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EIGHTH OIL SHALE SYMPOSIUM

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President

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# CONTENTS

Foreword ......................................................................................................................... v

Energy Input-Output Relationships in Shale Oil Production  
*Albert G. Melcher* ........................................................................................................ 1

Net Energy and Oil Shale  
*C. E. Clark and D. C. Varisco* .................................................................................. 3

Energy Requirements in an Oil Shale Industry: Input-Output  
Relationships Based on the Paraho Direct Combustion Retorting Process  
*S. Kumar Kunchal* ....................................................................................................... 21

Energy Efficiency of the Garrett In Situ Oil Shale Process  
*Chang Yul Cha and Donald E. Garrett* ........................................................................ 31

Energy Self-Sufficiency: the Goal for 1985  
*Granville Dutton* .......................................................................................................... 41

Resource Appraisal of Oil Shale in the Green River Formation,  
Piceance Creek Basin, Colorado  
*C. William Keighin* .................................................................................................... 57

Dawsonite: Its Geochemistry, Thermal Behavior, and Extraction  
from Green River Oil Shale  
*John Ward Smith and Neil B. Young* ......................................................................... 69

Recovery of Alumina from Dawsonitic Oil Shales  
*Frank C. Haas and Mark T. Atwood* ......................................................................... 95

The Thermo-Oxidizing Pyrolysis of Oil Shales  
*Vladimir Kashirsky and Aleksandr Koval* .................................................................. 109

In Situ Oil Shale Process Development  
*Richard D. Ridley and R. T. Chew, III* ...................................................................... 123

The Use of the Lurgi-Ruhrgas Process for the Distillation of Oil Shale  
*P. Schmalfeld* ................................................................................................................ 129

Accelerated Oil Shale In Situ Program of the U.S. Government  
*Andrew W. Decora and Harry R. Johnson* ................................................................. 147
Research and Development on Rubble In Situ Extraction of Oil Shale (RISE) at Lawrence Livermore Laboratory

Albert J. Rothman ................................................................. 159

The New Colorado Administration's Thoughts on Oil Shale

Harris D. Sherman ............................................................... 179

Simulated In Situ Retorting of Oil Shale in a Controlled-State Retort

J. J. Duvall and H. B. Jensen .............................................. 187

Excess Heat Generation in Retorting Oil Shale in Air

A. Lamont Tyler ................................................................. 207

Thermal Behavior of Oil Shale Blocks Heated in Air

Richard G. Mallon and William C. Miller .......................... 221

In Situ Retorting of Oil Shale Rubble: A Model of Heat Transfer and Product Formation in Oil Shale Particles


A Mathematical Model of an Oil Shale Retort

Donald W. Fausett ............................................................... 273
FOREWORD

After over 50 years of predictions that shale oil production in the United States is on the threshold of commercial development, there is still no commercial size plant scheduled for construction. In 1920, technical problems were the main roadblock to commercialization of shale oil production, while today the major obstacles also include environmental and political problems as well as the lack of necessary economic incentives.

In spite of the importance of environmental impact with respect to shale oil development, it was a deliberate decision not to include papers on environment in the program of the Eighth Oil Shale Symposium. This decision was made for two reasons: (1) the Seventh Oil Shale Symposium had dealt heavily with environmental and land-use planning, and (2) a survey of companies involved with field work in environmental aspects of oil shale development indicated more complete and definitive papers would be available in the fall of 1975 after another spring and summer of data collection. As a result the decision was made to limit the April meeting to papers that dealt with areas of shale oil production other than environmental and to schedule a special symposium on October 9th and 10th, 1975, restricted to “Environmental Aspects of Oil Shale Development.”

The need for efficient use and conservation of our energy resources is apparent to everyone today. In the past little attention was paid to energy efficiency of various sources of energy supply and no general ground rules were developed so that true comparisons could be made among energy sources. The keynote session of the Eighth Oil Shale Symposium was devoted to reporting “Input-Output Energy Studies for Development of Oil Shale Resources” and guideline discussions were encouraged. This provided a series of papers on net energy relationships as well as the limitations and restrictions of each of the studies. Hopefully this has given a better insight into the items that should be considered in all net energy studies and their relative importance.

Efficient use of other minerals found in oil shale deposits is also a necessary restriction on development of energy sources from oil shale. If properly handled, the recovery of these minerals can help defray part of the costs of mining and land reclamation as well as provide minerals needed for this country’s economic progress. Papers are included that pertain to other minerals found with oil shale as well as improvements in technology that will serve to make shale oil production more efficient and less costly.

The success of the symposium is due largely to the interest and dedication of the authors of the papers and the support of their employers which
permits and encourages them to make the results public. Appreciation is expressed to everyone participating, either as author, speaker or sponsoring company, who made this symposium possible. Special thanks are given to Jon Raese and the reviewer, Mark T. Atwood, who provided prompt and efficient publication of the proceedings.

James H. Gary  
Vice President for Academic Affairs  
Colorado School of Mines
ENERGY INPUT-OUTPUT RELATIONSHIPS IN SHALE OIL PRODUCTION

Comments by Panel Chairman

Albert G. Melcher

As our technological society moves from a period of cheap energy into a period in which energy will become more costly to deliver for end use, we are asking a number of questions which we did not ask 10 and 20 years ago. Some of these relate to resource depletion, some relate to international politics and economics, some relate to the ways in which we use our energy, and some relate to the technologies and economics of new sources of energy.

This latter subject—bringing major quantities of a new fuel to the American public—is the concern of this entire symposium. This panel, which will commence the entire session, melds that concern with the question of how we use our energy. One of the uses of energy is for making more energy. Another aspect of "use" is "wise use": do we waste energy, do we use it frivolously, do we use it with the welfare of future generations in mind? How and where can we use our energy, which is becoming more limited as resources are depleted, and more costly, in more effective ways?

These are major social concerns, and within the past year nearly everyone has recognized the need to conserve energy. Some talk of a 1985 reduction from trend consumption of 125 Q to 108 Q, others talk of 95 Q, but there is little basic disagreement on energy conservation. Nor is there significant disagreement on the need to develop new sources and new technologies.

So, in our oil shale programs, we now have the issue before us: "How much energy does it take to produce how much energy?" A number of people have addressed the matter, and some have quantified their assessment. We are fortunate in having three of them on the program today. Further, there has been a tremendous amount of heat without much light generated by some people, and a tremendous amount of misinformation. Should I say that we are fortunate that the protagonists of misinformation are not on the program?

Albert G. Melcher, Deputy Director for Operations, Colorado Energy Research Institute, P.O. Box 366, Golden, Colorado 80401.
Bear in mind that the speakers today are talking only about oil shale, not about all fossil fuels or all energy systems. Also, they will be talking about a portion of the total system which commences with geologic exploration and terminates with the end use, or final demand, for energy.

At the Colorado Energy Research Institute, we are conducting a study on “Net Energy Balances in Fossil Fuels.” Our study will be published late this year; hence, we do not have any definitive findings on data, study methodology or policy-related issues and “energy accounting systems” at this time. I will say, however, that there are a number of ways of defining the boundaries of the systems to be studied and of accounting methods for displaying the results of the balance or energy input-output calculations. Some of these will be discussed today. Also, there are a number of ways in which energy balance studies may be useful, and there are a number of reasons why they are of limited use and why other decision-making tools are more important. I am delighted to join with you in what should be a fascinating learning experience for all of us.
INTRODUCTION

Net energy is a concept that has received much attention lately in both technical circles and in the popular press. Much confusion has resulted from the many conflicting statements regarding the conclusions of net energy studies. It has frequently been stated or inferred that net energy analysis provides significant information not available from conventional economic analysis techniques. There are some persons who would have net energy analysis become the basis for major planning decisions. More specifically, the results of net energy studies, also known as energy balance studies, have been cited as the basis for not developing a shale oil industry.

We will define the concept of a net energy ratio and will apply it to a shale oil complex. Emphasis will be placed on the boundary problem and how it gives rise to some of the apparent discrepancies in quoted results. It is hoped that this discussion will help clarify some of the questions that have been raised regarding net energy yield of a shale oil complex.

DEFINITION OF THE NET ENERGY RATIO

The subject of net energy is frequently discussed in terms of the net energy yield and net energy ratio. Briefly, the net energy yield is the difference between the energy output of a project and the external energy supplied to the project. Since the numerical values normally quoted refer to net energy ratios, this method of expressing net energy will be used here. The basic definition of the net energy ratio is very simple. The formula is:

\[
\text{Net Energy Ratio (NER)} = \frac{\text{Energy Produced}}{\text{Energy Consumed in Production}}
\]
This ratio measures the energy received from a system for a unit of energy required by the system. Published estimates of the net energy ratio for a shale oil complex have varied widely. The major reason for this is differences in the calculation of the amount of energy consumed in production. These differences arise for two reasons. The first is a variation in the actual direct energy requirements of the system. The second is variations caused by differences in the boundaries used to calculate energy flows. With all due respect to the law of the conservation of energy, consumption, as used here, means the "conversion of energy from a readily usable form to an unusable form."

