varied from a high of 60 percent in quadrant 2-7 to a low of 27 percent in quadrant 3-8. Air injection flow was typically 180 scfm (5.09 m³ pm) at 30 psig (2.1 Kgscm) injection pressure. Flow from quadrant 3-8 was reduced in several steps, and when oxygen utilization did not improve, 3-8 was completely shut off (56th day).

The second phase of the operation began on the 60th day when the air injection was moved to well 10 and flow from individual wells was shut off or throttled in the attempt to control the location of the combustion zone. At that time, the combustion zone was burning strongly in quadrant 2-7, weakly in quadrants 5-6 and 4-9, and was nearly out in the 3-8 quadrant. The new location of the injection point resulted in higher oxygen utilization. While the gas analyses from the two western quadrants improved, the location of the injection point probably caused retort products from quadrant 2-7 to flow from quadrants 5-6 and 4-9. Air injection flow rates and pressures are shown in figure 6. Air injection flow and retorting rate are shown in figure 7. Average rate of advance of the retorting front is shown in table 9.

Material and Energy Balances

Hourly flows and analyses were integrated to produce material and energy balances which represent the first 150 days, April 5 to September 2, 1976, of in situ retorting of Rock Springs site 9. During this period, 39 MMscf (1.1 MM m³) of air were injected with an average nitrogen recovery of 93 percent. An estimated 3,260 tons (2,964 metric tons) of shale were retorted, representing 21 percent of the 15,616 tons (14,210 metric tons) in the target zone within the pattern.

Material balance calculations were based on carbon and hydrogen balances between gas, oil, and shale. Rates of oxidation of kerogen (CH₂) were calculated by subtracting the measured propane combustion and using the chemical formula, CH₂, to represent the kerogen. Carbon dioxide, released by mineral carbonate decomposition, was calculated as the difference between total carbon
FIGURE 4. - TEMPERATURE PROFILE OF OBSERVATION WELL 03

FIGURE 5. - TEMPERATURE PROFILE OF OBSERVATION WELL 10.
FIGURE 6. - INJECTION HISTORY.

FIGURE 7. - RETORTING RATE AND AIR FLOW.

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Table 9. - Retorting advance rate.*

<table>
<thead>
<tr>
<th>Path</th>
<th>Distance</th>
<th>Time,</th>
<th>Rate,</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>feet</td>
<td>hours</td>
<td>in/hr</td>
</tr>
<tr>
<td>Well 1 to Obs. well 3</td>
<td>16</td>
<td>480</td>
<td>0.40</td>
</tr>
<tr>
<td>Well 1 to Obs. well 10</td>
<td>26</td>
<td>624</td>
<td>.50</td>
</tr>
<tr>
<td>Well 1 to well 2</td>
<td>35</td>
<td>2328</td>
<td>.18</td>
</tr>
<tr>
<td>Well 1 to well 11</td>
<td>60</td>
<td>2760</td>
<td>.26</td>
</tr>
<tr>
<td>Quad 2-7 to well 11</td>
<td>25</td>
<td>288</td>
<td>1.04</td>
</tr>
</tbody>
</table>

*Assuming linear path between designated points.

dioxide produced and carbon dioxide from oxidation of kerogen. The validity of these calculations will be tested when core samples from the site are analyzed after completion of the burn. Material balance summary is shown in Table 10.

The bases for the material balance calculations were:

1. Hydrocarbon resource is represented by the chemical formula, CH2.
2. Gas, flowing from the formation, is saturated with water vapor.
3. Oil and gas, recovered from the production wells, are representative of oil and gas retorted from the oil shale.

4. The raw shale had the following properties:
   a. Oil content of 21.3 gpt (.097 m³ metric ton) Fischer assay.
   b. Water content of 2.3 percent by weight by Fischer assay.
   c. Total hydrogen content of 1.66 percent by weight.
   d. Mineral CO2 content of 19.23 percent by weight.

5. Assumed oil properties were:
   a. Specific gravity of 0.9.
   b. Carbon content of 85.56 percent by weight.
   c. Hydrogen content of 12.01 percent by weight.

6. The atomic ratio of carbon to hydrogen remaining on the spent shale was assumed to be 1.0.

7. The contribution of hydrogen and oxygen from migrating groundwater was neglected.

8. Oil retorted from the shale is not more than 65 percent of Fischer assay of the raw shale. This assumption was based on results of runs simulating in situ retorting in the LERC 150-ton retort.

Table 10. - Material balance summary.

<table>
<thead>
<tr>
<th></th>
<th>Cu m</th>
<th>Mscf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen used:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Burning propane</td>
<td>12,503</td>
<td>442</td>
</tr>
<tr>
<td>Forming CO from CH2</td>
<td>11,355</td>
<td>401</td>
</tr>
<tr>
<td>Forming CO2 from CH2</td>
<td>73,604</td>
<td>2,605</td>
</tr>
<tr>
<td>Forming H2O from CH2</td>
<td>48,153</td>
<td>1,696</td>
</tr>
<tr>
<td>Total oxygen reacted</td>
<td>145,613</td>
<td>5,155</td>
</tr>
<tr>
<td>Percent oxygen reacted</td>
<td>65.0</td>
<td>65.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Kgs</th>
<th>Lbs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas production:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>19,759</td>
<td>43,521</td>
</tr>
<tr>
<td>Combustion CO</td>
<td>26,935</td>
<td>59,328</td>
</tr>
<tr>
<td>Combustion CO2</td>
<td>137,185</td>
<td>302,170</td>
</tr>
<tr>
<td>Combustion H2O</td>
<td>53,616</td>
<td>118,098</td>
</tr>
<tr>
<td>Mineral CO2</td>
<td>94,808</td>
<td>208,829</td>
</tr>
</tbody>
</table>

| Oil shale retorted: |        |       |
|                    | Metric tons | Tons  |
|                    | 2,964        | 3,260 |

| Retorted oil:       |        |       |
|                    | Liters   | Barrels |
|                    | 170,859  | 1,075   |
Table 11 shows a wide variation of the fraction of shale retorted between quadrants. The low 8 percent of the oil shale retorted in quadrant 3-8 reflects the poor oxygen utilization in that quadrant resulting in the wells being shut in early in the experiment. The quantity of oil shale retorted in quadrant 2-7 is probably greater than the 1,132 metric tons reported, as a result of moving the air injection to well 10 on the 60th day of operation. The calculations of the amount of shale retorted depend upon gas flow from the wells. Any gas generated in quadrant 2-7, which flowed out other wells, would result in shale being calculated as retorted in other quadrants.

The high air-to-shale use rate in quadrant 3-8 reflects the short burn time in that quadrant. The flame front moved through area 3-8 so rapidly that the stage of most efficient air utilization was not realized, i.e., the stage where air transfers heat from hot spent shale to raw shale. Also limiting the air use efficiency during the early part of the experiment was the use of propane injection to supplement combustion. Propane increased the hydrocarbon content of the injection gas above the lower combustion limit nearer the injection well, which meant the flame could be sustained closer to the injection well. The gas which was heated near the injection well could not absorb heat as it moved across the hot shale, resulting in reduced heat transfer.

This point is also born out in Table 12 which shows much less air was used to retort a ton of shale in the latter part of the test. The heat transfer mechanism brought the 150-day average air use down to 11,700 scf air per ton of shale retorted.

The large discrepancy between the calculated oil retorted and the oil actually recovered cannot be explained fully until core samples are taken and evaluated. It is known that much oil migrated beyond the pattern and oil has been found in downhole equipment in the form of a thick layer of heavy grease. It is probable that much of the oil was carbonized or burned.

Laboratory tests (Wise and others 1971) measured the heat required to bring oil shale from 50°F (10°C) to 1,000°F (538°C). For 21.3 gpt (86.5 l/metric ton) oil shale 0.6 MM Btu/ton (0.167 Kcal/metric ton) is needed. The laboratory data agree closely with the results from site 9 which are shown in Table 13. However, the laboratory tests did not include heat recovered when the spent shale was cooled from 1,000°F (538°C). Because site 9 shale bed was still hot at the time this data was collected, it should be possible to retort with less net heat input if waste heat is recovered from spent shale.

Table 11. - Evaluation of Rock Springs site 9.

<table>
<thead>
<tr>
<th>Site</th>
<th>Total</th>
<th>Quad 2-7</th>
<th>Quad 3-8</th>
<th>Quad 4-9</th>
<th>Quad 5-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shale resource, metric tons</td>
<td>14,210</td>
<td>3,552</td>
<td>3,552</td>
<td>3,552</td>
<td>3,552</td>
</tr>
<tr>
<td>Shale retorted, metric tons</td>
<td>2,964</td>
<td>1,132</td>
<td>275</td>
<td>507</td>
<td>1,054</td>
</tr>
<tr>
<td>Percent shale retorted</td>
<td>21</td>
<td>32</td>
<td>0</td>
<td>14</td>
<td>30</td>
</tr>
<tr>
<td>Air used, MM m³</td>
<td>1.08</td>
<td>.40</td>
<td>.13</td>
<td>.19</td>
<td>.34</td>
</tr>
<tr>
<td>M m³ air used/metric ton shale retorted</td>
<td>.36</td>
<td>.36</td>
<td>.49</td>
<td>.38</td>
<td>.32</td>
</tr>
<tr>
<td>Air used, MMScf</td>
<td>38.2</td>
<td>14.2</td>
<td>4.7</td>
<td>6.8</td>
<td>12.1</td>
</tr>
<tr>
<td>Mcsf air used/ton shale retorted</td>
<td>11.7</td>
<td>11.4</td>
<td>15.7</td>
<td>12.2</td>
<td>10.5</td>
</tr>
<tr>
<td>Percent oxygen reacted</td>
<td>65.0</td>
<td>65.4</td>
<td>63.5</td>
<td>64.0</td>
<td>65.6</td>
</tr>
<tr>
<td>Oil available, bbls</td>
<td>7,808</td>
<td>1,952</td>
<td>1,952</td>
<td>1,952</td>
<td>1,952</td>
</tr>
<tr>
<td>Oil retorted, bbls</td>
<td>1,076</td>
<td>411</td>
<td>99</td>
<td>184</td>
<td>382</td>
</tr>
<tr>
<td>Oil recovered, bbls</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Net heating value of gas:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MM Kcal</td>
<td>382</td>
<td>148</td>
<td>34</td>
<td>62</td>
<td>138</td>
</tr>
<tr>
<td>MM Btu</td>
<td>1,515</td>
<td>587</td>
<td>134</td>
<td>247</td>
<td>547</td>
</tr>
<tr>
<td>Kcal/m³</td>
<td>338</td>
<td>331</td>
<td>239</td>
<td>296</td>
<td>364</td>
</tr>
<tr>
<td>Btu/scf</td>
<td>38.0</td>
<td>37.2</td>
<td>26.9</td>
<td>33.3</td>
<td>40.9</td>
</tr>
</tbody>
</table>

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Matzick and Dannenberg (1960) reported heat required in an aboveground gas combustion retort was only 400,000 Btu per ton of shale retorted with efficient heat recovery. This permitted operation with only 3,800 to 4,300 scf of air injected per ton of shale retorted.

Conclusions
After the first 150 days of sustained in situ retorting at Rock Springs site 9, the following conclusions were drawn:
1. There were significant differences among quadrants in the capability to support retorting. This is shown by the differences in quantity of retort product gases flowing from the various quadrants.
2. The portions of oil shale retorted varied from 32 percent of the shale bed in quadrant 2-7 to 8 percent in quadrant 3-8.
3. Only a small percentage of the oil retorted from the shale was recovered.
4. In situ retorting conditions can be sustained where the shale bed has sufficient surface area.
5. Improvements in fracturing and recovery techniques are needed to achieve...


Table 13. - Energy balances for Rock Springs site 9 (in 10⁶ Kcal)

<table>
<thead>
<tr>
<th></th>
<th>Site total</th>
<th>Quad 2-7</th>
<th>Quad 3-8</th>
<th>Quad 4-9</th>
<th>Quad 5-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation CH₂ to CO</td>
<td>25.4</td>
<td>9.9</td>
<td>2.5</td>
<td>3.8</td>
<td>9.2</td>
</tr>
<tr>
<td>Oxidation CH₂ to CO₂</td>
<td>293</td>
<td>111</td>
<td>35</td>
<td>53</td>
<td>93</td>
</tr>
<tr>
<td>Oxidation CH₂ to H₂O</td>
<td>234</td>
<td>90</td>
<td>27</td>
<td>41</td>
<td>77</td>
</tr>
<tr>
<td>Propane combustion</td>
<td>51.6</td>
<td>17.1</td>
<td>8.8</td>
<td>9.8</td>
<td>16.1</td>
</tr>
<tr>
<td>Water condensation</td>
<td>31.4</td>
<td>10.0</td>
<td>4.1</td>
<td>5.7</td>
<td>11.3</td>
</tr>
<tr>
<td>Total heat input</td>
<td>636</td>
<td>238</td>
<td>78</td>
<td>113</td>
<td>205</td>
</tr>
<tr>
<td>Sensible heat of gas</td>
<td>(1.08)</td>
<td>(1.18)</td>
<td>0</td>
<td>.03</td>
<td>.18</td>
</tr>
<tr>
<td>Carbonate decomposition</td>
<td>(84.3)</td>
<td>(31.8)</td>
<td>(8.4)</td>
<td>(13.5)</td>
<td>(30.6)</td>
</tr>
<tr>
<td>Net heat input</td>
<td>551</td>
<td>205</td>
<td>70</td>
<td>100</td>
<td>175</td>
</tr>
<tr>
<td>Retorting heat:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MM Kcal/m. ton</td>
<td>.187</td>
<td>.181</td>
<td>.256</td>
<td>.197</td>
<td>.166</td>
</tr>
<tr>
<td>MM Btu/ton</td>
<td>.674</td>
<td>.652</td>
<td>.922</td>
<td>.710</td>
<td>.599</td>
</tr>
</tbody>
</table>

...yields that can be economically attractive.

6. The mechanical lift pumps used for liquid recovery did not function during periods of the experiment.

Acknowledgments

We wish to express our appreciation to all who contributed to the experiment. While it is not possible to name everyone, the following made sustained contributions: E. Boden, D. Clarke, R. Collins, R. Cummings, L. Gitke, W. Jussila, P. Kerr, D. McClintock, and E. Williams.

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References


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MINERAL AND ORGANIC RELATIONSHIPS THROUGH COLORADO'S GREEN RIVER FORMATION ACROSS ITS SALINE DEPOSITIONAL CENTER

W. A. Robb and J. W. Smith
Laramie Energy Research Center
Laramie, Wyoming

Abstract

Stratigraphically correlated profiles of organic matter concentration and the distribution and relative abundance of 8 major minerals in oil shales, through Colorado's Green River Formation near its saline depositional center, were used to evaluate relationships among these components in Colorado oil shales. Strong direct relationships between the volume of organic matter in Colorado's Green River Formation oil shales and the relative amounts of the silicate minerals—quartz, soda feldspar, and potash feldspar—were demonstrated singly and collectively. The silicate minerals were also shown to be directly related to each other. Dawsonite, in the saline zone of the Formation, was also shown to be directly related to the volume of organic matter and, indirectly, to the amount of nahcolite. These relationships were all interpreted as resulting from CO₂ arising from organic matter in the sediment. A strong direct relationship, demonstrated between dawsonite and quartz, was credited to both the organic CO₂ mechanisms and to ash-fall decomposition. Significant non-correlation with organic matter or any of the other minerals was found for calcite and analcime. Lack of significant correlation among any of the components in a particular horizon demonstrated absence of geochemical control during its deposition.

In addition to their geochemical value, these relationships provide an additional interpretive tool for the Green River Formation deposits.

Introduction

Stratigraphic profiles of organic matter concentration and major mineral distribution and relative abundance in Green River Formation oil shales have been developed for 7 cores, transecting the center of saline deposition in the northern part of Colorado's Piceance Creek Basin. While the profiles themselves will be reported in a LERC/ERDA Report of Investigations, they provide the massive data base necessary for statistical evaluation of relationships among 8 authigenic minerals and organic matter in the sampled Green River Formation oil shales. Relationships disclosed by the statistical evaluation are interpreted in terms of the geochemistry of oil-shale development.

Only three previous mineral profile studies obtained data bases large enough for realistic evaluation of general mineral relationships in Green River Formation oil shales. One, completed on a single core, sampling the entire Green River Formation in Colorado, is a preliminary to the present study (Robb and Smith 1974). The second one of two completed on Utah samples, was performed on 3 sets of selected core samples by Desborough (1976) and covered too large and complex an area to permit summarizing relationships. In addition, statistical methods were not employed for evaluation. The third presents mineral profiles of a core through Utah's Green River but no statistical evaluation of material relationships (Smith and others 1972).
Other studies giving Colorado mineral profiles and relationships on a limited basis, insufficient for statistical evaluation, include those by Brobst and Tucker (1973) and Dyni (1974).

This study was limited to the saline depositional center of Colorado's Green River Formation to simplify interpretation of the significant relationships. Figure 1, a map of Colorado's oil-shale-bearing Piceance Creek Basin, shows the location of the selected coreholes in relation to the Formation's saline depositional center, as defined by Smith (1974). Table 1 identifies and locates each corehole. The initial depositional center of ancient Lake Uinta, whose sediments became the Green River Formation, lay near the solid ring in figure 1. Deposition around this center persisted to form thick, rich oil shales, bearing the saline minerals, nahcolite and dawsonite. Nahcolite and dawsonite became more concentrated around the depositional center. Figure 2 shows the locations of the 7 coreholes in relation to the existing thickness of the nahcolite-bearing interval. Beard, Tait, and Smith (1974) show that these rings parallel the relative concentrations of nahcolite and dawsonite and thus define the saline depositional center. During the time of deposition of these minerals, clastic incursion into the lake was limited. Geochemical control of mineral deposition predominated, reducing the number of variables affecting the mineral profiles and their evaluation.

Experimental Procedures

Both oil-yield assays, used to estimate organic matter content, and x-ray diffraction studies were completed on samples selected to represent the cores continuously. Selection of the assay samples of 6 cores was based on visible lithologic variations so that each sample was as lithologically uniform as possible. The resulting samples, representing about one foot (0.3 m) of core, provide detailed representation of the oil yield and lithologic variations present in the cores. The assay samples were crushed to pass an 8-mesh screen, mixed and air-dried before oil-shale assay by the modified Fischer retort method (Stanfield and Frost 1949). Skyline No. 1 core (No. 4) was sampled by Atlantic Richfield Company. These samples were selected at exact one-foot (0.3 m) intervals instead of by visible lithologic variations.

(Metric units have been specified for this volume, but our data were accumulated using the foot as the unit for depth and elevation and gallons per ton as the oil-yield unit. Depth and elevation measures may be converted from feet to meters by multiplying by 0.3048. The unit, gallons per ton, can be converted to liters-per-metric ton by multiplying by 0.417. It can also be converted into a weight unit, kilogram/tonne, by multiplying by 0.29, a factor agreed upon at the World Energy Conference, 1974. This conversion is approximate because the variable density of the oil is ignored.)

Samples for x-ray diffraction analysis were split from the assay samples, pulverized by a standard procedure and packed identically to insure comparable diffraction results (Robb and Smith 1974; Smith and Robb 1973). In the intervals containing dawsonite and nahcolite, detectable by x-ray diffraction, every sample was analyzed. Above and below those intervals, either every fifth sample or one sample every five feet (1.5 m) was analyzed.

X-ray diffraction patterns were obtained with a diffractometer using CuKa radiation. Patterns were recorded under standardized conditions on 10-inch (25.4 cm) 100-unit chart paper at a goniometer scanning speed of 2°20 per minute and a chart speed of one inch (2.54 cm) per minute. The data control unit was set at 100 counts full scale, multiplier at 1, and time constant of 5. Peaks off the chart were rerun with a higher multiplier, then converted to their equivalent in 100 counts full scale. Individual peak heights were measured above background in chart units for the primary peak of each of the 8 minerals being investigated. The 002 locations for the primary peaks of these minerals are given in table 2. The measured mineral peak heights, while not quantitative without calibration, give a
Figure 1. Core hole locations, northern Piceance Creek Basin, Colorado.
LEGEND

Thickness of Nahcolite-bearing Interval, feet

Outline of Green River Formation

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Figure 2. - Core hole locations in relation to nahcolite-bearing interval.

Reliable relative measure of the amount of a mineral from sample to sample. The peak heights of the minerals and the organic content in volume percent estimated from oil yield were used to determine relationships between each mineral and organic content and between minerals.

Deposit Correlation

Mineral composition of oil shales is not uniform throughout the thickness of Colorado's Green River Formation. To avoid comparing oranges with camels, similar mineral compositions must be compared for all 7 coreholes. This requires defining com-
Table 1. - Location and elevation of coreholes across the Piceance Creek Basin’s depositional center.

<table>
<thead>
<tr>
<th>Core Number</th>
<th>Company or Agency</th>
<th>Name</th>
<th>Sec.</th>
<th>T</th>
<th>R</th>
<th>Elevation, ft.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Shell Oil Co.</td>
<td>J. M. Greeno No. 1-4</td>
<td>4</td>
<td>3</td>
<td>S</td>
<td>97 W</td>
</tr>
<tr>
<td>2</td>
<td>Equity Oil Co.</td>
<td>Boies No. 1</td>
<td>19</td>
<td>2</td>
<td>S</td>
<td>97 W</td>
</tr>
<tr>
<td>3</td>
<td>Marathon Oil Co.</td>
<td>Square S No. 1</td>
<td>4</td>
<td>2</td>
<td>S</td>
<td>97 W</td>
</tr>
<tr>
<td>4</td>
<td>Atlantic-Richfield Oil Co.</td>
<td>Skyline No. 1</td>
<td>26</td>
<td>1</td>
<td>S</td>
<td>98 W</td>
</tr>
<tr>
<td>5</td>
<td>Shell Oil Co.</td>
<td>Corehole 4x-9</td>
<td>9</td>
<td>1</td>
<td>S</td>
<td>97 W</td>
</tr>
<tr>
<td>6</td>
<td>Humble Oil Co.</td>
<td>Yellow Creek No. 1</td>
<td>2</td>
<td>1</td>
<td>S</td>
<td>98 W</td>
</tr>
<tr>
<td>7</td>
<td>Bureau of Mines-Atomic Energy Commission</td>
<td>Colorado No. 1</td>
<td>13</td>
<td>1</td>
<td>N</td>
<td>98 W</td>
</tr>
</tbody>
</table>

Table 2. - Primary x-ray peak locations for 8 Green River Formation minerals.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Peak Location, °2θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dawsonite</td>
<td>15.6</td>
</tr>
<tr>
<td>Analcime</td>
<td>26.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>26.6</td>
</tr>
<tr>
<td>Potash Feldspar</td>
<td>27.6</td>
</tr>
<tr>
<td>Soda Feldspar</td>
<td>28.0</td>
</tr>
<tr>
<td>Calcite</td>
<td>29.5</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>30.4</td>
</tr>
<tr>
<td>Dolomite</td>
<td>30.9</td>
</tr>
</tbody>
</table>

Comparable sections which can be done by correlating the core data. Table 3 gives specific depth locations for widely used stratigraphic markers occurring in the Green River Formation (Smith and others 1968). These markers more or less divide the Formation into zones containing specific mineral suites. Illite clay is the dominant mineral below the Blue Marker (at 2590 feet (790 m) in Core No. 7, for example). The saline minerals, nahcolite and dawsonite, occur primarily in the saline section, bounded on the bottom by the Blue Marker, and, on the top, by the base of the leached zone at 17/5 feet (529.7 m) in Core No. 7. The leached zone from which nahcolite has been dissolved lies between the bottom of B-groove and the base of the leached zone (table 3). The Mahogany Zone, lying between A-groove and B-groove (table 3), is characterized by dolomite-calcite mineralization.

On the basis of the markers in table 3 and the oil-yield histograms, corehole samples were correlated, as described by Trudell and others (1970). Figure 3 shows the resulting correlation of the oil-yield histograms. The base of B-groove was chosen as the common reference point (datum) for this figure.

In their initial Green River Formation, mineral profile study on Colorado Corehole No. 1 (Core No. 7), Robb and Smith (1974) selected six horizons to represent the various mineral suites encountered through the Formation. Table 4 gives descriptions and depths for sections A through F, selected for study in Colorado Corehole No. 1. These sections are diagrammed in figure 3 on the oil-yield histogram for Core Number 7. By stratigraphic correlation of oil yields, sections A through F were extended to define comparable sections in the other six coreholes along the cross-section. Table 5 gives depths for mineral correlation sections, A through F, in each of the seven coreholes.

The lines bounding all the correlated sections are time lines; consequently, the sediments in all of the comparable sections, like all seven sections labeled C, were deposited during the same time period (Trudell and others 1970). Around the center of deposition, the geochemical conditions which created the Green River Formation tended to be uniform. Consequently,
Figure 3. - Oil yield profiles across the Green River Formation saline depositional center.
Table 3. - Stratigraphic markers for coreholes across the Piceance Creek Basin's saline depositional center.

<table>
<thead>
<tr>
<th>Core number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marker</td>
<td>Marker depth, ft.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-groove</td>
<td>1058.0-1066.7</td>
<td>1/ 634.4-648.0</td>
<td>1409.0-1418.0</td>
<td>2/ 735.3-752.0</td>
<td>989.5-1018.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-groove</td>
<td>1240.0-1260.0</td>
<td>770.0-783.2</td>
<td>820.9-840.0</td>
<td>1602.0-1621.0</td>
<td>1522.0-970.8</td>
<td>1250.0-1285.7</td>
<td></td>
</tr>
<tr>
<td>Base leached zone, approx.</td>
<td>1810.3</td>
<td>1370.0</td>
<td>1382.2</td>
<td>1815.0</td>
<td>1750.0</td>
<td>1522.0</td>
<td></td>
</tr>
<tr>
<td>Blue</td>
<td>2268.7</td>
<td>1750.0</td>
<td>1889.2</td>
<td>2998.0</td>
<td>2750.0</td>
<td>2155.5</td>
<td>2590.0</td>
</tr>
<tr>
<td>Orange</td>
<td>2483.9</td>
<td>1933.5</td>
<td>2057.6</td>
<td>3172</td>
<td>3172</td>
<td>2852</td>
<td></td>
</tr>
</tbody>
</table>

1/ Above top of core
2/ Abnormal section

Table 4. - Mineral correlation sections USBM-AEC Colorado No. 1 (Core No. 7)1/.

<table>
<thead>
<tr>
<th>Section</th>
<th>Depth, ft.</th>
<th>Interval, ft.</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1021.4-10400</td>
<td>601.0-677.0</td>
<td>Mahogany zone</td>
</tr>
<tr>
<td>B</td>
<td>1290.0-1295.0</td>
<td>94.9</td>
<td>Bottom of leached zone</td>
</tr>
<tr>
<td>C</td>
<td>1475.0-1539.0</td>
<td>68.4</td>
<td>Top of saline zone</td>
</tr>
<tr>
<td>D</td>
<td>1600.0-1675.0</td>
<td>78.7</td>
<td>Saline zone, nahcolite-free</td>
</tr>
<tr>
<td>E</td>
<td>1777.7-1846.1</td>
<td>78.7</td>
<td>Lower Saline zone</td>
</tr>
<tr>
<td>F</td>
<td>1913.3-1993.0</td>
<td>395.5</td>
<td>Garden Gulch-Douglas Creek</td>
</tr>
</tbody>
</table>

1/ Robb and Smith (1974).

Table 5. - Mineral correlation sections for coreholes on profiles.

<table>
<thead>
<tr>
<th>Core number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Section</td>
<td>Section depth, ft.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1066.7-1119.1</td>
<td>601.0-677.0</td>
<td>650.4-735.7</td>
<td>1418.0-1506.0</td>
<td>1300.0-1400.0</td>
<td>753.4-845.8</td>
<td>1021.4-1150.5</td>
</tr>
<tr>
<td>B</td>
<td>1475.0-1501.1</td>
<td>998.0-1092.0</td>
<td>1040.8-1978.0</td>
<td>1930.0-1724.0</td>
<td>1640.0-1506.0</td>
<td>2434.2-2506.0</td>
<td>1919.0-2302.1</td>
</tr>
<tr>
<td>C</td>
<td>1539.3-1616.1</td>
<td>1037.0-1103.0</td>
<td>1132.8-2104.0</td>
<td>1908.0-2011.5</td>
<td>2642.0-2711.0</td>
<td>2600.0-2995.5</td>
<td>2448.9</td>
</tr>
<tr>
<td>D</td>
<td>1913.3-1993.0</td>
<td>1508.0-1640.0</td>
<td>1564.0-2711.0</td>
<td>2642.0-2711.0</td>
<td>2711.0-2820.0</td>
<td>2506.0-2603.0</td>
<td>1993.0-2105.1</td>
</tr>
<tr>
<td>E</td>
<td>1993.0-2105.1</td>
<td>1508.0-1640.0</td>
<td>1564.0-2711.0</td>
<td>2642.0-2711.0</td>
<td>2711.0-2820.0</td>
<td>2506.0-2603.0</td>
<td>1993.0-2105.1</td>
</tr>
<tr>
<td>F</td>
<td>2301.6-2641.6</td>
<td>1759.0-2011.5</td>
<td>1908.8-2219.7</td>
<td>1/ 1/</td>
<td>1/ 1/</td>
<td>2168.0-2464.0</td>
<td>2600.0-2995.5</td>
</tr>
</tbody>
</table>

1/ not reached
center of deposition. Another geologic factor, complicating the evaluation of mineral relationships, is the fact that sedimentation was extremely slow. A one-foot (0.3 m) oil-shale sample may represent hundreds or perhaps thousands of years of deposition (for example, see Bradley 1963). Any evaluation made on a one-foot (0.3 m) sample must represent an average of conditions over many annual deposition cycles. Consequently, analyses of one-foot (0.3 m) samples yield only generalizations in spite of comparing simultaneously deposited sections.

One additional complicating geologic factor is the change in mineral distribution in some of the selected sections created by post-depositional nahcolite leaching. Figure 3 shows the approximate depth of nahcolite leaching for each core. This division is not sharp. The initial selection of mineral correlation sections, A through F, in Core No. 7 placed section B at the bottom of the leached zone and section C at the top of the nahcolite-bearing saline zone. In Core No. 4, section B is in the saline zone, largely coinciding with the upper salt cap (Trudell and others 1974); Section C is in the leached zone in Cores 1, 2, 3, and 6 and partially in the leached zone in Core No. 5. This discrepancy was compensated for in our calculations.

Calculations Procedures

Regression and correlation analyses were enlisted to determine significant relationships between organic matter and minerals and among minerals. However, two corrections were necessary to make the data directly comparable. The first is associated with the widely varying quantities of organic matter occurring through the Formation (figure 3). The volume of this organic matter in an individual sample controls how much of its mineral fraction is available to x-ray diffraction. If its effect was not compensated, all minerals would show an intense inverse correlation with organic matter because of its diluting effect. All relationships between organic matter and the individual minerals would be overridden. To remove the organic matter's diluting effect, mineral peak heights were corrected for the volume of organic matter in the sample. This volume was estimated from the oil yield using the following equation:

\[
\text{Organic content, volume percent} = \frac{164.85}{X} + 111.46
\]

where \(X\) = oil yield from Fischer assay in gallons-per-ton (liters per metric ton).

This equation is modified from Smith (1969), using a mineral density of 2.72 gm/cc, and an organic matter density of 1.07 gm/cc (Smith 1976). After correction, the mineral peak heights represent the peak heights that would have been obtained on an organic-free sample. This correction permits testing relationships between organic matter and mineral quantities.

Nahcolite requires the other data correction. In the saline zone, the quantity (volume) of nahcolite, from sample to sample, varies even more widely than the organic matter. The diluting effect of nahcolite was eliminated by correcting the other mineral peak heights and the organic volume for the percent by weight of nahcolite. The percent by weight of nahcolite was estimated from the peak heights of nahcolite and dolomite, using an equation derived from x-ray diffraction peak heights on samples with chemically-determined percentages of nahcolite and dolomite. After correction, the mineral peak heights represented the heights that would have been obtained on a nahcolite-free sample. This correction also permitted testing the relations between nahcolite and the other minerals. Some samples, containing huge amounts of nahcolite and only minor amounts of organic matter and other minerals, were omitted from the calculations.

Linear regression equations were calculated by standard techniques (Ezekial and Fox 1959) to relate the peak heights of the individual minerals to each other and to the volume of organic matter. These calcu-
lations were performed on results available in each of the sections, A through F. More than 1800 data sets were evaluated. The relations developed were tested for significance, using a standard method (Arkin and Colton 1950; Smith and Robb 1973), independent of the number of samples. Correlations showing less than a 5 percent probability of being zero were deemed significant.

Mineral Relationships and Their Origin

Mineral relationships, detected by regression analysis, are evaluated in terms of geochemical mechanisms postulated for development of oil shale and its minerals by Smith (1974) and Smith and Robb (1973). These mechanisms depend on development and persistence of a stratified lake with a density-stabilized lower layer, composed of a sodium carbonate solution sufficiently basic to dissolve in-coming, air-borne, fine-particle silicates. The regression analyses revealed both strong, significant correlation and some equally strong absence of significant correlation. Non-correlation tends to be simpler to evaluate, so these cases will be discussed first.

Two minerals showed no significant correlation with any of the other minerals or with organic matter. These minerals were analcime and calcite. Analcime occurred sporadically through the Mahogany Zone down to the top of the saline zone. In the dawsonite-bearing section (the saline zone), only one occurrence of analcime was noted in all seven cores. This was in a dawsonite-free specimen from Core No. 7. Below the dawsonite section, analcime occurred occasionally. Analcime formed by modification of clastic material arriving in bulk from volcanic ash falls. At times when the lake was sufficiently basic (Smith 1974), ash-fall minerals were dissolved and destroyed; when less basic, ash-fall minerals were altered to form analcime. A borderline case is the occurrence of large-crystal dawsonite, in thin layers resembling ash falls, near the bottom of the saline zone. Since elsewhere analcime is the product of instantaneous events (ash-falls), occurring sporadically, its lack of relationship to the other minerals and to organic matter is reasonable.

Calcite occurs sporadically but in correlateable zones up to the top of the saline mineral section. Above this point, calcite occurs more frequently, and it is ubiquitous in the Mahogany Zone. Robb and Smith (1973) and Smith (1974) describe calcite as a direct chemical precipitate, resulting from the release of calcium into strongly basic sodium carbonate brine. This calcium was brought into the lake continuously in air-borne dust. Direct and immediate precipitation of calcite in the water of the lake's lower layer produces correlateable zones but eliminates the possibility of calcite relationships with organic matter and most other minerals. Dolomitization of calcite to produce an inverse relationship between these minerals was not verified statistically.

A third negative result, revealed by the comprehensive statistical analysis, is the absence of any significant relationship among the minerals and organic matter for samples in correlation section B. This section differs markedly from the other sections. Robb and Smith (1974) described this, in Core No. 7, as resulting from a heavy clastic influx, overriding the geochemical control which produced the observed relationships in the other five sections. The seven-core study of section B verifies this observation. The clastic influx appears to originate from the north. Section B thins progressively toward the south (figure 3). It is largely replaced by halite in Core No. 4. Because section B offers no useful relationships, it will be eliminated from further discussion.

Several positive relationships were indicated by the statistical study. The most emphatic were those demonstrated between the volume of organic matter and each of the silicate minerals, quartz, soda feldspar, and potash feldspar. All of these relationships were direct; that is, as organic matter increases, the amounts of
individual silicate minerals increase correspondingly. Three-variable, multiple regressions, relating organic volume as the dependent variable to peak heights of each of the three silicates, showed strong significance in all 33 cases where the test could be run. Thirty-one were significant at the 99.9 percent level and the other two at the 98 percent level. Also strongly indicated were direct relationships between all pairs of the silicate minerals, although this is complicated by the difficulty inherent in completely resolving the feldspar peaks.

Direct relationships between organic matter and the silicate minerals, quartz, albite, and potash feldspar, are a natural consequence of the geochemical development pattern postulated by Smith (1974). In this pattern, the silicates are formed from materials dissolved in strongly basic interstitial water, trapped by organic-rich sediments. The organic matter decomposes to yield CO₂. This lowers the pH of the trapped interstitial water, sharply decreasing the solubility of silica and aluminates and initiating silicate formation. The more organic matter in the sediment, the more CO₂ is available, and the more effective is the pH decrease to form silicates. The direct and strong relationships between amounts of organic matter and amounts of quartz, albite, and potash feldspar would be a product of this mechanism.

Dawsonite shows significant relationships with organic matter and with quartz. Dawsonite is strongly zoned, occurring largely in the correlation sections of the saline zone. These are sections C, D, and E. Smaller amounts were found in and immediately below the Mahogany Zone. Direct relationships between amounts of organic matter and dawsonite were determined in more than half of the correlation units of the saline zone. This is a strong demonstration of the existence of a relationship between organic matter and dawsonite. Dawsonite is a relatively small fraction of the total rock, occurring primarily, but not exclusively, as a matrix mineral. That which occurs as a matrix min-

eral is associated in amount with organic matter. Smith and Young (1975) associated dawsonite formation with events accompanying CO₂ evolution from organic matter in sediment. The following equation depicts the equilibrium which came to exist between dawsonite and two other sediment components:

\[ \text{NaAl(OH)}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{CO}_3 + \text{Al(OH)}_3 + \text{NaHCO}_3 \]

Both materials on the right are produced by CO₂ being absorbed into the aluminate-carbonate lake water. More CO₂ forms more dawsonite. Statistical evaluation of x-ray diffraction results supported this pattern by detecting significant inverse relationships between dawsonite and nahcolite in three of the unit C evaluations. Since dawsonite only formed in the presence of large excesses of sodium bicarbonate (nahcolite), detection of this relationship in unit C is a fortunate occurrence.

Quartz was even more strongly related to dawsonite than was organic matter. Part of this direct relationship results from the CO₂ balance described above. Part may result from the local decomposition of ash falls to produce dawsonite and quartz, respectively, from the alumina and silica present in the deposit. Neither soda feldspar (albite) nor potash feldspar showed significant associations with dawsonite.

Dolomite usually showed some correlation with volume of organic matter, with quartz, with soda feldspar, and with potash feldspar, but not always directly. Apparently, CO₂ contributions by the organic matter provided only part of the conditions necessary for dolomite formation.

Detecting nahcolite relationships statistically appeared unlikely because nahcolite solubility and mobility would tend to obscure possible relationships. In addition, the accumulation of nahcolite in crystal knots also fogs the detection of mineral relationships. The mineral peak height corrections for nahcolite could not compensate for these two effects. Nevertheless, in addition to the inverse relationship with dawsonite described above,
strong, direct nahcolite correlation with dolomite was found in units C and E. We reserve evaluation of this correlation until the mineral profiles for these cores can be presented.

Summary

Strong direct relationships between the volume of organic matter in Colorado's Green River Formation oil shales and the relative amounts of the silicate minerals, quartz, soda feldspar, and potash feldspar, were demonstrated singly and collectively. The silicate minerals were also shown to be directly related to each other. Dawsonite, in the saline zone of the Formation, was also shown to be directly related to the volume of organic matter and indirectly to the amount of nahcolite. A weaker relationship between dolomite and organic volume was also detected. These relationships were all interpreted as resulting from CO₂ arising from organic matter in the sediment. This lowers the pH of the interstitial water, sharply decreasing the solubility of silica and alumina and initiating the formation of quartz and the feldspars. Dawsonite formation and its relationship with organic matter were also shown to result from this CO₂ evolution by a process which incorporates dawsonite's indirect relationship with nahcolite as part of the process. A strong direct relationship demonstrated between dawsonite and quartz was credited to both the organic effect and ash-fall decomposition. Dolomite showed some relatively weak relationships with organic matter and the silicate minerals. A direct relationship of dolomite with nahcolite was found but not evaluated. Significant non-correlation with organic matter or any of the other minerals was found for calcite and analcime. Lack of significant correlation among any of the components in a particular horizon demonstrated absence of geochemical control during its deposition.