**SHALE OIL COMPLEX ENERGY FLOWS**

The energy flows shown in figure 1 were developed for a 100,000 barrel per stream day plant producing a high quality, fully refined, full range distillate fuel oil from 35 gal/ton Colorado oil shale. The processing scheme uses underground room and pillar mining, the TOSCO II retorting process, and surface disposal of the processed shale. The information is based on a definitive commercial design developed by a major independent engineering contractor at a cost exceeding $10 million. The energy flows shown in figure 1 quantify all the direct energy requirements associated with the construction, operation, and completion of a commercial shale oil plant and mine. Other than plant size, no changes have been made from the pro-

![Figure 1. Shale energy flows.](image)
posed 50,000 bbl/day Colony design. The products are shown exiting the complex on the right-hand side. They are oil, coke, and other products which include LPG and ammonia. Two energy inputs enter the complex from the left. These are electrical power and what has been termed "other external input." The energy flows can be treated in two categories—in-ternally provided energy and externally provided energy.

Internal energy consumptions are those quantities of energy that are generated and consumed within the physical boundaries of the shale oil complex. Examples include process fuel, boiler fuel, and diesel fuel for operation of the heavy equipment required in mining and process shale disposal. These items have been lumped together as fuel in figure 1. The magnitude of these energy flows was determined at each step from detailed calculations performed by the engineering contractor based on experimental data, which were developed during extensive operations of a semiworks scale experimental unit at a cost exceeding $25 million.

The external energy consumptions are those quantities of energy that are generated outside the boundaries of the shale oil plant. Examples include the energy components of exploration, research and development, plant construction, mine development, capital goods, and operating materials. In figure 1 the external energy flows are seen to be electric power which is 50 billion Btu per stream day and what we have classified as "other externals" which is 13 billion Btu per day. The electric power is the 200 megawatts of energy required for routine plant operations. This energy has been expressed at the fossil fuel equivalent of 10,000 Btu per kilowatt-hour required to produce the electric power. The actual energy delivered to the plant is approximately one-third of this value. The difference is accounted for by the low efficiency of the electric power generation step.

In the area of external energy consumption or subsidies, as they are sometimes referred to, one is faced with the problem of determining the energy components of nonenergy commodities. In most practical situations the actual consumptions of materials are difficult to determine. Even with the extensive engineering calculations performed to date on the proposed commercial shale oil plant, on many occasions we are forced to rely on the dollar values for determining material consumptions. However, whenever possible, we have used the actual estimated quantities of specific materials. An example of this is the explosives used in the mining operation. The subject of the actual energy requirements per dollar of expenditure in the various sectors of the economy is receiving much attention in several major universities. For the purposes of this study, we have used a value of 45,000 to 65,000 Btu per dollar. No expertise in this area of computation is claimed or implied. This conversion factor was taken directly from the
Oregon Energy Study. Since this value equates to a direct energy contribution to a commodity price in the order of 5 to 10 percent, it seemed reasonable for most sectors of the economy. If one prefers a different Btu per dollar conversion factor, sufficient detail is included in the Appendix to allow a recalculation of these results. Our experience has shown the outcome of the calculations to be relatively insensitive to reasonable variations in this conversion factor.

Estimates of the external energy inputs to a 100,000 barrel per stream day shale oil complex are shown in figure 2. These have been compared to the values presented in the Oregon Energy Study mentioned earlier. This study has been widely quoted as showing a shale oil facility to be a zero or negative net energy producer. The value of $456.7 \times 10^{12}$ Btu for the total external energy supplied during the plant life equates to the $63 \times 10^9$ Btu per stream day of electric power and other energy shown in figure 1, using a 20-year plant life. The two estimates of the external

<table>
<thead>
<tr>
<th>A.R.Co. Estimate</th>
<th>$\text{M} \text{Btu} \times 10^{12}$</th>
<th>Interim Oregon Energy Study</th>
<th>$\text{M} \text{Btu} \times 10^{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exploration and Research</td>
<td>30</td>
<td>2.0</td>
<td>2,920</td>
</tr>
<tr>
<td>Mining</td>
<td>61</td>
<td>18.7</td>
<td>26</td>
</tr>
<tr>
<td>Retorting and upgrading Capital goods</td>
<td>281</td>
<td>12.6</td>
<td>267</td>
</tr>
<tr>
<td>Construction fuel</td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating materials</td>
<td>6.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Subtotal</td>
<td>21.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pipelines and distribution</td>
<td>49.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total electric power</td>
<td>365</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total external energy input</td>
<td>456.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>External consumption</td>
<td>$4,044$</td>
<td>$8.8$</td>
<td>$3,842$</td>
</tr>
<tr>
<td>Net energy ratio</td>
<td>$\frac{456.7}{1,378}$</td>
<td>$2.8$</td>
<td></td>
</tr>
<tr>
<td>External Btu's consumed per 1,000 Btu output</td>
<td>113</td>
<td></td>
<td>359</td>
</tr>
</tbody>
</table>

Nominal Output — 100M b/d

Figure 2.—Comparison of external energy inputs.

energy inputs differ by a factor of three. The major contributors to this difference are in the estimate and treatment of construction energy, operating energies, and the energy component of operating materials.

ENERGY BOUNDARIES

To apply the concept of net energy, it is necessary to refine the definition presented previously. The ratio is sensitive to the boundaries imposed on an energy system. Two boundaries have frequently been used. In figure 3 the first boundary is superimposed on the energy flows shown previously in figure 1. The boundary is drawn so that all energy used by the complex, including internally generated fuel, crosses the boundary. This is called the "total consumption boundary" and produces a ratio called the "total consumption net energy ratio." The quantities used to calculate the ratio are shown in figure 4. The result is a value of 2.6 for the total consumption net energy ratio. In this definition the heating value of the processed shale is treated as an energy flow-through and not a consumption. The processed shale is handled in this way because, as in the case of the raw shale left unrecovered in the mine, the decision not to recover the energy is the result of economic and technical limitations. The energy of the shale, though lower in concentration, is not consumed.

A second boundary is superimposed on the basic shale oil energy flows to yield figure 5. The boundary is drawn to include the fuel internally
Output | External Consumption
---|---
Oil 480 | Electric power 50
Coke 42 | Other external 13
Other 32 | 
Total 554 | 63

Net energy = \( \frac{554}{63} = 8.8 \)

(All values in Btu's \( \times 10^9 \) per stream day)

**Figure 4.**—External consumption definition, net energy ratio.

**Figure 5.**—Shale energy flows with external consumption boundary.
produced and consumed by the complex. Using this boundary, the only energy defined as consumed is that energy which society makes available external to the physical boundary of the shale oil complex. This boundary leads to what is called the "external consumption definition." The quantities listed in figure 6 are identical to those shown in figure 4, except that the fuel produced and consumed within the complex is not listed as a consumption. The resulting external consumption net energy ratio is 8.8.

It should be noted that the electrical power is generated external to the energy boundaries of the shale oil complex. We believe this to be appropriate when considering only one plant. However, if one is examining a shale oil industry, it is reasonable to assume that power would be generated using products from the shale oil industry itself. The boundary could then be redrawn to include the power plant. In this case, the external net energy ratio would be in the range of 35 to 39. The decision not to generate captive power was an economic one based on the incompatibility of a power plant with a single shale oil facility. This problem would not exist when a number of plants are in operation. The contrast between this net energy ratio and those discussed previously illustrates the sensitivity of a net energy analysis to boundary definitions. This characteristic is a limitation of net energy analysis.

<table>
<thead>
<tr>
<th>Output</th>
<th>Consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>Fuel</td>
</tr>
<tr>
<td>480</td>
<td>148</td>
</tr>
<tr>
<td>Coke</td>
<td>Electric power</td>
</tr>
<tr>
<td>42</td>
<td>50</td>
</tr>
<tr>
<td>Other</td>
<td>Other external</td>
</tr>
<tr>
<td>32</td>
<td>13</td>
</tr>
<tr>
<td>Total</td>
<td></td>
</tr>
<tr>
<td>554</td>
<td>211</td>
</tr>
</tbody>
</table>

Net energy \( = \frac{554}{211} = 2.6 \)

(All values in Btu's \( \times 10^9 \) per stream day)
APPLICATION OF THE TOTAL CONSUMPTION DEFINITION

The basic energy flows developed for a 100,000 bbl/day shale oil complex have been presented. Results have been developed using two possible definitions of the net energy ratio. The interpretation and application of these results will be discussed next.

The total consumption definition is a measure of the energy output of a system compared to the total energy consumed by the system. In this definition, a large contributor to the energy consumption is the energy content of the resource used in the operation of the energy system. In considering the areas where this definition provides useful information, two are apparent. The first is in reserve calculations. The total consumption definition recognizes that a considerable portion of an energy reserve may be consumed in making a reserve available to society. The total consumption definition provides a measure of this. However, it should be noted that the results of such an analysis agree with the conclusion that would be arrived at using a standard thermal efficiency calculation. A second area where the total consumption definition can provide additional information is in ranking alternative recovery systems for a particular resource. Because this definition considers all of the consumptions required to produce a unit of energy output, the energy efficiency of alternative recovery systems can be compared. The most efficient system will have the highest net energy ratio. However, it should be emphasized that because a system has a high net energy ratio it is not necessarily superior to another system. Economics must remain the final basis for such a judgment.

APPLICATION OF THE EXTERNAL CONSUMPTION DEFINITION

The external consumption definition considers only those energies generated external to the energy system as consumptions. In doing so, this definition recognizes the fact that reserves in place are not available to society and thus, in the economic sense, have no opportunity costs. This is not to say that they do not have value. It only recognizes the fact that in order to make an energy resource available to society, it is essential to consume a portion of that resource. This energy consumption is not charged against the project. The external consumption definition is a measure of the energy returned to society for a unit of energy taken from society. As the calculation shown previously demonstrates, a shale oil facility would make available 8.8 Btu for every Btu it received.

The external consumption definition sheds light in two areas. First, in comparing alternative resources for development it provides an indication of the energy investment that will be required on the part of society to achieve the desired increase in energy output. It should be noted that this
is the only form of a net energy ratio for which the value of 1.0 has significance. By this definition, a project having a net energy ratio less than one is receiving more energy from society than it is returning. It thus can be properly termed a “negative net energy contributor.” However, because of the many factors not considered by net energy analysis, a negative net energy contribution is not necessarily undesirable. Using any other definition of a net energy ratio, it is possible for a project to have a ratio less than one and still provide a net positive flow of energy. This is true of the total consumption definition.

An extension of comparing alternative resources is the use of this information in social planning. Society can use the information provided by net energy analysis as one factor in making decisions regarding the placement of its available energy investments.

THE VALUE OF NET ENERGY ANALYSIS

Net energy analysis techniques can be helpful in certain areas. The concept stresses the total system approach to solving large-scale energy problems. As uncertainties in the energy sector become more complex, narrow analysis of the components of energy systems must be augmented with consideration of the system as a unit. Net energy analysis stresses this point of view. Reserve analysis benefits from net energy concepts. As was discussed earlier, looking at in-place reserves can be deceptive. Sometimes net energy analysis can also provide insight not furnished by conventional analysis. For example, under existing pricing conditions, it is possible to burn 10 million Btu of natural gas to make the electricity to pump 6 million Btu out of a stripper well. The process would be a net energy loser, but still can return a profit of $5.80 (1 x $10/bbl − 10 x $.42/MCF).

Net energy analysis also has many shortcomings. The concept neglects the quality of an energy source as well as the time and place of availability. Energy in the form of electricity is more useful to society than an equivalent amount of energy in the form of fossil fuel. Energy available in Alaska is not the same as energy available at the marketplace. However, net energy analysis would value them equally. Side effects are neglected by net energy analysis. Some energy sources have low concentrations of polluting elements like sulfur and nitrogen, but these differences are not considered by energy accounting.

Using the ratio method of displaying net energy magnifies differences. The net energy ratio for four systems is shown in figure 7. There is a 5 percent difference in thermal efficiency between the first two systems and the last two systems. However, the net energy ratios magnify the differences between the two systems. Some discussions of net energy have used inconsistent comparisons. It is necessary that product and location be comparable. Comparisons have been made between unrefined Middle
Eastern oil at the wellhead and the refined product of a shale oil complex. Neither location nor product is similar in this example.

The net energy ratios for a number of energy sources are compared in figure 8. Because complete information is not available on all of these systems, they have not been analyzed in the same detail as the shale oil complex. However, care has been taken to identify all of the direct energy requirements. The calculation of the shale oil case demonstrated that for this type of project the energy contribution of nonenergy commodities is small compared to the large energy flows generated within an energy delivery system. Therefore, these results are believed to be comparable.

All of the results presented in figure 8 will not be discussed here. However, it is worthy of note that our calculations show conventional offshore petroleum to have a net energy ratio in the range of 7 to 15. This is considerably different than some of the values that have been compared to those for a shale oil complex in the popular press. Frequently, quoted values for conventional petroleum neglect the energy required for refining the crude to marketable products. Our calculations indicate that in situ retorting would have a higher external net energy ratio than surface processing facilities. Its total consumption net energy ratio is approximately equal to surface retorting. The net energy yield of western coal is high compared to other sources of energy. This is because the coal is low sulfur and requires no processing before consumption. Coal gasification has a low net energy yield because of its inherent low thermal efficiency.

The list in figure 8 is not exhaustive. Furthermore, as was pointed out earlier, different net energy ratios are possible by redefining the energy delivery system or drawing a different energy boundary. This characteristic

<table>
<thead>
<tr>
<th>System Thermal Efficiency</th>
<th>Net Energy Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>95%</td>
<td>19</td>
</tr>
<tr>
<td>90%</td>
<td>9</td>
</tr>
<tr>
<td>65%</td>
<td>1.9</td>
</tr>
<tr>
<td>60%</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure 7.—Net energy ratios of four systems.
Table:

<table>
<thead>
<tr>
<th>Source</th>
<th>External Consumption Definition</th>
<th>Total Consumption Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stripper well (3 b/d)</td>
<td>1.9</td>
<td>1.7</td>
</tr>
<tr>
<td>Offshore well refined product</td>
<td>14.9</td>
<td>7.4</td>
</tr>
<tr>
<td>Shale complex</td>
<td>8.8</td>
<td>2.6</td>
</tr>
<tr>
<td>In-situ retorting</td>
<td>15.0</td>
<td>2.7</td>
</tr>
<tr>
<td>tar sands</td>
<td>15.9</td>
<td>5.6</td>
</tr>
<tr>
<td>Western coal (delivered)</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>Coal gasification</td>
<td>1.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Figure 8.—Net energy ratio comparison with conventional petroleum products.

is a serious limitation of the net energy concept as an analysis tool. The results can be manipulated to arrive at misleading conclusions. Net energy has been used, we believe unjustly, to oppose the development of a shale oil industry. As the results presented here demonstrate, shale oil plants will be significant net energy producers.

APPENDIX

I INTRODUCTION

The energy flows shown in figure 1 were developed for a 100,000 barrels per stream day (BPSD) plant producing high quality shale oil from 35 gallons per ton Colorado oil shale using underground room-and-pillar mining and the TOSCO II retorting process. The information is based on a definitive commercial design developed from experimental data by an independent engineering contractor at a cost exceeding $10 million. The objective of these calculations is to quantify all of the direct energy...
flows associated with the construction, operation and completion of a commercial shale oil plant and mine.

II Methodology and Definitions

A. Internal Energy Flows

Internal energy flows and consumptions are those quantities of energy that are generated and consumed within the boundaries of the shale oil complex. Examples include process fuel, boiler fuel, plant fuel and diesel fuel for heavy equipment operation in mining and processed shale disposal operations. The magnitude of these energy flows was determined at each step from detailed engineering calculations performed by an independent engineering contractor using experimental data. This data was developed during extensive operations of a semiworks scale experimental unit at a cost exceeding $25 million.

B. External Energy Flows

The external energy consumptions are those quantities of energy that are generated outside the boundaries of the shale oil plant. Examples include the energy components of exploratory research and development, plant construction, mine development, capital goods, and operating materials. The methodology used in developing these energy flows differs from that of the Oregon Interim Energy Study.* Where energy consumptions were in the form of energy products, such as construction fuel or explosives, the amounts were based on engineering estimates. For capital goods and operating materials, the dollar values were converted to energy flows using the Btu to dollar conversion factors presented in the Oregon report. The actual quantity of capital goods and operating materials was again based on contractor estimates. Pipeline construction and operating costs were developed from Atlantic Richfield Company information.

III Internal Energy Consumption

During operation, the shale oil plant provides all its own operating fuel requirements from the resource base. Those requirements include:

(1) diesel fuel for mining equipment;
(2) process fuel for retorting and upgrading;
(3) boiler fuel of process steam;
(4) hydrogen plant feed and fuel;
(5) mobil equipment fuel for processed shale disposal.