In addition to their geochemical value, these relationships provide an additional interpretive tool for the Green River Formation deposits. For example, they demonstrate that attempting to select a section to maximize dawsonite and minimize organic matter or the silicate minerals would be difficult.

References


, and Young, N. B., 1975, Dawsonite: its geochemistry, thermal behavior, and extraction from Green River oil shale: Colorado School Mines Quart., v. 70, no. 3, July, p. 69-93.


DYNAMICS OF OIL GENERATION AND DEGRADATION DURING RETORTING OF OIL SHALE BLOCKS AND POWDERS*

J. H. Campbell, G. H. Koskinas, T. T. Coburn† and N. D. Stout
Lawrence Livermore Laboratory
University of California
Livermore, California

Abstract
The evolution of oil during pyrolysis of blocks and powders of oil shale has been investigated, using heating rates from 2 to 180°C/h. Blocks (in the form of right circular cylinders) ranged in size from 3.2 to 17.2 cm in diameter and from 58 to 2041/ metric ton (14 to 49 gal/ton) in grade. The results show that coking reactions are the major source of intraparticle oil degradation. Furthermore, the degree of coking depends strongly on the heating rate, but is nearly independent of particle size and grade for the conditions used.

Experimental results from the 17.2 cm blocks are analyzed, using a simple mathematical model, based on kinetic results from powder retorting experiments and thermal data reported in the literature. The model calculations agree closely with the experimental data.

Finally, the practical implications of this work for field retorting are discussed.

Introduction
The Lawrence Livermore Laboratory is currently doing research and development on modified in-situ shale oil recovery (Lewis and Rothman 1975; Rothman 1975). The modified in-situ method calls for partial mining of an oil shale bed, followed by rubblization of the remaining material into the mined void space. By choosing a proper mining configuration, it is possible to create vertical, packed beds of oil shale, which can be processed by either combustion or hot gas retorting methods. A schematic of one proposed process is shown in figure 1.

The rubblized shale in the retort columns (fig. 1) will consist largely of blocks of material whose size will depend on the rubblization technique. During processing, these blocks are heated at a rate that depends on the thermal wave velocity through the retort. Results from model calculations and retorting experiments (Rothman 1976; Braun 1977) show that the heating rate (dT/dt) through the oil formation region is nearly constant for a given thermal wave velocity (fig. 2).

A factor of major importance to in-situ oil shale processing is the effect of various retorting rates on the oil yield. Although a number of investigators have attempted to study this problem, most work has been done on powders and small particles (<2.5 cm) and, usually, under isothermal conditions (Stout and others 1976; Hill and others 1967; Cummins and Robinson 1972; Johnson and others 1975).

A limited amount of information is available on larger particles. Johnson and others (1975) described an experiment on a
Symbol Table

$A_p$ = particle surface area ($m^2$)  

$C_s$ = shale heat capacity (kcal/kg K)  

$C_g$ = heat capacity of evolved gaseous products  

(kcal/kg K)  

$E$ = activation energy (kcal/mole)  

$F$ = dimensionless fraction of decomposed kerogen  

$\Delta H$ = enthalpy of kerogen decomposition (kcal/kgm)  

$OC_{char}$ = percent organic carbon converted to char  

$R_{oil}$ = rate of liquid oil formation (intraparticle)  

(kg/s$^3$m$^{-3}$)  

$R_{og}$ = rate of gas phase oil formation  

(intraparticle) (kg/s$^3$m$^{-3}$)  

$R_c$ = rate of intraparticle coke formation  

(kg/s$^3$m$^{-3}$)  

$R_g$ = rate of non-condensible gas formation during  

coking (kg/s$^3$m$^{-3}$)  

$R_{op}$ = rate of oil release (kg/s$^3$m$^{-3}$)  

$T$ = temperature (K)  

$T_0$ = initial particle temperature (K)  

$V_p$ = particle volume ($m^3$)  

$W_k$ = weight fraction kerogen in raw shale  

$I-X$ = fraction of liberated oil as liquid or in  

liquid-vap equilibrium.  

$Y_L$ = percent oil yield loss  

$b$ = heating rate (K/s)  

$f_o$ = fractional conversion of kerogen-bitumen  

to oil  

$f_c$ = fractional conversion of degraded oil to coke  

$k$ = shale thermoconductivity (kcal/s$^3$m$^3$K)  

$k_1$ = rate constant for oil production via liquid  

vaporization (s$^{-1}$)  

$k_2$ = rate constant for oil production as initial  

gas products (s$^{-1}$)  

$k_c$ = rate constant for coke formation (s$^{-1}$)  

$q$ = rate of heat generation (kcal/s$^3$m$^3$)  

$r$ = radial position (m)  

$r_o$ = block radius (m)  

$r_s$ = radius of equivalent spherical particle (m)  

t = time (s)  

$\rho_s$ = density of shale particle (kg/m$^3$)  

$\rho_{min}$ = mass concentration of mineral matter (kg/m$^3$)  

$\rho_{org}$ = mass concentration of organic matter (kg/m$^3$)  

$\rho_{s0}$ = initial shale particle density (kg/m$^3$)  

$\rho_{f0}$ = final shale particle density (kg/m$^3$)  

$\rho_{io}$ = mass concentration of intraparticle liquid  

oil (kg/m$^3$)  

$\rho_c$ = mass concentration of coke (kg/m$^3$)  

$\rho_{kb0}$ = initial mass concentration of kerogen-bitumen  

(kg/m$^3$)  

$\rho_{kb}$ = mass concentration of kerogen + bitumen  

(kg/m$^3$)  

$\rho_{vol}$ = mass concentration of kerogen-bitumen  

converted to volatile products (kg/m$^3$)  

$\bar{\rho}_{vol}$ = average mass flux rate of gas products  

from shale (kg/m$^3$ sec)
10.2-cm-diameter spherical shale particle, retorted at a constant heating rate in a hot gas. Unfortunately, their results are reported in undefined units of dimensionless time; from the discussion in the text, it can be estimated that the block was retorted between 2 and 3 hours. They report the weight loss vs dimensionless time and the temperature distribution in the sphere. Recently, Needham and others (1976) carried out a number of experiments on "pseudo" blocks, i.e., 0.8 cm cores, 53 cm long, sealed in a retort vessel by the thermal expansion during heating. However, the shale bedding planes were perpendicular to the core axis, hence, restricting flow to the nearly impermeable cross-bedding-plane direction. Huang (1976) has recently studied the retorting of 15-cm cubes under isothermal and non-isothermal conditions in both nitrogen and air. His main objectives were to study oxygen penetration and the previously-reported anomalous fast heating in blocks (Mallon and Miller 1975). However, yield data are reported for the heating rate of about 3 to 5°C/min. Recently, Minster and others (1976) retorted blocks of mine run shale (100-300 kg), packed in a bed of crushed shale inside a 0.45 metric ton retort. The blocks were retorted by either igniting the crushed shale (oxidizing conditions) or using a preheated inert gas. Data on the temperature distribution in the block and product gas composition are reported.

In this paper, we report the results of a study of the effects of heating rate and particle size on oil yield from Colorado oil shale. Experiments were carried out on material ranging in size from powders to 17.2-cm blocks and in grade from 58 to 204 l/metric ton (14 to 49 gal/ton). Furthermore, heating rates used in this work were chosen to mimic expected in-situ conditions for both combustion and hot gas retorting (i.e., heating rates from 2 to 180°C/h).

Most of the data in this report deal with the dynamics of oil formation and degradation processes. On the basis of these results, a simple mechanistic picture of oil formation and degradation under various heating rates is developed. Application of this simple picture to block retorting via a calculational model gives excellent agreement with the experimental results.

**Experimental**

**Sample Preparation** - The oil shale used in this study was obtained from the Anvil Points Mine in Colorado. Cylindrical blocks, ranging in size from 3.2 to 17.2 cm in diameter, were cut from mine-run pieces of shale, using a pneumatically operated, diamond-tipped core drill. Care was taken to insure that the sides of the cores were perpendic-
ular to the shale bedding planes and that the material lacked any large mineral inclusions. The 7.2- to 17.2-cm-diameter blocks were cut to a length of between 17 to 18 cm; the 3.2-cm cores to a length of 9.1 cm.

Before retorting, the oil grade of a block was determined by two methods: assay of satellite cores and immersion density. For the first method, satellite cores (2.5 cm in diameter) were cut from the periphery of the slab containing the larger core holes. The bedding planes of the satellite cores were then matched to those of the corresponding block and cut to an equal length. Each core was crushed to a fine powder and assayed, using a modified Fischer method (Koskinas and others 1976). The average of the satellite assays provided one measure of the grade of the corresponding block.

For the second method, the density of each block was determined and a yield predicted on the basis of the oil yield/density correlation developed by Smith (1969). The yields predicted on the basis of the above two methods agreed to within 4 percent.

In certain cases, a further check of the expected yield could be made, following retorting, by comparing the organic carbon remaining in the spent shale with values predicted, using the correlation developed by Stout and others (1976). Using this method, predicted yield generally agreed closely with the assay and density results.

The powdered shale comes from a masterbatch of 91.7 1/metric ton (22 gal/ton) material. The method by which it was prepared and assayed is described elsewhere (Koskinas and others 1976). Particle size of the powder material was less than 800 μm (-20 mesh).

**Apparatus** - A schematic diagram of the apparatus used for the large block (7.2 - 17.2 cm diameter) retorting experiments is given in fig. 3. It consists of four main parts: the furnace and controller, the retort-reactor, a product collection system, and a sweep gas flow control and measurement system.

The furnace is a Heavy Duty Equipment

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*Reference to a company or product name does not imply approval or recommendation of the product by the U. of California or the U.S. ERDA to the exclusion of others that may be suitable.*

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![Figure 3. - Schematic of block retorting apparatus.](image-url)
block. Five thermocouples were centered vertically in the block while a sixth was placed vertically one-fourth the length of the block down from the top (fig. 3). Radial distribution of the thermocouples is given in table 1.

During an experiment, a constant flow of nitrogen (-300 cm³/min) sweeps through the system. Input flow is measured by a calibrated flow gauge and output flow by a wet test meter.

Liquid products are collected in a graduated cylinder, attached to the base of two water-cooled condensers (fig. 3). The graduated collector is connected to the condenser by a Cajon O-ring seal (so collectors can be changed during the course of an experiment) and immersed in a 0°C ice bath. Three other cold traps, one at 0°C and two at -78°C (CO₂ - isopropyl alcohol) collect any mists or vapors swept past the first graduate. These traps contain glass wool to increase the available surface area for condensation.

The apparatus used to retort the powders and 3.2-cm-diameter cores is simply a smaller version of the above equipment. It is described in detail elsewhere (Koskinas and others 1976).

**Retorting Procedure** - Once a block sample has been selected and cut to size, it is drilled to accommodate the thermocouples and then weighed. The thermocouples are attached to the retort lid and cemented in pre-drilled holes in the block using saueriesen; the lid of the retort is then welded to the main vessel body. The mass of the retort is great enough to provide an effective heat sink during welding and, hence, prevent premature heating of the block. Following welding, the retort chamber is immersed in a tank of water and leak tested with compressed air.

The traps, condensers, connection tubing and retort chamber are individually weighed and then assembled as shown in fig. 3.

During retorting, continuous readings are made of the thermocouples in the block, the oil and water generated and total gas flow (sweep plus product gas). In certain of the experiments, the oil was collected in 20 to 60 g fractions for chemical analyses. (Results of these analyses are the subject of another report, dealing with chemistry of the oil products, Campbell and others, to be published.)

At completion of an experiment, the apparatus is disassembled and each piece of retort equipment reweighed. The volume of gas generated is calculated from the total gas produced minus the volume of sweep gas. A mass balance of the evolved products is completed from these data; the balance is within 3 percent on an evolved product basis (i.e., weight loss vs weight collected).

**Results and Discussion**

**Dynamics of Oil Release from Blocks and Powders** - The observed evolution of oil during retorting of 17.2-cm-diameter right-cylinder blocks is shown in fig. 4. The data are for heating rates, varying from 2 to 60°C/h; the abscissa scale refers to the block surface temperature. Since the grade and mass of the blocks were slightly different, the yield is plotted as percent Fischer Assay (FA).

Although one experiment was carried out at a heating rate of 180°C/h, the rate of oil generation was too fast to monitor accurately; consequently, only total yield is reported (table 2).
Table 2. - Yield results for block of various sizes and grades retorted at different heating rates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grade</th>
<th>Block Dimensions, cm</th>
<th>Heating rate, °C/h</th>
<th>Oil yield, l/ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>III - 2</td>
<td>121. (29.0)</td>
<td>17.2 × 18</td>
<td>180</td>
<td>99.0</td>
</tr>
<tr>
<td>III - 18</td>
<td>135. (32.4)</td>
<td>17.2 × 18</td>
<td>6</td>
<td>91.0</td>
</tr>
<tr>
<td>III - 30</td>
<td>139. (33.3)</td>
<td>17.2 × 18</td>
<td>18</td>
<td>94.4</td>
</tr>
<tr>
<td>III - 38</td>
<td>122. (29.2)</td>
<td>17.2 × 18</td>
<td>2</td>
<td>83.8</td>
</tr>
<tr>
<td>III - 55</td>
<td>17.2 (13.8)</td>
<td>17.2 × 18</td>
<td>2</td>
<td>82.2</td>
</tr>
<tr>
<td>III - 63</td>
<td>156. (37.5)</td>
<td>17.2 × 18</td>
<td>60</td>
<td>96.0</td>
</tr>
<tr>
<td>III - 81</td>
<td>204. (48.8)</td>
<td>17.2 × 18</td>
<td>2</td>
<td>81.5</td>
</tr>
<tr>
<td>III - 85</td>
<td>156. (37.4)</td>
<td>7.2 × 18</td>
<td>2</td>
<td>84.9</td>
</tr>
<tr>
<td>III - 91</td>
<td>118. (28.2)</td>
<td>3.2 × 9.1</td>
<td>2</td>
<td>83.4</td>
</tr>
<tr>
<td>III - 93</td>
<td>152. (36.5)</td>
<td>11.8 × 18</td>
<td>2</td>
<td>82.0</td>
</tr>
</tbody>
</table>

The temperature at which oil evolves varies with heating rate (fig. 4). This is not an indication of a change in the oil generation mechanism but, instead, results from the longer time in which the kerogen can decompose (at a given temperature) when heated at a slow rate. Also, at higher heating rates, the thermal gradient through the block gives the appearance of oil generation at high temperatures.

It is apparent (fig. 4) that lower heating rates cause a greater yield loss. This trend is better shown in fig. 5 where total oil yield is plotted vs the log of the heating rate. Note the approximate asymptotic approach to 100 percent Fischer Assay at higher heating rates.

![Figure 4. - Oil evolution (as percent Fischer Assay) vs surface temperature for 17.2 cm x 18 cm right cylindrical blocks. Data are for four different heating rates: (0) 2°C/h, (a) 6°C/h, (Q) 10°C/h, and (c) 60°C/h. The solid lines are smooth curves drawn through the experimental points.]

Figure 5. - Oil yield vs. log of the heating rate for 17.2 cm x 18 cm blocks and for powdered material (<800 μm). The dashed line is the yield calculated for the powder experiments, based on the mechanism and kinetics discussed in the text; the solid lines are not calculated but are just smooth curves drawn through the experimental points.

Heating rate, per se, should not affect oil yield. Rather, the heating rate must control some other mechanism by which oil becomes degraded before being collected. To gain a better understanding of what this mechanism might be, a series of experiments was carried out on powdered shale samples under the same heating conditions and without an external sweep gas (autogenous environment). Results are shown in fig. 5. Note that nearly the same trend (within experimental error) is observed for both powdered and block shale samples. Apparently, the degradation process is nearly independent of particle size.

To confirm that this agreement was not just fortuitous, we measured the effects of slow heating (2°C/h) on material 3.2, 7.2, and 11.8 cm in diameter. To within experimental error, all particle sizes gave the same yield (table 2).

During previous experiments on powder shale samples, we observed similar oil degradation (i.e., yield loss) during prolonged isothermal heating under autogenous conditions (Stout and others 1976). However, sweeping the sample with an inert gas reduced the yield loss since the liberated oil was
removed from the pyrolysis region before being degraded.

The ability of a sweep gas to reduce oil degradation in powders was also observed in these non-isothermal experiments. Powdered shale samples, heated at 5°C/h, showed a near linear increase in yield with gas sweep rate (table 3, fig. 6). Hence, the effects of gas sweep rate and heating rate closely parallel each other.

These results indicate that a higher heating rate may allow the recovery of more oil in both powders and blocks because it produces higher self-generated (i.e., autogenous) gas sweep rates during retorting. Furthermore, if the oil products are removed in the vapor phase,* then the flow rate would be approximately proportional to the heating rate. The low permeability of oil shale makes it impossible for an external sweep gas to significantly penetrate a shale block. Autogenous gas sweep and oil vaporization processes are the only effective means of removing oil from a block. As a result, the more rapid the heating conditions, the faster oil is removed from the block; consequently, less oil degrades.

We were also interested in the effect of the shale grade on yield. To determine this, two 17.2-cm-diameter blocks, one 58 l/metric ton (14 gal/ton) and another 204 l/metric ton (49 gal/ton) were retorted at 2°C/h and compared with experimental data from the approximately 125 l/metric ton (30 gal/ton) material (table 2, fig. 7). To within experimental error, the yield is independent of grade over the 58-204 l/metric ton range.

In summary, the experimental data show that oil degradation depends principally on heating rate (as it effects autogenous gas

*We have been able to partially verify that the oil products are removed in the vapor phase by carrying out retort experiments (heating at 19°C/h) on a powdered shale sample in an inverted retort can. In this operating mode, the oil must be in a vapor phase in order to be removed; a metal frit was used to help break any aerosols. The yield from the inverted retort was the same as that from the standard retort, i.e., 91 percent vs 90.8 percent, respectively (see Appendix, table A).

Table 3. - Summary of oil shale powder experiments on 91.7 l/t\(^b\) (22 gal/ton) material under linear heating conditions, i.e., \(dT/dt = \text{constant}\).

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Heating rate, °C/h</th>
<th>External flow rate, cm³/min</th>
<th>Oil yield % FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP-1</td>
<td>0.60</td>
<td>0</td>
<td>78.8</td>
</tr>
<tr>
<td>TC-22</td>
<td>5.0</td>
<td>0</td>
<td>86.1</td>
</tr>
<tr>
<td>TC-18</td>
<td>5.0</td>
<td>0</td>
<td>85.7</td>
</tr>
<tr>
<td>TC-30</td>
<td>19.3</td>
<td>0</td>
<td>90.8</td>
</tr>
<tr>
<td>TC-14</td>
<td>63.5</td>
<td>0</td>
<td>96.1</td>
</tr>
<tr>
<td>TC-12</td>
<td>185.0</td>
<td>0</td>
<td>98.4</td>
</tr>
<tr>
<td>Fischer assay</td>
<td>720.0</td>
<td>0</td>
<td>100.0</td>
</tr>
<tr>
<td>TC-28</td>
<td>5.0</td>
<td>2.0</td>
<td>86.7</td>
</tr>
<tr>
<td>TC-24</td>
<td>5.0</td>
<td>5.2</td>
<td>89.8</td>
</tr>
<tr>
<td>TC-34</td>
<td>3.0</td>
<td>5.0</td>
<td>91.9</td>
</tr>
<tr>
<td>TC-16</td>
<td>5.0</td>
<td>15.0</td>
<td>92.9</td>
</tr>
<tr>
<td>TC-18</td>
<td>5.0</td>
<td>18.6</td>
<td>97.4</td>
</tr>
<tr>
<td>TC-46  (^c)</td>
<td>19.3</td>
<td>0</td>
<td>91.0</td>
</tr>
</tbody>
</table>

\(^a\)Zero flow indicates autogenous conditions.
\(^b\)0.916 wt% organic carbon in raw shale.
\(^c\)Retort vessel inverted.

Figure 6. - Oil yield vs external gas flow rate (argon) for powdered oil shale samples heated at 50°C/h. A flow rate of 18 cm³/min corresponds to about one retort void volume per minute at 400°C and 1 bar.
swEEP rate) and not on particle size* or grade.

**Intraparticle Oil Degradation - Cracking vs Coking Reactions** - A realistic picture of oil release from oil shale can be developed only when one understands the mechanism of intra-particle oil degradation. Once the mechanisms that lead to major oil loss are determined, one can then attempt to design processing conditions that minimize loss effects.

A recent study of the effects of thermal histories on oil shale pyrolysis showed that the yield was determined by the time-temperature history of the liberated oil and not by the thermal history of the kerogen (Stout and others 1976). Using this work as a basis, we have confined our investigation to the loss in yield due to reactions in the liberated oil.

The principal non-oxidative means by which the liberated shale oil can be degraded are cracking and coking reactions. Because coking and cracking often have slightly different meaning (depending on the material being processed) we define the terms as they will be used here: By cracking, we mean vapor-phase, bond fission reactions that eventually lead to a distribution of molecular units (mostly units smaller than the original molecule) plus, possibly, some carbonaceous residue. Coking, we define as liquid or condensed phase reactions resulting in fusion of two or more molecular species with the ultimate formation of a carbonaceous product plus minor amounts of lower molecular weight gases.

An important difference in the above two mechanisms is the distribution of final products. As defined, cracking reactions lead to greater evolution of lower molecular weight hydrocarbon fragments (CH₄, C₂H₆, etc.) whereas, coking reactions produce mainly a carbonaceous residue.

Experiments reported in the Appendix show that coking is the principal intra-particle oil degradation process. Evidence for this comes from several observations, principally: product distribution from powder and block retorting experiments, and shale oil distillation at different heating rates.

**Proposed Oil Production Mechanism** - From the experimental data given above and in the Appendix, it is possible to formulate a simple mechanistic picture of oil production and degradation:

\[
(k_{1} + k_{g}) \frac{d}{dt} \text{(oil)}_{ip} = k_{c} \text{coge} + \text{gas} \rightarrow \text{carbonaceous residue} + \text{gas}
\]

The term (oil)_{ip} refers to the liberated oil in-place (intraparticle). The in-place oil is subjected to two competing processes: oil degradation leading to coke and gas formation, and oil removal from the particle giving recovered product. In the event of negligible degradation, the oil produced would equal 100 percent of Fischer assay.

The experimental results in the preceding section show that coke is formed primarily from the oil liquid or condensed phase. Therefore, one can rewrite the oil generation and degradation steps given in (1) as
follows:

\[
\begin{align*}
\text{Oil precursors} & \xrightarrow{k_{d}} \text{oil}^l + \text{oil}^g \\
& \xrightarrow{k_{c}} \text{coke} + \text{oil produced.}
\end{align*}
\]

(2)

Since we are concerned only with reactions involving oil, the term oil precursors is used to refer to that portion of the kerogen plus bitumen that decomposes to oil (i.e., condensable product at 0°C).

The stoichiometries (table 4) for the reactions given in Equations (1) and (2) were determined from experiment. Details leading to this formulation are given elsewhere (Campbell and others 1977).

In the proposed mechanism, the oil precursors decompose at some rate, \(k_d\), giving a distribution of oil in the gas (oil\(^g\)) and liquid (oil\(^l\)) phase. This distribution of products is some function of temperature \(X(T)\) times the total oil present.

\[
\text{Oil}^g = (X(T)) \text{oil}
\]

(3a)

\[
\text{Oil}^l = (1 - X(T)) \text{oil}
\]

(3b)

The term oil\(^g\) here refers to the material that is above its boiling point, i.e., that material which cannot coexist in liquid-vapor equilibrium at 1 bar and the retort temperature, \(T\). The oil vapor in equilibrium with a liquid oil phase is considered separately in the \(k_1\) rate step. Since the void space in the sample is small, the vapor products are assumed to exit the material at some rapid rate (\(k_g\)) giving "produced" oil.

Inside the shale material, the oil in the liquid phase is subject to two competing reactions, one of rate, \(k_c\), which leads to coke formation, and another, \(k_1\), which leads to oil produced. The rate of coking, \(k_c\), is for a reaction and, hence, varies as \(\exp\left(-E/RT\right)\); whereas, \(k_1\) is essentially independent of temperature, depending only on the gas flow rate (or heating rate).

The process governed by the rate, \(k_1\), can be considered a vaporization step represented by:

\[
\text{Oil}^l \rightarrow \text{oil}^{\text{vap}} + \text{oil produced}, \quad (4)
\]

where step 2 depends on the flow rate. Oil\(^{\text{vap}}\) is the vapor material in coexistence with some liquid phase and, hence, is distinguished from oil\(^g\), the oil totally in the gas phase - i.e., above its boiling point.

From the above-proposed mechanism, it is apparent that increasing the flow rate (by either rapid heating or, in the case of powders, introducing an inert gas) increases the rate of oil production and reduces the likelihood of competing coking reactions.

To carry out meaningful calculations, using the mechanism in Equation (2) one must know the values of the various rate constants as well as the boiling-point distribution for the produced oil (i.e., \(X(T)\)). These have recently been reported by Campbell and others (1976, 1977) and are summarized in Table 5. The rate constant for liquid removal, \(k_1\), does not have the common exponential form; instead, \(k_1\) is proportional to the autogenous gas flow rate, which is, in turn, proportional to the heating rate. A value for the proportionality constant, \(a\), of 0.12 K\(^{-1}\) was found to give good agreement with the constant-heating rate experiments.

**Table 4.** - Stoichiometries for the reactions given in equations (1) and (2) of the text.

<table>
<thead>
<tr>
<th></th>
<th>A. Oil generation</th>
<th>B. Oil degradation</th>
<th>C. Oil removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}<em>{1.56}^g\text{N}</em>{0.028}^g\text{S}_{0.006}^g)</td>
<td>(\text{CH}<em>{1.56}^g\text{N}</em>{0.020}^g\text{S}_{0.002}^g)</td>
<td>(\text{CH}<em>{1.56}^g\text{N}</em>{0.024}^g\text{S}_{0.002}^g)</td>
<td></td>
</tr>
<tr>
<td>(\text{CH})</td>
<td>(0.2\text{CH}_0]0.006]0.018</td>
<td>(0.36\text{CH}_0]0.024]0.004</td>
<td>(0.725\text{CH}_0]0.020]0.002</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>(0.019\text{H}_2)</td>
<td>(0.013\text{H}_2)</td>
<td>+0.010 (\text{H}_2)</td>
</tr>
<tr>
<td>(\text{CO})</td>
<td>(0.018\text{CO}_2)</td>
<td>(0.014\text{C}<em>{3.8}^0\text{H}</em>{7.5})</td>
<td>(0.014\text{C}<em>{3.8}^0\text{H}</em>{7.5})</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>(0.036\text{H}_2)</td>
<td>(0.036\text{H}_2)</td>
<td>(0.019\text{H}_2)</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>(0.019\text{H}_2)</td>
<td>(0.036\text{H}_2)</td>
<td>(0.014\text{C}<em>{3.8}^0\text{H}</em>{7.5})</td>
</tr>
<tr>
<td>(\text{Vapor})</td>
<td>(\text{Gas})</td>
<td>(\text{Gas})</td>
<td>(\text{Gas})</td>
</tr>
</tbody>
</table>
Table 5. - Summary of rate constants for proposed mechanism (Equation (2)) and fractional distribution of oil in the gas phase.

A. Rate constants

\[ \begin{align*}
  k_a (\text{cm}^3 s^{-1}) &= 2.8 \times 10^{13} \exp(-54400/RT) \\
  k_b (\text{cm}^3 s^{-1}) &= 3.1 \times 10^7 \exp(-35000/RT) \\
  k_c (\text{cm}^3 s^{-1}) &= a \cdot b \\
  a &= 0.12 \text{ cm}^{-1} \\
  b &= \text{heating rate}
\end{align*} \]

B. Oil fraction in gas phase

\[ \begin{align*}
  X(T) &= 0.38 + (T - 598) \cdot 0.0007, \quad 773 \geq T \geq 600K \\
  &= 1.0, \quad T > 773K
\end{align*} \]

Activation energies are in cal/mole.

The distribution of oil in the liquid and vapor phases was estimated from a simulated distillation of a Fischer assay oil (Campbell and others 1977). Examining these data, we found that the percent by weight of oil above its boiling point at a given retorting temperature, T, (and 1 bar) could be accurately represented by the relationship in Table 5.

The oil yield versus heating rate for powder retorting experiments was then calculated, using the data in Table 5 and a standard numerical routine for solving ordinary differential equations (Hindmarsh 1974). The yield calculated, using the simple mechanism in equation (2) agrees well with the experimental data (fig. 5).

Although the above mechanism is oversimplified, the complexity of the system precludes a more detailed picture with the data now available. Nevertheless, this simple mechanism helps immensely in forming a picture of the processes that may be occurring as well as defining retorting conditions that may lead to low yields.

Analysis of Block Retorting Via a Simple Mathematical Model - In this section, we analyze the results from the block experiments, using a simple mathematical model. The model incorporates the kinetic results from the powder experiments (Equation (2) and Tables 4 and 5) and thermal data reported in the literature. The model calculates the volume of evolved oil, the degree of intra-

particle oil degradation, the coke distribution, and the thermal profile through the material. By carrying out such a numerical analysis, we can check the ability of our simplified model to describe the experimental results. If there is good agreement, the model can then be used to gain further valuable insight on processing conditions and block sizes leading to optimum oil recovery.

Particle Size - To make the problem numerically tractable, we assume the block can be treated as a sphere (i.e., one dimensional). Sohn and Szekely (1972) showed that particles, having equal dimensions in three directions, can be analyzed by assuming that the particle is a sphere with a radius given by:

\[ r_s = \frac{3V_p}{A_p} \tag{5} \]

where \( V_p \) and \( A_p \) are the values for the volume and area of the particle, respectively. The 17.2 cm diameter blocks have a length-to-diameter ratio of about one and, therefore, can be treated using this assumption.

Governing Equations - The equation describing energy conservation for a solid spherical particle with a chemical heat source is given in part A, Table 6. The three terms on the right-hand side refer to energy transport by conduction, convection, and chemical reaction, respectively.

In the analysis given here, the convective heat transport term is assumed to be small and, hence, neglected. This assumption has been shown to be quite valid for the heating rates and grade of material used here (Campbell and others 1977).

Organic reactions and rate of heat generation during retorting of an oil shale particle (below the dolomite and calcite decomposition temperatures) can be described by the set of equations given in parts B and C, Table 6. These equations come directly from the experimentally-derived mechanism for oil generation and degradation given in the previous section (Equation (2)) and the stoichiometries given in Table 4.
Table 6. - Governing equations for 1-D model of block retorting.

A. Heat transport

\[ \rho \cdot C_p \frac{\partial T}{\partial t} = V \cdot k \nabla T - \frac{V}{8} \rho \cdot C_p \nabla T + \dot{q} \]

B. Chemical reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate equation</th>
<th>Physical Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil ( \rightarrow ) (1 - ( X(T) )) Oil</td>
<td>( R_{\text{oil}} = f_o(1 - X(T)) \cdot k_d \cdot \rho_{\text{kb}} )</td>
<td>Intra-particle oil formation from the organic material (i.e., Kerogen + bitumen) in the shale.</td>
</tr>
<tr>
<td>Oil ( \rightarrow ) ( X(T) ) Oil</td>
<td>( R_{\text{og}} = f_o \cdot X(T) \cdot k_p \cdot \rho_{\text{kb}} )</td>
<td></td>
</tr>
<tr>
<td>Oil ( \rightarrow ) ( f_c ) coke</td>
<td>( R_c = f_c \cdot k_c \cdot \rho_{\text{lo}} )</td>
<td>Intraparticle oil degradation leading to formation of coke and non-condensible gas.</td>
</tr>
<tr>
<td>Oil ( \rightarrow ) ( 1 - f_c ) gas</td>
<td>( R_g = \frac{(1 - f_c)}{f_c} R_c )</td>
<td></td>
</tr>
<tr>
<td>Oil ( \rightarrow ) ( f_l ) Oil produced</td>
<td>( R_{\text{ol}} = R_{\text{og}} + k_l \cdot \rho_{\text{lo}} )</td>
<td>Oil evolution from the block.</td>
</tr>
<tr>
<td>Oil ( \rightarrow ) ( f_l ) Oil produced</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C. Rate of heat generation

\[ \dot{q} = \Delta H \cdot k_d \cdot \rho_{\text{kb}} \]

The density of the shale block at a particular temperature is given by:

\[ \rho_S(T) = \rho_{\text{min}} + \rho_{\text{org}} \cdot (1 - X(T)) \] (6)

Assuming negligible decomposition of mineral species (\( T < 600^\circ \text{C} \)), the block density can be rewritten as:

\[ \rho_S(T) = \rho^0_S - \rho_{\text{vol}}(T) + \rho_c(T) + \rho_{\text{lo}}(T) \] (7)

The volatile mass loss under zero degradation conditions is given by \( \rho_{\text{vol}} \) where

\[ \rho_{\text{vol}}(T) = 0.78 \cdot (1 - F) \cdot \rho_{\text{kb}} \] (8)

The coefficient, 0.78, represents the mass fraction of volatile matter released per unit weight of initial organic material (Allred 1976). At the end of retorting, the intra-particle oil has either vaporized or coked and, hence:

\[ \rho_S^F = \rho_S^0 - \rho_{\text{vol}} + \rho_c \] (9)

The above system of equations, describing the particle retorting process, was solved using a partial differential equation routine implemented by Sincovec and Madsen (1975). The particle was zoned into 21 equal volume segments. The boundary condi-
results given here (e.g., kinetics from powder shale experiments) or data previously reported in the literature (e.g., heat capacity, thermal conductivity, etc.). Therefore, a comparison of the calculated and experimental results provides a sensitive test of the model.

Figures 8 and 9 are plots of calculated and experimental results showing the oil evolution, total oil yield, and temperature data for a set of block retorting experiments. The experimental data are for the 17.2-cm-diameter blocks, heated at rates of 2, 6, 18, and 60°C/min (corresponding to experiment numbers III-38, 18, 30, and 63, respectively; table 2). The grade of the blocks ranged from about 120 to 136 l/metric ton (29-33 gal/ton).

The calculated evolution of oil vs block surface temperature agrees well with the experimental results (fig. 8). The biggest discrepancy between the model calculation and experimental data is for the high heating rate experiment (60°C/h). The model predicts oil release at a slightly lower temperature (~20°C) than is observed.

![Figure 8](image.png)

**Figure 8.** - Comparison of oil evolution vs block surface temperature, calculated from the mathematical model with experimental observation for surface heating rates of (a) 2, (b) 6, (c) 18, and (d) 60°C/h. Blocks are 17.2 cm in diameter and between 120 to 136 l/metric ton (29 to 33 gal/ton) in grade (see text). The experimental points are from fig. 4.

Model Calculation vs Experimental Results - It is important to note that there are no free parameters in the model. All input to the model was from experimental

\[
\frac{\partial T}{\partial r} \bigg|_{r=0} = 0 \quad (10)
\]

and

\[
\frac{\partial T}{\partial r} \bigg|_{r = r_s} = T_0 + bt. \quad (11)
\]

The second boundary condition, Eq. (11), is set by the experiment, where \( T_0 \) is the initial block temperature and \( b \) is the heating rate, determined from the thermocouple readings near the block edge \( (r/r_s = 0.97) \).

The other necessary initial conditions include block density and concentration of organic matter. Block density was determined experimentally (see experimental section) and the concentration of organic matter was calculated from the oil grade, using the correlation reported by Stanfield and others (1951).

A value of 80.0 kcal/kg was used for the heat of decomposition of kerogen. This value is based on an analysis by Carley (private communication 1976) of shale enthalpy data reported by Wise and others (1971).

**Oil Shale Physical Properties** - The heat capacity of the shale is taken to be:

\[
C_s = [(216.8 + 120.9 \ W_k)/(1.0 - F)]
+ 197.8 \ F] + [(0.1478]
+ 1.329 \ W_k] (1.0 - F]
+ (0.220 \ F)] \cdot [T - 298], \quad (12)
\]

where \( W_k \) is weight fraction of kerogen in the raw shale and \( F \) is the fractional conversion (decomposition) of kerogen at temperature \( T \). This equation is also from Carley's (1976) analysis of Wise's (1971) data.

The thermal conductivity of the shale is assumed to be given by:

\[
k = 1.25 \times 10^{-4} \cdot (1 - F]
+ 0.83 \times 10^{-4} \ F \quad (13)
\]

based on data reported by Tihen and others (1968) for 125 l/metric ton (30.0 gal/ton) material.
Accurate data for the difference between block center and surface temperatures were not available for the heating rate of 2°C/h. The error in the thermocouple readings was too large to quantitatively determine a difference except to note that it was less than 10 to 15°C, hence, only calculational results are shown in fig. 9a.

Carbon Distribution in Spent Shale - The radial distribution of organic carbon in the spent shale blocks was determined at the completion of several retorting experiments. Analyses were performed on drill corings taken at different radial positions; the procedure used in the coring operations is similar to that reported by Mallon and Braun (1976). The results (fig. 10) are for two 17.2-cm-diameter blocks; one heated at a rate of 2°C/h, the other at 60°C/h.

Note that the concentration of organic carbon residue is independent of radial position in the block. This phenomena was also observed in blocks having a smaller diameter (fig. 11). The spatial independence of organic carbon deposition indicates that the oil that degrades is apparently not diffusing through the block, but instead remains near the site of initial formation. This observation supports the proposed mechanism for oil degradation (Equation (2)). The mechanism assumes that oil degradation due to coking occurs in the relatively immobile condensed or liquid phase and not in the mobile gas phase. The 1-d model calculations, based on this mechanism, show good agreement with the experimental data (fig. 10).*

From the above data, it becomes clearer why particle size has little effect on oil yield. Since the degradation process is not occurring in the gas phase, longer intra-

*Carbon distribution for the 7.2-cm block (fig. 11) could not be calculated via the 1-d model because the length to diameter ratio was not 1. However, the carbon concentration in the block can be estimated from the observed yield loss and the calculated organic carbon conversion to char (see Appendix).
particle residence times - i.e., larger blocks - have little effect on the degradation process. This conclusion pertains only to block sizes and heating rates similar to those used in this study. One can easily think of conditions (e.g., very fast heating rates and large blocks) where the surface temperature of the shale becomes very hot (>700°C) while the inside is still retorting. Under these conditions, cracking of the gas phase products diffusing from the interior of the block may be an important oil degradation process. It is also probable that extra-particle oil oxidation (burning) will become a major oil loss mechanism.

Water Evolution During Block Retorting -

The amount of water released during retorting of the 17.2-cm-diameter blocks is given in table 7. The weight of water released is about 1.9 percent of the total weight loss (to ~500°C) from the 121-154 l/metric ton (29 to 37 gal/ton) material. The water is released in approximately equal amounts in two steps (fig. 12), one below ~240°C and the second during retorting (i.e., above 240°C).

Note the similarities in the evolution profiles for water with those for oil (fig. 4). Water, released at high temperatures (~240°C), apparently forms during the kerogen decomposition process. Water released below 240°C, may come from hydrated mineral species or nahcolite in the shale.

**Practical Implications of the Results** -

The results of this study have a great deal of practical significance in relation to proposed methods of in-situ shale processing. As mentioned in the introduction, there are two principal means of processing shale: combustion and hot inert gas retorting. The movement of the pyrolysis front during combustion retorting is quite fast, the shale heating rates being of the order of several degrees per minute. On the other hand, heating rates during hot inert gas retorting may be much slower - only a few degrees (or few tenths of a degree) per hour.
Table 7. - Quantity of water released during retorting of 17.2-cm-diameter blocks.