---

The total fuel requirements are:

\[
\text{Total fuel} = \frac{24,667 \text{ BPSD} \times 6.0 \text{ MM Btu/bbl}}{148 \times 10^6 \text{ Btu/D}}
\]

IV \hspace{1em} \textbf{EXTERNAL ENERGY CONSUMPTIONS}

\textit{A. Exploration Research and Development}

The total expenditures for exploration, research and development for the proposed Colony Development Shale Oil Complex* are $30 million. Since much of the R&D expenditures will not have to be repeated for future plants, these funds should be amortized over the expected number of plants. However, because of the uncertainty in oil shale development, and to be conservative regarding any additional future expenditures, the total amount will be charged to the one plant. Using the general energy charge rate of 68,000** Btu/$, energy flow becomes:

\[
\frac{\$30 \times 10^8}{x 68 \times 10^3 \text{ Btu/} $} = 2.0 \times 10^{12} \text{ Btu}
\]

\textit{B. Mining and Crushing}

\textit{Capital Goods}

The total capital equipment and facilities cost for a 132,000 ton/day room-and-pillar mine and associated crushing plant is estimated to be $61 million. Using the energy conversion factor for manufactured goods of 45,000 Btu/$ and an erected capital cost to capital goods factor of 55 percent, we get:

\[
\frac{\$61 \times 10^8}{x 45 \times 10^3 \text{ Btu/} $} = 2.7 \times 10^{12} \text{ Btu}
\]

\textit{Operating Material}

- Explosives

Room-and-pillar mining of 132,000 T/D is estimated to require 37 T/D of explosives. Using the estimated energy conversion factor of 50 x 10^6 Btu/ton (25,000 Btu/lb).

---

*Colony Development Operation is a four-company venture consisting of Atlantic Richfield Co., The Oil Shale Corp., Shell Oil Co., and Ashland Oil Co.

Total explosives = (37 T/D)(20 yr)(365 D/yr)* = 268,000 ton

Energy flow
\[
\begin{align*}
&= 268 \times 10^3 \text{ ton} \\
&\times 50 \times 10^6 \text{ Btu/ton} \\
&= 13.4 \times 10^{12} \text{ Btu}
\end{align*}
\]

- Maintenance Materials

Maintenance materials are estimated to be $1.9 million per year.
\[
\begin{align*}
&= \frac{\$1.9 \times 10^8 \text{ per year}}{20 \text{ year}} \\
&= \frac{\$38 \times 10^6}{x 45 \times 10^3} \\
&= 1.7 \times 10^{12} \text{ Btu}
\end{align*}
\]

Construction Energy

Direct construction fuel requirements are estimated to be 1.4 percent of capital goods costs. Contractor estimates of construction fuel requirements for the 30-month construction period received after this calculation was made, show the amount to be 0.8 percent. Using a conversion factor of \(1 \times 10^6 \text{ Btu/\$} (6/bbl)\), we get:
\[
\begin{align*}
&= \frac{\$61 \times 10^8}{x 0.014} \\
&= \frac{0.88 \times 10^6}{x 1 \times 10^6 \text{ Btu/\$}} \\
&= 0.88 \times 10^{12} \text{ Btu}
\end{align*}
\]

Operating Fuel

All operating fuel (diesel) is generated by the complex rather than being purchased and thus is not an external consumption.

Summary of Mining and Crushing Energy
\[
\begin{align*}
\text{Capital goods} & \quad 2.7 \\
\text{Operating material} & \quad 13.4 \\
\text{Maintenance} & \quad 1.7 \\
\text{Construction fuel} & \quad 0.9 \\
\text{Total} & \quad 18.7
\end{align*}
\]

*Assumed 365 stream days/year, downtime will extend required operation life.
C. Retorting and Upgrading

Capital Goods
The total capital goods for a 100,000 barrels per stream day retorting and upgrading facility producing a premium low sulfur fuel oil is $281 million. Thus, the energy flow is:

\[
\frac{281 \times 10^8 \times 45 \times 10^3 \text{ Btu} / \$}{12.6 \times 10^{12} \text{ Btu}}
\]

Maintenance Material
The total operating materials for a 20-year life are estimated to cost $135 million.

\[
\frac{135 \times 10^8 \times 45 \times 10^3 \text{ Btu} / \$}{6.1 \times 10^{12} \text{ Btu}}
\]

Construction Fuel
Construction fuel for the retort and upgrading sections was estimated to be 1 percent of capital goods.

\[
\frac{281 \times 10^8 \times 0.01}{2.8 \times 10^6 \times 1 \times 10^6 \text{ Btu} / \$}
\]

Operating Fuel
All operating fuel is generated by the complex rather than being purchased and thus is not an external consumption.

Summary of Retorting and Upgrading Energy

<table>
<thead>
<tr>
<th></th>
<th>Btu x 10^{12}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital goods</td>
<td>12.6</td>
</tr>
<tr>
<td>Maintenance material</td>
<td>6.1</td>
</tr>
<tr>
<td>Construction fuel</td>
<td>2.8</td>
</tr>
<tr>
<td>Total</td>
<td>21.5</td>
</tr>
</tbody>
</table>

D. Transportation
Shipment of the product from the previously planned plant location will require 200 miles of new pipeline to connect with existing pipeline networks. The energy cost of constructing these 200 miles, plus the operating costs for a 1000-mile delivery radius, was calculated.
New Pipeline Capital

200 mi of 8" schedule 40 pipe

\[(200 \text{ mi})(22 \text{ lb/ft})(5280 \text{ ft/mi}) = 23 \times 10^9 \text{ lb} \]

\[(11.6 \times 10^3 \text{ ton})\]

\[
\begin{align*}
&11.6 \times 10^3 \text{ ton} \\
&\times 56 \times 10^6 \text{ Btu/ton} \\
&= 65 \times 10^{12} \text{ Btu}
\end{align*}
\]

Construction Energy

The 200-mile pipeline is estimated to cost $50 \times 10^8$ dollars. Because of the large amount of excavation required for construction, fuel costs were estimated to be 6 percent of total capital.

\[
\begin{align*}
&\$50 \times 10^8 \\
&\times 0.06 \\
&= 3.0 \times 10^8 \text{ Btu/\$} \\
&\times 1 \times 10^8 \text{ Btu/\$} \\
&= 3.0 \times 10^{12} \text{ Btu}
\end{align*}
\]

Maintenance Materials

Maintenance materials for the 20-year life are assumed to equal the initial materials costs. Therefore:

\[
\text{Maintenance materials} = 0.65 \times 10^{12} \text{ Btu}
\]

Operating Energy

Pipeline operating energies were estimated from the energy requirements of existing Atlantic Richfield Company pipeline information. These energy requirements are estimated to be 30,000 Btu/bbl for the 1000-mile delivery.

\[
\begin{align*}
&730 \times 10^6 \text{ Bbl} \\
&\times 30 \times 10^3 \text{ Btu/bbl} \\
&= 21.9 \times 10^{12} \text{ Btu}
\end{align*}
\]

Summary Pipeline Costs

<table>
<thead>
<tr>
<th></th>
<th>Btu $10^{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital goods</td>
<td>0.7</td>
</tr>
<tr>
<td>Construction energy</td>
<td>3.0</td>
</tr>
<tr>
<td>Maintenance materials</td>
<td>0.7</td>
</tr>
<tr>
<td>Operating energy</td>
<td>21.9</td>
</tr>
<tr>
<td>Total</td>
<td>26.3</td>
</tr>
</tbody>
</table>

Distribution Costs

Since the final distribution system is existing, it is not normally included as part of the shale oil complex and thus no definitive contractor esti-
mates are available. Therefore, it was assumed that the final distribution energies calculated in the Oregon report\(^*\) are accurate.

**Distribution:**

\[
\text{Energy} = 23.2 \times 10^{12} \text{ Btu}
\]

**E. Electrical Requirements**

As stated earlier, the shale oil complex provides all of its own operating fuel requirements. However, electric power requirements are satisfied by purchase from a local electric utility. For simplicity of calculation, rather than report these power usages for each plant section, they are reported collectively here. The total operating electric load has been estimated by a contractor to be 200,000 kw. As is convention, electric power is charged at its fossil fuel heat rate of 10,400 Btu/kwh.

Total kilowatt-hours

\[
(200,000 \text{ kw})(24 \text{ hr/day})(365 \text{ day/yr})(20 \text{ yr}) = 35 \times 10^9 \text{ kwh}
\]

Fossil fuel energy required

\[
\frac{35 \times 10^9 \text{ kwh}}{365 \times 10^{12} \text{ Btu}}
\]

**F. Construction Fuel**

The construction fuel requirements were estimated as a percentage of capital costs for the plant sections. They total 3.7 \times 10^{12} \text{ Btu} for mining, crushing, retorting and upgrading. Subsequent to making these estimates, the actual energy requirements were estimated by a contractor for site preparation, road construction, mine development, plant construction and plant startup. The sum is 1.8 \times 10^{12} \text{ Btu}. Thus, the estimates made as a percent of capital are seen to be on the high side.