<table>
<thead>
<tr>
<th>Run number</th>
<th>Ir</th>
<th>Grade</th>
<th>H₂O yield, ml H₂O/kg raw shale</th>
</tr>
</thead>
<tbody>
<tr>
<td>III-2</td>
<td>121</td>
<td>(29.0)</td>
<td>25</td>
</tr>
<tr>
<td>III-10</td>
<td>135</td>
<td>(32.4)</td>
<td>21</td>
</tr>
<tr>
<td>III-10</td>
<td>139</td>
<td>(33.3)</td>
<td>17</td>
</tr>
<tr>
<td>III-38</td>
<td>122</td>
<td>(29.2)</td>
<td>17</td>
</tr>
<tr>
<td>III-41</td>
<td>156</td>
<td>(37.5)</td>
<td>17</td>
</tr>
<tr>
<td>III-55</td>
<td>57.6</td>
<td>(13.8)</td>
<td>12</td>
</tr>
<tr>
<td>III-81</td>
<td>204</td>
<td>(48.8)</td>
<td>10^9</td>
</tr>
</tbody>
</table>

*Accurate determination of the total water released was complicated by the large quantity of oil evolved. Hence, this number represents a lower limit on the total water evolved.

From the results of this study, it is apparent that significant intraparticle degradation may occur during hot gas retorting, whereas, relatively little will probably result from combustion processing.

A least squares fit of the data for oil yield versus logarithm of the heating rate (fig. 5, tables 2 and 3) gives a valuable empirical relation that can be used to estimate the intraparticle yield loss at various heating rates:

\[
\begin{align*}
Y_L & \approx 100 - (81.1 + 8.24 \log b), \\
& \quad \text{when } b \leq 190^\circ C/h \quad (13) \\
Y_L & \approx 0.0, \quad \text{when } b > 190^\circ C/h
\end{align*}
\]

Furthermore, the percent of organic carbon converted to char within the block can be estimated as:

\[
\begin{align*}
OC_{\text{Char}} & = -0.606 \times (81.1 + 8.24 \log b) \\
& + 80.54, \quad \text{when } b \leq 190^\circ C/h \quad (14) \\
OC_{\text{Char}} & = 19.9, \quad \text{when } b > 190^\circ C/h
\end{align*}
\]

The above expressions are valid over the range of heating rates and grade of material used in this study. Caution should be used in applying these relationships to very large shale particles since the material used in this study was less than 18 cm in diameter. LLL is currently conducting experiments to check the validity of this work when applied to particles approaching 60 cm (2 ft) in diameter.

The data here also only apply to intraparticle degradation. Oxidation of the oil, once it leaves the blocks (extra-particle), can become important for large-size material processed at a high heating rate. Under this condition, a large thermal gradient develops, resulting in kerogen pyrolysis occurring on the interior of the block while the exterior is being oxidized (i.e., burned). LLL is currently developing a detailed retorting model, which takes into account both of the above processes (Braun and Chin 1977).

Summary and Conclusions

The principal conclusion of this study is that particle size (up to 17.2 cm) and grade (14-49 gal/ton) have little effect on the degree of intraparticle oil degradation during shale retorting. On the other hand, the rate at which the shale is heated has a pronounced effect on yield. For example, retorting at a rate of 180°C/h gives a yield of ~99 percent, while retorting at 2°C/h gives only about 83 percent yield.

The principal degradation product is a carbonaceous residue, which we term coke. Evidence showed that oil degradation occurs mainly in the liquid or condensed phase and not in the vapor phase. Furthermore, we found that the degree of degradation is controlled by the rate of gas sweep through the...
particle, which, in turn, is controlled by the rate of particle heating.

We propose a mechanism to explain the observed oil degradation during retorting. Our rate equations, characterizing the various mechanism steps, were determined from experimental data on powdered shale and incorporated into a mathematical model describing oil shale block retorting. The model contains no free parameters. Calculations carried out with the use of the model agree very well with experimental results.

Acknowledgments

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NOTICE

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APPENDIX

Evidence for Shale Oil Coking During Retorting

I. Organic Carbon Distribution in Retorting Products

The amount of organic carbon converted to char under various retorting conditions is given in table A1 for powders and table A2 for four of the block experiments. Stout and others (1976) report that 83 percent of the carbon lost from oil by degradation processes appears as char, and 17 percent as gas (mainly CH₄). Furthermore, they showed that the percent organic carbon converted to char (OC_char) could be correlated with oil yield by the empirical relation:

\[ OC_{\text{char}} = -0.606 \cdot \text{OY} + 80.54 \]

where, OY, is the oil yield as percent Fischer assay. Using this correlation, a predicted value of organic carbon converted to char has been calculated for the experiments in tables A1 and A2. As shown in the tables, the agreement between the predicted and observed values is quite good.

The important point is that over 80 percent of the carbon lost from the oil goes to form carbonaceous residue - this strongly indicates coking as the major oil degradation process. Furthermore, Stout and others (1976) found that the H₂ concentration in the evolved gas increased by roughly two-fold with a 20 percent loss in FA yield. There was no observable increase in Cₙ, n > 1, gas-phase hydrocarbons. Hence, it is probable that for the experiments reported here, little loss in yield results from cracking of the produced oil.

II. Shale Oil Distillation Experiments

Coking of shale oil is readily observed when distilling it at various heating rates. Figure A1 shows the percent by weight of coke produced vs log of the heating rate for a shale oil still. Also plotted (dashed line) is the equivalent amount of carbonaceous residue formed by oil degradation during retorting of shale powders. The dashed curve was obtained using the expression:

Weight Coke = YL \cdot (0.83) \cdot (13.0/13.5)

where, YL, is the percent yield loss observed at a given heating rate (fig. 5 - main text), 0.83 is the fractional conversion of organic carbon in oil to organic carbon in coke, and 13.0 and 13.5 are approximate empirical weights for 500°C carbonaceous residue (CH) and oil (CH₂₅), respectively.

The agreement between the weight of carbon residue formed by retorting powdered shale and coking shale oil is quite good. This tends to further support coking as the major intraparticle oil degradation process.
Table A1. - Summary of oil shale powder experiments on 91.7 l/metric ton (c) (22 gal/ton) material retorted under linear heating conditions (i.e., $\frac{dT}{dt}$ = const.).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating rate, $^\circ$C/h</th>
<th>External flow rate, $^3$ cm/min</th>
<th>Oil yield, TFA</th>
<th>Predicted (b) organic C converted to char wt%</th>
<th>Oil yield, (wt%)</th>
<th>Char yield, (wt%)</th>
<th>Total Organic C converted to char wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP-1</td>
<td>0.60</td>
<td>0</td>
<td>78.8</td>
<td>32.8</td>
<td>85.85</td>
<td>12.74</td>
<td>1.56</td>
</tr>
<tr>
<td>TC-22</td>
<td>5.0</td>
<td>0</td>
<td>86.1</td>
<td>28.3</td>
<td>84.38</td>
<td>12.00</td>
<td>1.59</td>
</tr>
<tr>
<td>TC-18</td>
<td>5.0</td>
<td>0</td>
<td>87.7</td>
<td>28.6</td>
<td>84.85</td>
<td>12.45</td>
<td>1.60</td>
</tr>
<tr>
<td>TC-20</td>
<td>19.3</td>
<td>0</td>
<td>90.8</td>
<td>25.5</td>
<td>83.54</td>
<td>11.98</td>
<td>1.64</td>
</tr>
<tr>
<td>TC-14</td>
<td>63.5</td>
<td>0</td>
<td>91.1</td>
<td>22.3</td>
<td>85.86</td>
<td>12.08</td>
<td>1.75</td>
</tr>
<tr>
<td>TC-12</td>
<td>185.0</td>
<td>0</td>
<td>98.4</td>
<td>20.9</td>
<td>86.51</td>
<td>11.66</td>
<td>1.56</td>
</tr>
<tr>
<td>Fisher Assay</td>
<td>720</td>
<td>0</td>
<td>100.0</td>
<td>19.9</td>
<td>86.38</td>
<td>11.22</td>
<td>2.06</td>
</tr>
<tr>
<td>TC-28</td>
<td>5</td>
<td>2</td>
<td>86.7</td>
<td>28.0</td>
<td>86.17</td>
<td>11.98</td>
<td>1.71</td>
</tr>
<tr>
<td>TC-52</td>
<td>5</td>
<td>5</td>
<td>89.8</td>
<td>26.1</td>
<td>84.07</td>
<td>12.12</td>
<td>1.62</td>
</tr>
<tr>
<td>TC-34</td>
<td>5</td>
<td>7</td>
<td>91.9</td>
<td>24.8</td>
<td>84.65</td>
<td>11.62</td>
<td>1.79</td>
</tr>
<tr>
<td>TC-38</td>
<td>5</td>
<td>18.6</td>
<td>97.4</td>
<td>21.5</td>
<td>83.60</td>
<td>11.65</td>
<td>1.85</td>
</tr>
<tr>
<td>TC-56</td>
<td>5</td>
<td>15.0</td>
<td>92.9</td>
<td>24.2</td>
<td>84.48</td>
<td>12.36</td>
<td>1.74</td>
</tr>
<tr>
<td>TC-48</td>
<td>19.3</td>
<td>0</td>
<td>91.0</td>
<td>25.6</td>
<td>84.87</td>
<td>11.94</td>
<td>1.83</td>
</tr>
</tbody>
</table>

(a) A zero flow indicates autogenous conditions.

(b) Based on Stout and others (1976), organic C converted to char = -0.606 x Oil Yield + 80.54.

(c) 9.914 wt% organic carbon in raw shale.

Table A2. - Organic carbon converted to char for several block retorting experiments (a)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grade 1/t (gal/ton)</th>
<th>Heating rate, $^\circ$C/h</th>
<th>Yield, % FA</th>
<th>% Organic carbon converted to char</th>
</tr>
</thead>
<tbody>
<tr>
<td>III-2</td>
<td>121.</td>
<td>29.0</td>
<td>99.0</td>
<td>20.3</td>
</tr>
<tr>
<td>III-38</td>
<td>122.</td>
<td>29.2</td>
<td>83.8</td>
<td>29.3</td>
</tr>
<tr>
<td>III-63</td>
<td>156</td>
<td>37.5</td>
<td>96.0</td>
<td>20.2</td>
</tr>
<tr>
<td>III-85</td>
<td>156</td>
<td>37.4</td>
<td>84.9</td>
<td>29.4</td>
</tr>
</tbody>
</table>

(a) Block dimensions are given in Table 2 of main text.

(b) Based on work by Stout and others (1976), organic C converted to char = (-0.606 x Oil Yield) + 80.54.

Figure A1. - Percent by weight of coke produced during distillation of shale oil at different heating rates compared to the calculated percent by weight of coke formed by retorting powdered shale.
References


Campbell, J. H., Coburn, T. T., and Koskinas, G. H., Oil Shale Retorting 2. Variation in Shale Oil Chemical and Physical Properties during Retorting of Blocks: Lawrence Livermore Laboratory, to be published.


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Raley, J. and Braun, R., 1976, Oil Degradation During Oil Shale Retorting: UCRL-78098.


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Abstract

A one-dimensional mathematical model has been developed, simulating the chemico-
physical processes involved in the concurrent, vertical retorting of a rubblized bed of oil shale. Both hot-gas retorting and combustion retorting can be simulated. The flow rate of the gas stream and the composition and temperature of both the gas stream and the shale particles are calculated as a function of time and location in the retort. Rates of recovery of oil and water from the retort are also computed.

The model is used to predict commercial in-situ retorting phenomena for typical conditions of shale composition, particle size, packing fraction, and input-gas properties. The predicted effects of introduced gas properties (flow rate, temperature, and composition) are examined in detail here. The model indicates that introduced air, diluted with steam or CO₂, is effective in controlling the temperature and maximizing the oil yield, without causing the large decrease in retorting rate associated with the use of a mixture of air and recycle gas. The air and steam mixture is also attractive because it yields a retort product gas with a higher heating value.

Introduction

The oil shale program at the Lawrence Livermore Laboratory (LLL) is concerned with oil recovery by means of a modified in-situ oil shale retorting process (Lewis and Rothman 1975; Rothman 1975). In this so-called RISE process, a portion of the oil shale is removed by underground mining, and the remainder is rubblized and retorted in place by a forward combustion technique. The rubble is created by a continuous mining process, using a modified sublevel caving method, with removal of approximately 20 percent of the oil shale to the surface. This process is believed capable of producing large volumes of rubble, with uniform and controlled void space, suitable for commercial-scale retorting of the thick, medium-grade resources within Colorado's Piceance Creek Basin. Construction of the large, in-situ retorts is time-consuming and expensive. Therefore, we must learn to control and perfect the retorting process with a minimum of experimentation in the field. A keystone in this effort is the development of a mathematical model for simulating the chemical reactions and physical processes in the concurrent, vertical retorting of a rubblized bed of shale.

Process simulation models for oil shale retorting have been developed independently by several private corporations - in particular, Mobil (Kondis and others 1975); Johnson and others 1975) and Occidental (McCarthy and Cha 1976). Because these

*This work performed under auspices of U.S. ERDA, under contract No. W-7405-Eng-48.
models are proprietary, however, they are not available to the public. Some modeling work has been done at the Laramie Energy Research Center, but no publication of that work has yet appeared. Other work (Fausett 1975; Nuttall 1976) has not been comprehensive enough to permit making predictions of in-situ retorting. In previous work at LLL, Bowman (1975) formulated a set of governing equations for oil shale retorting. However, the numerical solution of those equations proved to be excessively time-consuming. Since then, we have adopted another approach in developing a retort model. The purpose of this paper is to describe the LLL model and to illustrate its use in determining the effects of the composition of introduced gas on in-situ retorting.

Modeling Philosophy

There are several important reasons for developing a mathematical model of the oil shale retorting process. Such a model is a good frame of reference in an experimental program. It can be used to identify sensitive variables that may require further laboratory measurements. It can be used in planning expensive laboratory retort experiments so that they yield the most significant information. The model can also be used to predict the results of in-situ retorting under various conditions; this would help establish design criteria for a field program, leading to the demonstration of commercial-scale, in-situ retorting. A well-developed model can be expected to suggest basic process changes that will produce significant improvements in yield and cost. Finally, such a model can be used to guide the actual operations of an in-situ retort.

In developing our model, we have kept three essential requirements in mind: First, it must be versatile enough to describe and predict all of the selected aspects of the process. To meet this requirement we adopted a mechanistic approach, based on fundamental chemical and physical properties rather than on empirical scaling. Secondly, the number of adjustable parameters must be low (preferably zero). Finally, the model must be computationally tractable within a reasonable time and level of effort. The importance of this requirement must not be underestimated, for even a very sophisticated model has little value if it cannot be executed in real time. The LLL model has been developed by starting with a few process mechanisms and gradually including additional ones. Thus, at each stage of development, a working computer version of the model has been available.

Description of the Model

A rigorous mathematical treatment of the model is beyond the scope of this paper. The interested reader is referred to Braun and Chin (1977) for those details.

The present model is a transient, one-dimensional description of a packed-bed retort. Variable properties in the vertical (axial) direction are considered. Thus, the model is probably valid for in-situ retorts that have been prepared with fairly uniform lateral distribution of shale particle sizes and void volume. However, it is not valid for laboratory retorts having appreciable heat loss at the wall, since the resulting effects of the lateral temperature gradients cannot be treated properly.

The model's main role is to calculate (as a function of time and location in the retort) the flow rate of the gas stream and the composition and temperature of both the gas stream and the shale particles. A given shale particle size distribution is represented by several (typically 2 or 3) discrete sizes and the governing equations for all those size classes are solved simultaneously. From these calculations, one obtains the desired information regarding the composition, temperature, and flow rate of the output gas as well as the net rate of recovery of oil and water from the retort.

The processes included in the present model are those believed to have the greatest effects in either the hot-gas retorting
mode or the combustion retorting mode. The physical processes are:

1. axial convective transport of heat and mass due to the bulk gas flow,
2. axial conductive transport of heat,
3. heat transfer between the gas stream and the shale particles, and
4. water evaporation and condensation.

The chemical reactions in the shale particles are:

5. decomposition of kerogen,
6. decomposition of carbonate minerals,
7. reaction of carbon with \( \text{CO}_2 \),
8. reaction of carbon with \( \text{O}_2 \),
9. thermal degradation of oil, and
10. release of fixed water.

The chemical reactions in the gas stream are:

11. combustion of \( \text{CO} \) produced from the above reaction of carbon with \( \text{CO}_2 \),
12. combustion of the fuel components in recycle gas, and
13. combustion of oil.

Chemical reactions in the shale particles are modeled on the following basis: For kerogen decomposition, we used the first-order kinetics measured experimentally by Campbell and others (1976). Although much simpler than other recent investigations of the kinetics and mechanism of kerogen decomposition (Faussett 1975; Finucane and others 1977), the first-order kinetics have demonstrated good accuracy in predicting oil production rates.

For the decomposition of carbonate minerals, we limit our treatment to two components: One (designated \( \text{MgCO}_3 \)) represents the \( \text{MgCO}_3 \) portion of dolomite, as well as the generally minor amounts of other carbonates that decompose at relatively low temperatures. The other (designated \( \text{CaCO}_3 \)) represents the \( \text{CaCO}_3 \) portion of dolomite, as well as the initial calcite content. We use the simple first-order decomposition kinetics, which were found to predict adequately the rate of \( \text{CO}_2 \) evolution from blocks of oil shale (Mallon and Braun 1976). Additional experimental work on carbonate decomposition is in progress.

The reactions of the carbon residue of spent shale are handled by means of a spherical particle model. The reaction with \( \text{O}_2 \) occurs at the surface of a shrinking core of unburned carbon, and the reaction rate is largely controlled by the rate of \( \text{O}_2 \) diffusion through the reacted shell. The chemical kinetics of the reaction are also included, because, with eventual cooling of the shale particle, the rate of the chemical reaction becomes the limiting step. The reaction between carbon and \( \text{CO}_2 \) occurs within the unburned carbon core and is assumed to be first-order with respect to both carbon and \( \text{CO}_2 \). The carbon reaction model has been experimentally calibrated and verified for oil shale blocks (Mallon and Braun 1976).

The oil yield may be reduced because of thermal degradation (coking) of oil within a shale particle. Experiments show that the magnitude of the loss depends upon the heating rate of the shale particle at the time of oil generation (Campbell and others 1977). This fact is taken into account in the retort model. The products of the coking reaction are carbon residue, which is deposited within the particle (and which may undergo further reaction with \( \text{O}_2 \) or \( \text{CO}_2 \)), and combustible gas, which may be burned upon leaving the particle, if \( \text{O}_2 \) is present in the gas stream.

The fixed water content of raw shale is assumed to be released linearly with increase in temperature of the shale particle, between a low starting temperature (-120°C) and a higher final temperature (-360°C). This is in approximate agreement with measured release of water from blocks of oil shale (Campbell and others 1977).

The chemical reactions in the gas stream are modeled on the following basis. Six gas species are considered: \( \text{N}_2 \), \( \text{O}_2 \), \( \text{H}_2\text{O} \), \( \text{CO}_2 \), \( \text{CO} \), and "GAS." This last term includes \( \text{H}_2 \), \( \text{CH}_4 \), and all other gaseous hydrocarbons and gaseous combustible compounds (except \( \text{CO} \)) produced during the complete pyrolysis of kerogen.

Detailed composition of this component has been deduced from Fischer assay data and char pyrolysis data (Raley, written commun-
ication 1977), and from that, the heat of combustion was deduced. Combustion of CO and "GAS" is permitted to occur in the model whenever O₂ is also present, if the temperature is above a specified threshold value. This combustion proceeds until either the fuel or the O₂ is consumed. If any O₂ is still present in that part of the retort where oil is being generated, then all of the remaining O₂ is consumed by oil combustion.

The preceding physical and chemical processes are used in formulating the governing equations for conservation of energy and mass. Separate equations are used for the gas phase and for each class of shale particle size. For the gas equations, we use the quasi-steady-state approximation. This approximation should be valid because the small mass of the gas, compared with that of the solid, causes the gas properties to be primarily determined by interaction with the solid phase rather than by the past history of the gas phase. The governing equations are solved by means of a semi-implicit, finite-difference computer program. The program is written in LRLTRAN (an LLL version of FORTRAN) for use on a CDC-7600 computer.*

Several processes not included in the model should be mentioned here. For example, flow of oil, either as vapor, mist, or liquid, is not addressed. That is, once the oil has been generated, it is assumed to have no further role in the process, except that a certain amount undergoes intraparticle coking or extraparticle combustion. Secondly, because the pressure drop within the retort is expected to be low, it is neglected. A constant gas pressure of one standard atmosphere is assumed. Change in bed permeability, due to compaction or plugging with liquid products, needs further assessment. Thirdly, chemical reactions of water with carbon in the spent shale, with CO in the gas stream, or with any other reactants have not been included. Experimental work is underway to help guide the formulation of an appropriate model for these reactions.

### Table 1. - In-situ combustion retort conditions for the reference case (case 184).

<table>
<thead>
<tr>
<th>Composition of shale</th>
<th>Kerogen</th>
<th>13.9 percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>30</td>
<td>&quot;</td>
</tr>
<tr>
<td>Calcite</td>
<td>13</td>
<td>&quot;</td>
</tr>
<tr>
<td>Water</td>
<td>2</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bed properties</th>
<th>Initial temperature</th>
<th>25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>20 percent by volume</td>
<td></td>
</tr>
<tr>
<td>Shale particle diameters</td>
<td>50 percent by weight—6.4 cm (2.5 in.)</td>
<td>50 percent by weight—61 cm (24 in.)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Input-gas properties</th>
<th>Composition</th>
<th>Air (containing 1 percent by volume of H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>25°C</td>
<td></td>
</tr>
<tr>
<td>Flow rate</td>
<td>0.68 ml/s² (3.17 scfm/ft²)</td>
<td></td>
</tr>
</tbody>
</table>

Application of Model

The model has been tested in several recent laboratory retort experiments performed with controlled heat loss at the wall. Reasonable agreement was found for retorting rate, oil yield, gas composition, and temperature profile. Much more testing will be done to determine the accuracy of the model and to help establish which aspects of the model need improvement. This work will be reported in a later paper.

The model can be used to predict retorting results for operating conditions typical of commercial in-situ retorting. As a reference case, we have selected the set of conditions shown in table 1 for combustion retorting with air as the introduced gas. The kerogen content (i.e., total organic material) of 13.9 percent by weight corresponds to an organic carbon content (Smith 1961) of 11.2 percent by weight and Fischer

*Reference to a company or product name does not imply approval or recommendation of the product by the U. of California or the U.S. ERDA to the exclusion of others that may be suitable.
assay oil yield (Cook 1974) of about 100 liters per metric ton (24 gal/ton). Note that the reference-case flow rate is 0.68 mol/m²·s.*

In the ensuing calculations, all the rate quantities (such as retorting rate, rate of oil recovery, etc.) and the gas composition data are reported as average values since zero time. This enables us to calculate the integrated quantities quickly if desired. Unless otherwise noted, all of the results presented are at an elapsed retorting time of 25 days. At that elapsed time, most of the quantities have reached steady-state values.

When the exit gas stream leaves the retort, a substantial part of the potential oil product may be either in the vapor state (since the temperature will generally be 45°C or more) or carried along as a mist. In calculating the oil recovery, we have assumed that the oil mist is completely recovered and that liquid petroleum products are condensed from the gas stream at 0°C. The latter condition is in line with the derivation of the stoichiometry for kerogen decomposition from Fischer assay data. In practice, however, the actual condensation temperature will probably not be this low. Therefore, the actual rate of oil recovery may be somewhat less than calculated. The reported rate of oil recovery is the net rate after mist separation and further condensation outside of the retort, and after allowing for loss in oil yield both by direct combustion of oil outside a shale particle and by thermal degradation (cooking) of the oil within a shale particle. The reported rate of water recovery is the sum of the rate of water condensation in the retort and the rate at which water vapor exits the retort.

Table 2. - Retorting results for air input at various flow rates (elapsed retorting time =25d)

<table>
<thead>
<tr>
<th>Case No.:</th>
<th>199</th>
<th>184</th>
<th>198</th>
<th>197</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input gas flow rate (mol/m²·s)</td>
<td>1.36</td>
<td>0.68</td>
<td>0.34</td>
<td>0.17</td>
</tr>
<tr>
<td>Retorting rate (m/d)</td>
<td>4.11</td>
<td>2.05</td>
<td>1.03</td>
<td>0.51</td>
</tr>
<tr>
<td>Percentage loss of oil, by combustion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot; &quot; &quot; &quot; , coking</td>
<td>19.9</td>
<td>20.0</td>
<td>20.1</td>
<td>20.2</td>
</tr>
<tr>
<td>Total percentage loss</td>
<td>22.2</td>
<td>23.0</td>
<td>24.0</td>
<td>25.7</td>
</tr>
<tr>
<td>Rate of oil recovery (kg/m²·d)</td>
<td>496</td>
<td>246</td>
<td>121</td>
<td>59</td>
</tr>
<tr>
<td>Rate of water recovery (kg/m²·d)</td>
<td>324</td>
<td>163</td>
<td>82</td>
<td>41</td>
</tr>
<tr>
<td>Output gas, dry (mol/m²·s)</td>
<td>1.87</td>
<td>0.93</td>
<td>0.46</td>
<td>0.23</td>
</tr>
<tr>
<td>Lower heating value (kJ/mol)</td>
<td>56</td>
<td>57</td>
<td>58</td>
<td>59</td>
</tr>
<tr>
<td>Composition: N₂ + Ar (percent by volume)</td>
<td>57.0</td>
<td>57.1</td>
<td>57.2</td>
<td>57.5</td>
</tr>
<tr>
<td>CO₂ (percent by volume)</td>
<td>30.3</td>
<td>30.0</td>
<td>29.5</td>
<td>29.0</td>
</tr>
<tr>
<td>CO (percent by volume)</td>
<td>6.7</td>
<td>6.8</td>
<td>7.1</td>
<td>7.2</td>
</tr>
<tr>
<td>&quot;GAS&quot; (percent by volume)</td>
<td>6.0</td>
<td>6.1</td>
<td>6.2</td>
<td>6.3</td>
</tr>
</tbody>
</table>

*SI metric units are used throughout this report. Conversion factor: 1 mol/m²·s = 4.662 scfm (60°F)/ft².
The values for rate of gas exiting from the retort are similarly based on the above condensation conditions, and they are reported on a water-free basis. The lower (net) heating value of the dry output gas is based on 283.0 kJ/mol CO and 616.2 kJ/mol "GAS."

Air Input - The results for reference case 184 and for air input at various other flow rates are shown in Table 2. The rate of oil recovery is essentially proportional to the input-air flow rate, the slight deviation being caused by the somewhat greater oil loss by coking at the lower flow rates. At all four flow rates, the total loss in oil yield (as percent of Fischer assay) caused by oil combustion is substantial. As a direct consequence, the calculated retort bed temperatures are very high, as illustrated in Figure 1 for reference case 184. The two temperature curves are for the two shale particle sizes selected for the calculation. The temperature plotted for a given particle size is the average temperature of the particle. In reality, the surface temperature of the larger particles at a given location in the retort will be closer to the temperature of the smaller particles than is indicated. The temperature of the smaller particles is particularly high near the retorting front, where both combustion of carbon in the smaller particles and combustion of oil from the larger particles are occurring. The width of the thermal wave continues to increase with advancement of the retorting front. The possible effect of the high temperatures and broad thermal waves on the retort walls should be considered. Since lowering the flow rate of the air alone did not give the desired capability for temperature control in the range of flow rates considered, we investigated alternative gas compositions.

Diluted-Air Input - Diluted-air input is effective in controlling the maximum temperature reached in the retort. This fact is illustrated in Figures 2 to 5, where the effect of dilution with 50 percent by volume of CO₂, steam, N₂, and recycle gas, respectively, is represented. As with 100 percent air input, the width of the thermal wave continues to increase with further propagation of the retorting front. Additional predicted results for these diluents are shown in Table 3. We will now discuss some of the advantages and disadvantages of each of these input-gas options.

50-Percent Air and 50-Percent CO₂ - From the results in Table 3, it is obvious that the CO₂ diluent gives the highest retorting rate, the lowest loss in oil yield, and the highest rate of oil recovery. In fact, the rate of oil recovery exceeds that of reference case 184, even though the rate of advance of the retorting front has decreased from 2.05 to 1.76 m/d. This favorable aspect is due to a decrease in oil combustion from 20 percent to 4.6 percent. These beneficial

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Figure 1. - Calculated retort bed temperatures for reference case 184 (see Table 1) after 25 days.

*Conversion factor: 1 kJ/mol = 1.134 Btu/scf (60°F).
effects are primarily due to the high heat capacity of CO$_2$. It is very effective in transporting heat downstream. The principal disadvantage of CO$_2$, as a diluent, is the expense involved in removing enough of it from the exit gas for use as input. However, removal of the 60.9 percent by volume of CO$_2$ from the exit gas would raise the heating value of that gas from 41 kJ/mol to 105 kJ/mol. Much greater increases in the heating value can be obtained by using pure O$_2$, with CO$_2$ diluent, as the input gas; followed by CO$_2$ removal from the output gas. This will be discussed in more detail later.

Table 3. - Effects of input gas composition for a total input gas flow rate of 0.68 mol/m$^2$.s (elapsed retorting time = 25 d).

<table>
<thead>
<tr>
<th>Case No.:</th>
<th>184</th>
<th>201</th>
<th>209$^a$</th>
<th>223</th>
<th>192</th>
<th>196</th>
</tr>
</thead>
<tbody>
<tr>
<td>Components:</td>
<td>Air</td>
<td>Air</td>
<td>Air</td>
<td>Air</td>
<td>Hot</td>
<td>+ + + + recycle</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Steam</td>
<td>N$_2$</td>
<td>Recycle (500°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$ content of input gas (percent by volume)</td>
<td>20.8</td>
<td>10.4</td>
<td>10.4</td>
<td>10.4</td>
<td>10.4</td>
<td>0</td>
</tr>
<tr>
<td>Retorting rate (m/d)</td>
<td>2.05</td>
<td>1.76</td>
<td>1.56</td>
<td>1.45</td>
<td>1.11</td>
<td>0.94</td>
</tr>
<tr>
<td>Percentage loss of oil by combustion</td>
<td>20.0</td>
<td>4.6</td>
<td>8.0</td>
<td>8.2</td>
<td>1.3</td>
<td>0</td>
</tr>
<tr>
<td>&quot;&quot;&quot;&quot;&quot;&quot;&quot;&quot; coking</td>
<td>3.0</td>
<td>4.1</td>
<td>4.5</td>
<td>4.1</td>
<td>7.8</td>
<td>19.4</td>
</tr>
<tr>
<td>Total percentage loss</td>
<td>23.0</td>
<td>8.7</td>
<td>12.5</td>
<td>12.3</td>
<td>9.1</td>
<td>19.4</td>
</tr>
<tr>
<td>Rate of oil recovery (kg/m$^2$.d)</td>
<td>246</td>
<td>250</td>
<td>212</td>
<td>198</td>
<td>156</td>
<td>117</td>
</tr>
<tr>
<td>Rate of water recovery (kg/m$^2$.d)</td>
<td>163</td>
<td>90</td>
<td>619</td>
<td>84</td>
<td>90</td>
<td>47</td>
</tr>
<tr>
<td>Output gas, dry (mol/m$^2$.s)</td>
<td>0.93</td>
<td>0.84</td>
<td>0.50</td>
<td>0.83</td>
<td>0.79</td>
<td>0.74</td>
</tr>
<tr>
<td>Lower heating value (kJ/mol)</td>
<td>57</td>
<td>41</td>
<td>69</td>
<td>37</td>
<td>32</td>
<td>364</td>
</tr>
<tr>
<td>Composition: N$_2$ + Ar (percent by volume)</td>
<td>57.1</td>
<td>31.5</td>
<td>53.5</td>
<td>72.7</td>
<td>59.5</td>
<td>3.4</td>
</tr>
<tr>
<td>CO$_2$ (percent by volume)</td>
<td>30.0</td>
<td>60.9</td>
<td>32.7</td>
<td>20.0</td>
<td>34.0</td>
<td>34.9</td>
</tr>
<tr>
<td>CO (percent by volume)</td>
<td>6.8</td>
<td>1.7</td>
<td>4.9</td>
<td>2.4</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>&quot;GAS&quot; (percent by volume)</td>
<td>6.1</td>
<td>5.9</td>
<td>8.9</td>
<td>4.9</td>
<td>4.2</td>
<td>56.9</td>
</tr>
</tbody>
</table>

$^a$The temperature of the input gas was 100°C in this case.
Figure 2. - Calculated retort bed temperatures for case 201 after 25 days. (All parameters were the same as in table 1, except that the input gas was 50 percent by volume of air and 50 percent by volume of CO₂.

50-Percent Air and 50-Percent Steam - Steam is a more practical diluent from the standpoint of availability and has some beneficial effects. Compared to air input, the steam and air combination results in a lower loss in oil yield and a smaller volume and higher heating value for the dry exit gas. Furthermore, the calculated heating value will probably be even higher than that indicated in table 3, when we include in the model the chemical reaction of water. With a steam diluent, good temperature control can be achieved within the retort, both in terms of lower maximum temperatures and narrower thermal waves. The disadvantage is that more water must be handled, mainly in the form of water vapor that has to be condensed outside of the retort. The use of steam injection in proportions other than 50 percent is discussed in a later section.

Figure 3. - Calculated retort bed temperatures for case 209 after 25 days. (All parameters were the same as in table 1, except that the input gas was 50 percent by volume of air and 50 percent by volume of steam at 100°C).

50 Percent Air and 50 Percent N₂ - As a diluent, N₂ is inferior to both steam and CO₂ because of its lower heat capacity, although it still provides some temperature control. Furthermore, it yields an exit gas of much lower heating value. Thus, it is of interest mainly in laboratory retorting. It does, however, have some practical interest because the steady-state composition of the exhaust gas from a gas turbine happens to be largely N₂, with smaller amounts of CO₂ and H₂O mixed in. A gas turbine might provide a convenient source of inert gas for use in retorting, and, if this exhaust gas were used with air, the results would be slightly more attractive than those given in table 3 for a pure air and N₂ mixture.
Figure 4. - Calculated retort bed temperatures for case 223 after 25 days. (All parameters were the same as in table 1, except that the input gas was 50 percent by volume of air and 50 percent by volume N₂).

50 Percent Air and 50 Percent Recycle - It has often been suggested that air and direct recycle gas (i.e., gas exiting from the retort) might be used as input gas in retorting. Table 3 shows that recycle gas is the least effective diluent of those considered. This is because of the additional fuel (i.e., CO, H₂, and hydrocarbons) present in recycle gas. This fuel consumes a substantial portion of the already diluted O₂ input, thereby slowing down the rate of advancement of the other combustion reactions. Furthermore, although oil loss by combustion is very low in this case, oil loss by coking is relatively high because of the more gradual heating of the shale particles during the time of oil generation (fig. 5). A more satisfactory air/recycle ratio than that considered here may be found, but the added fuel would still cause some retardation of the retorting rate. In experimental (small) retorts, the presence of extra fuel would perhaps be beneficial at first, because it would provide an alternative fuel to oil, but except in that instance, the use of recycle gas would be wasteful.

Hot-Gas Retorting

Another possible candidate for input retorting gas is direct recycle gas preheated to 500°C (case 196 in table 3 and fig. 6). A higher temperature for a given flow rate would, of course, give a higher rate of heat input. However, the rate of carbonate decomposition would also be increased, producing an offsetting effect. The serious objection to hot-gas retorting is the large, calculated oil loss from coking. At an elapsed time of 25 days, when the retorting front has advanced 23.5 m, total calculated oil loss from coking is 19.4 percent. Earlier, when the temperature profile of the bed is steeper, the calculated coking loss is less. It
worsens progressively, however, with advancement of the thermal wave, and this loss would probably make hot-gas retorting unsuitable for deep retorts, unless a flow rate high enough to keep a reasonably steep temperature profile in the bed could be used. The attractive feature of hot-gas retorting is the heating value of the gas exiting from the retort. Furthermore, since most of the gas is directly recycled (after suitable treatment for use in compressors), only about 9 percent of the dry exit gas, which has relatively high heating value, would need to be disposed of.

Additional Study of Water Injection

We have seen that steam has attractive properties as a diluent with air. We will now illustrate some of the effects of varying the steam content of a gas introduced into the retort at a temperature of 100°C.

Pertinent results of the retort model are shown in the first four columns of table 4 for steam contents of 0, 25, 50, and 75 percent by volume. From these results, it is not at all clear what the optimum composition is. For example, going from 0 to 75 percent by volume of steam, the retorting rate decreases by a factor of 2 because of the decrease in O₂ flux; however, oil losses due to combustion decrease from 25 percent to only 3.5 percent. Thus, the rate of oil recovery actually decreases only by a factor of 1.8. Note also that the oil-coking loss becomes quite important as we go from 50 to 75 percent by volume of steam. Generally, a higher steam-to-air ratio increases the heating value of the exit gas and results in smaller volumes of dry product gas to be handled in any further gas-using process.

One effect of water addition that may have an important bearing on the successful operation of an in-situ retort is to increase the temperature of the bed downstream from the retorting region. For straight air input, this steam plateau is at 46°C. For 25, 50 and 75 percent by volume of steam input, downstream steam plateaus are at 76, 80 and 91°C, respectively. This elevation in temperature should have the desirable effect of reducing the viscosity of the oil product, thus allowing it to flow more readily out of the retort.

Considering all these things, optimum steam content is probably between 25 and 50 percent by volume of the input gas. This question will be addressed in detail once we have included the full water chemistry in the retort model.

One other variation, the use of straight air with water, seems promising. Case 200 in table 4 shows the effects of air input at a rate of 0.68 mol/m²·s, coupled with water input at a rate of 0.28 mol/m²·s. Comparing these results with those of air without water injection (case 184), we see that there is a substantial increase in retorting rate, rate of oil recovery, and heating value of the dry exit gas. Furthermore, using water has the desired effect of narrowing the thermal wave and lowering the maximum bed temperatures. The narrowing is due to the latent heat of vaporization of the water. Only part of this
Table 4. - Effects of water addition for a total input-gas flow rate of 0.68 mol/m².s (elapsed retorting time = 25 d).

<table>
<thead>
<tr>
<th>Case No.:</th>
<th>184</th>
<th>209A</th>
<th>209</th>
<th>209B</th>
<th>200a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input gas (percent of air by volume)</td>
<td>100</td>
<td>75</td>
<td>50</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td>(percent of steam by volume)</td>
<td>0</td>
<td>25</td>
<td>50</td>
<td>75</td>
<td>0</td>
</tr>
<tr>
<td>O₂ content of input gas (percent by volume)</td>
<td>20.8</td>
<td>15.7</td>
<td>10.4</td>
<td>5.2</td>
<td>20.8</td>
</tr>
<tr>
<td>Retorting rate (m/d)</td>
<td>2.05</td>
<td>1.84</td>
<td>1.56</td>
<td>1.02</td>
<td>2.49</td>
</tr>
<tr>
<td>Oil percentage loss by combustion</td>
<td>20.0</td>
<td>13.0</td>
<td>8.0</td>
<td>3.5</td>
<td>15.1</td>
</tr>
<tr>
<td>&quot; &quot; &quot; &quot; coking</td>
<td>3.0</td>
<td>3.6</td>
<td>4.5</td>
<td>9.6</td>
<td>3.3</td>
</tr>
<tr>
<td>Total percentage loss</td>
<td>23.0</td>
<td>16.6</td>
<td>12.5</td>
<td>13.1</td>
<td>18.4</td>
</tr>
<tr>
<td>Rate of oil recovery (kg/m².d)</td>
<td>246</td>
<td>239</td>
<td>212</td>
<td>137</td>
<td>316</td>
</tr>
<tr>
<td>Rate of water recovery (kg/m².d)</td>
<td>163</td>
<td>379</td>
<td>619</td>
<td>843</td>
<td>606</td>
</tr>
<tr>
<td>Output gas, dry (mol/m².s)</td>
<td>0.93</td>
<td>0.73</td>
<td>0.50</td>
<td>0.26</td>
<td>0.96</td>
</tr>
<tr>
<td>Lower heating value (kJ/mol)</td>
<td>57</td>
<td>60</td>
<td>69</td>
<td>84</td>
<td>64</td>
</tr>
</tbody>
</table>

*a Case 200 is the same as case 184, except that liquid water is also input at a rate of 432 kg/m².d.

heat is redeposited downstream by condensation. Once the temperature of the shale has been raised sufficiently (to about 70°C in this example), all further water leaves the retort as vapor.

One serious problem associated with water injection is distributing the liquid over the entire cross-section of the retort. Localized injection would have the effect of developing cool channels through which the water would simply flow from top to bottom. And, even if successful distribution were achieved, there might be a high hold-up of water in the porous spent shale above the combustion zone.

Using O₂ Instead of Air - The effects of O₂ input, diluted by steam, CO₂, or recycle gas to give a total input flow rate of 0.68 mol/m².s are shown in table 5. For each of the three diluents, two O₂ concentrations are used, corresponding to the O₂ concentrations in the previous cases of 50 and 100 percent air input. We will limit this discussion to the following salient features.

Steam and CO₂ both appear to be attractive diluents with O₂. In fact, the retorting rate for case 203 (20.8 percent by volume of O₂ and 79.2 percent by volume of CO₂) is the highest we have seen for this total input flow rate. Yet, the maximum temperature is not excessively high, and the oil loss from combustion is modest. With steam and 20.8 percent O₂, oil loss and maximum temperatures are probably too high; thus, less than 20.8 percent by volume of O₂ should be used. The attractive result associated with steam and O₂ input is the relatively high heating value of the dry output gas. If O₂, rather than air, were used to burn gas, exiting from the retort, in the surface processing unit, the exhaust from that process would be almost exclusively CO₂ and steam, and this, in turn, could then serve as a source of diluent gas for input to the retort. Alternatively, CO₂
Table 5. - Effects of pure O₂ input, diluted by steam, CO₂ or recycle gas for a total input flow rate of 0.68 mol/m²·s (elapsed retorting time = 25 d).

<table>
<thead>
<tr>
<th>Case No.:</th>
<th>Steam</th>
<th>CO₂</th>
<th>Recycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent</td>
</tr>
<tr>
<td>Input gas (percent by volume, O₂)</td>
<td>10.4</td>
<td>10.4</td>
<td>10.4</td>
</tr>
<tr>
<td>(percent by volume, diluent)</td>
<td>89.6</td>
<td>89.6</td>
<td>89.6</td>
</tr>
<tr>
<td>Retorting rate (m/d)</td>
<td>1.64</td>
<td>1.89</td>
<td>1.07</td>
</tr>
<tr>
<td>Percentage loss of oil, by combustion</td>
<td>8.0</td>
<td>2.4</td>
<td>0.7</td>
</tr>
<tr>
<td>&quot; &quot; &quot; &quot;&quot;, by coking</td>
<td>4.9</td>
<td>4.6</td>
<td>14.6</td>
</tr>
<tr>
<td>Total percentage loss</td>
<td>12.9</td>
<td>7.0</td>
<td>15.3</td>
</tr>
<tr>
<td>Rate of oil recovery (kg/m²·d)</td>
<td>222</td>
<td>273</td>
<td>141</td>
</tr>
<tr>
<td>Rate of water recovery (kg/m²·d)</td>
<td>1037</td>
<td>85</td>
<td>124</td>
</tr>
<tr>
<td>Output gas, dry (mol/m²·s)</td>
<td>0.23</td>
<td>0.86</td>
<td>0.73</td>
</tr>
<tr>
<td>Lower heating value (kJ/mol)</td>
<td>157</td>
<td>42</td>
<td>43</td>
</tr>
<tr>
<td>Lower heating value after removal</td>
<td>494</td>
<td>561</td>
<td>441</td>
</tr>
<tr>
<td>of CO₂ (kJ/mol)</td>
<td></td>
<td></td>
<td>530</td>
</tr>
</tbody>
</table>

could be removed from gas exiting from the retort, resulting in a gas fuel of relatively smaller volume and much higher heating value.

Using direct recycle gas as a diluent with O₂ does not look attractive. In case 193 (10.4 percent by volume of O₂), most of the O₂ is consumed by burning of fuel components in the recycle gas near the top of the retort. The resulting thermal wave is similar to that described in connection with hot-gas retorting; oil loss from coking is rather high. With 20.8 percent by volume of O₂, there is sufficient O₂ to support propagation of a combustion front, but, again, because of the large amount of recycle combustion near the top of the retort, a very broad thermal wave is produced.

Further Development of Model

The present model encompasses enough of the most important processes to make it of significant value in predicting the design of in-situ retorting operations. The model will be developed further to increase its versatility and accuracy.

New items to be included are: the chemical reactions of water and the variations of
initial bed properties (particularly shale grade) in the axial direction. In addition, although the number of gas and solid components must be held to a minimum, several more components may be included. This would make more accurate treatment of the gas source terms from kerogen decomposition and oil degradation possible. We may also take into account other mechanisms affecting oil yield: effects of softening or thermal expansion of the raw shale, effects of accumulation of tar or high-viscosity oil, sweep efficiency of the input gas, loss of gas or heat to surroundings, and water intrusion from surroundings. Our modeling effort will be guided by further analysis and experimentation.

Summary and Conclusions

We have described the LLL oil shale retort model and its use to predict the effects of the composition of introduced gas on retorting rate, loss in oil yield, net rate of oil recovery, heating value of the input gas, and other in-situ retorting results. Air input, even at a low rate as low as 0.17 mol/m²·s, produces high temperatures and broad thermal waves that may be of concern in retort operation and wall stability.

The use of recycle gas to accomplish the desired temperature control has long been practiced in experimental retorts. There, the recycle gas not only serves as a diluent, but also serves as a fuel source in preference to air for supplying part of the required heat for retorting. This is desirable because even in the largest of the above-ground experimental retorts (12 m long), the zone of combustion of carbon residue is quite thin, and it is therefore inefficient in depleting the oxygen from the gas stream before it reaches the zone of oil production. However, in the much larger, commercial-size retort (100 to 300 m long), the zone of carbon combustion soon becomes thick enough so that the carbon fuel is largely consumed, either by direct oxidation in the smaller particles of shale or by oxidation of CO, which evolves from the reaction between CO₂ and carbon in the larger particles. Therefore, after start-up, the fuel value of recycle gas is not needed as input to a commercial retort. Its continued use would not only be an unnecessary consumption of a potentially valuable resource, but it would further slow down the retorting rate.

This problem is avoided if CO₂, steam, or N₂ are used as the diluent. Model calculations indicate that all of these are effective in achieving temperature control. A direct benefit of the use of dilute air is a substantial decrease in the amount of oil combustion. Because of the lower O₂ flux for a given total gas flow rate, the retorting rate is also decreased, but the decrease is not nearly as great as with recycle input. The most practical diluent appears to be steam because it is easy to produce. From the commercial point of view, steam is also attractive because it can be readily condensed from gas exiting from the retort to yield a product gas of higher heating value.

Some further gains could be achieved by using CO₂, steam, or recycle gas as diluents with O₂, rather than with air, but the gains probably do not justify the cost of an O₂ plant.

The results presented in this report are to be considered as preliminary estimates for use in the design of in-situ retorts. Further development and verification will increase our confidence in the model predictions.

Acknowledgment
Technical discussions with A. E. Lewis and all members of the LLL Oil Shale Group are gratefully acknowledged.

References


NOTICE
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MODELING OF VERTICAL PRESSURE DISTRIBUTION IN LARGE IN-SITU RETORTS

J. F. Carley and L. Thigpen
Lawrence Livermore Laboratory
Livermore, California

Abstract

Deformation of oil-shale rubble and its consequent permeability loss depends upon rock pressure. This pressure distribution in oil-shale rubble columns is therefore important to modified in-situ oil extraction from oil shale. Pressure distribution in unretorted columns of oil-shale rubble has been modeled using the theory of bins. Dependence of vertical pressure on column geometry and shale properties was examined. A major finding is that, at room temperature for a given geometry and properties, pressure approaches an asymptotic limit regardless of overburden forces.

The model has been extended to include variations in density and frictional properties of shale that accompany the temperature changes occurring during retorting, and this expanded model has been programmed for the CDC 7600 computer. Parametric studies with this program point up the urgent need for data on the dependence of interparticle frictional properties on temperature and pressure.*

Directions of further development and improvement of this modeling effort are discussed.

Introduction

The modified in-situ process plans the extraction of oil from rubblized shale containing about twenty-percent voids in large vertical columns that may be developed under hundreds of meters of overburden. A potential problem that concerns us is the possible compaction of the rubble under its own weight and that of the overburden, with loss of porosity and consequent slowing or even stopping of processing. The report of Burwell, Tihen and Sohns (1974); work done on a smaller scale in our own laboratories (Trimmer and Heard 1977) and by Needham (1976), show that, at high temperatures and at applied pressures of 2 to 6 Mpa,* a laboratory column of small shale particles tends to contract and become less permeable as the kerogen is pyrolyzed. Permeability loss increases with increasing pressure. A key question that arises in trying to assess the seriousness of this processing hazard is: "What pressures will actually be felt in the standing rubble as the thermal front moves through?" It is mainly this question, rather than the effects of such pressures, to which this paper is addressed.

Theory

To begin with, consider the rubble bed, in place, before processing begins. Imagine it to be rectangular in cross-section with vertical walls of length, L, and width, W, and a height, H, from the bottom of the column to the top surface of the rubble. One might at first suppose that the rubble pressure at the bottom is simply the weight of

* Nomenclature given immediately before references.

*SI metric units used throughout.
the rubble divided by the cross-sectional area, LW. However, this rubble column is not free-standing, but is closely confined by the solid shale walls within which it was created. In fact, the column is very much like an enormous bin or storage silo. In tall bins, vertical pressure at the bottom is much less than the distributed weight of the stored particulate matter and any downward movement of this matter is strongly resisted by internal friction among the particles and by the frictional drag of the particles against the bin walls. The theory of vertical bin pressure was worked out eighty years ago by Janssen (1895) and is explained in detail in McCabe and Smith's text, "Unit Operations" (1967). We believe the same basic equation is applicable to vertical pressure in rubble columns, but some preliminaries should be dealt with first.

One of these is that Janssen (and McCabe and Smith) assumed that the top surface of the solids bed would be a free surface, whereas, we have to consider the possibility of overburden bearing on the rubble. Another is that, in most silos and bins, the materials making up the bin are rather different from those being stored, whereas, ours are the same. Third is that many of the commodities stored in bins, such as grain, plastic pellets and the like, are regular in shape and size, whereas our rubble particles will be broken rock ranging in size from perhaps a meter, down to fifty microns and less. Fourth is that temperature variations in storage bins seldom cause serious changes in the distribution of vertical pressure, while in RISE processing, temperature variations will be tremendous - many hundreds of degrees - and the shale itself will undergo profound chemical and physical changes. Finally, there is the meaning here of the term, "pressure", itself. This is a very rough use of a term from fluid mechanics, but we conceive of it here as a force exerted by the rubble on an area whose dimensions are considerably larger than those of the largest particles, divided by that area. With a grasp of the restrictions this definition imposes, we can treat the rubble as a continuum, with vertical and horizontal components of pressure at any point of interest.

Figure 1 is an idealized drawing of such a bed, with the coordinate, z, being the distance, measured downward, from the top surface to a horizontal slice of thickness, dz. The vertical pressure at z is PV, acting on the upper face of the slice, and at depth z + dz, the pressure, PV + dPV, acts upward on the lower face. The mass of this slice results in weight acting downward through its center. Finally, the frictional force of the walls acts upward around all the edges. This force is caused by horizontal pressure of the rubble against the walls and the coefficient of friction between the rubble and the walls. The equation of vertical equilibrium for the slice is:

\[ WLDV = WLP_b \frac{g}{g_c} dz - 2(W+L)uPH dz \]  

Rearranging,

\[ \frac{dPV}{dz} - \rho_b \frac{g}{g_c} + \frac{2(W+L)}{WL} uPH = 0 \]  

McCabe and Smith (1967) show that in beds of noncohesive, solid particles at rest, the ratio of horizontal pressure, PH, to vertical pressure, PV, is given by:

\[ \frac{PH}{PV} = K = \frac{1 - \sin \phi}{\cos \phi} \]  

in which \( \phi \) is the angle of internal friction of the particle mass. If the substitution, \( PH = KPV \), is made in Equation (2), we have the differential equation:

\[ \frac{dPV}{dz} + \frac{2(W+L)uK}{WL} PV - \rho_b \frac{g}{g_c} = 0 \]  

with the boundary condition, \( PV = P_0 \) at \( z=0 \).

In the operating retort, the properties, K, \( \mu \) and \( \rho_b \), will depend on the grade of the shale and on operating conditions, especially temperature. But, in the rubble column before retorting, we can get an estimate of pressure distribution by making a few simplifying assumptions, integrating Equation (4), and exploring the integrated form's parameters. We do this in the next section; in the following section, Equation 4 is
Figure 1. - Cutaway sketch of in-situ rubble column, with rectangular cross-section, showing forces acting on differential element at depth, z, below the top surface of the rubble. Presence of overburden is represented by pressure, $P_0$. 
solved for assumed retorting conditions.

Pressures in Cold Rubble Columns

Our first simplifying assumption is that vertical variations in the grade of the shale may be ignored and the mass-average grade may be used to represent the entire column. Another is that porosity is uniformly distributed; this makes the bulk density the same everywhere and equal to the shale-rock density, times (1-\(\varepsilon\)), where \(\varepsilon\) is the porosity. Rock density may be estimated from grade by means of the data of Smith (1956). Little is known about the frictional properties of granular shale. The angle of internal friction, \(\phi\), is the angle whose tangent is the coefficient of friction of adjacent particles within the mass. It can be determined from measurements of vertical and horizontal pressures within piles of particles, as Equation 3 implies. It is also nearly equal to, but usually slightly larger than, the easily measured angle of repose, \(\alpha\), illustrated by figure 2.

As the figure suggests, one builds up a conical pile of particles by pouring them from containers onto a central point on a flat horizontal surface; then measures the angle with the horizontal of the base of the cone. We have done this for several piles of particles, some small, some in the two-centimeter size range and some piles of mixed-size shale pieces up to 0.6 meter, but without attempting to sort the shale as to grade. Average grade is close to 0.08 m\(^3\)/metric ton. Eighteen measurements of angle of repose ranged from 33 to 39 degrees and averaged 35.0 degrees. In making some of the plots that follow, we assumed that the tangent of this angle was equal both to the tangent of the internal angle of friction and also to the coefficient of friction between the particles and the sidewalls of the retorts. The corresponding values of \(\mu\) and \(K\) are 0.700 and 0.2710.

Under the assumption that shale properties are constant throughout the column, Equation 4 becomes separable and is easily integrated to give

\[
P_v = P_0 e^{-2(W+L)\mu K z/WL} + \left[ WL\mu g/2(W+L)g_c \mu K \right] \left[ 1 - e^{-2(W+L)\mu K z/WL} \right]
\]

(5)

The first term of this equation is the effect of overburden pressure while the second gives the effect of the stacked-up rock mass. The dimensional group, \(WL/2(W+L)\), appearing in both terms, is the ratio of cross-section to perimeter and reduces to \(W/4\) for a square cross-section. It is easy to show that it also equals \(W/4\) for a circular cross-section, where \(W\) is the diameter. For a very long, narrow mine, in which sidewall support of the rubble would tend to be very strong, this ratio approaches \(W/2\).

Curves plotted from this equation are shown in figure 3 for a shale whose grade was assumed to be 0.08 m\(^3\)/metric ton, with a corresponding density of 2308 kg/m\(^3\). Void fraction was taken as 0.2, making the bulk density 1846 kg/m\(^3\). The bed was assumed to be square, with \(W = L = 37\) meters, values which we believe to be close to those of Occidental Oil's Retort 4 (McCarthy and Cha 1976).

Perhaps the most striking feature of this plot is the convergence of all the curves, regardless of overburden pressure, to a common asymptote, 0.88 Mpa, at depths
greater than 250 meters. If overburden pressure is high, it dominates the vertical pressure in the rock for the first 200 meters; if it is low, the rubble weight dominates. The Occidental No. 4 retort had no overburden; calculated rubble pressure at the bottom of that column is indicated by the small circle marked on the lowest curve.

We have made similar plots for different combinations of shale properties and found that they change only slightly over the range of reasonable expectation for material properties (Carley 1976). However, the pressure distribution is sensitive to the ratio of column cross-section to its perimeter, $WL/(W+L)$, which appears in both the exponential parts of Equation 5 and in the coefficient of the second term. We have calculated such distributions for the case of zero overburden pressure, but with rubble properties the same as for figure 3, for values of cross-section/perimeter up to 50 meters. This value corresponds to a column 200 meters square, or a rectangular one, with $W = 125$ and $L = 500$ meters, columns much larger than any now being contemplated for in-situ retorting. The results of these calculations for several depths are shown in figure 4. These curves show that rubble pressures at all depths climb rapidly as the length and width of the retort, particularly the width, increase. The small open circle in figure 4 has the same meaning as the one in figure 3; the circle with a cross in it represents conditions at the bottoms of retorts whose dimensions are reasonable for commercial-scale development. The dashed line represents the asymptotic pressure for any retort geometry, while the small arrows at the left mark the so-called "lithostatic" pressures for this same rubble at depths of 100, 200 and 300 meters. Clearly, actual pressures are far less than these values until the retort is very large in cross section or is relatively shallow.

**Rubble Pressures During Retorting**

Estimating rubble pressures during retorting is much more complicated than room-temperature estimates for several reasons:

![Figure 3](image-url)  
**Figure 3.** - Pressure profiles for rubble column at room temperature under different pressures. $P_0$, exerted by overburden at top surface of rubble. Grade of shale is 0.08 m³/metric ton, porosity is 0.2. Bed is square with its side = 37 m. "Lithostatic" pressure at 300 m, for $P_0 = 0$, would be 5.43 MPa.

![Figure 4](image-url)  
**Figure 4.** - Influence of ratio of cross-section to perimeter on cold rubble pressure at several depths for shale of grade = 0.08 m³/metric ton, porosity = 0.2, with no pressure from overburden. Open circle gives bottom pressure for a retort 37 m square, 93 m deep; closed circle gives the same for a retort 46 m wide, 183 m long, 220 m deep.
(1) Temperatures vary widely throughout a working retort, not only with vertical position, but also with time from the start of retorting.

(2) Because retorting drives the kerogen out of the shale and causes decomposition of the mineral carbonates, the spent shale is quite a different material from raw shale and can be expected to exhibit different dependence of density and frictional properties on temperature.

(3) Density and frictional properties may depend not only on material composition and temperature, but also on the rock pressure itself.

(4) Since no one has as yet published measurements of rock composition and temperature during actual retorting of a full-scale, rubble column in situ, these important quantities must be estimated.

(5) No actual measurements have been made of internal or external frictional properties of shale rubble at elevated temperatures, so a way must be found of estimating these.

(6) The differential equation (Equation 4), set up to describe rubble pressure, is based on an assumption that rubble particles are noncohesive; that is, they do not stick together. This assumption may not hold in the burnt-shale region of the working retort.

(7) Below the retorting front, oil and water, extracted from the kerogen, will be condensing and draining. We do not know how the presence of these liquids may affect the frictional behavior of rubble.

We shall now discuss these questions. Items (1), (2) and (4) are closely related. Two of our colleagues at LLL, Robert Braun and Raymond Chin, have constructed an elaborate computer model of the in-situ retorting process, some details of which are presented elsewhere in this volume (Braun and Chin 1977). Among the outputs of their program are rock composition and temperature throughout the retort at any time after heating begins. The retorting model assumes that events, at any level z, are the same over that entire plane, that initial porosity is the same throughout the rubble column, and that there is no subsidence during processing. In our modeling of rubble pressure, we have used composition and temperature distributions calculated by the model of Braun and Chin from reasonable operating and initial conditions.

Item (3) remains an open possibility, neglected in the absence of definitive data. The same applies to Items (5) and (7). As to (6), there is evidence, both from LLL research and work done elsewhere, to indicate that burnt shale partially fuses and develops substantial cohesion among particles when exposed to the extremely high temperatures anticipated in the combustion front during retorting with air. There is additional evidence that burnt shale, exposed to carbon dioxide and steam, undergoes cementing reactions with substantial strength development. While we recognize that these cohesion-producing phenomena may act to greatly reduce the pressure of over-standing burnt shale on the reaction zone below, we have not, at this time, allowed for their effects in our modeling of rubble pressure.

While Item (5) of the above list is true as stated, there do exist some data from triaxial testing of small, more or less homogeneous specimens of shale rock. While rock and rubble are not identical macroscopically, it seems reasonable to assume that interparticle frictional behavior will be approximately the same as intraparticle frictional behavior. We have collected the available data, some from published literature and some from as-yet-unpublished sources, and analyzed it. Details of that analysis will be presented by Thigpen and Heard (1977) elsewhere. Avoiding duplication, we can summarize as follows:

(1) From about two dozen measurements, at temperatures from 35 to 400°C, of which three are coefficients of external friction and the rest are tan φ as derived from triaxial tests, we find that coefficient of friction and tan φ are equal within the substantial scatter of the data.

(2) Tan φ and μ decrease from about 0.6-
0.7, at room temperature, at a rate of about 0.0015/°C for 0.1 m³/metric ton shale.

(3) Tan φ decreases with increasing grade, but appears to be only slightly influenced by the orientation of the principal stress to the bedding planes of the shale and by rate of strain during testing.

(4) At temperatures of 300° C and above, tan φ is strongly influenced by whether or not the oil formed from kerogen breakdown is permitted to escape from the specimen. At 400° C, tan φ becomes very small (less than 0.1) if the oil is retained.

(5) Spent shale has high friction coefficients, 0.5 to 0.7, at all temperatures. Although tan φ drops to 0.1 or less in oil-retaining specimens at 400° C, we believe that there are two reasons why such low extremes may not be encountered in-situ rubble: The first is that the oil formed in the rubble will drain off as it is formed, probably as vapor, until it reaches cooler regions below the retorting front. The second is that, in our own experiments with retorting of small beds of fine shale particles at pressure up to 6 Mpa (Trimmer and Heard 1977), the final porosity was at least ten percent, whereas if tan φ and μ truly fell to zero, we would expect all the porosity to be gone.

The third property that must be evaluated at the various temperatures pervading an operating retort is, ρ_b, bulk density. We have found no data on the densities of shales at elevated temperatures. However, the composition of various grades of Colorado shale has been reported and compiled in the Synthetic Fuels Data Handbook (Cameron Engineers 1975). Considerable information also exists on the decomposition of kerogen and the carbonate minerals of oil shale, calcite and dolomite. Most of the remaining mineral content consists of silicates of sodium, calcium and aluminum, plus quartz. From this information, it is possible to estimate densities at certain temperatures; temperatures at which the decomposition of kerogen, dolomite and calcite is complete after times that are mostly shorter than those expected in in-situ retorts. Assuming that these endothermic decompositions are equilibria, whose constants increase exponentially with temperature, these points can be connected, as in figure 5. The curves shown here are for the two grades of shale considered in our simulation. Each of the curved sections has four stages; representing, in succession, the loss of free water, kerogen decomposition, dolomite decomposition and calcite decomposition. At the end of this sequence we have remaining burnt shale, consisting mainly of sodium aluminosilicate minerals that will probably be partially fused after the passage of the flame front. Using averaged mineral compositions for burnt shales (Cameron Engineers 1975), a volume-weighted, average coefficient of cubical expansion was calculated and applied to the densities at 700° C to get the dashed lines of figure 5. Mineral properties were taken from Clark's "Handbook of Physical Constants" (1966).

![Figure 5 - Estimated dependence of oil shale density on temperature for two grades of shale. Values are believed to be representative of the densities that would be measured after several hours at the given temperature. Solid curves represent density changes that would take place with slow, progressive heating as a result of decomposition reactions that would never be reversed in in-situ processing, so are unidirectional. Dashed lines are usable for burnt shale regardless of direction of temperature change.](image-url)
Equation 4 was numerically integrated, using the Runge-Kutta method (Henrici 1962) for the following set of conditions. Details of the computer programming will be given by Thigpen and Heard (1977).

Retorting dimensions: width = length = 37 m; depth = 100 m
Shale grade: 0.63 m$^3$/metric ton. No overburden pressure.
Retorting rate: approximately 0.5 m/day with air.
Tangent $\phi$ and $\mu$: 0.6 in burnt shale at $25^\circ$C (upper region);
0.5 for hot burnt shale;
0.3 for burnt shale in combustion zone;
0.1 for shale in retorting zone;
0.7 for raw shale below 300°C.
Density: values given by upper curve of figure 5, multiplied by 0.8 (porosity taken - 0.2 throughout rubble).
Stage in process: retorting front (300°C) at 95 m, very close to end of run.

Figure 6 shows temperature and rock-pressure profiles for this simulated run. The temperature profiles in these plots were calculated from the model of Braun and Chin (1977) for these conditions. Since that model computes separate profiles for different-sized particles, those shown represent mass-averaged temperatures for all material at any level, $z$. As Braun and Chin point out, the narrow peak at the right edge of the hump is the region in which residual carbon is being burned off. The steeply falling temperatures, just to the right of that peak, are in the retorting front, where kerogen is decomposing to form oil and gas. It is in this very narrow region that practically all of the mass lost by the shale -- oil, gas, carbon dioxide and water -- is driven off. Hence, it is here that all large changes in density occur. To the left of the combustion peak, the material is all burnt shale and its composition is essentially constant; its densities are given by the dashed lines of figure 5, the upper one for this particular case.

As retorting nears its conclusion after 190 days, bottom pressure is 0.6 Mpa, 80 percent of starting value (see open circle, fig. 4). This occurs, in spite of the fact that most of the remaining rubble mass stands over the oil-rich retorting front, because the shale has lost about one-third of its initial mass during retorting and the gravity term in Equation 4 is correspondingly less. Final pressure at the bottom is about one-half of the "lithostatic" pressure at this time in the process.

Figures 7 and 8 show similarly calculated profiles for a larger, rectangular retort whose dimensions are in the range practical for in-situ production of oil from shale at useful commercial rates. The conditions are:

Retort dimensions: $W = 46$ m, $L = 183$ m, $H = 220$ m
Shale grade: 1 m$^3$/metric ton. No overburden pressure.
Retorting rate: approximately 2 m/day with air.
Frictional properties as in preceding case.
Density: given by lower curve of figure 5, times 0.8 for a porosity of 0.2.
Stage in process: 15th day in fig. 7; 100th day in fig. 8.

The assumption of no overburden pressure is based on assurance by mining experts that the overburden will be fully supported by the pillars surrounding each rubble column for at least as long as it will take to retort the rubble, even though there are several hundred feet of overburden over most of the rich shale deposits in the Piceance Basin.

These profiles are much like the one in figure 6, though the pressures reached are considerably higher because of the greater ratio of cross-section to perimeter and the greater depth of this retort. These factors are slightly offset by the lower density of the richer shale filling this retort. The loss of 34 percent of the original mass of this shale makes the total mass of rubble almost that much less after 100 days, near the end of retorting, than after only 15 days of processing. The resulting lower densities make the bottom pressure lower at the end of retorting than at the start. Note that it is only about 40 percent of the estimated "lithostatic" pressure for the 100th-day condition.

Discussion

Clearly pressures calculated from Equation 4 depend strongly on the frictional properties throughout the rubble. At present, these properties are not well known. We need better information about them, particularly the friction coefficients. This work is progressing at LLL, but we would like to see others interested in oil from shale doing this work.

While it now appears that there will be no pressure from overburden during retorting, such pressure, if it were high, would seriously change the calculated profiles. For example, if all the weight of a 150-m overburden thickness had to be supported by the rubble column, the pressure at \( z = 0 \) in figures 7 and 8 would be about 3 Mpa and would diminish exponentially toward almost the same bottom pressures shown. The effects, in the early stages of retorting, could be serious, based on the evidence we
now have relating porosity and permeability to pressure at retorting temperatures. However, that evidence was gathered entirely on rather small particles, 2.5 centimeters and less in size, and it is known that in packed beds, permeability increases with the square of the particle size for particles which do not change shape.

For there to be losses of porosity of, say, half the starting amount of 20 percent, there will probably have to be major deformations of particles. Material properties other than density and the friction coefficients may then play a role in rubble pressure. These phenomena are just beginning to come under study in oil shale. It appears that it will be very difficult to incorporate particle deformation into our model of rubble pressure. At this time, the main directions for development of the model are: (1) improvement of information on frictional properties and, (2) linking pressure and temperature to porosity and permeability through further experimentation with those properties.

Our model makes no effort to allow for conditions within the walls that contain the rubble. Since these walls are themselves shale, we expect that retorting will penetrate them to some depth as the front moves down through the rubble. We can envision a situation, somewhere within the walls, where the temperature reaches 400°C and oil is generated without much chance to escape. Under these conditions, the internal coefficient of friction in a vertical plane, approaches zero and, if the outer layer of the wall were free to move, it might slump downward. Fortunately, these layers are completely restrained. In addition, after the front passes, the 400°C plane is constantly moving outward, because of heat flow from the hot spent shale behind the front; so the extent of the oily region in the vertical direction is very limited. For these reasons, the specter of wall slump may be more imaginary than real; but it cannot be wholly discounted at this time.

Conclusion

We have developed a model for rock pressures in rubble columns and used it to compute such pressures at various depths in oil-shale rubble. Within the limitations imposed by paucity of frictional-properties data, the model seems to be realistic. The highest pressures computed for commercial-size retorts of reasonable design are not very different during processing than before retorting is begun. From our present knowledge of permeability as a function of particle size, temperature and pressure, it appears that these pressures should not cause serious losses of permeability. Such losses might occur, however, if the rubble were subjected to a large overburden pressure during retorting, especially in the early stages.

Nomenclature

\[ g \] = the acceleration due to gravity, \( 9.806650 \text{ m/s}^2 \)

\[ g_c \] = the proportionality constant in Newton's second law of motion, \( 1.000000 \text{ kg/m N s}^2 \)

\[ H \] = the depth of a rubble column, m

\[ K \] = the ratio of horizontal pressure to vertical pressure in a static mass of noncohesive particles; \( K = (1 - \sin \phi) / (1 + \sin \phi) \)

\[ L \] = the horizontal length of a rectangular rubble column, m

\[ P_{h}, P_{v} \] = the horizontal and vertical components of rubble pressure at any depth \( z \), N/m²

\[ P_0 \] = the vertical overburden pressure at \( z = 0 \), N/m²

\[ W \] = the horizontal width of a rectangular rubble column, m

\[ z \] = the depth to any level below the top surface of the rubble, m

\[ \alpha \] = the angle of repose in a pile of particles, ordinarily slightly less than the internal angle of friction, degrees

\[ \mu \] = the external coefficient of friction of shale rubble on rough shale walls at any depth \( z \)

\[ \rho_b \] = the bulk density of the rubble at any point \( z \); \( \rho_b \) = rubble-rock density multiplied by \( (1 - \epsilon) \), where \( \epsilon \) the fraction of void space in the rubble, kg/m³
The angle of internal friction at any depth $z$, degrees; in this work, $\tan \phi$ was assumed to be equal to $\mu$.

NOTE: Although SI units have been used throughout this paper, any consistent system is satisfactory in all the equations.

The term "spent shale" refers to shale that has been retorted but still contains its residual char; "burnt shale" has had the char removed by oxidation and/or reaction with carbon dioxide.

References


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OIL SHALE RETORTING UNDER ADIABATIC CONDITIONS

V.V. Mahajan, R.E. Lumpkin, F.M. Gragg, R.J. Fraser
Occidental Research Corporation
1855 Carrion Road
La Verne, California 91750

Abstract

A small pilot plant has been designed and constructed to simulate the retorting of oil shale under conditions pertinent to a modified vertical in-situ shale oil recovery process. The pilot plant consists of a 6-inch diameter (15.2 cm) fixed bed reactor, 4 feet (1.2 m) long with provision for heat supply along the wall. This external heat supply balances the heat losses so that the retort operates like an in-situ retort. Results from typical pilot plant runs are included. These runs are characterized by high oil yields and excellent mass, energy and heat balance closures.

Introduction

Oil shale reserves in the western United States constitute one of the most promising future domestic sources for liquid fuels. Many processes have been proposed to tap this resource, and a number of above ground and in-situ methods have been tested on a pilot scale. Occidental Petroleum Corporation has developed a process, combining features of both true in-situ and above ground processing, called the vertical, modified in-situ retorting process.

Since mid-1972, Occidental has formed and burned four in-situ retorts, and a fifth will be ignited this month. Processing results (McCarthy and Cha 1976; Fernandes and Cha 1977) and plans for commercial development (Sass and Lumpkin 1977; Ashland and Occidental 1977) have been published previously. This paper discusses one aspect of oil shale research being conducted by Occidental Research Corporation (ORC) in support of the continuing field tests.

ORC, the central research division of Occidental Petroleum, was responsible for the initial development of the Oxy oil shale process. In January 1975, Occidental Oil Shale, Inc. was formed to continue the development; ORC retained responsibility for medium and long-range supporting research. A major facet of ORC's extensive oil shale program has been the design, construction and operation of small-scale, batch retorts capable of simulating in-situ processing.

This paper briefly reviews the history of batch retorting experiments, explains the rationale behind the ORC design, and presents some of the experimental results.

Early Work on Batch Retorting

Occidental's vertical, modified in-situ process involves preparing a packed bed of shale underground and retorting this bed in place to produce the oil. The retorting process is somewhat similar to the N-T-U process, studied by the Bureau of Mines, for above ground batch retorting of oil shale (Ruark and others 1956). The Bureau constructed two identical 40-ton (36.2 metric ton) retorts, shaped like inverted truncated cones, 16 feet (4.8 m) high, with internal diameters of 8 2/3 feet (2.6 m) at the top and 10 1/3 feet (3.1 m) at the bottom. Experiments in these retorts
proved that a combustion front can be propagated through a bed of oil shale particles, and the recovery of oil from such a unit could be a self-sustaining operation. Useful information was obtained on the effects (on retorting) of air flux, air to recycle gas ratio, grade of shale and particle size of shale.

A 10-ton (9 metric ton) retort was constructed by the Bureau of Mines, at what is now the Laramie Energy Research Center (LERC) of ERDA, specifically to simulate in-situ retorting. This retort was built to study the processing of shale ungraded in size and varying in oil content, and to examine slow retorting of large shale particles. The work was generally successful. A number of reports have been published (Carpenter and Sohns 1974; Dockter and others 1972). Maximum recovery of oil in this retort was approximately 52 percent of Fischer assay at a superficial gas velocity of 4 SCFM/ft$^2$ and an oxygen concentration of 16 percent by volume in the inlet gas. Low- to medium-grade shale, containing 10-25 gal (0.04-0.11 m$^3$)/ton oil, was used in most of the runs in this retort.

LERC researchers have also operated a bigger retort, with a nominal capacity of 150 tons (135 metric tons), using shale in chunks as large as 4 feet (1.2 m) across (Harak and others 1970; Harak and others 1974). Maximum oil recovery was 65.8 percent of Fischer assay at a superficial gas velocity of 1.25 SCFM/ft$^2$ and an oxygen concentration of 15 percent by volume. The Fischer assay oil content of the shale charged was in the 20-30 gal (0.08-0.12 m$^3$)/ton range.

Some similarities have been observed in the operation of these two LERC retorts, such as the linear dependence of the retorting rate on the oxygen flux (Carpenter and Sohns 1974). However, a recent attempt (Dockter and Harak 1976) to correlate results from these two units led to the conclusion that they have different operating characteristics. A major reason for the observed discrepancies appears to be heat losses of unknown magnitude in these two vessels. Estimates of these losses range from 25-40 percent of the total heat content of the shale bed. Such losses are likely to distort the retorting behavior and limit the applicability of the data.

Other investigations, less extensive than those in the big retorts at LERC but employing batch processing with significant heat losses at the walls, have been reported by researchers at Sandia (Arnold 1975); LERC (Wise, Miller and George 1976); Phillips Petroleum (Needham and others 1976); the University of California (Branch and Ness 1976); and the University of New Mexico (Nuttall 1976). Operating small scale units in this manner complicates the analysis of the data and makes the extension of the work to larger retorts difficult. Proper modelling can be used to predict the behavior of retorts with non-adiabatic walls, but using data from such an experiment to confirm or evaluate the model is very risky.

Rationale for Adiabatic Operation

It is usually possible to derive many different process models for a system as complex as in-situ oil shale retorting. Normally, the simplest model chosen for use is the one that satisfactorily predicts the system's behavior over the expected range of operating conditions. It is frequently very difficult to determine acceptable level of simplicity (or complexity) because mechanisms that are important in laboratory or pilot plant work may not be important in the field. It is therefore desirable to avoid making analysis of small-scale experimental data any more difficult than is inherent in the process. Allowing heat losses through the walls of a batch retort seriously complicates the necessary model. Radial temperature profiles become significant and a two-dimensional, rather than a one-dimensional, treatment of the process is required. A two-dimensional model can be avoided by proper experimental design.

Two laboratories, other than Occidental Research, have reported data from retorts
constructed to eliminate, or at least control, heat losses through the vessel walls. A small retort has been built at Laramie (Duvall and Jensen 1975), with a series of separately controlled, six-inch (15.2 cm) long heaters over its 15-foot (3.9 m) length. The vessel is three inches (7.6 cm) in diameter, with a one-inch (2.5 cm) pipe down the center; the shale is placed in the annulus, which is only one inch (2.5 cm) across. Only limited data have been published, and, if adiabatic operation has been attempted, it has not yet been reported.

Lawrence Livermore Laboratory (LLL) has constructed two retorts, one with a capacity of 6 tons (5.4 metric tons) and the other capable of holding 275 lbs (125 kg) of shale (Ackerman and Sandholtz 1976). This work also appears to be promising, but the published data are not sufficient to evaluate how well the systems work in controlling heat losses.

Occidental developed a mathematical model for in-situ oil shale retorting (McCarthy and Cha 1976) and used this model in the design of the early field experiments. Parameters in the model were primarily derived from Laramie data. Subsequently, we refined the model by using results from the field tests, but felt that additional information would help to extend and improve it. Field work is notoriously difficult to instrument and analyze properly, and the tests are so expensive and time-consuming that the effects of many variables cannot be adequately explored. Consequently, ORC decided that a pilot retort, two feet (0.6 m) in diameter and 10 feet (3.0 m) long, holding approximately one ton (.9 metric ton) of shale, was large enough to provide a good simulation and small enough to permit many runs within a short span of time. ORC began preliminary design of this retort in late 1974.

Occidental's Pilot Retort (1 ton; .9 metric ton)

We decided to build a retort with heavily insulated walls rather than resort to heaters to control the wall temperature and prevent heat loss. This route seemed to offer ease of operation and lower cost. Construction was started in May 1975 and completed in November. The first run was made during the last week of November; the seventh and last run was completed in March 1976. Analysis of temperature profiles observed during the seven runs indicated that almost half of the heat generated at the burn front was used to raise the temperature of the refractory lining of the retort. This loss imposed severe radial temperature profiles and made it difficult, if not impossible, to extrapolate the results to the behavior of in-situ retorts. We concluded that heaters would be required to generate meaningful data.

The features of our first pilot retort vessel are shown in figure 1. There are three layers of insulation. The inner layer is a hardened fire brick, 4 1/2 inches (11.4 cm) thick, backed by insulating brick of equal thickness, and a 1-inch (2.5 cm) layer of fiber insulation. Since the surface temperature of the steel shell never rose above ambient temperature, the insulation was quite effective in preventing loss of heat from the vessel. Nonetheless, a significant quantity of heat was required to raise the temperature of the refractory lining as the flame front passed through.