**G. Summary-External Energy Consumptions**

<table>
<thead>
<tr>
<th>Item</th>
<th>Btu \times 10^{12}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exploration &amp; research</td>
<td>2.0</td>
</tr>
<tr>
<td>Mining and crushing</td>
<td>18.7</td>
</tr>
<tr>
<td>Retorting and upgrading</td>
<td>21.5</td>
</tr>
<tr>
<td>Pipeline</td>
<td>26.3</td>
</tr>
<tr>
<td>Distribution</td>
<td>23.2</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td><strong>91.7</strong></td>
</tr>
<tr>
<td>Electric power</td>
<td>365.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>456.7</strong></td>
</tr>
</tbody>
</table>

Daily Energy Flows

Days = (365)(20) = 7300

Power: \( \frac{365 \times 10^{12}}{7300} = 50 \times 10^9 \text{ Btu/D} \)

Other: \( \frac{91.7 \times 10^{12}}{7300} = 12.6 \times 10^9 \text{ Btu/D} \)

These values appear as daily energy flows in figure 1.
ENERGY REQUIREMENTS IN AN OIL SHALE INDUSTRY: BASED ON PARAHO’S DIRECT COMBUSTION RETORTING PROCESS

S. Kumar Kunchal

The objective of an oil shale industry is to produce an alternate source of energy to help alleviate dependence on imported hydrocarbons. During the process of mining, crushing, retorting and refining, the industry must consume energy to operate the facility. The purpose of the author is to identify the source, amount, and the net energy balance of an oil shale industry. Energy requirements for coal and natural crude oil, and alternate sources of fossil fuel are also analyzed on a comparable basis as major suppliers of energy, and an overall energy balance is computed. To compare coal, oil shale, and natural crude oil, all have been converted to a common Btu index* of substitute natural gas (SNG), electricity, and liquid fuels (gasoline, jet fuel, etc., for transportation).

Oil shales contain varying amounts of kerogen. This energy content of oil shale is generally defined as so many gal/ton grade. However, total energy present in oil shale is a combination of heating value of the kerogen, gases and other combustible matter present. For example, although low in sulfur, sulfur content of oil shale has a heating value of 4,000 Btu/pound. Heating value varies from grade to grade. A 28 gal/ton oil shale grade has a gross heating value of 2,600 Btu/pound of rock. By comparison, typical Indiana and Illinois coal has a heating value of 10,000 Btu/pound. Lignite in the western states has a heating value of 6,000 to 7,000 Btu/pound.

S. Kumar Kunchal, Paraho Oil Shale Demonstration, Inc., 300 Enterprise Building, Grand Junction, Colorado 81501.

*For this comparison, energy is defined in Btu. For example, 1 cubic foot of natural gas contains about 1,000 Btu of energy and 1 barrel of crude contains about 6,000,000 Btu of energy.
MINING

For this study underground mining has been assumed. Preliminary mine design dictates that one mine would be required to support each 50,000 bbl of refinery capacity. It would produce about 70,000 tons/day of rock. Energy required to mine oil shale is in the form of electric power for hoisting converted matter, ventilation and lighting, and diesel fuel for hauling, loading, scaling, and roof bolting equipment, etc. Total energy required in mining represents about 1 to 1.5 percent of the energy extracted or has a thermal efficiency of about 98.5 to 99 percent. This does not include oil shale left (about 40 percent) for roof support which, by comparison, is far less than natural crude oil (about 66 percent of crude oil is left behind in the ground during the production process). A detailed breakdown of the energy required follows:

<table>
<thead>
<tr>
<th>Electric Power</th>
<th>70,000 tons/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production shaft &amp; hoisting</td>
<td>10,500 hp</td>
</tr>
<tr>
<td>Men &amp; material shaft</td>
<td>1,100</td>
</tr>
<tr>
<td>Mine ventilation</td>
<td>7,950</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>19,550 hp</td>
</tr>
</tbody>
</table>

**Electric Power**

<table>
<thead>
<tr>
<th>Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ventilation heating during winter</td>
</tr>
<tr>
<td>Drilling</td>
</tr>
<tr>
<td>Fuel oil used in blasting mixture</td>
</tr>
<tr>
<td>Roof bolting</td>
</tr>
<tr>
<td>Scaling</td>
</tr>
<tr>
<td>Loading</td>
</tr>
<tr>
<td>Hauling</td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
</tbody>
</table>

CRUSHING

Paraho's retorting process requires crushed rock in the range of +½ and -3½ inch. Crushing requires energy in the form of electric power for crushers and conveyor belts. Fines produced are in the range of 6 to 10 percent of the material fed to crushers. Thermal efficiency* of this step is in the range of 89.5 to 93.5 percent depending upon fines produced, that is, less than ½ inch in size and not usable in the retorting process.

*Thermal efficiency = \[
\frac{\text{total Btu output from the process}}{\text{total Btu input to the process}} \times 100
\]
RETORTING

Paraho's direct combustion retort is assumed. In this process raw oil shale is fed cold to the retort. The rock descends by gravity and the oil-gas mixture flows upwards. Retorting heat is supplied by combustion of about 40 percent of the carbon residue in the retorted shale. A part of the gas produced is circulated through the bottom of the retort thus recovering sensible heat from retorted shale.

Two cases using different parameters have been developed. For a 28 gal/ton and a 90 percent Fischer assay liquid yield, the overall thermal efficiency of retorting jumps to about 92 percent.

PREREFINING

Prerefining reduces the pour point and viscosity of shale oil so that it can be transported by pipeline. It usually consists of converting crude shale oil to synthetic crude and removing sulfur and nitrogen. Synthetic crude is a more desirable feed stock to refineries and can readily be converted to motor gasoline, jet fuel or heating oil.

Shale oil can be processed to synthetic crude by using a combination of crude distillation, coking, and hydrotreating. Overall thermal efficiency of such a refinery is estimated to be in the range of 95 percent.

RETORTED SHALE DISPOSAL

Energy required to dispose of retorted shale, including putting a layer of natural cover over it and watering to revegetate (pumping costs, etc.) is estimated to be less than ½ percent of the energy recovered from the oil shale industry.

FINAL REFINING OF SYNTHETIC CRUDE TO LIQUID FUELS

Studies compiled by various oil companies indicate overall thermal efficiency of a typical sweet crude based refinery is in the range of 93 percent. Synthetic crude is a more desirable feed stock since it has already been partially refined. A refinery based on synthetic crude as feed stock is expected to have an overall thermal efficiency of about 95 percent.

OVERALL THERMAL EFFICIENCIES

For an oil shale complex starting with mining and producing synthetic crude, the overall thermal efficiency is in the range of 67 to 78 percent, depending upon the shale grade, fines loss, and liquid yield.
In figures 1 and 2, we summarize the energy requirement for a nominal 100,000 barrel per day synthetic crude oil shale complex. In Case A (fig. 1), we assume a conservative approach, namely:

1. A 28 gal/ton oil shale grade;
2. 10 percent of oil shale extracted is in fine gravel and is used to cover retorted shale;
3. 90 percent Fischer assay liquid yield.

In Case B (fig. 2), we assume a more optimistic approach, namely:

1. A 35 gal/ton oil shale grade;
2. 6 percent of oil shale extracted is in fine gravel and is used to cover retorted shale;
3. 100 percent Fischer assay liquid yield.

COMPARISON WITH OTHER FOSSIL FUELS

In tables 1 through 3, we summarize conversion of oil shale, coal and natural crude to transportation liquid fuels (motor gasoline, jet fuels, etc.), substitute natural gas, and electricity, respectively.

CONCLUSION

In converting to liquid fuels, the oil shale industry is expected to use 25 to 35 percent of the energy it produces. Coal requires about 35 percent or more. As the technology progresses and experience is gained, there is a good probability of improving these overall thermal efficiencies. There are already some designs on the drawing board (such as steam and oxygen injection) which have a potential of cutting down the energy requirements in retorting oil shale.

In converting oil shale to substitute natural gas, 30 to 40 percent of the energy is consumed compared to 35 to 45 percent for coal, owing to the much greater amount of hydrogenation required to convert coal to methane (CH₄), since coal has less hydrogen than oil shale kerogen.

In converting oil shale or high sulfur coal to electricity via the clean fuels route, about 75 percent of the energy available is consumed because the thermal efficiency of producing electricity by burning fuel under a boiler is only 35 percent.