A radial temperature profile from the second run is shown in figure 2. Temperatures were measured by moving a thermocouple across the radius and therefore are corrected for the flame front movement. The temperature falls over 800°F (302.4°C) from the center of the retort to the wall. Most of the heat removed from the bed stays within the fire brick, and, as the flame front passes, it flows back into the shale. Thus, little heat is lost to the atmosphere but the refractory lining distorts the process results by acting as a heat storage device.

Significant improvements to a number of the peripheral systems were made during the seven runs. Flow control and oil collection systems were developed that satisfied all of the requirements for good mass
balances and steady operation. The gas chromatographic analysis of gas exiting from the retort was fine-tuned; a system for data collection and logging was developed. Data from this unit were recorded on magnetic tape cassettes for later playback onto time-shared computers. The software for collating and manipulating such data was also developed during these runs.

The "Adiabatic" Mini-Retort

A decision was made in mid-January 1976 to construct an "adiabatic" pilot plant capable of accurately simulating in-situ retorting behavior. The design incorporated a series of separately-controlled heating sections to maintain the reactor skin temperature equal to the center line temperature. Ideally, no heat would be added to the shale bed in the retort, only enough energy to balance heat losses. The reactor was to be six inches (15.2 cm) in diameter and four feet (3.1 m) long, with 16 separate heating sections, each 3 inches (7.6 cm) high.

We recognized one limitation of this equipment at the time of its design: particle sizes would probably be restricted to less than 1/2 inch (12.7 mm). The 1-ton (.9 metric ton) pilot retort would have to be rebuilt to examine the behavior of large rocks. The new unit had its own advantages,
however. Construction would be faster and cheaper; time required to perfect the operation and achieve temperature control would be reduced. In addition, turnaround time would be shorter; more runs could be made within a given time span.

The "adiabatic" retort assembly is shown schematically in figure 3. Total length of the retort vessel is 7 feet (2.1 m). The top and bottom portions, 18 (45.7 cm) and 12 (30.5 cm) inches long, respectively, are heated to control the temperatures of the inlet and exit gases. A gas preheater, provided at the top, doubles as a steam generator. Gas flows are metered both into and out of the retort; provision is made for recycling the gas exiting from the retort. Part of this is diverted through an oxygen meter and then to the gas chromatograph. The oxygen meter is used to monitor bed ignition which is achieved through the use of a Calrod coil heater.

Construction of this pilot plant was completed on schedule at the end of April. Tests without shale occupied the first week of May; the first retorting run was made May 9-10, 1976. The mass balance for this run closed to within 1 percent. Unfortunately, it took until the 19th run on November 10 before the heat and energy balances

Figure 3. - Schematic Diagram of the Adiabatic Pilot Retort.
The graphs show that air consumption by the process decreases and rate of advance of the flamefront increases as the heat balance closure improves. The three runs, included in these figures, were nominally identical. Only the control techniques were changed. In absence of a similar run, after control techniques were perfected, predictions of the computer model under the same conditions are included for comparison. These predictions seem to be generally consistent with the pattern established by the data.

Five tests were applied to the run data to determine if the system was operating satisfactorily. Our criteria were:

1. Radial temperature profiles for an ideal retort should be flat. During the initial phases of the development of this retort, radial temperature gradients of up to 100°F/foot (37.8°C/2.5 cm) were observed, demonstrating the severity of the heat losses. The worst gradients observed during current operation are less than 5°F/foot.

2. Overall energy balances should close. The early runs showed that 20 to 30 percent of total system energy was lost as heat through the walls. This was not a significant improvement over earlier LERC retorts. Improvements in the design of the mini-retort have led to closures within 5 percent, indicating that losses are minimal.

3. Overall heat balances should close. Heat that flows into the vessel, plus heat generated by exothermic reactions, should equal heat consumed by endothermic reactions plus heat that flows out of the vessel. Early runs showed heat losses of 40 to 50 percent of input; later runs closed to within 10 percent. Greater scatter is expected in these balances than in energy balances because parameters are im-

![Figure 4. Retorting rate as a function of heat loss in the mini-retort.](image1)

![Figure 5. Air consumption as a function of heat loss in the mini-retort.](image2)
olved that are not directly measured. For example, the extent of various reactions as a function of time must be estimated to produce final heat balance.

4. Intermediate energy and heat balances should also close. These balances were not computed in the early phases of the work, but they are now incorporated in the main data analysis program and close to within 10 percent of perfect balance. They require a knowledge of the extent of each of the chemical reactions throughout the bed and accurate values for the oil production and hold-up rates.

5. The combustion front should propagate steadily. The earliest runs in the mini-retort were characterized by an irregular propagation rate of combustion and retorting fronts through the bed. The situation was caused by poor temperature control, and, in fact, some runs were abandoned to prevent damage to the retort. More recent runs have shown that this control problem is solved; retorting and flame fronts move in a steady progression through the shale.

One criterion, avoided in deciding when the retort reached a satisfactory level of operation, was a comparison between experimental results and computer simulation model. Our purpose in building the pilot plant was to test and extend the model, and we felt that it was necessary to establish independent criteria for evaluating effectiveness of our pilot plant temperature control.

Current Operations
Since adiabatic operation was demonstrated, more than 25 additional runs have been made. Two runs per week are routine; occasionally three runs can be made in that time. Data are logged on magnetic tape and fed to a time-shared computer for collation and initial data analysis, a technique developed for the 1-ton (.9 metric ton) pilot plant.

Data for four runs are summarized in Table 1. These runs were selected to demonstrate the capabilities of the unit; the data have no other special significance. Two diluents for inlet air were used and two replicate tests made with each gas. The same shale was charged in all runs; inlet oxygen concentration and flow rate were maintained as constant as possible. Oil yields with steam averaged 95 percent; those with nitrogen 92 percent. Retorting rates did not vary significantly. Gas exiting from the retort has a higher heating value when steam is used because one of the diluents (water) is condensed out. Gaseous products from retorting are very similar in all cases on an inert-free basis.

Mass, energy and heat balance closures for all of these runs were satisfactory. Reproducibility was excellent; even though average yields for both diluents are above 90 percent, the difference between diluents is significantly greater than the difference between replicate runs. These yields should only be regarded as proof of experimental precision. Both absolute and relative values for oil yield may change significantly under field operating conditions.

Summary and Conclusions
Occidental Research has built and operated an adiabatic mini-retort for oil shale. Mass, energy and heat balance closures are good; reproducibility of runs and consistency of data appear to be excellent. We believe that this retort can adequately simulate in-situ operation, within limits imposed by the size of the equipment.

We are currently making a series of minor modifications to the retort to streamline our operation. A PDP-11/34 dedicated computer is being installed to improve data handling and analysis. We will then be able to make real-time comparisons between theory and experiment.
Table 1. - Adiabatic mini-retort runs: comparison of effect of diluent gases.

<table>
<thead>
<tr>
<th>Diluent</th>
<th>Run No.</th>
<th>Nitrogen</th>
<th>Steam</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>MR-19</td>
<td>MR-21</td>
<td>MR-20</td>
</tr>
<tr>
<td>Total inlet gas flow rate SCFM/ft²</td>
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<td>0.726</td>
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<td>0.551</td>
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<tr>
<td>Oxygen concentration at inlet, mole %</td>
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<td>13.50</td>
<td>14.99</td>
</tr>
<tr>
<td>Oil Yield, % of Fischer assay</td>
<td>91.59</td>
<td>92.73</td>
<td>95.16</td>
</tr>
<tr>
<td>Retorting rate, ft/day</td>
<td>2.52</td>
<td>2.59</td>
<td>2.90</td>
</tr>
<tr>
<td>Air required, SCF/ton shale</td>
<td>9370</td>
<td>9496</td>
<td>9750</td>
</tr>
<tr>
<td>Off-gas heating value, BTU/SCF</td>
<td>36</td>
<td>42</td>
<td>55</td>
</tr>
<tr>
<td>Mass balance closure, %</td>
<td>96.93</td>
<td>97.66</td>
<td>97.09</td>
</tr>
<tr>
<td>Energy balance closure, %</td>
<td>91.05</td>
<td>95.07</td>
<td>94.93</td>
</tr>
<tr>
<td>Heat balance closure, %</td>
<td>92.78</td>
<td>91.03</td>
<td>91.52</td>
</tr>
</tbody>
</table>

References


Arnold, C., 1975, Preliminary studies on the recovery of oil from Chattanooga shale: Sandia Laboratories, SAND 75-0344.


EFFECTS OF THERMAL HISTORY ON OIL SHALE PYROLYSIS PRODUCTS

R. M. Coomes and F. H. Sommer
Tosco Corporation
18200 West Highway 72
Golden, Colorado 80401

Abstract

This laboratory study determined the effects of mild thermal treatment of oil shale on quantity and quality of subsequently produced Fischer assay oil. It was determined that heating oil shale, at 70 to 180°C in air, reduced Fischer assay oil yield as much as 58 percent. Similar thermal histories in oxygen-free atmospheres gave unchanged Fischer assay oil yields. Specific gravity of product shale oil was increased when oil shale was preheated in an oxygen-containing atmosphere.

Introduction

Production of oil from oil shale requires that the kerogen in the oil shale undergo thermal decomposition. All retorting processes, above ground or in situ, produce a great deal of waste heat, generally used to preheat oil shale before it actually reaches retorting temperatures. A knowledge of the effects various preheating conditions have on product oil is fundamental to proper design and operation of an oil shale preheating system. These studies were undertaken at temperatures in the range of 70-180°C at which oil shale is generally believed to be unreactive.

Previous investigators have studied effects of temperature and preheating in the temperature range of 200 to 525°C. These studies have included kinetics of kerogen decomposition and effects of heating rate and preheating on oil yields. Johnson and others (1975) studied the effect of heating rate on oil yield of 30 gpt (0.14 m³) shale when retorting with a terminal temperature of 470°C under inert atmosphere. They reported that, when the heating period was shortened from 14 days to 40 minutes, oil yield increased from 70 to 100 percent of Fischer assay by weight.

A series of experiments by Hubbard and Robinson (1950) showed the effect of terminal temperature on oil yield. Samples containing 13.9 percent by weight of kerogen were rapidly heated to terminal temperature under an inert atmosphere and held at temperature for various lengths of time. A modified Fischer assay of this shale sample gave 26.7 gallons (0.12 m³) of oil per ton of shale, or an 83.4 percent conversion of kerogen to oil plus gas. Rapid heating to terminal temperature resulted in kerogen conversions of 71 percent in 150 minutes at 400°C, and 83.4 percent in 7 minutes at 525°C. It was also determined that kerogen conversion continued for 24 hours when shale was heated to 350°C.

Hubbard and Robinson's results (1950) were verified in a series of experiments by Hill and others (1967) using 35 gpt (0.16 m³) shale. Hill determined that only 34 percent of Fischer assay oil yield could be obtained by heating the shale to 350°C, after heating for 425 hours.

Stout and others (1976) determined the effect on oil yield of interrupting the Fischer assay heating profile for a hold period of isothermal heat soaking. At holding temperatures of 250°C or below, little
effect on oil yield was noted. At holding temperatures between 300 and 425°C, a significant decrease in oil yield was noted, up to a maximum of 19 percent. Robinson and Hubbard (1951), and Stout and others observed that if sufficient quantity of inert sweep gas is passed through the shale during an isothermal soaking period, oil yield upon subsequent Fischer assay is not affected. Oil yield loss, noted in non-sweep experiments, was attributed to thermal degradation of liberated oil and not to the thermal history of the kerogen.

Robinson and Hubbard (1951) also noted that if oxygen were present in the sweep gas, oil yield decreases would be observed. Oil yield decreases were dependent on heating temperature, heating time, shale particle size and oxygen content of heating gas. Heat soaking temperatures studied ranged from 200 to 350°C, for periods of 15 to 240 minutes. Oil losses of up to 26 percent, compared to Fischer assay of untreated shale, were observed and were attributed to oxidation of the kerogen. This effect was noted for oxygen content in sweep gas as low as 1 percent.

The literature shows that various thermal factors have definite effect on decomposition of kerogen and quantity of oil produced in a Fischer assay. Experiments reported in this paper examined the effects of thermally treating oil shale at 70 to 180°C, in air and nitrogen atmosphere, on the quantity and quality of oil produced by subsequent Fischer assay. These temperatures are much lower than those used in previously reported studies. According to Cumming and Robinson (1972), these conditions are too mild to cause significant conversion of kerogen to bitumen and oil. Raw shale weight and organic carbon content were monitored during preheat; any changes noted were small. Fischer assay product yields of shale, preheated in a nitrogen atmosphere, were unchanged. Oil yields from subsequent Fischer assay of air preheated shale were as low as 42 percent of Fischer assay, while gas and water yields were increased. Quality of oil was altered by this mild air preheating treatment, as determined by an increased density compared to Fischer assay oil of untreated shale.

Experimental

Shale Sampling - The oil shale used in this research was 32 gpt (0.145 m³) shale from the Colony Mine, Piceance Creek Basin area, Colorado. With the exception of shale used in a particle size study, all shale was processed through a jaw crusher and Raymond mill to minus 65 mesh size before preheating. As shown in table 1, the shale sample was characterized by the following analyses: mineral carbon, organic carbon, oxygen, and Fischer assay.

Fischer assay determinations were performed on samples that were minus 65 mesh in particle size. The procedure used at Tosco has been previously described by Goodfellow and Atwood (1974). This procedure allows all product gas to be collected and analyzed by gas chromatography. Gas analysis, along with recovery of oil, water and spent shale, allows complete material balances to be made around the Fischer assay procedures.

Shale samples for particle size studies were obtained by crushing and then fractionating the shale into various particle sizes by screening. Size ranges selected for study were: U.S. Mesh sizes -1/4"+8m; -8m+20m; and -65m. Samples for control Fischer assay determinations were taken from each fraction and assayed in the normal manner before preheating treatments.

Procedure - Shale to be preheated in air was spread in a thin layer (5 mm) on aluminum trays and placed in an oven for the required length of time. Shale to be preheated under an inert atmosphere was placed in a sealed container with fittings that allowed a nitrogen purge. This container was sealed and purged before and during the preheat period. The shale was not stirred during preheating. When preheating was complete, samples were split for various analyses. Fischer assay was performed, as described by Goodfellow and Atwood (1974).
Bitumen content was determined by a 24-hour benzene Soxhlet extraction. Benzene was removed from bitumen by reduced pressure, rotary evaporation.

Carbon analysis was used to determine amount of hydrocarbon volatilized during the heating period, since no significant weight losses were observed. Losses in organic carbon, during preheating, were expressed as oil losses by dividing by 0.85. These oil losses, called preheating losses, were added to actual Fischer assay oil yields of preheated samples to give reported total oil yield values.

Results and Discussion

Samples were heated in air at 120°C for up to 25 days. Analyses of these samples at days 5 and 25 are given in table 2. Samples preheated in a nitrogen atmosphere showed no change or were within experimental error of the analyses. After five days of 120°C treatment in air, samples had oil yields of only 81 percent Fischer assay. At 25 days, oil yield was 66 percent of Fischer assay, while gas and water yields had increased to 164 percent and 217 percent, respectively, of those determined for fresh shale. Weight changes, during 120°C preheat, were within experimental error, and organic carbon losses during preheat were small, when compared to loss of oil yield by Fischer assay.

Although not shown in the table, the amount of organic carbon in the Fischer assay residue increased 90 percent with 25 days of heating. When fresh shale was assayed, spent shale accounted for 84 percent of the material balance. Spent shale, from shale preheated 25 days at 120°C in air, accounted for 87 percent of the material balance. The increase can be entirely accounted for as unretorted or carbonized organic carbon on the spent shale. Table 2 also shows that oxygen content of the raw shale increased from 17.8 percent for fresh shale to 21.5 percent in shale heated for 25 days. Using the value of 5.8 percent given by Smith (1961) for organic oxygen in oil shale, and, assuming that oxygen gained during heating is organic, there was a 64 percent increase in organic oxygen at 25 days.

When shale was preheated and then stored at ambient temperatures for six months, the same Fischer assay products were obtained as for shale promptly assayed after preheating. The necessity of oxygen for altered yields, and the irreversibility with time suggest a partial oxidation of the kerogen during the preheat process. Heat of combustion, as determined by a Parr bomb calorimeter, confirms that shale is partially oxidized during preheating. Heat of combustion of shale, preheated for 25 days at 120°C, is 88 percent of that of fresh shale (1440 versus 1630 cal/g, table 8). It is concluded that a non-volatile, partial oxidation product of kerogen is formed during the preheating treatment.

There were significant differences in the character of Fischer assay oils from fresh oil shale and preheated oil shale. As shown in table 3, specific gravity of oil increases after treating oil shale only 5 days at 120°C. Initially, the increase in specific gravity was thought to be due to a loss of light ends during preheat treatment, even though no weight losses were observed. Microdistillations on Fischer assay oils

Table 1. - Characterization of oil shale.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Value(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral Carbon</td>
<td>5.6</td>
</tr>
<tr>
<td>Organic Carbon</td>
<td>14.8</td>
</tr>
<tr>
<td>Oxygen</td>
<td>17.8</td>
</tr>
<tr>
<td>Bitumen</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Fischer Assay

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil(2)</td>
<td>12.0</td>
</tr>
<tr>
<td>Gas</td>
<td>2.8</td>
</tr>
<tr>
<td>Water</td>
<td>1.2</td>
</tr>
</tbody>
</table>

(1) Expressed as weight percent of raw oil shale
(2) Specific Gravity, 0.9071
Table 2. - Analysis of shale preheated in air at 120°C.

<table>
<thead>
<tr>
<th>Product Yield(1)</th>
<th>Fresh Shale</th>
<th>Preheated 5 days (% of Fresh)</th>
<th>Preheated 25 days (% of Fresh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fischer Assay Oil</td>
<td>12.0</td>
<td>9.2 (77)</td>
<td>5.4 (45)</td>
</tr>
<tr>
<td>Preheating Losses</td>
<td>---</td>
<td>0.5 (--)</td>
<td>2.5 (--)</td>
</tr>
<tr>
<td>Total Oil</td>
<td>12.0</td>
<td>9.7 (81)</td>
<td>7.9 (66)</td>
</tr>
<tr>
<td>Fischer Assay Gas</td>
<td>2.8</td>
<td>3.6 (129)</td>
<td>4.6 (164)</td>
</tr>
<tr>
<td>Fischer Assay Water</td>
<td>1.2</td>
<td>1.6 (133)</td>
<td>2.6 (217)</td>
</tr>
<tr>
<td>Bitumen on Raw Shale</td>
<td>1.3</td>
<td>0.6 (46)</td>
<td>0.4 (31)</td>
</tr>
<tr>
<td>Oxygen Content Raw Shale</td>
<td>17.8</td>
<td>---</td>
<td>21.5 (9.5)</td>
</tr>
<tr>
<td>Organic Oxygen</td>
<td>5.8(2)</td>
<td>---</td>
<td>9.5(3)</td>
</tr>
</tbody>
</table>

(1) Given as weight percent of raw oil shale
(2) Smith (1961)
(3) Additional oxygen content at 25 days assumed to be organic

Table 3. - Microdistillation inspection data for Fischer assay oil.

<table>
<thead>
<tr>
<th>Oil Fraction</th>
<th>Fresh Shale Wt%</th>
<th>Gravity</th>
<th>Preheated Shale (5 days - 120°C) Wt%</th>
<th>Gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole Oil</td>
<td>--</td>
<td>0.907</td>
<td>--</td>
<td>0.933</td>
</tr>
<tr>
<td>IBP - 200°C</td>
<td>12</td>
<td>0.772</td>
<td>14</td>
<td>0.777</td>
</tr>
<tr>
<td>200 - 315°C</td>
<td>17</td>
<td>0.858</td>
<td>18</td>
<td>0.870</td>
</tr>
<tr>
<td>315 - 425°C</td>
<td>25</td>
<td>0.918</td>
<td>22</td>
<td>0.930</td>
</tr>
<tr>
<td>425 C+</td>
<td>46</td>
<td>0.973</td>
<td>46</td>
<td>0.991</td>
</tr>
</tbody>
</table>

Table 4. - FJA analysis* of oil product.

<table>
<thead>
<tr>
<th>Component (vol%)</th>
<th>Fresh Shale</th>
<th>Preheated Shale (25 days - 120°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturates</td>
<td>26</td>
<td>22</td>
</tr>
<tr>
<td>Olefins</td>
<td>48</td>
<td>46</td>
</tr>
<tr>
<td>Aromatics</td>
<td>26</td>
<td>32</td>
</tr>
</tbody>
</table>

* ASTM D-1319

from fresh and preheated oil shales proved that light ends were not lost. The specific gravities of various fractions were determined, and are also reported in table 3. The data show that the relative amount of material in each temperature range is approximately the same for each oil, and that the specific gravity of each fraction, throughout the boiling range, has increased with preheating. The microdistillation technique, developed at Tosco, provides distillation curves and data in agreement with those obtained by ASTM D-2892, but requires only 50 ml of oil.

A fluorescent indicator analysis (FIA), ASTM D-1319, was made on oils from fresh and 25-day, 120°C, preheated shales. These data, given in table 4, show increased concentrations of aromatic or polar materials, and decreased concentrations of saturated or non-polar materials with preheating. This analysis is consistent with the increased specific gravity of oils formed from preheated shale.

An elemental analysis of oils from fresh and 25-day, 120°C, preheated shales supports the contention that oils from preheated shales are more polar. Analyses, given in table 5, show a significant increase in oxygen content for oil from preheated shale.

It may be concluded from the oil analyses that oil from preheated oil shale is of a lower quality than oil from fresh shale. This is shown by increased specific gravity throughout the entire boiling range which may be due to increased concentrations of aromatic compounds, oxygenated compounds,
Table 5. - Elemental analysis of shale oil.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fresh Shale (wt%)</th>
<th>Preheated Shale (25 days - 120°C) (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>84.7</td>
<td>83.7</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>11.6</td>
<td>11.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.0</td>
<td>1.8</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.8</td>
<td>1.6</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>

or both.

Product gas, formed by Fischer assay of fresh and 25-day, 120°C, preheated oil shale, was analyzed by gas chromatography (GC). GC analyses are given in table 6. Preheating oil shale causes significant changes in Fischer assay product gases: hydrogen and hydrogen sulfide are decreased; carbon monoxide and carbon dioxide are increased. The decrease in hydrogen and hydrogen sulfide may be due to a hydrogen deficiency caused by increased formation of water (table 2). More than 60 percent of the sulfur that did not form hydrogen sulfide in the preheated shale Fischer assay product gas was accounted for as other unidentified forms of gaseous sulfur products. Total sulfur content of Fischer assay product gas was determined by microcoulometry. The increased gas production of preheated shale is essentially accounted for by increased amounts of carbon monoxide and carbon dioxide.

The greatly increased concentrations of carbon monoxide and dioxide, and water, suggest that an oxidation reaction, begun during preheating, was either completed or the combustion products released during Fischer assay. These products result from normal combustion or oxidation; their increased yields support the hypothesis that kerogen is partially oxidized in air at relatively low temperatures.

Apparent, oxidation of kerogen can take place at temperatures approaching those attainable on shale exposed to the summer sun, or generated by spontaneous combustion in stockpiled raw oil shale. For example,

Table 6. - GC analysis of Fischer assay gas product.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fresh Shale (mole %)</th>
<th>Preheated Shale (mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>28</td>
<td>9</td>
</tr>
<tr>
<td>CO</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>CO₂</td>
<td>23</td>
<td>53</td>
</tr>
<tr>
<td>H₂S</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>C₁</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>C₂</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>C₃</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>C₄*</td>
<td>7</td>
<td>4</td>
</tr>
</tbody>
</table>

Total 100 27.9 100 45.9

Table 7. - Effect of low temperature heating on oil yield.

<table>
<thead>
<tr>
<th>Length of Preheat</th>
<th>% of Fischer Assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mo</td>
<td>94</td>
</tr>
<tr>
<td>2 mo</td>
<td>90</td>
</tr>
<tr>
<td>3 mo</td>
<td>84</td>
</tr>
</tbody>
</table>

* -65 mesh shale @ 70°C

when samples of -65 mesh oil shale were heated in air to 70°C for 1, 2 and 3 months, product oil yield was lowered. Fischer assay oil yields of these preheated oil shales are shown in table 7. After 3 months, preheating at 70°C Fischer assay produced only 84 percent of the oil produced from identical fresh shale.

Oil shale samples were preheated in air at various temperatures from 100 to 180°C for five days in order to determine temperature effects. Results of these experiments are shown graphically in figure 1. While there was essentially no change in oil yield after five days preheat at 100°C or less, at higher temperatures, oil yield decreased rapidly. At 180°C preheat for five days, oil yield was only 42 percent that of fresh shale.

The effect of particle size on Fischer assay oil yield losses due to preheating was examined in a series of 28-day experiments at 140°C. Results of these experiments are shown in table 8. It was determined that greatest losses were associated with smallest particle size (or greatest surface
Figure 1. - Effect of preheat temperature on oil yield.

Table 8. - Dependence of preheating effect on particle size.

<table>
<thead>
<tr>
<th>Mesh Size (U.S.)</th>
<th>Oil Yield (wt% Fischer Assay)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1/4&quot; + 8m</td>
<td>81</td>
</tr>
<tr>
<td>-8m + 20m</td>
<td>65</td>
</tr>
<tr>
<td>-65m</td>
<td>50</td>
</tr>
</tbody>
</table>

area). The direct relationship with surface area also supports the hypothesis that kerogen is partially oxidized under these mild preheating conditions.

Page (1967) has shown that oil yield is related to particle size. When a sample of shale is ground, the larger particles are richer in kerogen than the finer particles. For this reason, special precautions were taken in these particle size experiments. Individual Fischer assays were performed on each particle size fraction, with and without the preheating. The values in table 8 are comparisons of fresh and preheated shales of identical particle size, and obtained from the same grinding operation.

Conclusions

When oil shale is exposed to relatively mild thermal conditions in the presence of oxygen, a partial oxidation of kerogen occurs which is detrimental to subsequent oil production. A summary of data, supporting a partial oxidation hypothesis, is given in table 9. The decline in Fischer assay oil yield, noted with preheating in air at temperatures of 70 to 180°C, is accompanied by increased production of combustion products: CO₂ and water. Factors affecting this oxidation are: preheating temperature, preheat time, surface area, and presence of oxygen. Conditions need not be severe before a significant oil loss is noted. In addition to lower oil yield, quality of oil also decreases. Both of these factors would affect the economics of commercial oil shale processing.

Factors affecting oil yield and quality should be considered in the design of preheat systems for above ground retorting operations, where the presence of small amounts of oxygen could have an adverse effect on oil yield and quality. In in-situ
Table 9. Evidence for partial oxidation.

<table>
<thead>
<tr>
<th></th>
<th>Fresh Shale (25 days)</th>
<th>Preheated Shale (120°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Shale</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fischer assay oil yield (wt%)</td>
<td>12.0</td>
<td>5.4</td>
</tr>
<tr>
<td>Oxygen content (%)</td>
<td>17.8</td>
<td>21.5</td>
</tr>
<tr>
<td>Heat of combustion (cal/g)</td>
<td>1630</td>
<td>1440</td>
</tr>
<tr>
<td>Fischer Assay Products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ (kg/t)</td>
<td>10.5</td>
<td>31.4</td>
</tr>
<tr>
<td>Water (kg/t)</td>
<td>12.2</td>
<td>26.4</td>
</tr>
</tbody>
</table>

operations, where large amounts of shale are exposed to varying thermal conditions for long periods of time before retorting, there is also cause for concern. Above ground storage of shale from in-situ or stockpiling for above ground retorting, where summer sun can provide necessary thermal input, can result in oxidation of kerogen and may be an important factor in subsequent retorting operations. In the storage, handling and drying of shale samples for Fischer assay, it is necessary to remember that mild thermal conditions affect oil yield.

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ASSAYING GREEN RIVER OIL SHALE WITH MICROWAVE RADIATION

A. Judzis, Jr. and B. Williams  
Dept. of Chemical Engineering  
University of Michigan  
Ann Arbor, Michigan 48109

R. E. Hiatt  
Dept. of Electrical and Computing Engineering  
University of Michigan  
Ann Arbor, Michigan 48109

Abstract

Microwave radiation may be an alternate means of assaying the organic content of Green River oil shale. Preliminary results show a strong correlation between the dissipation of microwave energy in shale and its richness, as determined by Fischer assay, in the frequency range investigated (0.3 to 1.0 GHz). The loss tangent, an index of a material's ability to absorb electromagnetic radiation energy and a function of the complex dielectric constant, increases by a factor of six as shale richness increases from 0.034 to .261 m³/metric ton of shale (10 to 76 gal/short ton).

There is an indication also that radiation of oil shale with high-power microwave energy may aid in the recovery of oil and gas by the decomposition of kerogen.

Introduction

The potential oil yield of western shales is presently determined by Fischer assay—a pyrolytic method that measures the quantity of oil evolved during a heating process. Its success is largely due to the accuracy and reliability of the oil yield determinations which are within 1.7 l/metric ton (0.5 GPT) for lean and intermediate richness shales. A period of at least two hours, however, is necessary to assay a single specimen. This time includes sample crushing and drying as well as the actual retorting.

A new assaying technique with comparable accuracy has not yet been discovered. The search goes on, however, as there is a need in the industry to simplify and shorten the procedure for determining the oil yield of these western shales. Siggia and Uden (1974), in discussions at a National Science Foundation workshop on oil shale, cite the need for the "replacement of the modified Fischer assay procedure for oil yield determinations by a simpler, more reliable and more informative procedure."

Weak correlations between various physical and thermal properties and the organic content of shales have been found; the results are in the literature. J. W. Smith (1956) determined that specific gravity of shale from the Green River formation is related to Fischer assay oil yield. The relationship's accuracy is at best ±14 l/metric ton (±4 GPT). R. J. Shaw (1947) correlates specific heats with organic richness; Prats and O'Brien (1975) use thermal conductivities. Both, however, are weak for assaying purposes. F. P. Miknis and others (1974) have estimated potential oil yields with pulsed NMR* measurements. Instantaneous assays are possible, but standard errors are between 0.0069 and 0.0137 m³/metric ton (2 and 4 GPT). R. L. Hanson and others (1975) have correlated acetylene production, during pulsed ruby laser pyrolysis, with Fischer assay results. Again, a strong relationship was not found. J. B. Sellers and others (1972) measured compressive strengths

* nuclear magnetic resonance
of different grade shales; only a general trend in the relationship is seen.

In preliminary work, we discovered that there is a significant dissipation of radiation energy in the microwave frequency range as it propagates through oil shale samples. This study correlates the relative amount of energy dissipated at 500 MHz with shale richness. The correlation is strong and accurate to 0.0058 m³/metric ton (1.7 GPT) with the described procedure. The microwaves used for this analysis are of low power, on the order of 5 milliwatts. There exists a great potential for the application of high-power microwave radiation in the actual break-up of kerogen for the production of oil and combustible gases from shale.

Microwave Theory

The oscillating field of electromagnetic radiation induces an electric displacement of dipoles, generally out of phase with the field, in the irradiated medium. This never-ending effort of dipoles to stay aligned with the oscillating field, sometimes called dipole relaxation, will result in a maximum absorption of energy when the dipoles resonate between the extremes of completely random and perfect alignment. The energy is dissipated as heat. The microwave frequency range of 0.3 to 300 GHz encompasses the vibrational and rotational frequency range of typical organic bonds (R. P. Bauman 1962).

The precise structure of the polymeric macromolecule, kerogen, is unknown. However, polarity is clearly evident from structural studies of kerogen by Schmidt-Collerus and Prien (1976) and by T. F. Yen (1976). Furthermore, the numerous sulfur-, nitrogen-, and oxygen-hetero atoms present in kerogen (Robinson and others 1963) greatly augment the polarization characteristics of this substance. The polar nature of kerogen enhances dipole relaxation and, hence, the observed energy dissipation. Such high polymers usually exhibit "orientation polarization" where segments of the macromolecule change orientation rather than the entire molecule itself. This produces a distribution of relaxation time values (C. P. Smith 1955) and, consequently, energy loss is fairly constant over a wide range of frequencies.

Another interesting and successful application of dipole relaxation has been reported by R. W. Parsons (1975). He used a microwave attenuation technique to measure water saturations in Berea sandstone slabs. Water is quite polar and, therefore, "lossy" at microwave frequencies.

The complex permittivity, or dielectric constant $\varepsilon^*$, is a measure of the ability of a material to store radiation energy. The imaginary term of this constant is an index of the amount of energy actually absorbed. The relative permittivity is usually of importance and is defined as

$$\varepsilon'_r = \varepsilon^*/\varepsilon_0 = \varepsilon' - j\varepsilon''$$

where $\varepsilon_0$ is the permittivity of free space and equals $8.85\times10^{-12}$ farads/meter and $j = \sqrt{-1}$. It is often useful to define the relative dielectric constant as:

$$\varepsilon''_r = \varepsilon'(1-j\tan\delta)$$

where $\tan\delta = \varepsilon''/\varepsilon'$.

Here, the loss tangent, $\tan\delta$, is the ratio of power lost in heat per cycle to power stored per cycle. It is a measure of the "lossy" characteristics of the dielectric material.

Assaying Apparatus and Procedure

Mine-run shale samples from both the Anvil Points and Colony mines in Colorado were assayed with the modified Fischer retort, described by Stanfield and Frost (1949).

Permittivity measurements were taken with a General Radio, Type 874-LB slotted line, fitted with a 200-ohm crystal detector and an adjustable stub attenuator. The microwaves were generated with a Hewlett-Packard Model 612A UHF signal generator, externally modulated by an HP Model 200-CD oscillator. A Hewlett Packard Model 415B standing wave indicator was used to measure voltage standing wave ratios (VSWR) and to locate wave troughs in the slotted line.
The VSWR is the ratio of maximum voltage to minimum voltage in the transmission line. Figure 1 shows the arrangement of the apparatus. Since the measurement of permittivity by this technique is standard procedure, further details are not included here. Sucher and Fox (1963) describe the various techniques available quite well. The necessary data, however, include null position shifts and standing wave ratios. This data is taken with the sample backed, first, by a "short circuit" and, then, by an "open circuit" (see figure 1). A homemade, variable position short facilitated the measurements with the short, one-quarter wavelength behind the sample. An Ames gauge insured accurate length measurements in the slotted line.

A technique for preparing the shale samples to proper dimensions was also developed. The sample holder, attached at the right end of the slotted line, was designed for a sample filling the annular space, as shown in figure 2. Thickness, \(d\), should be no greater than \(\lambda_m/4\); \(\lambda_m\) being the wavelength in the sample. A 1.588 cm O.D. (5/8 in.) diamond coring drill was used to core shale specimens perpendicular to the bedding. The cylindrical samples were then drilled through the center with a size "C" (0.6147 cm, 0.2420 in.) carbon steel drill bit. A jig was used to guide the bit and to hold the cylinders securely. This minimized breakage of lean shales. Moisture-free samples were used for all measurements.

Mathematical manipulation to compute the dielectric constant from raw data involves complex variables but is easily handled by a computer program. Impedances are first calculated by the following relationship:

\[
Z = \frac{1/(\rho - 1/\rho_o) - j\tan(2\pi l/\lambda_o)}{1-j(1/\rho-1/\rho_o)\tan(2\pi l/\lambda_o)},
\]

where \(\rho\) = measured VSWR with the slotted line containing a sample (open or short circuit)

\(\rho_o\) = measured VSWR without a sample

\(l\) = null position shift (open or short circuit)

\(\lambda_o\) = measurement frequency.

The complex permittivity is then calculated from

\[
e^{*} = \frac{j\lambda_o \arctan\left(\frac{Z_{sc}^{*}}{Z_{oc}}\right)^{1/2}}{2\pi d(Z_{sc}^{*}Z_{oc})^{1/2}},
\]

where \(d\) = sample length.

Results of Microwave Study

The richness of Green River oil shales, as determined by Fischer assay, correlates strongly with the shale's loss tangent and the imaginary term of the relative dielectric constant at 500 MHz. This assumes the

![Figure 1. Permittivity measurement apparatus.](image-url)
sample is maintained at room temperature, about 24°C. Figure 3 shows the latter relationship. Repeated permittivity measurements, with 0.113 m³/metric ton (33 GPT) samples, produced standard deviations of 0.0049 for the loss tangent, tan δ, and 0.0020 for the imaginary term of the dielectric constant, ε''. This corresponds to an accuracy of approximately ±0.0058 m³/metric ton shale (±1.7 GPT). The magnitude of the relative complex dielectric constant of the available oil shale varied between 3.5 and 4.7.

Discussion

Shale samples, between 0.034 and 0.261 m³/metric ton (10 and 76 GPT) richness, were studied. The sensitivity of the relationship, with respect to shale richness, is partially responsible for the accuracy of this new assaying technique. The loss tangent, for example, increases by a factor of six as shale richness increases from 0.034 to 0.261 m³/metric ton (10 to 76 GPT). Such sensitivity has not been found with other physical and thermal properties, described previously.

The method measures the concentration of kerogen directly, without interference from the mineral matter. This factor is also responsible for the accuracy of the assay in determining the potential oil yield of Green River oil shales. The absorption of radiation energy in the microwave frequency range by minerals in these shales is negligible. The carbonates, of which the inorganic matrix is predominantly made, contribute practically nothing, therefore, to the imaginary term of the dielectric constant. The same is true for other minerals present, such as nahcolite and dawsonite. Compositional variations in the mineral make-up should not significantly affect the outcome of shale assays using microwaves. It is
assumed, however, that kerogen and its structure are fairly uniform throughout the deposit.

The extension of the correlation to other shale deposits is feasible, provided the kerogen is similar in structure to that found in the Green River formation. This assaying technique is certainly applicable, however, to many other hydrocarbon deposits.

Permittivity measurements at frequencies of 300 and 1000 MHz produced similar relationships, but accuracy suffered. At the higher frequencies, the electrical short that terminated the transmission line was not sufficiently effective; at the lower frequencies, the slotted line was not long enough to obtain reliable data. Alternate equipment for obtaining the complex dielectric constant must be used for these other microwave frequencies.

Another parameter which will be incorporated in further studies is geometric orientation of the bedding planes with respect to the direction of the incident radiation. Pulverization of larger rocks, riffling, and subsequent compaction into the required doughnut shapes should be pursued. Problems in sampling severely stratified shale would then be eliminated. In this study, homogeneous samples were carefully chosen to eliminate effects of variation of kerogen content.

The ability of kerogen to absorb radiation energy in the microwave frequency range presents an interesting possibility for the future. High power applications of microwaves should decompose the organic matter in shale to oil and various gaseous products. The rotational and vibrational energy of irradiated kerogen is manifested as heat which will serve to sever bonds of the organic macromolecule. These higher energy fluxes in the radiation are necessary to compensate for heat losses by conduction while sufficient "quanta" of energy are collected by the bonds for breakage to occur. In-situ application of this phenomena might be possible if fragmented shale could be irradiated by microwaves transmitted from a centralized borehole.

Conclusions
1. The relationship between shale richness, as determined by Fischer assay, and the imaginary term of the dielectric constant is strong at a radiation frequency of 500 MHz and a temperature of 24°C.
2. The measurement of permittivity enables one to determine the concentration of kerogen in Green River oil shale directly. It, therefore, is an alternate and powerful assaying method. Extension of this technique to other hydrocarbon deposits is feasible.
3. High power microwave applications may aid in the recovery of oil and combustible gases in the future, perhaps on an in-situ basis.

Acknowledgment
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References


UNIVERSITY DISPOSAL OF RETORTED OIL SHALE

H.W. Earnest, V. Rajaram, and T.A. Kauppila
The Cleveland-Cliffs Iron Company
Western Division
Rifle, Colorado 81650

J.R.M. Hill
Bureau of Mines
U.S. Department of the Interior
Spokane, Washington 99207

Abstract

Methods for underground disposal of retorted oil shale from a gas combustion retorting process have been investigated under Contract No. J0265052 for the U.S. Bureau of Mines. These methods include transport and stowing by hydraulic, mechanical, and pneumatic means for a deep mine in the Piceance Creek Basin of northwestern Colorado. Mechanical transport and stowing, using conveyors, was determined to be the most promising system, based on a ranking analysis which included subjective and objective technical analysis, and capital and operating costs.

The various backfilling methods were studied as an integral part of two mining methods: chamber and pillar, and sublevel stoping. Excessive water and energy requirements, poor pillar support characteristics of the backfill, and high costs were the principal reasons for rejecting hydraulic transport and stowing. Excessive energy requirements, severe dust problems, and high costs resulted in the rejection of the pneumatic transport and stowing methods. The surface and underground environmental effects of the various methods were considered in all evaluations. Underground disposal of retorted shale may reduce the amount of material placed on the surface by as much as 85 percent. Resource recovery may be increased up to 16 percent when backfilling provides supplementary pillar support and the opportunity to reduce the size of rib pillars.

Preliminary operating cost estimates for underground disposal ranged from $0.3101 per ton, for conveyor transport and stowing, to $1.1855 per ton for pneumatic transport and stowing. Operating costs for total surface disposal are estimated to be $0.2438 per ton.

Introduction

The waste material remaining after shale oil has been extracted by retorting, which amounts to approximately 82 percent of the retort feed, must be disposed of in a manner that is environmentally acceptable and economically feasible. The Cleveland-Cliffs Iron Company, under U.S. Bureau of Mines Contract No. J0265052, is investigating various methods of underground disposal of retorted shale from a gas combustion retorting process. Two mining methods suitable for mining the deep oil shale deposits in the center of the Piceance Creek Basin (chamber and pillar, and sublevel stoping), were specified for this study. The results include costs and other considerations for partial surface disposal since it is not possible to put all the retorted shale back into the mined-out areas.

This report is based on the Phase I investigations for USBM Contract No. J0265052 entitled "Underground Disposal of Spent Shale from the Paraho Retorting Process." Phase I of this contract dealt primarily with the selection of the more promising methods for underground disposal of retorted oil shale. A more detailed analysis of the selected systems and related problems is being performed in Phase II of the contract.
Conditions and Assumptions

Since a gas combustion retorting process was specified, the physical and chemical characteristics of retorted shale from this process were used. Therefore, the results and conclusions discussed here are applicable to that process but may not be applicable to retorted shale from other processes. All parameters are based on actual data, except where assumptions are stated explicitly.

Physical Properties - Due to mine environmental and safety restrictions, retorted shale must be cooled to approximately 100°F (38°C) before being transported into the mine. Holtz (1975) determined that the size of the material, as it comes from the retort, ranges from approximately 2.5 inches (63.5 mm) maximum size to a fineness of about 40 percent minus 4-mesh (4.76 mm) and 15 percent minus 325-mesh (0.044 mm). The density of retorted shale, as it leaves the retort, is about 70 pounds per cubic foot (1.12 g/cm³) (Holtz, 1975).*

Mine Conditions - The mine is assumed to be located in the center of the Piceance Creek Basin in northwestern Colorado. The surface elevation is 6,200 feet (1,890 meters) above sea level, and the mining-backfilling activities will be at a depth of 2,000 feet (610 meters) in the lower saline zone of the Green River formation. The recorded ambient rock temperature is in the range of 90°F (32°C) to 100°F (38°C).

Economic Assumptions - All capital and operating costs are based on 1976 dollars. In some instances where data were not available, relative or factored costs are used. Labor rates are comparable to the current wage scales for mining in western Colorado. No attempt has been made to escalate wages to account for the effects of an energy-impacted labor market.

Production Parameters - A commercial mining and retorting operation capable of producing shale oil at a rate of 50,000 barrels per day (7.95 m³/day) on a 365-day-per-year basis is used in this study. Assuming a retort efficiency factor of 0.95, 28 gallons per ton (0.117 m³/metric ton) of oil shale, 5 percent residual moisture, and a retorted shale to raw shale weight ratio of 0.82, the retort facility will produce 68,000 tons (61,690 metric tons) of retorted shale per day.

\[
\text{Tons/day} = \frac{50,000 \text{ bbl}}{\text{day}} \times \frac{42 \text{ gal}}{\text{bbl}} \times \frac{\text{ton}}{28 \text{ gal}} \times 1 \frac{1}{0.95} \times 0.82 \times 1.05 = 67,974
\]

Use: 68,000 tons per day

Mining Methods

The mining methods specified include chamber and pillar mining, and sublevel stoping. Both methods are suited to mining the deep deposits in the Piceance Creek Basin and to backfilling.

Chamber and pillar mining, with backfilling, is a modification of room and pillar mining in which drifts, driven normal to the main entries, are enlarged into chambers by fan drilling and blasting. Figure 1 is a schematic of a typical chamber and pillar system. The major advantage of this system is that it facilitates backfilling, which in turn has a stabilizing effect on the remaining pillars. This method is generally restricted to single-level mining.

Sublevel stoping with backfilling is a large-production, low-cost, open stoping method which is well suited to fairly regular ore bodies having both competent ore and host rock. Open stope production uses long hole drilling from levels and sublevels, and blasting in successive slices. Figure 2 shows a typical sublevel stope system during the mining and backfilling phases. The remaining pillars may be stabilized by properly backfilling the mined-out stopes. Multilevel mining is normally practiced with sublevel stoping.
Figure 1. - Chamber and Pillar Mining With Backfilling.

In both methods, the stopes or chambers will be mined in an alternating pattern so that backfilling may take place, and its supportive effect on adjacent pillars may be felt before the second alternating series of stopes are mined. Thus, the stabilizing effect of backfilling may be exploited during the mining phase, which, in turn, will allow minimal-sized pillars to remain for support, thus increasing overall extraction ratio. The result is an estimated increased resource recovery of up to 16 percent. In addition, underground disposal of retorted shale will reduce the amount of surface disturbance; however, it will also increase the overall mine operating costs.

Transport and Stowing Methods

Hydraulic, mechanical, and pneumatic transport and stowing methods have been considered for the underground disposal of retorted oil shale. Due to the rugged terrain in the Piceance Creek Basin and a desire to minimize surface disturbance, all methods studied provide for transport from a point near the surface retort facilities, directly to the backfilling level. Thus, nearly all lateral transport will be within the mine. An average transport rate of 2,900 tons per hour (2,630 metric tons/hour), with a peak capacity of 4,000 tons per hour (3,630 metric tons/hour), was anticipated in the design of the transport systems.
to remove any fugitive dust. Worker isolation may be required in some instances.

Hydraulic Transport and Stowing - The hydraulic transport system requires slurry preparation and removal of excess slimes on the surface before transporting the slurry to the backfilling area in the mine. The slurry is carried in large-diameter pipes, placed in a cased borehole, from the surface to the backfilling level and along the horizontal entries to the stopes. Preliminary work indicates that the retorted shale degrades readily when slurried and pumped. Pipe wear should not be excessive since the Bond Abrasion Index for the retorted oil shale is 0.006 as compared to 0.160 for dolomite or 0.634 for taconite. To effectively dewater the slurry by decanting and mousetrap drains, after placement in the stopes, past experience has shown that the slimes portion should be limited to approximately 20 to 25 percent minus 325-mesh (0.044 mm). Enough of the slimes can be removed by cyclones, or centrifuges, and disposed of in surface slimes ponds. It has been demonstrated that gas combustion retorted shale cannot be pumped effectively at densities greater than 50 percent by weight (Link, 1976, oral communication).

Slurry is placed in the chamber or stope from the upper level access drifts. Bulkheads strong enough to withstand the maximum hydrostatic head are installed in each access entry below the backfilling level. Preliminary work indicates that approximately 70 percent of the backfill material will pass through a 35-mesh (0.5 mm) sieve. Drainage characteristics of the backfill are so poor that men and equipment are unable to work on the fill. Therefore, the discharge pipe cannot be extended as backfilling progresses. As a result, coarser particles settle out near the discharge point and finer material migrates toward the rear of the chamber or stope. This saturated backfill will not provide adequate lateral support for the pillars separating the stopes.

Figure 2. - Sublevel Stoping with Backfilling.

Underground disposal of retorted shale will result in higher operating costs, less surface environmental disturbance, and increased resource recovery. Backfilling mined out areas is a common method of augmenting ground support in mines throughout the world. When the pillars are designed to fail gradually, so that lateral stresses are created in the backfill, the backfill can provide confinement and support for the pillars. This permits the design of smaller pillars than would be the case if no backfilling was planned. Resource recovery may be increased up to 16 percent by leaving smaller rib pillars which are partially supported by the retorted-shale backfill. Table 1 demonstrates the potential effects of increased resource recovery on the life and economics of the assumed project.

Dust generated during the transport and stowing of retorted shale will be controlled, wherever possible, with water. Dust collectors may be used at transfer points in the transport system. Dust, generated during backfilling, will be controlled by water and the ventilating air system will be used
Table 1. - Effects of Increased Resource Recovery Due to Retorted Shale Backfill.

Chamber and Pillar Mining
Conveyor Transport

<table>
<thead>
<tr>
<th>Stowing Method</th>
<th>% Increase</th>
<th>Added Years Of Operation**</th>
<th>Gross Added Revenue* $ x 10^3</th>
<th>Disposal Cost*** $ x 10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conveyor</td>
<td>16.0</td>
<td>3.20</td>
<td>931,840</td>
<td>197,744</td>
</tr>
<tr>
<td>Conveyor &amp; Pneumatic Topfill</td>
<td>15.6</td>
<td>3.12</td>
<td>908,544</td>
<td>264,569</td>
</tr>
</tbody>
</table>

Sublevel Stoping
Conveyor Transport

<table>
<thead>
<tr>
<th>Stowing Method</th>
<th>% Increase</th>
<th>Added Years Of Operation**</th>
<th>Gross Added Revenue* $ x 10^3</th>
<th>Disposal Cost*** $ x 10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conveyor</td>
<td>15.0</td>
<td>3.00</td>
<td>873,600</td>
<td>202,339</td>
</tr>
<tr>
<td>Conveyor &amp; Pneumatic Topfill</td>
<td>14.8</td>
<td>2.96</td>
<td>861,952</td>
<td>268,565</td>
</tr>
</tbody>
</table>

* Revenue based on $15/barrel.
** Operating life based on 20-year reserve without backfilling.
*** Disposal cost includes all capital and operating costs for total project life.
Percolation rate for backfill may be as low as $1.4 \times 10^{-3}$ feet per day ($0.04$ cm/day). Ultimately, approximately 65 percent of the water may be recovered from the stope or chamber by percolation and decantation. Tests indicate that the total dissolved solids in the reclaimed water will be about 2,200 milligrams per liter.

Water requirements for slurry transport amount to approximately 17,000 gpm ($64.35$ m$^3$/min) of which 11,000 gpm ($41.64$ m$^3$/min) can be recycled from the backfilling operation. The desliming operation will require about 7,000 gallons ($26.5$ m$^3$) of water per minute; about 2,000 gpm ($7.57$ m$^3$/min) can be reclaimed.

The principal advantage of hydraulic transport of retorted shale is the absence of dust. Excessive water consumption, surface disturbance associated with the slimes ponds, high operating costs for pumping the reclaimed water back to the surface, poor pillar-support characteristics of backfill, little or no increase in resource recovery, and the possibility of bulkhead failures and resulting mudflows into the active mining areas, are the major disadvantages of hydraulic transport and stowing.

Mechanical Transport and Stowing - Two mechanical transport and stowing methods, using belt conveyors or trucks, are considered for the underground transport of retorted shale. In both cases, retorted shale moves vertically from the surface to the backfilling level through a large-diameter, cased borehole. Retorted shale is transferred by pan feeders from borehole to surge bins and, ultimately, into the haulage system. Dust suppression and control facilities are used at all transfer points. The backfill material is mechanically compacted by self-propelled, tamping-foot, drum compactors to a final density of 90 pcf ($1.44$ g/cm$^3$) in the chamber and pillar mining method. Supplementary compaction is not possible, however, in the unsupported open stopes of the sublevel stope method of mining because of safety restrictions. Fill density with no mechanical compaction is estimated to be about 75 to 80 pcf ($1.20$ to $1.28$ g/cm$^3$). The increase in fill density with no mechanical compaction is due to the depth of the fill and limited travel on top of the fill. All lower level access entries are bulkheaded and monitored for ground water accumulation. Using modified dozers, final topfilling is accomplished by packing the retorted shale as close to the roof as possible.

In the case of chamber and pillar mining, alternating fill and compaction cycles are planned. Mechanical compaction results in a backfill of increased density and reduced permeability, and, as compared to uncompacted backfill, placement of more retorted shale underground. The ability of the backfill to restrain the rib pillars is increased by compaction.

Conveyor Transport and Stowing - Using this method, a system of main conveyors transports retorted shale from the borehole location to the areas being backfilled. Material is discharged from the main belts, through splitters, onto cross-belts that discharge into the chamber or stope being backfilled. Extendable belts are used for actual stope or chamber filling.

Advantages of conveyor transport and stowing are low manpower and water requirements, low operating costs, good pillar support potential, higher resource recovery, and favorable energy requirements. The disadvantages are the inherent inflexibility of a conveyor transport system and dust which may result from the backfilling operation.

A combination method, consisting of conveyor transport and conveyor stowing to the backfill level, with pneumatic topfilling, shows considerable promise. This method will be discussed in the final, detailed report for the contract.

Truck Transport and Stowing - This system uses diesel-powered haul trucks to transport retorted shale from the borehole transfer point to the chamber or stope being backfilled, dumping in the stope, and returning to the loading point. Fill
characteristics are comparable to those described for conveyor stowing.

The advantages of truck transport and stowing are improved fill strength and resource recovery when compaction is possible, and good haulage-system flexibility. The disadvantages are high manpower and equipment requirements, high energy consumption, increased ventilation requirements, more dust generated than with conveyors, large entries, and serious hazards, associated with high dumps.

**Pneumatic Transport and Stowing** - In pneumatic transport and stowing, the material is fed into a pipeline through an airtight feeder. Air, the transporting medium, is provided by high-volume, low-pressure blowers. The material may be transported pneumatically from the surface to the area being backfilled, or from the bottom of a borehole, as was described for the mechanical systems.

With current technology, a pneumatic unit, capable of transporting retorted shale over the required distances, has a nominal capacity of 200 tons per hour (181 metric tons/hr). Each unit includes a feeder and two 8,000-cfm (226.535 m³/min) blowers rated at 15 psig (1,055 g/cm²). Each blower is powered by a 700-horsepower (710 metric horsepower) motor. For the commercial application studied, a minimum of 15 operating units is required, with an additional four as backup units.

Backfill material is discharged directly into the mined-out chambers or stopes, and the discharge pipe is advanced as backfilling progresses. When the stope or chamber is filled to the level of the upper access entries, final topfilling is completed by retreating as the fill is placed. Dust is a severe problem during the stowing operation. The in-place density of pneumatically stowed material is estimated to be approximately 70 to 80 pcf (1.12 to 1.28 g/cm³), depending upon the degree of compaction due to fill depth and high velocity impact. Bulkheads are required in all lower access entries.

The principal advantages of this method are: complete chamber or stope filling is possible; little water is used. The major disadvantages of pneumatic transport and stowing are extremely high energy requirements, severe dust problems, excessive pipe wear, backfill susceptibility to saturation by ground water, and high operating and capital costs.

**Modification of Physical Properties**

Several methods for modifying the physical properties of retorted shale have been investigated. The scope of these investigations includes compaction, chemical additives, and controlled retort conditions to improve the self-cementing characteristics of the retorted shale.

**Compaction** - Compaction tests, performed on retorted shale from a gas combustion process, indicate that a dry density of 90 pounds per cubic foot (1.44 g/cm³) is possible when a compactive effort of approximately 12,000 foot pounds per cubic foot (5,864 g cm/cm³) is applied. The addition of water, up to the point of optimum moisture content, does not increase final dry density by more than about 3 percent for a given compactive effort (Holtz 1975). Therefore, water is added only for dust control, and no effort is made to reach optimum moisture content, approximately 22 percent. Compacting to a density of 90 pcf (1.44 g/cm³) enhances fill strength, reduces permeability to a rate of about 10 feet (3 meters) per year (Holtz 1975), and increases lateral pillar support.

**Chemical Additives** - The effects of additives on both hydraulically transported shale and dry retorted shale were investigated on a limited basis. Results indicate general trends rather than significant statistical differences in the effects of the various additives.

**Hydraulically Transported Retorted Shale.** The addition of a flocculant can improve the dewatering characteristics of the hydraulically transported shale. However, the high slimes content hinders flocculant effectiveness, and the water retained in the fill may be reduced slightly.
Polyacrylamide flocculants were more effective than calcium chloride in dewatering the samples. Portland cement, hydrated lime, and flyash did not produce significant cementation of the samples individually or in combination. The ratios of retorted shale to cementing agent used were 5:1 and 30:1.

Dry Retorted Shale. Portland cement, flyash, and hydrated lime were tested, individually and in various combinations, to determine their ability to cement dry retorted shale. Compressive strength test results indicate the strength increases when the moisture content of the retorted shale is increased from 15 to 25 percent. The cementing reaction is more complete at the higher moisture content. Of the samples tested, Portland cement, added at a retorted shale to cement ratio of 5:1, produced the highest unconfined compressive strength. Additional test work is needed. One study indicated that the addition of 5 percent hydrated lime produced a measurable increase in unconfined compressive strength (Holtz 1975).

Retort Effects. Variation in retort temperature may affect the self-cementing characteristics of the retorted shale. Some instances of self-cementing have been reported, although the reaction kinetics are not fully understood (Holtz 1975). Additional investigation is needed to define more clearly the retort operating conditions which affect the self-cementing characteristics of the retorted shale.

Environmental Effects

Ground Water Effects - Ground-water hydrology is a factor in any underground disposal plan. The effects of ground water on the emplaced retorted shale and the possible effects of the fill on the ground-water system must be considered. In addition, effects on the surface environment need to be investigated.

Effects of Ground Water on Backfilling. Inflow of ground water may cause operational problems during backfilling, but is more likely to cause saturation and leaching of the backfill. These problems diminish as inplace density is increased. The potential for saturation and liquefaction failure make it possible to increase the density of the fill as much as is reasonably possible.

Effects of Backfilling on Ground Water. The principal effect of backfilling on the ground-water system is the introduction of a saline leachate into the system, which may, or may not, affect the quality of the ground-water system. A relatively impermeable backfill minimizes leaching, whereas, a hydraulic stowing method, or a relatively pervious fill, present the greatest potential for ground water contamination.

Surface Environmental Effects

The surface environmental effects associated with an underground disposal system are generally favorable, but some adverse effects are also likely to occur. Underground disposal allows surface dumps to be reduced by 50 to 85 percent but, in the case of hydraulic transport and stowing, surface slimes ponds are required. Slimes ponds are objectionable for two reasons: they are difficult to vegetate, and they are a high-risk source of surface water contamination. Further, any underground disposal system will require some additional surface structures to house equipment. Air quality will not be affected to any appreciable degree by underground disposal and fugitive dust problems may be less severe than for complete disposal on the surface.

Economics

The capital and operating costs, which we have developed, were assembled to compare the various methods for disposal of retorted shale underground and also for comparison with total surface disposal. In many instances, costs are in relative magnitudes and do not represent the absolute costs of the method. The validity of costs is consistent from one method to another. Table 2 shows comparative costs for the various combinations of backfilling and mining methods, based on an estimated project life
Table 2. - Comparative Costs for Underground Disposal of Retorted Shale (20-year Operation at 50,000 Barrels per Day).

<table>
<thead>
<tr>
<th>Disposal Method</th>
<th>Capital Costs $ x 10^3</th>
<th>Operating Costs $/Ton Retorted Shale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chamber and Pillar Mining</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydraulic</td>
<td>85,908</td>
<td>0.7640</td>
</tr>
<tr>
<td>Conveyor</td>
<td>19,670</td>
<td>0.3101</td>
</tr>
<tr>
<td>Truck</td>
<td>43,895</td>
<td>0.5412</td>
</tr>
<tr>
<td>Pneumatic</td>
<td>60,883</td>
<td>1.1855</td>
</tr>
<tr>
<td>Conveyor With Pneumatic Topfill</td>
<td>23,015</td>
<td>0.4221</td>
</tr>
<tr>
<td>Sublevel Stoping</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydraulic</td>
<td>85,908</td>
<td>0.7640</td>
</tr>
<tr>
<td>Conveyor</td>
<td>22,328</td>
<td>0.3162</td>
</tr>
<tr>
<td>Truck</td>
<td>45,665</td>
<td>0.5331</td>
</tr>
<tr>
<td>Pneumatic</td>
<td>60,883</td>
<td>1.1855</td>
</tr>
<tr>
<td>Conveyor With Pneumatic Topfill</td>
<td>25,557</td>
<td>0.4276</td>
</tr>
<tr>
<td>Total Surface Disposal</td>
<td>19,055</td>
<td>0.2438</td>
</tr>
</tbody>
</table>

of 20 years and a daily production rate of 50,000 barrels (7,945 m³). All costs include an allowance for the portion of retorted shale that is disposed of on the surface. Costs for total surface disposal of retorted shale are included for comparative purposes. No effort has been made to attach a dollar value to any adverse environmental effects. It can be seen from Table 2 that the mechanical method, using conveyors, is the most economical underground disposal method.

Ranking Analysis

The underground disposal methods were ranked using the Least Total Divisor Ranking Analysis technique. Subjective and objective factors, and capital and operating costs were used as the basis for the ranking analysis. Safety, transport and stowing methods, underground and surface environmental effects, effects on the mining operation, and ground water considerations were the subjective factors considered. The objective factors studied were energy consumption, water usage, crew size, fill density, resource recovery increase, and volume of retorted shale for surface disposal. The ranking analysis indicated that mechanical transport and stowing, using conveyors, is the optimal method of those investigated.

Tables 3 and 4 show results for the final ranking of the combinations of transport and stowing methods reported. A more complete description of transport and stowing methods, including several not discussed in this report, will be published as part of the Final Report for U.S. Bureau of Mines Contract No. JO265052.

Conclusions

Underground disposal of retorted oil shale can be accomplished by several means. Of the methods investigated, this study concludes that conveyor transport and stowing, with mechanical compaction where possible, is the most desirable for the underground disposal of retorted shale.

Placing as much of the retorted shale as possible underground will reduce the surface environmental disturbance associated with
Table 3. - Ranking Analysis, Final Selection: Chamber and Pillar Mining.

<table>
<thead>
<tr>
<th>Transport - Stowing</th>
<th>Subjective Technical Analysis</th>
<th>Objective Technical Analysis</th>
<th>Capital Costs</th>
<th>Operating Costs</th>
<th>Total</th>
<th>Final Rank</th>
<th>Final Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conveyor - Conveyor</td>
<td>6.00</td>
<td>3.00</td>
<td>3.00</td>
<td>1.00</td>
<td>13.00</td>
<td>1.00</td>
<td>1</td>
</tr>
<tr>
<td>Conveyor - Conveyor &amp; Pneumatic Topfill</td>
<td>7.29</td>
<td>3.33</td>
<td>3.51</td>
<td>1.36</td>
<td>15.49</td>
<td>1.19</td>
<td>2</td>
</tr>
<tr>
<td>Truck - Truck</td>
<td>6.08</td>
<td>3.75</td>
<td>6.69</td>
<td>1.75</td>
<td>18.27</td>
<td>1.41</td>
<td>3</td>
</tr>
<tr>
<td>Pneumatic - Pneumatic</td>
<td>10.72</td>
<td>4.44</td>
<td>9.29</td>
<td>3.82</td>
<td>28.27</td>
<td>2.17</td>
<td>4</td>
</tr>
<tr>
<td>Hydraulic - Hydraulic</td>
<td>10.51</td>
<td>11.07</td>
<td>13.10</td>
<td>2.46</td>
<td>37.14</td>
<td>2.86</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 4. - Ranking Analysis, Final Selection: Sublevel Stoping.

<table>
<thead>
<tr>
<th>Transport - Stowing</th>
<th>Subjective Technical Analysis</th>
<th>Objective Technical Analysis</th>
<th>Capital Costs</th>
<th>Operating Costs</th>
<th>Total</th>
<th>Final Rank</th>
<th>Final Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conveyor - Conveyor</td>
<td>6.00</td>
<td>3.00</td>
<td>3.00</td>
<td>1.00</td>
<td>13.00</td>
<td>1.00</td>
<td>1</td>
</tr>
<tr>
<td>Conveyor - Conveyor &amp; Pneumatic Topfill</td>
<td>7.16</td>
<td>3.33</td>
<td>3.43</td>
<td>1.35</td>
<td>15.27</td>
<td>1.17</td>
<td>2</td>
</tr>
<tr>
<td>Truck - Truck</td>
<td>6.20</td>
<td>3.75</td>
<td>6.14</td>
<td>1.69</td>
<td>17.78</td>
<td>1.37</td>
<td>3</td>
</tr>
<tr>
<td>Pneumatic - Pneumatic</td>
<td>10.16</td>
<td>4.08</td>
<td>8.18</td>
<td>3.75</td>
<td>26.17</td>
<td>2.01</td>
<td>4</td>
</tr>
<tr>
<td>Hydraulic - Hydraulic</td>
<td>9.79</td>
<td>10.56</td>
<td>11.54</td>
<td>2.42</td>
<td>34.31</td>
<td>2.64</td>
<td>5</td>
</tr>
</tbody>
</table>

The strength and permeability characteristics of retorted shale can be altered by both mechanical and chemical means. Compaction increases unconfined compressive strength and lowers permeability, but the addition of water, beyond that required for dust control, is not necessary to attain a satisfactory compacted density. More investigation of chemical additives and their influence on the self-cementing characteristics of retorted shale is needed.

When evaluating surface versus underground disposal plans, the environmental implications associated with long-term, dump stability should be considered.

References


THE PARTITIONING OF As, Cd, Cu, Hg, Pb and Zn
DURING SIMULATED IN-SITU OIL SHALE RETORTING

J.P. Fox, R.D. McLaughlin, J.F. Thomas
University of California at Berkeley
621 Davis Hall
Berkeley, California 94700

R.E. Poulson
Laramie Energy Research Center
Box 3395, University Station
Laramie, Wyoming 82071

Introduction
Partitioning refers to the distribution of elements originally present in oil shale among the spent shale, shale oil, retort water and gas exiting from the retort as a consequence of oil shale retorting. The partitioning of trace elements during oil-shale retorting must be studied on a quantitative basis to effectively anticipate and control potential environmental residuals. The need for material balance studies has been indicated by Poulson and others (1977). In the present work, the effect of retorting variables on the partitioning of As, Cd, Cu, Hg, Pb, and Zn was investigated by completing mass balances for two small-scale, simulated in-situ retorts. Samples of raw oil shale, spent oil shale, shale oil and retort water were collected and analyzed for As, Cd, Cu, Hg, Pb, and Zn. Four runs of each of these retorts - Laramie Energy Research Center's (LERC) 20-kg controlled-state, simulated, in-situ retort and Lawrence Livermore Laboratory's (LLL) 125-kg simulated in-situ retort - were studied.

The retorting systems used in this work are discussed in the "Experimental" section. Information on sampling, sample handling and analytical methods, together with a list of acronyms and definitions are presented in Appendix B. Experimental results are summarized in terms of concentrations and mass balances in the "Results" section. An analysis of this data revealed two trends: sample contamination and inhomogeneities, and, element partitioning due to retort operating conditions. Each trend is discussed for the six elements and conclusions presented in the "Discussion" section. Study results are summarized in the "Summary" section.

Experiments
The two retorting systems studied are described below.*

The LERC 20-kg, controlled-state retort is a bench-scale, simulated, in-situ retorting facility with a capacity of approximately 20 kg. The retort consists of a 13-foot long (3.9 m), hinged electric heater that encloses a 3-inch ID (76.2 mm) stainless steel pipe. This assembly is fitted at the bottom to collect product oil and decant water and, at the top, to allow a gas to flow through during operation. This system is further described by Duvall and Jensen (1975).

Four runs of the controlled-state retort were analyzed in the present study. These runs are designated CS (controlled state) and pertinent retorting parameters are summarized in table 1.

The LLL 125-kg retort is a pilot-scale simulated in-situ retort. The retort is 12 inches (30.5 cm) in diameter and 60 inches (1.5 m) high; it can be operated to simulate

*A description of sampling techniques, sample preparation, analytical methods, and a list of symbols, acronyms, and definitions used in the text are summarized in Appendix B.
in-situ retorting with both externally-heated inert gas and internal combustion of carbon on the spent shale. Both operating modes are represented in this study. This system is further described by Rothman (1975).

Four runs of the LLL 125-kg retort were analyzed in the present study. These runs are designated, S, in the tabulations in this paper; pertinent retorting parameters are summarized in table 1.

Experimental Results

The results of this investigation are presented in terms of elemental concentrations and mass balances. Each of these is discussed below.

Concentrations - Concentrations in ppm for all samples analyzed for the eight runs are summarized in table 2, together with the acronyms used for each sample. The dashes (-) indicate an analysis was not performed. Values with an asterisk (*) in this table were done by XRF. These values represent a single determination on a 2-gm sample, except RAW-1 and SOS-CS-35, which were run singly on two separate days. The standard deviation reported for XRF results is two standard deviations for the counting error, or 4 percent experimental error, whichever is greater.

The values that are not asterisked are ZAA results. These values are the averages of two or more replicates. If the first two values obtained were within 5 percent of one another, no additional runs were made. If they differed by over 5 percent, replicates were run until good agreement was obtained and the source of the variation identified and resolved. Typically, variability due to all possible sources, was less than 10 percent, with the exception of some retort waters and Zn and Pb results. The standard deviation reported in table 2 for ZAA represents 10 percent experimental error or, one standard deviation, as determined from three or more runs of a single sample, whichever is greater.

Mass Balances - Mass balances were completed for the eight runs summarized in table 1 for As, Cd, Cu, Hg, Pb and Zn. Since gas samples were not analyzed, a modification of classical mass balance procedures was used.

Mass balance around the retorts in this work is given by:

\[ M_{IGAS} + M_{RAW} = M_{SOS} + M_{OIL} \]
\[ + M_{H_2O} + M_{OFFGAS} \] (1)

For definition of terms used in this equation and others that follow, see Appendix B.
### Table 2. Elemental concentrations of elements in oil shale materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Run S-7</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw oil shale (RAW-1)</td>
<td>37.3±2.0*</td>
<td>0.72±0.07</td>
<td>40.2±4.2*</td>
<td>0.077±0.008</td>
<td>23.6±2.7*</td>
<td>67.2±3.6*</td>
</tr>
<tr>
<td>Spent shale (SOS-7)</td>
<td>53.4±2.6*</td>
<td>0.87±0.09</td>
<td>52.1±4.8*</td>
<td>0.014±0.001</td>
<td>40.3±3.2*</td>
<td>111±4*</td>
</tr>
<tr>
<td><strong>Run S-9</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw oil shale (RAW-1)</td>
<td>37.3±2.0*</td>
<td>0.72±0.07</td>
<td>40.2±4.2*</td>
<td>0.077±0.008</td>
<td>23.6±2.7*</td>
<td>67.2±3.6*</td>
</tr>
<tr>
<td>Spent shale (SOS-9)</td>
<td>47.5±2.4*</td>
<td>0.87±0.09</td>
<td>53.5±4.6*</td>
<td>0.024±0.002</td>
<td>32.8±3.0*</td>
<td>89.0±4.0*</td>
</tr>
<tr>
<td>Shale oil (OIL-9)</td>
<td>6.2±0.6</td>
<td>&lt;0.01</td>
<td>4.7±0.4</td>
<td>0.10±0.01</td>
<td>1.37±0.23</td>
<td>0.53±0.11</td>
</tr>
<tr>
<td>Bound water (BOUND-9)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;0.01</td>
<td>0.01±0.01</td>
<td>3.3±0.4</td>
</tr>
<tr>
<td>Whole retort water (H₂O-9)</td>
<td>0.25±0.02 &lt;0.002</td>
<td>5.3±0.5</td>
<td>0.030±0.003</td>
<td>0.02±0.01</td>
<td>0.48±0.05</td>
<td></td>
</tr>
<tr>
<td>Filtered retort water (FILT-9)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;0.01</td>
<td>-</td>
<td>&lt;0.48</td>
</tr>
<tr>
<td><strong>Run S-10</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw oil shale (RAW-1)</td>
<td>37.3±2.0*</td>
<td>0.72±0.07</td>
<td>40.2±4.2*</td>
<td>0.077±0.008</td>
<td>23.6±2.7*</td>
<td>67.2±3.6*</td>
</tr>
<tr>
<td>Spent shale (SOS-10)</td>
<td>76.0±3.0*</td>
<td>0.84±0.08</td>
<td>56.4±4.2*</td>
<td>&lt;0.01</td>
<td>34.7±3.4*</td>
<td>87.6±4.6*</td>
</tr>
<tr>
<td>Shale oil (OIL-10)</td>
<td>4.7±0.5</td>
<td>0.035±0.005</td>
<td>12±1</td>
<td>0.22±0.02</td>
<td>2.11±0.33</td>
<td>0.84±0.11</td>
</tr>
<tr>
<td>Bound water (BOUND-10)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;0.01</td>
<td>0.05±0.05 &lt;0.85</td>
<td></td>
</tr>
<tr>
<td>Whole retort water (H₂O-10)</td>
<td>0.40±0.04 &lt;0.002</td>
<td>0.73±0.07 &lt;0.01</td>
<td>0.10±0.03</td>
<td>0.12±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filtered retort water (FILT-10)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;0.01</td>
<td>-</td>
<td>&lt;0.12</td>
</tr>
<tr>
<td><strong>Run S-11</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw oil shale (RAW-1)</td>
<td>37.3±2.0*</td>
<td>0.72±0.07</td>
<td>40.2±4.2*</td>
<td>0.077±0.008</td>
<td>23.6±2.7*</td>
<td>67.2±3.6*</td>
</tr>
<tr>
<td>Spent shale (SOS-11)</td>
<td>55.6±2.9*</td>
<td>0.77±0.08</td>
<td>55.2±4.6*</td>
<td>&lt;0.01</td>
<td>37.2±3.4*</td>
<td>116±4*</td>
</tr>
<tr>
<td>Shale oil (OIL-11)</td>
<td>7.0±0.7</td>
<td>0.025±0.003</td>
<td>7.9±0.8</td>
<td>0.35±0.04</td>
<td>1.10±0.29</td>
<td>3.6±0.8</td>
</tr>
<tr>
<td>Bound water (BOUND-11)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.029±0.003 &lt;0.02</td>
<td>7.7±2.0</td>
<td></td>
</tr>
<tr>
<td>Whole retort water (H₂O-11)</td>
<td>0.52±0.05 0.005±0.0005</td>
<td>160±20</td>
<td>0.016±0.004</td>
<td>0.83±0.18</td>
<td>15.1±2.0</td>
<td></td>
</tr>
<tr>
<td>Filtered retort water (FILT-11)</td>
<td>0.13±0.01</td>
<td>-</td>
<td>-</td>
<td>&lt;0.01</td>
<td>0.22±0.05</td>
<td>5.3±0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Run CS-35</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw oil shale (LOS-1)</td>
<td>51.0±2.2*</td>
<td>0.59±0.06</td>
<td>41.0±4.6*</td>
<td>0.078±0.008</td>
<td>24.0±2.6*</td>
<td>66.5±3.4*</td>
</tr>
<tr>
<td>Spent shale (SOS-35)</td>
<td>57.4±2.5*</td>
<td>0.91±0.09</td>
<td>55.3±4.8*</td>
<td>0.029±0.003</td>
<td>38.4±5.0*</td>
<td>84.6±4.0*</td>
</tr>
<tr>
<td>Shale oil (OIL-35)</td>
<td>2.8±0.3</td>
<td>&lt;0.01</td>
<td>0.35±0.04</td>
<td>&lt;0.06</td>
<td>0.71±0.08</td>
<td></td>
</tr>
<tr>
<td>Bound water (BOUND-35)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Whole retort water (H₂O-35)</td>
<td>6.5±0.7 0.001±0.0001</td>
<td>0.22±0.02 &lt;0.01</td>
<td>0.09±0.01</td>
<td>5.4±1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Run CS-56</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw oil shale (LOS-1)</td>
<td>51.0±2.2*</td>
<td>0.59±0.06</td>
<td>41.0±4.6*</td>
<td>0.078±0.008</td>
<td>24.0±2.6*</td>
<td>66.5±3.4*</td>
</tr>
<tr>
<td>Spent shale (SOS-56)</td>
<td>50.4±2.4*</td>
<td>0.87±0.09</td>
<td>51.8±4.6*</td>
<td>0.042±0.004</td>
<td>32.9±3.0*</td>
<td>84.8±4.0*</td>
</tr>
<tr>
<td>Shale oil (OIL-56)</td>
<td>2.5±0.3</td>
<td>0.030±0.003</td>
<td>0.54±0.05</td>
<td>&lt;0.06</td>
<td>-</td>
<td>&lt;0.68</td>
</tr>
<tr>
<td>Bound water (BOUND-56)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.39±0.08</td>
<td>&lt;1.5</td>
<td></td>
</tr>
<tr>
<td>Whole retort water (H₂O-56)</td>
<td>2.3±0.2 0.001±0.0001</td>
<td>0.46±0.05</td>
<td>0.012±0.002 &lt;0.05</td>
<td>&lt;0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Run CS-57</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw oil shale (LOS-1)</td>
<td>51.0±2.2*</td>
<td>0.59±0.06</td>
<td>41.0±4.6*</td>
<td>0.078±0.008</td>
<td>24.0±2.6*</td>
<td>66.5±3.4*</td>
</tr>
<tr>
<td>Spent shale (SOS-57)</td>
<td>57.5±2.4*</td>
<td>0.70±0.07</td>
<td>51.3±4.6*</td>
<td>&lt;0.01</td>
<td>34.5±3.0*</td>
<td>85.3±4.0*</td>
</tr>
<tr>
<td>Shale oil (OIL-57)</td>
<td>2.6±0.3</td>
<td>&lt;0.01</td>
<td>0.21±0.02</td>
<td>0.07±0.01</td>
<td>0.06±0.005</td>
<td></td>
</tr>
<tr>
<td>Bound water (BOUND-57)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.020±0.005</td>
<td>-</td>
<td>84±21</td>
</tr>
<tr>
<td>Whole retort water (H₂O-57)</td>
<td>0.6±3 0.001±0.0001</td>
<td>0.03±0.003 &lt;0.01</td>
<td>0.03±0.01</td>
<td>6.3±0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Run CS-59</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw oil shale (LOS-2)</td>
<td>28.1±1.8*</td>
<td>1.3±0.1</td>
<td>29.3±4.6*</td>
<td>0.063±0.009</td>
<td>17.0±2.8*</td>
<td>52.1±3.4*</td>
</tr>
<tr>
<td>Spent shale (SOS-59)</td>
<td>26.1±2.0*</td>
<td>0.63±0.09</td>
<td>38.9±4.6*</td>
<td>&lt;0.020</td>
<td>25.2±3.0*</td>
<td>68.5±4.0*</td>
</tr>
<tr>
<td>Shale oil (OIL-59)</td>
<td>-</td>
<td>&lt;0.0002</td>
<td>0.04±0.004</td>
<td>&lt;0.080</td>
<td>&lt;0.06</td>
<td>&lt;0.41</td>
</tr>
<tr>
<td>Bound water (BOUND-59)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;0.05</td>
<td>&lt;1.5</td>
<td></td>
</tr>
<tr>
<td>Whole retort water (H₂O-59)</td>
<td>0.5±2 0.001±0.002</td>
<td>0.04±0.004</td>
<td>0.03±0.005</td>
<td>&lt;0.02</td>
<td>0.9±0.31</td>
<td></td>
</tr>
</tbody>
</table>