OBSERVATIONS

Conservation of energy is of ever-increasing importance. Economic and technical viability are continuing essentials. Natural crude oil and natural gas, while ideal sources of liquid fuels for transportation and home heating, respectively, are declining in the United States. Low sulfur
西部煤炭最适合作为锅炉燃料来发电，但它位于远离市场的地区，运输或传输成本昂贵。为了减少我们对外国石油的依赖，所有可用的能源都必须被开采并转换成各种形式的燃料来满足我们的需求。石油页岩是一个有前途的热效率高且能为我们提供一小部分液态燃料需求的来源。页岩的副产品以氨的形式用于化肥和低热值天然气用于发电，将代表额外的好处给石油页岩国家。
CASE "B"
35 gal/ton oil shale
6% of Raw Shale as Fines to Disposal
100% Fischer Assay Liquid Yield

823x10^6 Btu/D
MINING
132,766 T/D
678 B.P.D.
671,396 KWhr/D

7,966 T/D
CRUSHING
124,800 T/D
407,748 KWhr/D
774x10^6 Btu/D

539,136 KWhr/D
RETORTING
Used + 50x10^6 Btu/D
100x10^6 Btu/D

104,000 B.P.D.
Crude shale oil

Sulfur 94 T/D

OVERALL THERMAL EFFICIENCY = 78%

Figure 2.—Case B: energy requirement for an oil shale complex at 35 gal/ton oil shale grade.
Table 1.—Fossil fuel to transportation liquid fuels (% energy required for each of the following steps)

<table>
<thead>
<tr>
<th></th>
<th>Oil Shale</th>
<th></th>
<th>Coal</th>
<th></th>
<th>Crude Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Case A</td>
<td>Case B</td>
<td></td>
<td>Eastern (Sub-bitu)</td>
<td>Western (Lignite)</td>
</tr>
<tr>
<td>Mining or Pumping</td>
<td>1.5</td>
<td>1.1</td>
<td></td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Crushing and/or</td>
<td>10.5</td>
<td>6.5</td>
<td></td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Transportation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Retorting and/or</td>
<td>16</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquification</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-refining to get</td>
<td>9</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Syn. Crude</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refining</td>
<td>5</td>
<td>5</td>
<td></td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Overall Thermal</td>
<td>64%</td>
<td>74%</td>
<td></td>
<td>65%</td>
<td>62%</td>
</tr>
<tr>
<td>Efficiency</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 2: Fossil fuel to synthetic natural gas (SNG) (% energy required for each of the following steps)

<table>
<thead>
<tr>
<th></th>
<th>Oil Shale</th>
<th></th>
<th>Coal</th>
<th></th>
<th>Crude Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Case A</td>
<td>Case B</td>
<td>Sub-bitu</td>
<td>Lignite</td>
<td>Sour</td>
</tr>
<tr>
<td>Mining or Pumping</td>
<td>1.5</td>
<td>1.1</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Crushing and/or</td>
<td>10.5</td>
<td>6.5</td>
<td>2.5</td>
<td>3.0</td>
<td>1</td>
</tr>
<tr>
<td>Transportation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Retorting</td>
<td>16</td>
<td>8</td>
<td>45</td>
<td>35</td>
<td>17</td>
</tr>
<tr>
<td>Gasification</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overall Thermal Efficiency</td>
<td>61%</td>
<td>70%</td>
<td>53%</td>
<td>63%</td>
<td>82%</td>
</tr>
</tbody>
</table>
Table 3.—Fossil fuel to electric power (% energy required for each of the following steps)

<table>
<thead>
<tr>
<th></th>
<th>Oil Shale</th>
<th></th>
<th>Coal</th>
<th></th>
<th>Crude Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Case A</td>
<td>Case B</td>
<td>High Sulfur Coal</td>
<td>Sweet</td>
<td>Sour</td>
</tr>
<tr>
<td>Mining or Pumping</td>
<td>1.5</td>
<td>1.1</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Crushing and/or Transportation</td>
<td>10.5</td>
<td>6.5</td>
<td>2.5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Retorting</td>
<td>16</td>
<td>8</td>
<td>22</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Clean Boiler Fuel Production</td>
<td>8</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel to Electric Power</td>
<td>65</td>
<td>65</td>
<td>65</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>Overall Thermal Efficiency</td>
<td>24%</td>
<td>27%</td>
<td>26%</td>
<td>34%</td>
<td>33%</td>
</tr>
</tbody>
</table>
ENERGY EFFICIENCY OF THE GARRETT IN SITU OIL SHALE PROCESS

Chang Yul Cha and Donald E. Garrett

The economic analysis of return on investment and total capital cost usually provides the principal data for comparing various processes. However, the continuing energy crisis is leading to a new awareness of how much energy is used in producing usable energy from alternate solid fuels resources. An energy analysis can reveal the specific energy inputs at each step in the process. The analysis can include the direct energy used for fuel and to run machinery, as well as the energy required to make available each of the input materials, tracing them back to their primary sources. An energy analysis is necessary to determine the energy required for each alternative, and can furnish new insights that can be used to develop quantitative parameters for private and public decision-making regarding energy use and recovery of energy resources. To begin an energy analysis it is necessary to define the system and its boundary.

The Garrett process consists of two basic steps:

(1) forming the in situ retorts by mining approximately 15 percent of the shale deposit, and by blasting to expand the remaining rock to fill the entire volume, and

(2) retorting the expanded oil shale in place using underground combustion.

Based upon the results of three actual in situ test retorts, a mining plan, retorting sequence, gas and oil handling equipment, and auxiliary facilities for producing shale oil at 30,000 barrels per day have been developed, and operating and capital cost estimates have been made. The retort is assumed to be approximately 120 by 120 feet in horizontal cross section, and 300 feet high. The retorting is accomplished by blowing a mixture of air diluted with recycle gas to a controlled oxygen concentration. The gas velocity entering the retorts is also closely controlled. The following energy analysis will be based upon the results of this study.

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Donald E. Garrett, President, Garrett Research and Development Company, Inc., 1855 Carrion Road, La Verne, California 91750.
ENERGY CONTENT OF OIL SHALE

One ton of rubblized oil shale is chosen as a basis for the energy calculations. The initial energy content of the oil shale can be evaluated from the elemental composition of its combustible constituents. A typical composition of the organic material in Colorado oil shale is shown in table 1 (Smith 1961).

Table 1.—Organic composition of oil shale.

(Mahogany Zone, Colorado)

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>80.5</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>10.3</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>2.4</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Since the Fischer assay is customarily used to measure oil shale grade, the concentration of kerogen may be approximately expressed in terms of its Fischer assay as follows (Cook 1974):

Concentration of kerogen = \(11.21F\) lb/ton

where \(F = \text{gal/ton}\).

Using the heat of combustion for the elements shown in table 1, and the above equation, the energy content of kerogen has been calculated as:

Energy content of oil shale = \(197,809F\) Btu/ton. \hspace{1cm} (2)

This energy is distributed into various products by the thermal decomposition of kerogen approximately as follows:

- Oil \(139,287F\)
- Combustible gases \(29,707F\)
- Residual carbon \(28,815F\)

Total \(197,809F\)

ENERGY INPUT

Conversion factors for the Btu requirements per dollar of equipment cost have been obtained from the 1967 Census of Manufacturer's data (Oregon Energy Study 1974), adjusted by the Wholesale Price Index for 1975:
Compressors, pumps, transmission lines 41,278 Btu per dollar of initial cost
Mining and construction equipment 36,203
Concrete and steel for construction 40,000
Engines and turbines 33,776

With these conversion factors, the energy input at various steps in the Garrett in situ oil shale process has been calculated from operating and capital cost estimates for producing the shale oil at 30,000 barrels per day for 20 years. The energy for life-support of manpower and for transportation of products has been neglected as a minor item. The electric energy required for gas compression and pumping was multiplied by 2.89 in order to convert to the equivalent Btu for their primary fuel sources. A list of energy inputs by such calculations follows:

A. Initial installation
   (1) Mine equipment = 967 Btu/ton
   (2) Retorting equipment and piping = 4,022 Btu/ton
      Subtotal = 4,989 Btu/ton

B. Operation
   (1) Equipment replacement and continuing construction of retorts = 10,872 Btu/ton
   (2) Electrical energy for pumps and blowers in the mine = 11,253 Btu/ton
   (3) Diesel fuel used for drilling and blasting = 5,693 Btu/ton
   (4) Explosives = 1,495 Btu/ton
   (5) Electrical energy for pumping of liquid products = 107 Btu/ton
   (6) Electrical energy for gas compression required for retorting = 22,722 + 5154F Btu/ton
      (7) Initial heatup of retort = 14,600 Btu/ton
         Subtotal = 66,742 + 5154F Btu/ton
         Total energy input = 71,731 + 5154F Btu/ton

F = Fischer assay, gal/ton.

It can be seen that the energy required for gas compression is more than 50 percent of the total energy input, and, unless carefully controlled, can represent a significant loss.
ENERGY OUTPUT

Since the amount of residual carbon resulting from the thermal decomposition of kerogen is more than enough to supply the heat required for the retorting process, and a significant amount of sensible heat is contained in the processed (retorted) shale, both primary and secondary recoveries should be considered.

PRIMARY ENERGY RECOVERY

Shale oil and combustible gases are produced from retorting. Also experimental data from three in situ tests indicate that much of the residual carbon can be recovered by a water gas reaction either during primary recovery, or later as a secondary recovery.

Shale oil energy output = $139,287F\eta$ Btu/ton

where $\eta$ is the fractional oil yield with respect to Fischer assay. The oil yield is dependent upon the Fischer assay, the operating conditions, the shale particle size and size distribution. This oil yield as a function of Fischer assay for a given set of operating conditions and particle size distribution is shown in figure 1. These values have been calculated from the mathematical model of the Garrett in situ process. The calculated values showed reasonably good agreement with the experimental data.