*X-ray fluorescence. All other values determined by Zeeman atomic absorption spectroscopy.*
<table>
<thead>
<tr>
<th>Retort Run</th>
<th>Raw Oil Shale (mg)</th>
<th>Spent Oil Shale (mg)</th>
<th>Oil (wet) (mg)</th>
<th>Whole Retort Water (mg)</th>
<th>Relative Imbalance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>COPPER</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>LLL 125-kg Retort</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run S-7</td>
<td>5110</td>
<td>5120</td>
<td>-</td>
<td>-</td>
<td>&gt;-0.2%</td>
</tr>
<tr>
<td>Run S-9</td>
<td>5050</td>
<td>5790</td>
<td>55</td>
<td>9</td>
<td>-16%</td>
</tr>
<tr>
<td>Run S-10</td>
<td>5000</td>
<td>4870</td>
<td>139</td>
<td>3</td>
<td>-0.2%</td>
</tr>
<tr>
<td>Run S-11</td>
<td>5030</td>
<td>4720</td>
<td>87</td>
<td>540</td>
<td>-6.3%</td>
</tr>
<tr>
<td><strong>LERC 20-kg Retort</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run CS-35</td>
<td>728</td>
<td>791</td>
<td>0.9</td>
<td>0.1</td>
<td>-8.8%</td>
</tr>
<tr>
<td>Run CS-56</td>
<td>712</td>
<td>717</td>
<td>1.0</td>
<td>0.1</td>
<td>-0.9%</td>
</tr>
<tr>
<td>Run CS-57</td>
<td>708</td>
<td>713</td>
<td>0.5</td>
<td>0.002</td>
<td>-0.8%</td>
</tr>
<tr>
<td>Run CS-59</td>
<td>545</td>
<td>610</td>
<td>0.1</td>
<td>0.002</td>
<td>-12%</td>
</tr>
<tr>
<td><strong>LEAD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>LLL 125-kg Retort</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run S-7</td>
<td>3000</td>
<td>3960</td>
<td>-</td>
<td>-</td>
<td>&gt;-32%</td>
</tr>
<tr>
<td>Run S-9</td>
<td>2960</td>
<td>3550</td>
<td>16</td>
<td>0.03</td>
<td>-21%</td>
</tr>
<tr>
<td>Run S-10</td>
<td>2940</td>
<td>3000</td>
<td>24</td>
<td>0.4</td>
<td>-2.9%</td>
</tr>
<tr>
<td>Run S-11</td>
<td>2960</td>
<td>3180</td>
<td>12</td>
<td>2.8</td>
<td>-7.9%</td>
</tr>
<tr>
<td><strong>LERC 20-kg Retort</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run CS-35</td>
<td>426</td>
<td>549</td>
<td>&lt;0.1</td>
<td>0.02</td>
<td>≥-29%</td>
</tr>
<tr>
<td>Run CS-56</td>
<td>417</td>
<td>455</td>
<td>&lt;0.1</td>
<td>&lt;0.01</td>
<td>≥-9.1%</td>
</tr>
<tr>
<td>Run CS-57</td>
<td>414</td>
<td>480</td>
<td>&lt;0.1</td>
<td>0.002</td>
<td>≥-16%</td>
</tr>
<tr>
<td>Run CS-59</td>
<td>316</td>
<td>395</td>
<td>&lt;0.1</td>
<td>&lt;0.001</td>
<td>≥-25%</td>
</tr>
<tr>
<td><strong>ZINC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>LLL 125-kg Retort</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run S-7</td>
<td>8540</td>
<td>10,900</td>
<td>-</td>
<td>-</td>
<td>&gt;-28%</td>
</tr>
<tr>
<td>Run S-9</td>
<td>8440</td>
<td>9630</td>
<td>6.2</td>
<td>0.8</td>
<td>-14%</td>
</tr>
<tr>
<td>Run S-10</td>
<td>8360</td>
<td>8430</td>
<td>9.7</td>
<td>0.4</td>
<td>-1.0%</td>
</tr>
<tr>
<td>Run S-11</td>
<td>8410</td>
<td>9920</td>
<td>39</td>
<td>51</td>
<td>-19%</td>
</tr>
<tr>
<td><strong>LERC 20-kg Retort</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run CS-35</td>
<td>1180</td>
<td>1210</td>
<td>1.8</td>
<td>1.3</td>
<td>-2.8%</td>
</tr>
<tr>
<td>Run CS-56</td>
<td>1160</td>
<td>1170</td>
<td>&lt;1.2</td>
<td>&lt;0.1</td>
<td>≥-1.0%</td>
</tr>
<tr>
<td>Run CS-57</td>
<td>1150</td>
<td>1160</td>
<td>1.9</td>
<td>0.4</td>
<td>-1.1%</td>
</tr>
<tr>
<td>Run CS-59</td>
<td>970</td>
<td>1070</td>
<td>&lt;0.7</td>
<td>0.1</td>
<td>≥-10%</td>
</tr>
</tbody>
</table>

**NOTE:** The symbol ≥ means that the actual value is slightly larger than the absolute magnitude of the recorded value.
<table>
<thead>
<tr>
<th>Retort Run</th>
<th>Raw Oil Shale (mg)</th>
<th>Spent Oil Shale (mg)</th>
<th>Oil (wet) (mg)</th>
<th>Whole Retort Water (mg)</th>
<th>Relative Imbalance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ARSENIC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>LLL 125-kg Retort</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run S-7</td>
<td>4740</td>
<td>5240</td>
<td>-</td>
<td>-</td>
<td>&gt;-11%</td>
</tr>
<tr>
<td>Run S-9</td>
<td>4690</td>
<td>5140</td>
<td>72</td>
<td>2.7</td>
<td>-11%</td>
</tr>
<tr>
<td>Run S-10</td>
<td>4640</td>
<td>6560</td>
<td>54</td>
<td>1.5</td>
<td>-43%</td>
</tr>
<tr>
<td>Run S-11</td>
<td>4670</td>
<td>4750</td>
<td>77</td>
<td>1.8</td>
<td>-3.4%</td>
</tr>
<tr>
<td><strong>LERC 20-kg Retort</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run CS-35</td>
<td>905</td>
<td>821</td>
<td>7.0</td>
<td>1.6</td>
<td>+8.3%</td>
</tr>
<tr>
<td>Run CS-56</td>
<td>886</td>
<td>698</td>
<td>4.5</td>
<td>0.6</td>
<td>+21%</td>
</tr>
<tr>
<td>Run CS-57</td>
<td>880</td>
<td>799</td>
<td>6.1</td>
<td>0.04</td>
<td>+8.5%</td>
</tr>
<tr>
<td>Run CS-59</td>
<td>520</td>
<td>409</td>
<td>-</td>
<td>0.03</td>
<td>+21%</td>
</tr>
<tr>
<td><strong>CADMIUM</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>LLL 125-kg Retort</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run S-7</td>
<td>92</td>
<td>85</td>
<td>-</td>
<td>-</td>
<td>&lt; +7.6%</td>
</tr>
<tr>
<td>Run S-9</td>
<td>90</td>
<td>94</td>
<td>&lt;0.1</td>
<td>&lt;0.003</td>
<td>&lt; -4.6%</td>
</tr>
<tr>
<td>Run S-10</td>
<td>90</td>
<td>73</td>
<td>0.3</td>
<td>&lt;0.01</td>
<td>&gt; +19%</td>
</tr>
<tr>
<td>Run S-11</td>
<td>90</td>
<td>66</td>
<td>0.3</td>
<td>0.02</td>
<td>+26%</td>
</tr>
<tr>
<td><strong>LERC 20-kg Retort</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run CS-35</td>
<td>11</td>
<td>13</td>
<td>&lt;0.02</td>
<td>&lt;0.001</td>
<td>&lt; -18%</td>
</tr>
<tr>
<td>Run CS-56</td>
<td>10</td>
<td>12</td>
<td>0.04</td>
<td>&lt;0.001</td>
<td>&lt; -20%</td>
</tr>
<tr>
<td>Run CS-57</td>
<td>10</td>
<td>10</td>
<td>&lt;0.02</td>
<td>&lt;0.001</td>
<td>&lt; -2.1%</td>
</tr>
<tr>
<td>Run CS-59</td>
<td>24</td>
<td>10</td>
<td>&lt;0.01</td>
<td>&lt;0.001</td>
<td>&gt; +14%</td>
</tr>
<tr>
<td><strong>MERCURY</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>LLL 125-kg Retort</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run S-7</td>
<td>9.8</td>
<td>1.4</td>
<td>-</td>
<td>-</td>
<td>&lt; +86%</td>
</tr>
<tr>
<td>Run S-9</td>
<td>9.7</td>
<td>2.6</td>
<td>1.2</td>
<td>0.05</td>
<td>+60%</td>
</tr>
<tr>
<td>Run S-10</td>
<td>9.6</td>
<td>&lt;0.9</td>
<td>2.5</td>
<td>&lt;0.04</td>
<td>&gt; +64%</td>
</tr>
<tr>
<td>Run S-11</td>
<td>9.6</td>
<td>&lt;0.9</td>
<td>3.8</td>
<td>0.05</td>
<td>&gt; +51%</td>
</tr>
<tr>
<td><strong>LERC 20-kg Retort</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run CS-35</td>
<td>1.4</td>
<td>0.4</td>
<td>&lt;0.1</td>
<td>&lt;0.01</td>
<td>&gt; +64%</td>
</tr>
<tr>
<td>Run CS-56</td>
<td>1.4</td>
<td>0.6</td>
<td>&lt;0.1</td>
<td>&lt;0.01</td>
<td>&gt; +69%</td>
</tr>
<tr>
<td>Run CS-57</td>
<td>1.4</td>
<td>&lt;0.2</td>
<td>0.2</td>
<td>&lt;0.01</td>
<td>&gt; +71%</td>
</tr>
<tr>
<td>Run CS-59</td>
<td>1.2</td>
<td>&lt;0.3</td>
<td>&lt;0.1</td>
<td>&lt;0.01</td>
<td>&gt; +66%</td>
</tr>
</tbody>
</table>

**NOTE:** The symbol ≤ or ≥ means the actual value is slightly less than or slightly greater than the absolute magnitude of the recorded value.
The offgas consists of two components. These are (1) input gas that passes through the retort (OGAS), and (2) gas generated from pyrolysis of the oil shale (SGAS). Therefore, the mass of an element in the offgas may be represented as:

\[ M_{\text{OFFGAS}} = M_{\text{OGAS}} + M_{\text{SGAS}} \] (2)

In those cases where the input gas (IGAS) is inert, N\(_2\), is at the same or a lower temperature than the material within the retort, and/or when the elemental concentration in the input gas is small, it may be assumed that the elemental mass in the input gas is not removed on passage through the retort. This gives:

\[ M_{\text{IGAS}} = M_{\text{OGAS}} \] (3)

The conditions required for equation (3) to be valid always held for the LERC controlled-state retort runs and all LLL 125-kg retort runs, except arsenic for run S-10. This will be addressed below in the "Discussion" section.

Substituting equations (2) and (3) in equation (1) gives the equation used for mass balance work in this study, or

\[ M_{\text{RAW}} = M_{\text{SOS}} + M_{\text{OIL}} + M_{\text{H}_2\text{O}} + M_{\text{SGAS}} \] (4)

Of the terms in this equation, \( M_{\text{RAW}}, M_{\text{SOS}}, M_{\text{OIL}}, \) and \( M_{\text{H}_2\text{O}} \) are computed directly from measured concentrations and product masses, while \( M_{\text{SGAS}} \) is unknown. Therefore, the difference between the inputs (\( M_{\text{RAW}} \)) and the outputs (\( M_{\text{SOS}}, M_{\text{OIL}}, \) and \( M_{\text{H}_2\text{O}} \)) is \( M_{\text{SGAS}} \), if equation (3) holds. For the more refractory elements, such as Cu, Zn and Pb, the elemental mass in the shale gas (\( M_{\text{SGAS}} \)) is approximately zero; equation (3) should give mass balance closure.

The relative imbalance in the mass balance (Kaakinen 1974), which is a measure of the degree of closure obtained, was computed from:

\[ RI = \left[ \frac{\text{Mass In} - \text{Mass Out}}{\text{Mass In}} \right] 100 \]

\[ RI = \left[ \frac{M_{\text{RAW}} - (M_{\text{SOS}} + M_{\text{OIL}} + M_{\text{H}_2\text{O}})}{M_{\text{RAW}}} \right] 100 \] (5)

A negative value for the relative imbalance ratio means that there is a net gain in elemental mass for the system: the outputs are greater than the inputs. This could occur for any one or more of the following reasons: (1) the spent shale was contaminated through sample handling relative to the raw shale, (2) elements in the input gas were transferred to system outputs other than the shale gas, (3) nonrepresentative sampling occurred, (4) inhomogeneities existed in the sample matrices, or (5) analytical errors biased outputs relative to inputs.

A positive value for the relative imbalance ratio means that there is a net loss in elemental mass for the system: inputs are greater than outputs. This could occur if: (1) there is an output which is not measured, (2) if nonrepresentative sampling occurred, (3) if homogeneities exist in the sample matrices, or (4) if analytical errors biased outputs relative to inputs. Recall that the shale gas was not analyzed and is not included in the balance. Therefore, positive, relative imbalance ratios would be expected for volatile elements, lost from the oil shale, and the magnitude of the index is a measure of the amount of each element lost.

Results of the mass balances are summarized in tables 3 and 4, in terms of elemental masses and relative imbalance ratios.

Discussion

The concentrations and mass balances summarized in tables 2-4 are discussed and interpreted below for each of the six elements. Classical treatment of experimental data (Daniels and others 1949) was used in assigning limits of error to relative imbalance ratios. Typically, maximum probable error for the relative imbalance ratio is 10 percent for As and Zn, 15 percent for Pb, Cd and Hg, and 20 percent for Cu.

Arsenic - Arsenic concentrations, found in the analyzed samples, range from 28 to 51 ppm in the raw oil shales; from 26 to 76 ppm in the spent oil shales; from 0.23 to 6.5 ppm in the whole retort waters; and
from 2.5 to 7.0 ppm in the oils. These observations are within the range of those reported by other investigators, including Poulson and others (1977); Fruchter and others (1977); Desborough and others (1976). Wildeman (1977) reports As levels of approximately 24 ppm in a Fischer assay shale oil. Approximately 75 percent of the As present in the retort water is particulate in nature. On a weight basis, less than 3 percent of the total As, originally present in the raw oil shale, is distributed to the oils and waters during retorting. The relatively high levels of As in the oil suggest that up to two percent by weight of the AS in the raw oil shale may occur as organometallic compounds.

Arsenic is associated with pyrite in the raw shale (Desborough and others 1976). Therefore, its loss from the oil shale matrix is probably controlled by the sulfides, As$_4$S$_4$ and/or As$_2$S$_3$, both of which have high vapor pressures at the retorting temperatures studied. Vapor pressure data, plotted in figure 1, show that arsenic sulfides are midway in volatility between Cd and Hg. Therefore, As losses from the raw oil shale should be midway between those for Hg and Cd. Mass balance calculations, shown in table 4, indicate that this is true, i.e., As volatility is midway between Hg and Cd for the LERC runs but not for the LLL runs.

The LLL runs have negative, relative imbalance ratios for As (gain in As), while LERC runs have positive, relative imbalance ratios (loss in As). The LERC results indicate that less than 10-21 percent of the As, present in the oil shales, is lost at around 550°C. Desborough and others (1976) reported a 15 percent As loss during pyrolysis by conventional Fischer assay. Wildeman (1977) reported a 12 percent gain in As for XRF analyses and a 1 percent loss in As for atomic absorption analyses on the same set of Fischer assay samples. Both reported As mass changes are within limits of experimental error and, therefore, are not conclusive. Predictions from thermodynamic data, such as those summarized in figure 1, suggest that As losses, sufficiently large to be detected by the experimental methods used here, should occur.

The negative, relative imbalance ratios for the LLL runs suggest that either a contamination, sampling, or analytical problem exists for the LLL samples. Arsenic is sometimes used as an alloying constituent in steel (Myers and Barnett 1953) and, therefore, could be introduced into the spent shales relative to the raw shales through sample processing. However, we do not feel that this is the source of the negative, relative imbalance ratios for As for the LLL runs; here, the largest relative imbalance ratio (-43 percent) occurs for run S-10, the least contaminated (see Appendix B - Sampling and sample preparation).

We do not believe that analytical bias is the source of the problem because neutron activation analysis was used to check As in these samples and the same negative relative imbalance ratios resulted. Inhomogeneities are probably not the cause of the consistently negative, relative imbalance ratios. Typically, error due to inhomogeneities would be randomly distributed, resulting in both positive and negative relative imbalance ratios. Additionally, the LERC and LLL runs both used Anvil Points raw oil shale with very similar composition (except LOS-2; see table 2). LERC runs showed consistently positive, relative imbalance ratios, while LLL runs showed consistently negative, relative imbalance ratios.

Two sets of mechanisms are required to explain the relative imbalance ratios obtained for As in LLL runs. The first mechanism involves run S-10 alone; the second mechanism involves all four LLL runs.

The largest negative, relative imbalance ratio occurs for run S-10. This value, -43 percent, is nearly four times larger than the other negative, relative imbalance ratios and is well outside the limits of experimental error. This run was a combustion run in which the gas introduced into
the retort consisted of a mixture of 10.5 percent oxygen and 89.5 percent of gas recycled after leaving the retort. This was the only run using "offgas" as "input" gas. Maximum retorting temperature was 935°C. At this temperature, most of the As in the oil shale should be volatilized, if sulfide or oxide forms control As volatility (fig. 1). Vaporized As would be swept ahead of the reaction front where the surrounding atmosphere is reducing. Here, it may react with H₂ to form AsH₃ (arsine, probably a major gaseous As species) and other arsenic compounds. The gas is then recycled through the retort, with air added. Oxygen, in the air stream, may react with arsenic and other compounds to form As₂O₃ (now probably a major As species) which could condense out of the gas phase onto the spent shale. In this manner, much of the As vaporized from the oil shale may be redeposited behind the reaction front in an inhomogeneous manner. This could bias the As level of the spent shale on the high side. Note that this invalidates equation (3).

The association of As with particulates in the retort water supports this type of mechanism and suggests that condensation of As₂O₃ may occur in the LLL product collection train. This type of mechanism also qualitatively agrees with data presented by Peterson and others (1976). Their data suggest that gaseous As is converted to particulate As in the "offgas" burner of the LERC 9.1 metric ton (10-ton) retort. They also indicate that most of the gaseous As
occurs as arsine, and that particulates collected after the "offgas" burner appear to be As₂O₃.

While this type of mechanism explains the anomalous behavior of run S-10, relative to the other three LLL runs, it does not explain the magnitude of the As gain. Arsenic, present in the recycle gas, originates in the raw shale; its redeposition would not cause an increase in mass in the retorting system.

On all four LLL runs, the mass of As in the spent shale is greater than in the raw oil shale. The only way to explain this mass increase is to postulate that: (1) As occurs at moderate levels in the "input" gases and condenses onto the spent shale, (2) As condenses onto the retort walls and elsewhere in the system and is released during subsequent runs, (3) As condensation on the spent shale results in inhomogeneities that bias the As concentration in the spent shales on the high side.

Order of magnitude calculations indicate that an As level of 25 ppm, at STP, be present in the "input" gas in run S-10 to account for the 43 percent increase in As mass (33 percent, given limits of error), and all of this would have to be transferred to the system outputs. Since this is unlikely, a combination of factors may be responsible for the As mass increase on LLL runs. This issue needs to be resolved experimentally.

**Cadmium** - Average cadmium concentrations, found in the analyzed samples, range from 0.59 to 1.3 ppm in the raw oil shale; from 0.63 to 0.91 ppm in the spent shale; from less than 0.01 to 0.30 ppm in the oil; and from 0.001 to 0.005 ppm in the whole retort waters. These values are within the range of those reported by Poulson and others (1977) and Desborough and others (1976). Less than 0.5 percent by weight of the Cd, originally present in the oil shale, is distributed to the oil and whole retort water on retorting.

Cadmium is less volatile than both As and Hg. Vapor pressure data (summarized, fig. 1) indicate that CdO and CdS are both relatively involatile at the retorting temperatures studied here. However, CdCl₂ would be vaporized at temperatures above 500°C. This suggests that CdCl₂, or another more volatile Cd compound, controls the vaporization of Cd from oil shale. This does not agree with Desborough's (1976) suggestion that Cd may substitute for Zn in ZnS.

Mass balance data for Cd (summarized, table 4) indicate that no statistically significant Cd loss occurs at around 550°C (runs S-9, CS-35, CS-56, CS-57, CS-59). Although CS-59 shows a 14 percent loss, this is within the limits of experimental error. Losses of less than 15, 19, and 21 percent occur at temperatures of 750°C, 950°C, and 1030°C, respectively. These data suggest that Cd loss is a function of temperature (vapor pressure) as predicted from thermodynamics.

**Mercury** - Average Hg concentrations found in analyzed samples range from 0.063 to 0.078 ppm in the raw oil shale; from less than 0.01 to 0.42 ppm in the spent shales; from 0.029 to 0.35 ppm in the oils; and from less than 0.01 to 0.34 ppm in the whole retort waters. These values are within the range of those reported by Poulson and others (1977) and Desborough and others (1976). Approximately 10 to 33 percent by weight of the Hg, originally present in the oil shale, occurs in the oils, less than 9 to 43 percent by weight remains in the spent shales, and less than 1 percent by weight occurs in the whole retort waters. More than two-thirds of the Hg present in the whole retort waters is associated with particulates. Typically, mercury concentrations in the oils are over three times greater than in the whole retort waters. Generally, the concentration of Hg in the bound water is less than, or equal to, that in the whole retort water. This suggests movement, from the oil to the closely-associated bound water, is negligible.

Mercury is the most volatile element studied. Vapor pressure data (summarized, fig. 1) indicate that all Hg forms consid-
ered are very volatile at the retorting temperatures studied and, irrespective of the form in which the Hg occurs in the parent rock, it would be significantly lost at 500°C. Mass balance data for Hg (summarized, table 4) indicate that from 51 to more than 71 percent of the Hg, originally present in the oil shale, probably leaves system in the "offgas".

Hg balances, unlike the Cd balances, do not show any trend as a function of temperature or other variables. Regardless of temperature, in the range of 500 – 1030°C, the same amount of Hg escapes from the retorting system as "offgas".

Data in table 4 indicate that the mass of Hg in the oil increases as a function of temperature (at 500°C the Hg mass in the oil is 0.2 – 1.2 mg; at 750°C, it is 2.5 mg, and, at 1030°C it is 3.8 mg). This, combined with the fact that 10 to 33 percent by weight of the Hg occurs in the oil, suggests that oil is a sink for Hg. This could be due to the occurrence of organic Hg in the raw oil shale or the incorporation of Hg into the oil, during oil production, due to the high vapor pressure of Hg species.

The conclusions presented above with respect to Hg should be checked experimentally under more controlled conditions since contamination from mercury manometers could bias reported data.

**Copper** - Average Cu concentrations found in analyzed samples range from 29 to 41 ppm in the raw oil shale; from 39 to 56 ppm in the spent shale; from 0.042 to 12 ppm in the oils; and from 0.03 to 160 ppm in the whole retort waters. Less than 1 percent by weight of the Cu in the original oil shale is distributed to the oil and whole retort water. The balance of the Cu remains with the spent shale.

Copper is relatively involatile, as shown by the vapor pressure data in figure 1. At the retorting temperatures studied, these data suggest that Cu would not be significantly volatilized. This is consistent with the mass balance data in table 3. All Cu balances show a negative, relative imbalance ratio which suggests that contamination from sample processing occurred. This is consistent with Wildeman's (1977) data that show an 8 percent increase in Cu for a Fischer assay mass balance. (The contamination discussion presented below for Pb and Zn probably applies to Cu also. However, the large experimental error for Cu [20 percent] prohibits a definite statement.) Any Cu loss would be masked by contamination or analytical errors and, therefore, would not be detected within the limits of experimental error.

Table 2 shows that concentrations of Cu in shale oils and retort waters are typically higher, by a factor of 10, for the LLL samples than for the LERC samples. This is believed to be due to contamination from the materials used in the LLL product collection system. Specifically, some fittings on the heat exchangers are copper, and brass and copper valves are used in the drain systems that collect the oil and water. Therefore, Cu could be introduced into the oils and waters through corrosion of the materials that they contact.

**Lead** - Average Pb concentrations in the analyzed samples range from 17 to 24 ppm in the raw oil shale; from 25 to 40 ppm in the spent oil shale; from less than 0.6 to 2.1 ppm in the oil; and from less than 0.02 to 0.22 ppm in the whole retort waters. These values are within the range of Poulson's reported values (1977); Smith and others (1977). Less than 1 percent by weight of the Pb in the original oil shale is distributed to the oil and whole retort water. The balance of the Pb remains with the spent shale. This is similar to the distribution noted above for Cu. Approximately 75 percent of the Pb in the whole retort water is associated with particulates. Lead concentrations are over ten times greater in the oil than in the whole retort water. Typically, the concentration of Pb in the bound waters is closer to that in the whole retort waters than to the oils. This suggests that ion movement, from the oil to the closely-associated bound water, is negligible.
Concentrations of Pb in the oils and whole retort waters for the LLL runs are significantly higher than in the LERC runs. This suggests, as discussed for Cu, that Pb is introduced into the products through corrosion of materials in the retorting system.

Negative, relative imbalance ratios were obtained for all eight runs. This means that no Pb loss, within the limits of experimental error, was detected. This agrees with Wildeman's (1977) data for Fischer assay mass balance. Most of the negative, relative imbalance ratios fall outside the limits of experimental error. Likewise, Cu and also Zn, have consistently negative, relative imbalance ratios. (However, they are not all outside the limits of experimental error.) This suggests a common cause.

The elements Cu, Pb and Zn are typically alloys in the stainless steels and brass that are used in grinding and sieving equipment. Hence, they could easily be introduced into samples during sample handling (Myers and Barnett 1953; Thompson and Bankston 1970). If both the raw oil shale and spent oil shale are handled identically, any contamination introduced during sample handling would not significantly affect the mass balance, since both samples would be contaminated approximately equally. If, however, the spent shale is processed to a greater extent than the raw shale, contamination introduced in the process would appear as a net increase in elemental mass (negative, relative imbalance ratio).

Given the above framework, we suggest the following evidence shows that contamination, during sample preparation, contributed to the negative, relative imbalance ratios in table 3 for Pb, and, possibly, Zn and Cu.

(1) In all runs, except S-10, spent shale was processed to a greater extent than raw shale. Typically, processing consisted of grinding and sieving with brass-rimmed sieves for the LLL samples and pulverizing and riffling for the LERC samples. The relative imbalance ratio that is closest to zero for Cu, Pb and Zn consistently occurred for run S-10 (-0.2 percent for Cu; -2.9 percent for Pb; -1.0 percent for Zn).

(2) Negative values were obtained for all eight runs for the relative imbalance ratio for Cu, Pb and Zn. Although some of these relative imbalance ratios are within the limits of experimental error (as noted previously), the consistent pattern of all negative values for these common alloying elements implies that they were introduced into the spent shale during its processing.

(3) If it is assumed that the imbalance in mass balance closure is due to contamination from sample preparation, contamination levels for Cu range from 3 to 6 ppm; for Pb, from 2 to 8 ppm; and for Zn, from 1 to 19 ppm. These contaminant levels agree with those in the literature (Thompson and Bankston 1970).

In addition to contamination, homogeneity problems probably contributed to the negative, relative imbalance ratios for Pb and, possibly, Cu and Zn, in runs CS-35 and CS-59. The raw oil shale sample for run CS-35 was selected from a different container than the one used to charge the retort (although all containers were produced from the same master lot). The spent shale sample on run CS-59 was taken before the material had been riffling. Therefore, both of these samples are probably not as representative of the retorted material as other LERC samples are. This is evident in the data for runs CS-35 and CS-59 for Pb (relative imbalance ratio, outside limits of error) and may also be true for Cu and Zn. In all cases, the largest imbalance ratios for the LERC runs occur for these two runs.

Zinc - Average Zn concentrations in the analyzed samples range from 53 to 67 ppm in the raw shale; from 69 to 111 ppm in the
spent oil shale; from less than 0.41 to 3.6 ppm in the oil; and from less than 0.12 to 6.3 ppm in the whole retort waters. These values are within the range of Poulson's (1977) reported values. Less than 1 percent by weight of the Zn in the original oil shale is distributed to the oil and whole retort water. The balance of the Zn remains with the spent shale. This is consistent with the distribution reported for the other refractory elements, Pb and Cu. Zinc concentrations, in the whole retort waters, are typically four times greater than in the oils. Approximately 50-85 percent of the Zn present in the retort waters occurs as particulates. This is consistent with the data for As, Hg and Pb which show that the majority of the elemental mass is associated with particulates. Typically, the concentration of Zn, in the bound waters, is greater than the concentration in the whole retort waters or the oils. This suggests that a significant fraction of the Zn, measured in the oils, occurs in the bound water and not in the oil matrix itself.

Desborough and others (1976) reported zinc, residing as a sulfide, in the oil shale matrix. Therefore, ZnS may control the partitioning of Zn during retorting. Vapor pressure data for ZnS (fig. 1) show little Zn will be volatilized at temperatures from 500° to 1350°C. This is consistent with the mass balance data (summarized, table 3) which show no Zn loss within experimental limits. This, however, is not consistent with Fruchter's (1977) or Wildeman's (1977) data. Fruchter and others measured the gaseous and particulate Zn in the "offgas" of LERC's 9.1 metric ton (10-ton) retort and found 40,000 ng/m³ gaseous Zn and 500 ng/m³ of particulate Zn. Wildeman (1977) reported a 13 percent Zn loss for the Fischer assay. Large amounts of Zn could be released from the shale matrix only if a more volatile Zn compound, such as ZnCl₂, controlled its release from the oil shale. Data presented here cannot resolve this discrepancy; it should be investigated experimentally.

Summary

In previous discussion we identified two types of trends: (1) trends due to sampling, sample preparation and sample inhomogeneities, and (2) trends due to element distribution among the spent shale, oil, water and gas caused by retort operating conditions. We will briefly summarize each of these within the framework of previous discussions.

Trends Due to Sample Contamination and Inhomogeneities - A number of significant problems exist in connection with performing precise trace element mass balances, using existing pilot-scale and bench-scale retorts. These are primarily due to the fact that these retorts are designed and operated for purposes other than mass balance work. Some of the problems of performing mass balances around existing simulated retorts, noted in this work, are:

- Sample processing, including crushing, grinding, pulverizing, sieving, riffling, and laboratory handling, may introduce contaminants. This is particularly troublesome if the spent shale is processed differently than the raw oil shale.
- It is difficult to obtain representative samples, particularly of the "offgas" and raw and spent oil shale. Generally, the larger the retort; the more serious the problem.
- Product collection systems may introduce contaminants in the oil and water. The materials used in construction of such units as collection tanks or heat exchangers may contain Cu, Pb, Zn and other trace elements that may be lost through corrosion.
- Volatilized components may condense on contaminant walls, or the spent shale, if a temperature gradient is encountered. This causes cross-contamination or spent shale inhomogeneities. Materials deposited during a previous run may be reactivated and incorporated into the products
of a subsequent run. Inhomogeneities in the spent shale may bias mass balances.
Trends suggested above for Cu, Pb and Zn are largely due to the first three items listed above; As results are influenced by the last item.

These types of problems suggest that for accurate mass balance work, carefully controlled experimental conditions are required. These should include a mass balance assay retort, designed to minimize cross-contamination and corrosion problems, high precision analytical techniques, and sample preparation procedure that will reduce sample inhomogeneities and contamination.

Trends Due to Retort Operating Conditions - The partitioning of trace elements in oil shales, during in-situ retorting, is largely controlled by (1) retort operating conditions, and (2) elemental mineralogical residence in the raw oil shale. These two factors determine if an element can be released from the oil shale matrix and, if released, what its subsequent fate will be.

The significant retorting parameters, from the standpoint of elemental partitioning, are thought to be retort thermal history, including maximum retorting temperature and heating rate, and input gas parameters, including flow rate and gas composition. Temperature is significant due to its relationship to vapor pressure which, in turn, controls the amount of an element vaporized. Qualitatively, the elemental mass vaporized increases as the temperature increases. Gas composition and gas flow rates are significant as they control the chemical reactions that occur at the solid-gas interface and in the atmosphere surrounding the oil shale. Both reducing and oxidizing conditions were studied here.

In the present work, observed effects of retort operating conditions on the volatilization of Cd, As, Hg, Pb, Cu and Zn were as follows:

- The amount of Cd volatilized from the oil shale is a function of temperature.
- The amount of Hg in the oils is a function of temperature.
- The As species present in the gas stream depend on gas composition.
- No loss of Cu, Pb or Zn occurs at retorting temperatures studied.

Each of these observations should be further investigated experimentally under controlled laboratory conditions.

Trace element chemical forms within the oil shale matrix, their mineralogical residence, determine the amount of energy that must be supplied as heat to release the elements from the matrix. Trace elements probably occur in oil shales in three forms, as they do in coals. These forms are (1) trace minerals, (2) substitution products in the major minerals, and (3) organometallic compounds. Desborough and others (1976) have completed preliminary work to determine the mineralogical residences of trace elements in Green River formation oil shales. This work, to date, has indicated that (1) Zn occurs as a sulfide, (2) the principal residence of As is pyrite, a sulfide mineral, and (3) Cd probably substitutes for Zn in ZnS. No data are yet available for Hg, Cd and Cu. Data presented here suggest that As$_2$S$_3$ or As$_4$S$_4$ may control the release of As from oil shales; that ZnS probably does not control the release of Zn, and that Cd release may be controlled by a more volatile chemical species than CdS.

Trace elements, distributed to the oil on retorting, are probably initially present in oil shales as organometallic compounds or have high vapor pressures (Hg, As). Trace elements, occurring in the shale gas, exist in the oil shale in forms that are easily volatilized at retorting temperatures (As, Cd, Hg). The gaseous species probably condense out as oxides before the gas stream is emitted to the atmosphere and, therefore, would occur as particulates, with the possible exception of Hg. Trace elements that remain in the spent shale are refractory at retorting temperatures or are otherwise trapped within the oil shale (Cu, Pb, Zn and, at 550°C, Cd).
The origin of trace elements that occur in the whole retort water is more complex. They may be incorporated into the water through dissolution of gases, contact with the oil phase or contact with the oil shale. Typically, trace element concentrations in the whole retort waters were significantly lower than in the oils, suggesting an organic origin, and over 50 percent of reported concentrations was particulate. The association of trace elements with particulates may be due to oxide formation in the product collection system or elsewhere. The low levels of all elements studied in the whole retort waters, relative to the oils, may be due to their occurrence in organometallic compounds within the oil shale. Elemental levels in the bound waters are probably largely controlled by ion movement across the oil-water interface. Results presented here indicate that Pb and Hg concentrations in bound waters are approximately the same as in the whole retort water, while Zn concentrations in the bound waters are greater than in the oils and whole retort waters.

All of these conclusions should be further investigated experimentally under controlled laboratory conditions in order to eliminate the problems of sampling, sample preparation, homogeneity, and contamination problems noted.

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NAHCOLITE USE DEVELOPMENT

B. E. Weichman
Manager, Oil Shale Department
The Superior Oil Company
P.O. Box 1521
Houston, Texas 77001

Introduction

Projecting the data on U.S. domestic energy supply-demand clearly shows a critical shortage of liquid energy beginning about 1985. In order to relieve some of the demand for liquid fuel, President Carter, in his energy message, proposed converting from the use of oil and gas, as much as possible, to the use of coal. He has proposed that the increased use of coal would reach 1 billion tons per year by 1985. One problem to overcome in reaching this rate of coal consumption is the unavailability of efficient sulfur-scrubbing technology to burn it as clean energy.

In the last 10 years, research and development on using nahcolite (a naturally occurring sodium bicarbonate) as a dry scrubbing agent for SO$_2$ and NO$_X$ has shown that it is potentially the simplest, cheapest and most efficient method of stack gas scrubbing available. In addition, there is a sufficient domestic resource of nahcolite in the Piceance Creek Basin of northwest Colorado to scrub 1 billion tons per year of average sulfur coal for nearly 300 years. This potential lends credibility to President Carter's energy proposal only if the scrubbing technology and nahcolite resource become available for use in a timely fashion.

Superior Nahcolite Testing Program

In 1967, The Superior Oil Company began testing nahcolite as a dry scrubbing agent for acid gases. Between 1967 and 1971, Superior completed 12 bench level testing studies on nahcolite that confirmed the commercial potential of nahcolite to remove SO$_2$ and NO$_X$ from combustion gases. In 1971, Superior began phase I of a nahcolite pilot program. Superior contracted for the pilot testing of direct injection of nahcolite into the furnace combustion zone and began in-house testing of a pilot cross-flow device for contacting nahcolite granules and power plant stack gases. These pilot tests confirmed only that a lot more information was needed about the physics and chemistry of reacting nahcolite with acid gases.

In 1972, Superior began an in-depth study of the basic nahcolite reaction kinetics and in 1973 started phase II of the pilot program that began with the construction of a pilot plant to test three separate process systems using nahcolite as a scrubbing agent. These three systems were:

1. Countercurrent contactor - This system tested the countercurrent flow of nahcolite granules and power plant stack gases.
2. Ductwork injection - This system tested the injection of powdered nahcolite into the gas stream ductwork and subsequent collection in a baghouse and in an electrostatic precipitator.
3. Direct combustion zone injection - This system tested two methods of injecting nahcolite into the combustion zone. The first was mixing powdered nahcolite with the fuel and the second was nahcolite injection.
into the combustion zone with the primary and secondary air.

The results of these pilot tests confirmed the bench-test data identifying nahcolite as an efficient dry scrubbing agent for SO\textsubscript{X} and NO\textsubscript{X} and that it is potentially the most efficient and lowest cost system available.

Of the three systems tested, the most inefficient in terms of use of nahcolite and SO\textsubscript{2} removal is the ductwork injection. This system was subsequently tested in full-sized hardware at the Stanton electric power plant at Stanton, North Dakota. Superior, Wheelabrator-Frye and Bechtel participated in this testing, with Bechtel representing an electric power group. The results of these full-size tests are not yet available; however, sufficient analysis has allowed Superior to conclude that they were successful in proving the economic and technical commerciality of this nahcolite scrubbing system.

Technical Discussion of Test Work

The first step in the research program was to determine chemical and physical phenomena taking place in the reaction of nahcolite with acid gases and the primary controlling factors.

The reaction between nahcolite and sulfur dioxide in flue gas takes place in two steps, as follows:

\[2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2\]
\[\Delta H = +31 \text{ kcal/mole}\] (1)

\[\text{Na}_2\text{CO}_3 + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2\]
\[\Delta H = -85 \text{ kcal/mole}\] (2)

The first reaction is an endothermic decomposition of nahcolite to a porous sodium carbonate. The second reaction (exothermic) is porous sodium carbonate with sulfur dioxide and the conversion to sodium sulfate. The exothermic reaction eliminates the need for flue gas reheat and prevents the granular bed from reaching dew point.

The second step was to define the physical phenomenon taking place. This was expected to be similar to the textbook gas to solid reaction models which are basic transport equations shown in Chemical Reaction Engineering by Octave Levenspiel.

The basic transport equation for mass or energy transfer is a function of three things:

1. Area available for transport.
2. Resistance, which is a function of length of resistance and a resistance term such as conductivity, diffusivity, etc.
3. Driving force, whether it is volts, temperature difference for heat transfer or gas concentration. Gas concentration is the driving force in the case of sulfur dioxide reaction with nahcolite.

Typically, there are two transport models that can be used for gas to solid chemical reaction. These models are used for molecular sieve, dryers, designs, catalyst poisoning, etc. One model is the continuous reaction model where the gas or fluid molecules, with time, diffuse into and react or convert the solid uniformly throughout its volume. The other model is the unreacted core model in which the reaction occurs first as the outer surface, forming a thickening "ash" layer of conversion material as the reaction progresses. During the reaction, the unreacted core of the material shrinks in size as shown on figure 1.

Three different methods were used to determine which of the two models was actually taking place in the reaction with nahcolite. The first was to take photomicrographs with an electron microscope of the reaction interface in the nahcolite granule. The photomicrographs showed a definite ash layer buildup on the surface leaving a porous unreacted core. The second method used was to obtain a plot (fig. 2) using a microprobe attachment on a scanning electron microscope. This shows a definite sulfate shell buildup and an unreacted core.

The third method was a basic equal penetration model that assumes, under identical
conditions, the depths of penetration (reaction or ash layer) for different size particles are the same. Therefore, based on a calculated volume of the ash and unreacted core volume, an analysis of sized particles would yield calculated penetration depths.

So, based on these three methods, it was concluded that the shrinking core model (fig. 1) was the correct model, and correct physical phenomenon taking place was mass transport.

The physical phenomenon having been defined, it was necessary to define the resistances to mass transport, which are shown on figure 3.

\[ R_1 = \text{gas film resistance (semistagnant layer of gas)} \]

\[ R_2 = \text{ash resistance (the resistance to diffusion of SO}_2\text{ through the ash layer)} \]

\[ R_3 = \text{chemical reaction resistance (resistance to reaction once the molecules come in contact with each other at the reaction interface).} \]

Fixed bed tests were used to determine the values of these resistances (diffusivity) and also the controlling or dominant resistance.

Figure 4 is a flow sheet of the fixed bed contactor used to test the values of the resistances. Flue gas from the power plant was compressed by a radial blade blower and forced through a baghouse filter to remove particulates. To produce various sulfur dioxide gas concentrations required for the test, SO\(_2\) was injected into the flue gas stream. The gas stream was electrically heated to the desired temperature and valved into the test units. Reacted gases were exhausted to the power plant stack through the existing ductwork. Data were recorded at regular intervals for each run. Data consisted of gas flow conditions, which included SO\(_2\) concentration, temperature and flow rate. These records also included the particle size and composition parameters. Analyses of time data for each sample were listed, and the conversion and the simplification functions, \(f(X_B)\) and \(g(X_B)\), were calculated.

\[ X_B, \text{ conversion, is defined as fraction of sodium as sulfate on a molar basis:} \]

\[ X_B = \frac{\text{wt}\%Na_2SO_4/142}{\text{wt}\%Na_2SO_4/142+\text{wt}\%Na_2CO_3/106+\text{wt}\%NaHCO_3/168} \]

where,

\[ \text{wt}\%Na_2SO_4 = 100-\text{wt}\%Na_2CO_3-\text{wt}\%NaHCO_3 \]

This method predicted that if conversion \((X_B)\) plotted versus time \((t)\) were a straight line, the overall rate would be controlled by gas diffusion. A straight line obtained by plotting the function \(f(X_B)\) versus time would indicate control by ash.
Figure 2. - Sulfate concentration profile through a partially reacted 6 mesh nahcolite granule using microprobe attachment on a scanning electron microscope.

diffusion, and a straight line obtained by plotting \( g(X_t) \) versus \( t \) would suggest that the reaction itself controls the rate. Data from test FB-20 are plotted in figure 5. It is typical and implies that overall the resistance owing to the sulfate shell or "ash" layer is the highest and may be considered rate limiting for granule sizes 1/2 inch to 20 mesh plotted in figure 5.

The test data used to generate the graphs, which were similar to that shown in figure 5, were further checked by a computer program that used a linear least square regression to fit the data into the form of

\[
SURFACE\ OF\ PARTICLE
\]
\[
MOVING\ REACTION\ SURFACE
\]
\[
GAS\ FILM
\]

Figure 3. - Resistances of various steps for unreacted core model.

the best straight line. This program also generated a statistical parameter, the correlation coefficient, that indicates an increased agreement between experimental and theoretical values as it approaches unity. A second statistical parameter, the standard error of estimate, approaches zero to indicate the best fit between experimental data and theory.

For a typical test, the results of the computer program are presented in table 1.

The standard error of estimate is the least and the correlation coefficient the highest for the ash diffusion controlled model. Again, ash diffusion resistance appears to govern the overall process for 1/2-inch to 20-mesh particles.

After the physical phenomenon was identified, Superior began phase II of the pilot testing program. The first of the three processes tested was the counter-current contactor.

Countercurrent Contactor

Figure 6 is a schematic of the pilot countercurrent contactor. It is a round cylindrical device with a feed seal at the top and a discharge seal at the bottom of
Figure 4. - Flow sheet of fixed bed contactor. Four tests could be run simultaneously at each set of operating conditions.

Figure 5. - Relationship among three possible overall rates indicating parameters and time. The straight line for ash diffusion shows that its modeling function \( f(X_B) \) predicts very well the experimental data.
the discharge hopper. Special grates operate within the unit to hold a column of nahcolite granules in the contactor and continually dump the contacted nahcolite into the discharge hopper. The combustion gas enters the contactor at the level of the grates and flows upward through the column of nahcolite granules to exit at the top of the unit.

Specifications for the countercurrent contactor are as follows:

- Contactor diameter: 3.50 ft
- Area: 9.62 ft$^2$
- Bed depth: 2.50 ft
- Bed volume: 24.05 ft$^3$
- Grate volume: 10.50 ft$^3$
- Total volume: 34.55 ft$^3$

This process was difficult to model on the computer for two basic reasons, as follows:

1. The granules in the bed are not just one size but a distribution of eight basic sizes. Equal penetration model allowed prediction of when the smaller particles were 100 percent converted and they could be dropped from the finite difference solution of the equation.

---

**Figure 6. - Pilot countercurrent contactor.**

**Table 1. - Results of Computer Program.**

<table>
<thead>
<tr>
<th>Controlling Resistance</th>
<th>Gas Film Diffusion</th>
<th>Ash Diffusion</th>
<th>Chemical Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical equation</td>
<td>$t = x_B$</td>
<td>$t = 1 + f(x_B)$</td>
<td>$t = 1 + g(x_B)$</td>
</tr>
<tr>
<td>Least square equation</td>
<td>$t + 5.6 \over 36.1 = x_B$</td>
<td>$t + 80.3 = 1.01 + f(x_B)$</td>
<td>$t + 5/3 = 0.95 + g(x_B)$</td>
</tr>
<tr>
<td>Correlation coefficient</td>
<td>0.945</td>
<td>0.998</td>
<td>0.988</td>
</tr>
<tr>
<td>Theoretical values</td>
<td>$t = 0$ at $x_B = 0$</td>
<td>$t = 0$ at $x_B = 0$</td>
<td>$t = 0$ at $x_B = 0$</td>
</tr>
<tr>
<td>Actual values</td>
<td>$t = 5.6$ at $x_B = 0$</td>
<td>$t = 0.9$ at $x_B = 0$</td>
<td>$t = -3.6$ at $x_B = 0$</td>
</tr>
<tr>
<td>Std. error of estimate</td>
<td>2.44</td>
<td>0.59</td>
<td>1.41</td>
</tr>
</tbody>
</table>
2. From top to bottom of the bed, SO₂ concentrations changed with bed height.

Therefore, there is a changing driving force, changing overall resistance due to ash layer thickness and the smaller particles dropping out of the equation or model when they are completely converted to sodium sulfate.

Results:
The general results of the countercurrent test program, using raw nahcolite, show the following removals:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>80-96%</td>
</tr>
<tr>
<td>NOₓ</td>
<td>40-50%</td>
</tr>
<tr>
<td>Particulates (behind E.S.P.)</td>
<td>99%</td>
</tr>
</tbody>
</table>

The conclusions are that the countercurrent system will:
1. Efficiently scrub SO₂.
2. Remove flyash at >90 percent efficiency behind modern E.S.P.
3. Be mechanically simple and reliable.
4. Be easy to control and operate.
5. Reaction can be modeled to predict removal, conversion and design parameters.
6. Produce marketable sodium sulfate.

Ductwork Injection
The second process is ductwork injection, shown on figure 7. The rate controlling resistances, as in all the processes, is a strong function of particle sizes. This process uses particle sizes in the -100 and +200 mesh ranges. This size range is used for ductwork injection with a baghouse used for removal of particulates from the stream. Removal could also be by electrostatic precipitator, wet scrubber or any final dust removal device.

In these applications, besides the physical arrangement of the equipment, gas film resistance and ash resistance are approximately equal for conversions up to 90 percent. This process was tested on full-sized hardware at the Stanton plant. The results of these full-size tests are not yet available.

Combustion Zone Injection
The third process is combustion zone injection. Figure 8 is a schematic of direct injection of nahcolite into the furnace combustion zone. During the furnace injection tests, a physical phenomenon was identified that was termed "thermal crushing". Particle sizes ranging from -400 to 15 mesh were injected with the fuel and via primary and secondary burner air. Generally, regardless of particle size injected through this size range, the particles produced resulted in a size reduction of 40 to 200 times, or sizes with an aerodynamic mean diameter of 2 microns were produced.

For conversion and removal of SO₂ in the 80-90 percent range at stoichiometric ratios of one, the reaction times were between 3 and 8 seconds, with 50 percent of the reaction taking place during the first second.

Thus, the controlling resistance for the thermally crushed particles is dominantly chemical reaction resistance controlled for the first 50 percent of the reaction (less than a second) and the remaining 40 percent conversion taking place in 2 to 7 seconds with gas film resistance controlling. These residence times fit well with power boilers since the length of time from burner to stack in a power boiler is 6 to 8 seconds.

The Superior Oil Company is currently involved in a number of nahcolite testing programs that have been keyed from these pilot tests. A comprehensive report on all of Superior's testing is currently being prepared and is expected to be available in a few months.
Figure 7. - SO₂ removal by injection of nahcolite into ductwork.

Figure 8. - SO₂ removal by injection of nahcolite into combustion zone.
APPENDIX A


Clark, R.E., Ground Water Laws: Problem Areas, p. 377.


Ross, J.F., Acquisition of Existing Water Rights, 13 Rocky Mt. Min. L. Inst. 477 (1967)


Delaney, R., Water for Oil Shale Development, 43 Den. L.J. 72 (1966)


3. Westwide Study, (n. 1)


Kneese and Brown, (n. 1)


U.S. Dept. of Interior, Final Environmental Statement for the Prototype Oil Shale Leasing Program (1973)


5. Moses (n. 1) p. 23

6. Westwide Study, (n. 1) p. 183-185


Waters and Water Rights (Clark, ed. 1967), p 127 ff

9. Westwide Study, (n. 1), p 188

10. Water for Energy, (n. 3), p 2

Weatherford and Jacoby, (n. 1), p 174


Boulder Canyon Project Adjustment Act, 43 U.S.C. sec 618 and ff (1928)

Colorado River Storage Project Act, 43 U.S.C. sec. 620 and ff (1956)


15. Fed. Power Comm. v Ore, 349 U.S. 435 (1955). Held: states' control over appropriation of water effected by Desert Land Act (see Cal. Ore Power, n. 7) did not affect water rights acquired by the US when it was proprietor of lands and waters of the west; rather, when federally-owned land was reserved from entry, the right to use the amount of water needed to accomplish the purposes of such reservation was also reserved. In Ariz. v Cal (n. 14), this ruling was expanded to allow such reservation even after statehood.


Clyde, E.W., Special Considerations Involving Indian Rights, VIII Nat. Res. Lawyer 237 (1975)

17. U.S. v Dist Ct. in and for Cty of Eagle; U.S. v Dist Ct. in and for Water Div. 5, 401 U.S. 520, 527 (1971)


18. Filings in Water Div. 7 include both federal and Indian reserved rights; rights for BuRecl. projects and Forest Svc and BLM appropriations.

19. Art. XIV, Upper Colorado River Compact (n. 12) covers delivery to New Mexico; Art. III, entitles Colorado to only 51.75% of the water available to the Upper Basin states, after deducting 50,000 acre feet per year for Ariz. Compact requires Upper Basin to deliver 75 million acre feet ann. to Lower Basin. Both compacts disclaim any effect on Federal and Indian rights.

20. Argued: On admission to statehood, Congress accepted Colo. Const., Art XVI, sec. 6 and by so doing, waived any and all reserved water rights in the state.

21. Question still open but reserved to federal courts to decide; Eagle City and Water Div. No. 5 (n. 17)

22. Water for Energy (n. 3) p 9-10

23. See n. 4

24. Argued: Congress has already done so; as in n. 20

25. Congress: 33 U.S.C. sec 1251 ff; (1972); 42 U.S.C. sec 300 f and ff

Exec. Order 11514(5/5/70); Exec. Order 11735(8/7/73); Exec. Order 11738 (9/12/73)

Judiciary: NRDC v Train, 396 F. Supp 1363 (1975) and others

26. Westwide Study (n. 1) p 175 and ff

Water for Energy (n. 3) p 34, 56-57

27. See n. 25

28. 33 U.S.C. Sec. 1311

29. 33 U.S.C. Secs. 1341, 1342

30. 33 U.S.C. Sec. 1311.

Under EPA regulations, Colorado River Basin states had until 10/18/76 to come up with numerical standards for salinity. Still not done, at least in Colorado

31. 33 U.S.C. sec. 1316

32. 33 U.S.C. sec. 1311

33. Water for Energy (n. 3) p. 35


35. Est. Loss: $230,000 per year per mg/l increase

Water for Energy (n. 3) p 34

36. See n. 25

37. Minute No. 242, Intnl. Boundary and Water Comm. (8/30/73) limits salinity of water delivered to Mexico at Imperial Dam to no more than 115 ppm (+30 ppm)

38. Colorado River Water Quality Improvement Program (CRWQIP), established by Bu-Rec. and Minute 242

Colorado River Basin Salinity Control Act, 43 U.S.C. sec. 1591 ff

39. Paradox Valley and Grand Valley Project in Colorado; Later study: Glenwood Spgs-Dotsero area.

40. McElmo Creek in Colorado

41. 43 U.S.C. sec. 1591


43. Same as n. 42

44. Particularly "Final Environmental Statement"; see n. 3

45. Established to advise the President on environmental concerns, 43 U.S.C. sec 4342

46. 43 U.S.C. sec 4332

47. 40 C.F.R. sec 1500.8(a)(1) sets out CEQ guidelines, already adopted by reference in the procedures of most other agencies, including Dept. of Interior and BuRecl.

49. Use of federal funds allows government to attach any conditions it likes to any money grant.

50. See n. 10

51. See n. 11

52. 43 U.S.C. sec 620a-1 Moses, (n. 2) p 25

53. To provide water for municipal use in Rifle-DeBeque area. Alternate plans include water for use in oil shale industry. Colorado Water Conservation Board has tied its approval of the project to the development of an oil shale industry.

54. CAP proceeding, although deleted from budget by Pres. Carter; West Divide project completely stalled

55. 43 U.S.C. sec 372 ff charges BuRecI with providing water for irrigation of arid western lands

56. See n. 54

57. See n. 55

58. See new Water Resources Council regulations concerning benefit-cost analyses

59. Generally, courts have held benefit-cost should not be included in NEPA actions. The CEQ, however, does seem to require this analysis in impact statements


61. 43 U.S.C. Sec. 391

62. Post, p. 36 (12/25/76)


64. See n. 7

65. Colo. Constit., Art. XVI, secs 5, 6


67. See n. 15 and 16

68. See n. 18


70. See text at nn. 15-24


76. Huerfano Valley, etc v Hinderlider, 81 Colo. 468 (1927)


79. A good example is Bond v Twin Lakes, 178 Colo. 160 (1972)


82. No precedent; remarks during oral argument; Wadsworth v Kuiper, No 27177, Colo. Sup. Ct. (pending)

83. C.R.S. 1973, sec. 37-92-401 and ff

84. Under earlier statutes, Colorado had 70-odd water districts, corresponding to various tributary basins; Act of 1969, C.R.S. 1973, sec. 37-92-201 and ff, divided state into 7 water divisions, one to each major river basin. A Div. Engineer is chief admin. officer for each division. Under old system, each district was administered separately with no formal basin-wide priority lists established


86. C.R.S. 1973, sec. 37-92-402


88. The question here is the effect that declaring a number of water rights in the Colorado River Basin (in Colo.) abandoned would have on the state's position in determining rights to Upper Basin water now in use in the Lower Basin.
89. Hutchins (n. 8) p 315-316, 343
90. Hutchins (n. 8) p 291 and ff

91. The statute (n. 87) makes the presumption of abandonment rebuttable. This can be done by showing positively that intent (to abandon) and non-use do not exist or Dist. Engineer can waive on such showing.


93. The reasoning behind allowing conditional water rights was to encourage large investments of time and money in water diversion projects. Where the right has been perfected, however, standards of abandonment could be stricter without threatening a heavy financial loss to the appropriator. Yet, courts have generally declined to find abandonment, lacking an extremely long period of non-use and failing the presumption the statute now provides.


95. But, see minimum stream flow decrees; text, n. 152 and ff

96. The constitution dedicates only the waters of natural streams to appropriation and use. (Art. XVI, secs. 5,6). For "natural stream" definition, see Pikes Peak Golf Club, Inc. v Kuiper, 169 Colo. 309 (1969) but note that "tributary" is not well-defined.

97. It is our understanding that because of the provisions of the Colorado Ground Water Management Act, an application to appropriate waters flowing on the surface of the land in an area designated as a ground water basin might be opposed by the State Engineer on the grounds that such water is subject to the 1973 law, not the 1969 act.

98. The courts have treated them as such: Buckers Irrigation, etc. v Farmers' Indep. Ditch, 31 Colo. 62 (1902). The 1969 Act agrees; C.R.S. 1973, sec. 37-92-103(13)

99. Hall v Kuiper, 181 Colo 130 (1973). Held: Tributary, water that would reach the stream in 40 years; Kuiper v Lundvall, 529 Pac. 2nd 1328 (Colo. 1974). Held: Water not reaching stream for 178 years not part of the stream.

100. The distinction between tributary and non-tributary has become so important that parties are using radioactive dating and other sophisticated methods to show whether water is part of a stream or not.

101. City of Colo. Spgs v Bender, 148 Colo. 458 (1962). Held: underground natural streams are covered by the constitutional provision. But, it is not clear that the water there was otherwise unconnected to surface waters.

102. City of Boulder v North Boulder Farmers' Ditch Co., 557 P.2d 1182 (Colo. 1976), further distinguishes between "waste" and "return flow".

103. See nn. 98, 99

104. For definition of "designated ground water", see C.R.S. 1973, sec. 37-90-105(6)

105. Designated ground water is subject to the appropriation doctrine, under strict administration by the Ground Water Commission under the Ground Water Management Act (n. 97) Surface water and tributary ground water, closely defined, are subject to the appropriation doctrine, under administration of the court and the division engineers under C.R.S. 1973, secs. 37-92-101 and ff

Non-tributary ground water is not clear

106. Westwide Study (n. 1) p. 185 Water for Energy (n. 3) p. 34-36

107. 153 Colo. 157 (1963)

108. Note: this case was decided before passage of both the Ground Water Management Act and the 1969 Act (n. 105)

109. The real issue in Whitten v Coit was whether the State Engineer was bound to administer the non-tributary wells by the priority system under the then-existing statutes. While the court said that non-tributary ground water was not part of a natural stream and, hence, not subject to appropriation, later decisions, based on the Ground Water Management Act, certainly call this language in question, if they do not expressly overrule it.

110. Under the English common law, water was part of the land and subject to virtually no control

111. Most American jurisdictions favor systems involving reciprocal rights among neighboring landowners in water questions

112. Colorado Ground Water Management Act, 1965 (n. 105)
113. Note: A Survey of Colorado Water Law (n. 63) argues that the definition of designated ground water indicates that the General Assembly intended to apply the appropriation doctrine to all non-tributary ground water. Considering Whitten v Coit (nn. 107, 109), it is not clear whether the General Assembly could do so even if it wanted to. Further, Senate Bill 213 (n. 120) seems to indicate the contrary.

114. See n. 107

115. See n. 105

116. See n. 71


118. Division Engineers are responsible for administration of water rights in their divisions, except designated ground water rights. C.R.S. 1973, sec. 37-92-301

119. C.R.S. 1973, sec. 37-92-501 authorizes the Division Engineers to administer the "waters of the state" and this does not include non-tributary ground water (n. 105)

120. Adding C.R.S. 1973, sec. 37-90-137(4)

121. See n. 104

122. C.R.S. 1973, sec. 37-90-137(2)

123. See n. 120

124. This is not a clear declaration of policy. The general definition of designated ground water in the act is no help, because S.B. 213 specifically refers to other than those waters. (n. 104, 113)

125. C.R.S. 1973, sec. 37-92-205(1) grants the Water Courts jurisdiction over the "waters of the state", defined so as to exclude non-tributary ground water. But, the Water Courts may still decide what waters are part of this category. Further, denial of a well permit under C.R.S. 1973, sec. 37-90-137, is not binding on the Water judge. C.R.S. 1973, sec. 37-90-205(6). S.B. 213 speaks only to the actions of the State Engineer.

126. Safranek v Town of Limon, 123 Colo 330 (1951)

127. De Haas v Benesch, 116 Colo. 344 (1947)

128. Water for Energy (n. 3) p 35-36

129. See definition of "waters of the state", n. 105

130. This has already given rise to much litigation in both the South Platte and Arkansas River basins. See Fellhauer v People, 167 Colo. 320 (1969) and Kuiper v Well Owners Conservation Assn, 176 Colo. 119 (1971). Proposed amendments to the rules and regulations of the Division Engineer for the Arkansas River basin are currently being litigated in the Water Court in Pueblo.

131. There are already far more claims than water in the entire Colorado River basin in Colorado. If only a portion of these projects, plus federal and Indian reserved rights claims, take effect, Division Engineers will be forced to actively administer all appropriations in their divisions, including wells

132. Water for Energy (n. 3) does not even make the connection between ground water and the river compacts

133. The inequity consists of the Upper Basin being deprived of more than half the water in the Colorado River. See Water for Energy (n. 3) p 11-12 Weatherford and Jacoby (n. 1) p 195, 196

134. See n. 12

135. Both compacts deal only with the surface flow in the river

136. To the extent no diminution of flow results, or is delayed, the compacts would not be involved

137. The fact that the Upper Basin compact (n. 12) is silent on the subject of interstate ground water aquifers, tends to support the argument that these aquifers must be separately apportioned among the states. See Fischer, W.H., Management of Interstate Ground Water, VIII Nat. Res. Lawyer 521 (1975)

138. This conflict is at least partly involved in Case No. W-2514, Water Div. No. 5 (n. 4)

139. See nn. 65, 66

140. Colo. Const., Art XVI, Sec. 4

141. See n. 105

142. "...any structure or device used for the purpose or with the effect of obtaining ground water for beneficial use from an aquifer." C.R.S. 1973, sec. 37-90-103(21)

143. See nn. 4, 138

144. The 1969 Act created special Water Courts for each Division to hear all water matters. (nn. 84, 117) The Court for Div. No. 5, the Colorado mainstream basin in Colorado, sits in Glenwood Spgs.
146. C.R.S. 1973, sec. 37-90-137(2)
147. See text at n. 126
149. Hall v Kuiper, 181 Colo. 130 (1973)

150. The constitutional provisions only guarantee the right to appropriate previously unclaimed water

151. C.R.S. 1973, sec. 37-92-305(6) and -304 (3). While the burden of proof is still on the applicant in Water Court, it is generally easier to persuade the Court than the State Engineer that there is some unappropriated water available.

152. S.B. 97 amended C.R.S. 1973, sec. 37-92-102, -103, in particular adding 37-92-102 (3) which seeks to preserve the natural environment to a reasonable degree by water appropriations (or acquisition), by the water conservation board, of waters of natural streams and lakes. A pending bill, S.B. 453, would considerably weaken this amendment.


154. Colorado River Water Conservation District v Rocky Mountain Power Co., 158 Colo. 331 (1965) held a provision similar to that in S.B. 97, authorizing in-stream appropriations for wildlife preservation, invalid. The case turned on the point that, under existing case law, there had to be a diversion in order to have an appropriation and that the provision in issue was not a clear enough expression of the legislature's intent to overturn the case law. S.B. 97 is an extremely clear expression of intent and, if constitutional, should withstand attack. See text, at nn. 158, 159

What a diversion is, is doubtful. See Genoa v Westfall, 141 Colo. 533 (1960)

Case law implies that any use that promotes the economic development of the state is a "beneficial use"


156. C.R.S. 1973, sec. 37-92-103(4) (amended 1973) modifies the definition of beneficial use to fit the demands of conservationists and outdoor sportsmen, including impoundment of water for recreational purposes, including fishery and wildlife and appropriation of minimum flows that are required to preserve the natural environment to a reasonable degree.

157. Colo. Const. Art XVI, Sec. 6 establishes a sort of priority system for water use when the waters of any natural stream are not sufficient to serve all those who need them: 1st, domestic purposes; 2nd, agricultural purposes, and 3rd, manufacturing purposes.

The argument is that since those are the only uses mentioned, they are the only valid "beneficial uses." Not so; see City and County of Denver v Sheriff, 105 Colo. 193 (1940). The requirement that a diversion is a necessary part of an appropriation has also been rejected; see Larimer Cty v Peo. ex rel Luthe, 8 Colo. 614 (1885). Nor are scenic beauty and environmental protection ruled out as permitted uses of water; see Empire Water and Power v Cascade Town Co, 205 F. 123 (1913). See also n. 160

158. Cases No. W-2770 and W-2721, and others, Water Div. No. 5, Colorado (pending)

159. This is the "futile call" question, covered by both case law and statute. C.R.S. 1973, sec. 37-92-502(2)

160. The rule is that an appropriator cannot command the entire flow of the stream to satisfy relatively small diversion requirements. If his diversion structure is faulty, so much the worse for him. See Empire (n. 157) and Bender (n. 101) for application of the principle

161. The constitutional preference (n. 157) has been held to allow condemnation of water rights used for less-preferred uses, but not out-of-priority administration. See Town of Sterling v Pawnee Ditch Extension Co., 42 Colo. 421 (1908)

162. See n. 130
163. See n. 159
164. See nn. 130, 162
165. See nn. 83-88
166. The 1974 tabulation for Water Div. No. 5 showed well over 4,893 water rights and did not include any of the nearly 3,000 filed since 1969

167. In Water Div. No. 5 there is little administration until late in the summer. When the Cameo Call from the Grand Valley Project goes out, everything junior to 1902 is shut down. See n. 131

168. See nn. 12, 19, 132, 133
169. See nn. 15-24

170. La Plata River and Cherry Creek Ditch Co v Hinderlider, 93 Colo. 128 (1933)
171. See n. 133

172. Overuse of a state's share under the Upper Colorado River Compact (n. 12) (ends 1983), could require that state to forego diversions in a later year if the Upper Basin came up short of its 75 million acre feet in each of the ten years.

173. The Mexican treaty (n. 13) guarantees delivery to Mexico of 1.5 million acre feet per year. This quantity is not covered by the Colorado River compact, except by the requirement that the Upper Basin pass an additional 3/4 of a million acre feet to the Lower Basin each year.

Water for Energy (n. 3) p. 11-12

174. Minute No. 242 (n. 37)

175. Especially the statutes (n. 11) and Ariz. v Cal. (n. 14)

176. See n. 131

177. See n. 76

178. A quasi-independent body charged with the responsibility for supplying water to Denver and several suburban water systems.

179. Denver has benefited from a number of landmark decisions, including important transmountain diversion cases. See Denver v Sheriff (n. 157)

180. 16 U.S.C. secs 1311 and ff (1964)

181. We hear of one estimate that cost will exceed $4,000 per acre-foot of yield, vs approx. $1,500 with gravity feed.

182. Such as the conflict between the Forest Service plans for Eagle-Aspen Planning Area and the Fryingpan-Ark. project (P.L. 87-590)


184. Colorado's major oil shale deposits are in the Piceance Creek basin, tributary to the White River.

Water for Energy (n. 3) p 9-10

Westwide Study (n. 1) p 182

185. Water for Energy (n. 3) p 25-26, 51-52

186. Water for Energy (n. 3) p 25-26, 51-52

187. Water for Energy (n. 3) p 46-47

188. 16 U.S.C. sec. 1531 and ff

189. As, the snail darter, a tiny fish, has halted the Tellico Dam on the Little Tennessee and an obscure little flower threatens progress on the Dicky-Lincoln project in Maine.

190. See n. 11

191. See nn. 51,52


193. See n. 53

194. Originally, this project called for building a large reservoir in the largely unspoiled canyon of the Crystal River at Placita, followed by construction of an expensive tunnel system to bring the water to the Divide Creek basin, south of the Colorado River in Garfield County. The reservoir immediately drew fire. Directors of the West Divide Water Conservancy Dist. and the Citizens "Advisory Panel" are included in the doubters.

195. Most of the alternatives proposed emphasize agriculture at the expense of the industrial.
APPENDIX B

Acronyms and Definitions

BOUND  water separated from shale oil by centrifuging at 80°C

bound water  water separated from shale oil by centrifuging

CS  Controlled State; descriptor used for LERC's 20-kg simulated in-situ retort

FILT  retort water filtered through Millipore Type HA 0.45-μ filter paper

H₂O  whole retort water*

IGAS  input gas

LERC  Laramie Energy Research Center

LLL  Lawrence Livermore Laboratory

M  elemental mass

NBS  National Bureau of Standards

OFFGAS  off gas; all gases leaving the retort, includes both shale gas and output gas

OGAS  output gas; that portion of the input gas that leaves the retort as offgas; excludes shale gas

OIL  shale oil

RAW  raw oil shale

S  Small; descriptor used for LLL's 125-kg simulated in-situ retort

SGAS  shale gas; gas generated from pyrolysis of oil shale, excludes input gas

SOS  spent oil shale

STP  standard temperature and pressure

USGS  United States Geological Survey

*whole retort water  decanted portion of the product water coproduced with shale oil

XRF  x-ray fluorescence spectrometry

ZAA  Zeeman atomic absorption spectroscopy

Sampling and Sample Preparation

Four sample types were collected from each retorting system, described under "Experiments", each as indicated. These are: (1) raw oil shale, (2) spent oil shale, (3) shale oil, and (4) retort water. Offgases and input gases were not collected. Oil and water samples were not available for LLL run S-7. Procedures used to collect and prepare these samples for analysis are described below for each set of samples (LERC, LLL). The letters in parenthesis, after each subheading, are the acronyms used in this paper for the samples discussed under that subheading. These acronyms were listed previously under "Symbols and Acronyms."

LERC 20-kg Controlled-State Retort - Sample collection and preparation for raw oil shale, spent shale, shale oil and retort water samples for the LERC-controlled-state retort runs (CS-35, CS-56, CS-57, CS-59) are described below:

- Raw Oil Shale (RAW)
  Anvil Points, mine-run, oil shale was fractured with a sledge hammer, reduced in size to pass a 13-mm (1/2 in.) screen and separated into the 3-mm (1.8-in.) to 13-mm (1/2-in.) size range, using a shaker screen. This material was then riffled, stored in cardboard containers and used in approximately 20-kg lots to load the controlled-state retort. A 50-gm sample was collected from the 20-kg retort charge, ground to less than 3-mm (1/8-in.) in an alumina-face shatter box and then to less than 0.15-mm (100 mesh), with a majority passing 0.074-mm (200 mesh), in an alumina-jaw pulverizer.

- Spent Oil Shale (SOS)
  After retorting, a 0.51-m (20-in.) section at the top and bottom of the retorted shale column was discarded and the remaining 3.0-m (120-in.) section removed, reduced in size to less than 0.15-mm (100 mesh) with a steel-ring pulverizer, and riffled. A 50-gm sample of the riffled material was collected for analysis. Spent shales for runs CS-35, CS-56, and CS-57 were prepared as above. On run CS-59, the 50-gm spent shale sample was taken from the 3.0-m (120-in.) section of spent shale before

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pulverizing and riffling. This 50-gm sample was then reduced to less than 3 mm (1/8 in.) in an aluminafaced shatter box and pulverized to less than 0.15-mm (100 mesh), with a majority passing 0.074 mm (200 mesh), in an aluminajaw pulverizer. Therefore, CS-59 spent shale is not as representative of the retort charge as the spent shales in runs CS-35, CS-56, and CS-57.

- Shale Oil (OIL, BOUND)

Oil and water were collected in a receiver at the bottom of the retort. The oil and water were separated and a 20-ml sample of each collected for analysis. The 20-ml aliquot was divided into two 10-ml samples. One of these was analyzed at 60°C for As, Cd, Cu, Hg, Pb and Zn. The other sample was centrifuged at 80°C at 3000 rpm for 15 minutes. The separated water, designated "bound water" (BOUND), was collected in polyethylene bottles and analyzed directly for Pb, Zn, and Hg.

- Retort Water (H₂O)

The 20-ml sample of retort water described above, whole retort water, was collected in a pyrex bottle and analyzed directly for As, Cd, Cu, Hg, Pb and Zn.

LLL 125-kg Retort

Detailed information on sample collection and preparation for the LLL 125-kg retort runs (S-7, S-9, S-10, S-11) is presented by Fox (1977). Pertinent aspects of this procedure are summarized below for each major sample type:

- Raw Oil Shale (RAW)

A 25-kg sample of raw oil shale was collected from LLL's master batch. This master batch was prepared by LLL by (1) separating a 136 metric ton (150-ton) lot of mine-run, Anvil Points, oil shale into greater than and less than 10.1 cm (4-in.) fractions with a grizzly; (2) passing the less than 10.1 cm (4-in.) material through a roll crusher; and (3) screening the material to 25.4-mm (1-in.) to 12.7-mm (1/2-in.) size range. The 12.7-mm (1/2-in.) to 25.4-mm (1-in.) master batch material was used in all LLL retorting work reported here. The 25-kg sample drawn from the master batch was mixed and split into 500-gm lots. One of these lots was selected for analysis in this work. The selected lot was ground to less than 3-mm (1.8-in.) in an aluminafaced shatter box, pulverized to less than 0.15 mm (100 mesh), with a majority passing 0.074-mm (200 mesh) and split into 15-gm lots. Several of these 15-gm lots were selected for analysis in this work.

- Spent Oil Shale (SOS)

The spent oil shale, with the exception of run S-10, was further ground after each retort run in a Sturtevant rotary grinder with a built-in splitter. In addition to this grinding, spent shales from runs S-7 and S-9 were sieved in 22.9-cm (9-in.) brass-rimmed sieves with stainless steel mesh. A 25-kg sample was split from the rotary-ground material and the unground S-10 material and prepared for analysis as described above for raw oil shales.

- Shale Oil (OIL, BOUND)

The oil-water emulsion from the retort was collected in a receiver at the bottom of the retort and the gaseous stream passed through a condenser-demister train. Each condenser and demister was fitted with a drain system; oil and water condensed at each point in the train were combined in a single product tank. The water was decanted and a 1-liter aliquot of the oil collected for analysis. Two 20-ml samples were taken from the 1-liter aliquot. One of these was analyzed at 60°C for
As, Cd, Cu, Hg, Pb and Zn. The other sample was centrifuged at 80°C at 3000 rpm for 15 minutes. The separated water, designated "bound" water (BOUND), was collected in polyethylene bottles and analyzed directly for Pb, Zn and Hg.

- Retort Water (H₂O, FILT)
  A 1-liter aliquot was obtained from LLL and refrigerated in doubly wrapped polyethylene containers. The 1-liter sample was carefully mixed and two 20-ml samples collected. One of these was filtered through Millipore, Type HA 0.45-μ, filter paper and the filtrate analyzed directly for As, Zn, Pb and Hg. This sample type is referred to as "filtered water" (FILT). The other 20-ml sample was analyzed directly and is referred to as "whole retort water" (H₂O).

Analytical Methods

Two instrumental methods were used to determine the concentrations of As, Cd, Cu, Hg, Pb and Zn in the four types of oil shale samples used in this study. All six elements, in oils and retort waters, and Hg and Cd, in raw and spent oil shales, were analyzed by Zeeman atomic absorption spectroscopy (ZAA). Raw and spent oil shales were analyzed by energy-dispersive, x-ray fluorescence, spectrometry (XRF) for As, Cu, Pb and Zn. The reasons these techniques were selected (Fox 1977) are as follows:

Zeeman Atomic Absorption Spectroscopy (ZAA) - This technique is an extension of the conventional atomic absorption method in which the light source is placed in a magnetic field. Details of this technique are presented elsewhere (Hadeishi 1972; Hadeishi and McLaughlin 1976). The background correction feature of this technique allowed water and oil samples to be run directly by measuring known volumes of weights of sample into a Massman-type, carbon-tube furnace. The only sample treatment required was dilution in those instances when the level of an element was not within the instrument's dynamic range. Standard addition procedures were used for oil and water samples.

The performance of ZAA on National Bureau of Standards (NBS) and other reference materials is summarized in table B1. Data are also presented comparing ZAA results with those obtained by x-ray fluorescence. This comparison is important for two reasons: First, the two techniques were used jointly in mass balances for As, Cu, Pb and Zn. Therefore, an inter-instrumental comparison is required to assess variations in the results due to any instrumental bias. Second, XRF is a well-established analytical technique and more data are available on its performance on standards. Comparing ZAA results with the XRF results is equivalent to using oil shale materials analyzed by XRF as secondary standards. Data presented in table B1 show no evidence of instrumental bias and all results are within reported limits of error.

Data not presented here suggest that ZAA results for As in oils are low, due to molecule formation in the carbon-tube furnace. We are at present investigating this possibility.

Energy-Dispersive X-ray Fluorescence Spectrometry (XRF) - The XRF technique, used in this study, is described in detail elsewhere (Giauque and others 1977). Samples are prepared by pressing 2 grams of powder into a lucite cylinder, 2.5-cm OD, 1.27-cm ID, and 1.3-cm high. Accuracies of 5 percent or better are typically obtained, using analysis periods of 20 minutes.

The performance of this technique on NBS standards is summarized in table B1. Results are also presented comparing ZAA and XRF results on oil shale samples.
Table B1. - Analysis of Reference Materials by Zeeman Atomic Absorption (ZAA) and X-Ray Fluorescence (XRF) and Inter-Instrumental Comparison (ppm±2σ).

<table>
<thead>
<tr>
<th>Element</th>
<th>NBS Fly Ash (SRM 1633)</th>
<th>Orchard Leaves (SRM 1571)</th>
<th>USGS Standard Rock (AGV-1-A)</th>
<th>Raw Oil Shale (RAW-1)</th>
<th>Spent Oil Shale (SOS-10)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XRF(1)</td>
<td>ZAA</td>
<td>NBS</td>
<td>XRF(2)</td>
<td>ZAA</td>
</tr>
<tr>
<td>As</td>
<td>63±7</td>
<td>57±6</td>
<td>61±6</td>
<td>10.6±0.8</td>
<td>—</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;4</td>
<td>—</td>
<td>1.45±0.06</td>
<td>—</td>
<td>0.13±0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>133±4</td>
<td>—</td>
<td>128±5</td>
<td>12.6±0.06</td>
<td>—</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;12</td>
<td>—</td>
<td>0.14±0.01</td>
<td>—</td>
<td>0.20±0.4(6)</td>
</tr>
<tr>
<td>Pb</td>
<td>72±5</td>
<td>69±18</td>
<td>70±4</td>
<td>45.4±2.0</td>
<td>45±3</td>
</tr>
<tr>
<td>Zn</td>
<td>216±14</td>
<td>241±24</td>
<td>210±20</td>
<td>23.7±0.8</td>
<td>—</td>
</tr>
</tbody>
</table>

NOTES:

(4) Values not referenced were run during the analysis of the oil shale materials.
(5) See Table 3; RAW-1 is the raw oil shale for runs S-7, S-9, S-10 and S-11 and SOS-10 is the spent oil shale for run S-10.