An examination of experimental data from three in situ retorts indicates that approximately 19,225 Btu/ton of combustible gases can be recovered from the residual carbon by water gas reactions. The energy output in the form of gas is as follows:

Energy output = 48,932F Btu/ton

then, total energy output from primary recovery is given by the equation:

$139,287F\eta + 48,932F$ Btu/ton

(4)

Energy Loss During Primary Recovery

The energy losses during primary recovery is dependent upon operating conditions and therefore has been included in calculating energy output in terms of the oil yield. However, in order to see some insight to what factors contribute to this energy loss, the approximate estimates of the energy loss at a typical operating condition are given as follows:

(1) Heat loss in the off-gas = $8,500 + 718F$ Btu/ton

(2) Heat loss in the liquid products = $9,000 + 438F$ Btu/ton

(3) Heat loss in the un-condensed water = $40,000 + 3,395F$ Btu/ton
Figure 1 - Oil yield as a function of Fischer assay.
Heat loss due to inorganic carbonates thermal decompositions = 197,000 Btu/ton

(5) Heat loss to the surroundings = 136,500 Btu/ton

These calculations assume that the initial oil shale temperature is 60°F and the inlet air temperature is 60°F. The gas leaves at 120°F while the oil and water products leave at 100°F. The inlet gas is assumed to be saturated with water.

As shown above, the energy loss due to thermal decomposition of inorganic carbonates is more than 40 percent of the total energy loss. Therefore, reducing the thermal decomposition of inorganic carbonates by reducing the retorting temperature can significantly decrease the energy loss.

SECONDARY ENERGY RECOVERY

Based upon theoretical calculations, approximately 14.3 percent of the residual carbon is available for secondary recovery when the Fischer assay of oil shale is greater than 10 gallons per ton. Assuming that the water gas reaction is used to recover the residual carbon, and 75 percent of residual carbon reacts with the water and oxygen, the energy output from residual carbon is 2318F Btu/ton. Run-2 data from Laramie Energy Research Center (Harak and others 1974) shows that the enthalpy of spent shale was on the average 343,100 Btu/ton. If we assume that 80 percent of this sensible heat can be recovered through air heat exchange or the water gas reaction, the total energy output from secondary recovery is

\[ 2318F + 274,480 \text{ Btu/ton} \]
D. Net energy efficiency by primary and secondary recovery
\[ \epsilon_2 = 0.70415\eta + 0.23303 + 1.0250/F \]  \hspace{1cm} (9)

Energy efficiency as a function of the Fischer assay of oil shale is shown in figure 2. It should be pointed out that equations (7) to (9) are applicable when the Fischer assay of oil shale is greater than 10 gallons per ton.

**RATIO OF ENERGY OUTPUT TO ENERGY INPUT**

The ratio of energy output to energy input from primary recovery can be obtained from equations (3) and (4):

\[
\text{Ratio} = \frac{\text{Total energy output}}{\text{Total energy input}} = \frac{139,287\eta + 48,932F}{71,731 + 5,154F} \]  \hspace{1cm} (10)

The ratios for the various Fischer assays of oil shale are calculated from equation (10) and plotted in figure 3.

As shown in figures 2 and 3, the energy efficiency and the ratio of energy output to energy input are dependent on both Fischer assay of oil shale and operating conditions. Net energy efficiency for the Garrett in situ oil shale process is from 55 to 80 percent for oil shale grades of 10 to 40 gallons per ton. The ratio of energy output to energy input is from 10 to 24 for oil shale grades of 10 to 40 gallons per ton. The energy analysis has revealed that the Garrett in situ oil shale process gives high energy efficiency. This energy efficiency can be increased by optimizing the process.

**ACKNOWLEDGMENT**

The authors wish to express sincere appreciation to Dr. A. Ruskin for providing valuable information on the energy analysis and to Dr. M. Gragg for his assistance during the preparation of the manuscript.

**REFERENCES**

Figure 2.—Energy efficiency.
Energy Efficiency of the Garrett In Situ Process

Figure 3—Ratio of energy output to energy input (primary recovery).
ENERGY SELF-SUFFICIENCY: THE GOAL FOR 1985

Granville Dutton

ABSTRACT

The adequacy of United States energy resources is dependent upon political rather than technological developments. The current energy shortage is a direct result of continuing governmental interference with the free market commencing with the 1954 Supreme Court decision directing federal control of natural gas prices. Recent congressional actions continuing excessive environmental restraints on the nuclear, coal and oil shale industries, while maintaining price controls and instituting punitive taxes on the petroleum industry, have virtually placed energy self-sufficiency in 1985 beyond our reach.

Petroleum, which currently supplies 75 percent of this nation’s energy needs, cannot fulfill its role in achieving energy self-sufficiency in the current political, economic and ecological climate; neither can nuclear, coal nor oil shale. Congressional panic measures—many of which are being considered in a lynching rather than a legislative atmosphere, such as the elimination of the percentage depletion allowance and the foreign tax credit, allocation, continuation of energy price controls at levels below those of the world market, unnecessary and untested ecological regulations, and the attempt to extend federal control over intrastate gas—continue to violate the law of supply and demand. Since such measures are doomed to failure, their proponents must seek to vilify others for the predictably disastrous results. If such demagogic expediencies are imposed on the American people as a “solution” to energy self-sufficiency, 1984 will arrive 10 years early . . . in the cold and the dark.

On the other hand, should an aroused citizenry insist that their federal representatives recognize the fact that there are no “free” lunches and renounce their efforts to perpetuate cheap energy by coercing sales at prices below replacement values, there will be adequate energy as well as other resources . . . including the greatest resource of them all: freedom under God.

The facts are that we are blessed with adequate potential petroleum

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reserves to sustain this country into the atomic era. The problem is that artificially depressed prices have prevented enterprising Americans from developing these resources. To develop these reserves will be costly, since the American people will not only have to pay the current costs of producing these more expensive resources, they will also have to make up the difference between the actual value of the resources used during the past 20 years and the government's controlled low prices. For it was during this period that the free market would have generated the capital necessary to make new and more expensive energy sources available ... resources which were uneconomical to develop at the artificially low prices set by the government. Higher prices would also result in a lesser demand for energy as ingenious Americans cope with facts instead of the federal fiction that energy will always be so cheap that there is no need to use it wisely.

For petroleum—including shale oil—to fulfill its role in making the United States self-sufficient will require achieving the critical balance between economic, energy and environmental conditions ... a balance that does not exist today. Restoration of the law of supply and demand and eliminating punitive taxes would provide the proper economic climate; proper revision of radical ecology laws would permit cooperatively working out rational solutions to energy-environmental problems.

A domestic capital investment of $330 billion of 1975 dollars will be necessary for petroleum to fulfill its energy resource role over the next 11 years. This will require $220 billion more than the total profits which would be generated during this period if profits are taxed back to the 1973 level. Even without any additional taxes, this would require over $460 billion more revenue as taxes would absorb more than half the additional revenue. Even so, the volumes are such that even these huge sums could be generated by an increase of 80¢ per MCF for natural gas and 21¢ per gallon of gasoline. This would result in average wellhead natural gas prices of approximately $1 per MCF and gasoline prices of 53¢ per gallon plus current taxes of 9 to 15¢ per gallon.

One thing is certain: prices will be substantially higher than these if federal taxes, price controls and allocations force further dependence on foreign, cartel-controlled oil and gas. Congressional activities have seriously reduced the incentive for Americans to attempt to increase domestic supplies, yet there is no way that the U.S. economy can sustain projected import costs. Unless Congress decides to free the market so that our domestic energy industry has an incentive to compete in the world market, we are destined to have disastrous financial trade balances and future energy shortages which will destroy life as we have known it in these United States. On the other hand, should government resume its constitutional role of protecting its citizens, including those engaged in the energy industry, from fraud and coercion, thereby allowing the free market to solve the energy dilemma, there would be a rapid balancing of demand
and supply with a concurrent efficient allocation of the available supply to the highest value end uses, two goals which have eluded the Federal Energy Agency and which must always elude any central planning agency attempting to cope with the independent daily market decisions of 150 million American purchasers.

NATURE OF THE ENERGY CRISIS

The energy crisis has had two facets. In the sense of a crisis being a severely disordered function, our government had relied on foreign oil imports supplying an average of 8.1 million barrels per day (8.1 MBPD), or 20 percent of our energy demand, during 1974. As a result of the Arabian embargo, only 6.3 MBPD were imported. However, realistic energy prices and the resultant conservation efforts reduced anticipated demand 2.8 MBPD so that crude and major product inventories actually increased during the year. With the termination of the boycott and the more representative energy prices, the immediate fuel shortage phase of the crisis is over, so long as the boycott is not reinstituted.

The second aspect of the crisis is that this is a crucial time in the state of our energy affairs: namely, will the federal government continue its attempts to abrogate the law of supply and demand and to add additional punitive taxes on the energy industry? To determine what history might indicate as the proper course, let us examine how the crisis developed.

![Figure 1.—United States energy demand.](image_url)
ENERGY DEMAND

The National Petroleum Council's historical and projected U.S. energy demand is shown on figure 1. The previous and forecasted increase in the electrical utilities share of the demand is interesting but only indirectly related to our subject in that coal and nuclear power, under proper economic and ecological conditions, could supply not only the future growth in energy required to generate electricity, but could also replace petroleum and natural gas in some current electrical generation stations.

Total energy demand as shown (fig. 1) increased at a rate of 3.6 percent per year between 1960 and 1970 and was projected to grow at a rate of 4.2 percent thereafter. Actually, the average growth in 1971-72 was 4.3 percent per year. A major factor in this increased growth rate is the additional energy required to protect the environment. For example, automobile pollution control devices are currently consuming 10 million gallons of gasoline per day.

ENERGY SUPPLY

United States energy supply sources are shown on figure 2. An interesting effect of tampering with the free market is shown with respect to increasing gas use. In the period when total energy use was increasing at a rate of 3.6 percent per year, natural gas consumption increased 2¾ times as rapidly.
at the rate of 9 percent per year. This was a direct and predictable result of the Federal Power Commission (FPC) dictating gas prices below their true value. However, this remarkable performance was reversed in 1971-72 when gas consumption increased only 3.2 percent, or 75 percent as much as all energy consumption. Why? Predictably there was not enough gas available to meet the demand, a fact proclaimed by full page ads in Washington and New York newspapers informing the people in those areas not to apply for new gas connections.

Even granting the startling growth of nuclear power as projected—a growth which will require considerable ecological enlightenment to overcome the rampant “Nader nonsense”—self-sufficiency would be 15 MBPD of imported oil away. As a matter of economic realism, the imports required to avoid a shortage simply cannot be obtained. To import the 9 MBPD projected for 1975, if the Organization of Petroleum Exporting Countries (OPEC) would sell it to us at their current landed price of $12 per barrel, would result in a trade deficit of $39 billion this year. By 1985, should we import 15 MBPD, the cost would likely be in excess of $100 billion per year and the cumulative costs during the 11 years would be over $800 billion. Obviously, the U.S. economy cannot support such deficits.

**Declining Supply**

The question is, “How did we become so dependent upon foreign energy?” The answer is, “Because the government decreed that natural gas should sell for a price below that established by the free market.” In a remarkably prophetic statement before the Investment Bankers Association on December 1, 1954, Humble President Hines Baker initiated a warning, which many energy industry spokesmen have reiterated over the years, when he stated what the effects of this short-sighted action would be: “It is clear that such low prices would increase the number of customers desiring gas and the demand for gas. By the same token, it would tend to lower the demand for oil and coal. But the low price would lessen the incentive to explore for and develop gas. This would lower the rate of discovery of gas reserves.”

And, lower the rate it did! Drilling was cut in half from 58,200 wells in 1956 to 27,300 in 1971. New gas reserves declined from an annual average of 22 trillion cubic feet (TCF) in 1956-57 to 9.7 TCF in 1971-72.

Concurrently, the inability of coal and oil to compete in the fuel market with the artificially low prices ordered by the FPC for the more desirable natural gas resulted in essentially dismantling the coal industry and lowering exploration for and discovery of oil. Shale oil development—plagued also by federal leasing indecision—was terminated. In figure 3, we show
Figure 3—Federally depressed crude price, wells drilled, and oil discoveries; gas and gasoline prices and gas discoveries.
that, as the real price of crude was pulled down by ridiculously low gas prices which averaged only one-third the cost of oil and even less than that of coal for equivalent heating values, oil discoveries declined 65 percent, from 2 billion barrels per year (BBPY) in 1956-57 to 0.7 BBPY in 1971-73. Fortunately, scientists and engineers, working under the adverse economic conditions resulting from natural gas price controls, devised ways of increasing recovery from prior discoveries so that the total oil reserves added declined 30 percent over this period. These improved recovery reserves represented two-thirds of the lower 48 states' reserves as of 1974.

PETROLEUM'S ROLE AS AN ENERGY RESOURCE

The role petroleum plays in fulfilling the United States' energy demand should be consistent with a free market operating under the law of supply and demand. Under such conditions the nation could be assured that petroleum would provide its proper share at the price set, not by a central bureaucracy, but by the people's dollar-votes in the marketplace. We could be equally certain that the petroleum mix between conventional hydrocarbons and more exotic sources, such as shale and coal oil, would be the one providing the most efficient supply for meeting specific energy demands. The overwhelming advantage of this solution is that it would be accomplished without bureaucratic expense, misallocation or favoritism and at the most reasonable price at which energy can be made available.

Worldwide, a free market does not seem attainable. The OPEC cartel which effectively controls the bulk of the world supply cannot be expected to surrender voluntarily the tremendous power that it now enjoys. Even should an improbable combination of economic and military pressure be exerted by a similar organization of free-world consumer countries so as to establish a worldwide free energy market, the current Communist naval strength would make it unwise for the United States to depend appreciably upon overseas sources.

Within the United States, conditions other than governmental tax, price and environmental constraints are ideal for operation of a free market. More than 7,000 firms are engaged in the search for and production of oil and natural gas, with the largest having less than 10 percent of the total. There are 127 companies operating over 250 refineries in 39 states and the largest has less than 9 percent of the total. There are 15,000 wholesale oil and gasoline jobbers, 18,000 fuel oil and liquified petroleum gas firms and 200,000 service stations. The largest single marketer only has a little over 8 percent of the nation's gasoline sales and it takes the top ten to account for 60 percent of the total sales. Comparing these figures to the television, automotive, aluminum and electrical equipment industries, it is indeed amazing that the petroleum industry continues to garner unfounded, ridiculous charges of being a monopoly or oligarchy.
With a free market at home, ingenious American traders would have no trouble competing for necessary imports on the world market... even under cartel conditions. The reason is that of all the industrialized free-world countries, only Canada supplies a larger percentage of its own energy needs. In addition, the higher cartel prices will make it economically expedient as well as desirable to expedite efforts to become self-sufficient.

**HISTORICAL ROLE**

Petroleum has been supplying more than 50 percent of the nation's energy needs for over 25 years and over two-thirds of these needs for 20 years. As shown on figure 2, petroleum accounted for nearly 75 percent of the U.S. energy supply in 1960 and 77 percent in 1970. During this period, gas increased its share from 29 to 34 percent while domestic oil, including gas liquids, declined from 38 to 33 percent, and imported oil increased from 8 to 10 percent. Preliminary figures for 1974 indicate gas decreased to 29 percent, of which imports constituted 1.5 percent, domestic oil decreased to 30 percent and imported oil rose to 17 percent of the total energy supply.

Volumes involved in gas are 8.7 TCF during 1954, increasing to 12.8 in 1960, 21.9 TCF in 1970, and 24 TCF in 1973 before decreasing to 22.8 in 1974 of which 0.94 was imported. Oil supplied 8.1 MBPD in 1954, increasing to 10.9 in 1960, 15.0 in 1970, and 17.4 in 1973 before declining to 16.8 in 1974. Imported oil volumes and percentages of total oil supplied for these same years were 1.0 MBPD and 12 percent; 1.8 and 18 percent; 3.4 and 23 percent; 6.2 MBPD and 36 percent; and 6.3 and 37.5 percent in 1974.

**PROJECTED ROLE**

As projected in 1970 by the National Petroleum Council, petroleum was to supply 62 percent of U.S. energy in 1985. Gas was to supply 17 percent, nonconventional oil 1 percent and domestic oil 18 percent, with imports supplying the remaining 26 percent. Although the projection shows a percentage decline for gas to 17 percent, or one-half the 1970 percentage, the increase in the projected total energy supply would still require the production of 22 TCF in 1985, or the same as produced in 1974. The percentage decline for domestic oil to 18 percent would require 1985 domestic production to be 10.4 MBPD, slightly under 1974 production of 10.5 MBPD. The really significant change projected was in imported oil which was scheduled to increase from 10 percent in 1970 to 26 percent in 1985 or from 3.4 MBPD to 15 MBPD. Recent events clearly indicate that U.S. imports cannot attain this level, so obviously the original projections will undergo some adjustments.
ADJUSTED ROLE

The National Petroleum Council (NPC) study, upon which the projections of figure 2 were based, used the data available at that time to show what the then current policies and prices would require in the way of future supplies. Should the federal government continue punitive taxes as well as price and allocation controls, the energy situation will continue to degenerate into chaos which will terminate the way of life we have known in these United States. If this is the direction we allow our government to take, there is no need to attempt to determine the adjustments necessary to solve our energy problem; under such conditions, no solution other than a miracle exists, and miracles do not lend themselves to analysis.

Should the government decide to free its citizens—including those in the energy industries—so that they can use their creative genius to solve our energy problem, then we can at least speculate on the nature of the adjustments required to accomplish the solution. In this speculation, it will be assumed that the siren song of radical ecologists will be sufficiently muted so that nuclear, hydro and coal power can be developed in the amounts shown on figure 2... since free market energy prices would permit the economic application of these sources in the time frame shown.

The NPC projection shows that petroleum would be called upon to supply the oil equivalent of 36 MBPD in 1985. This was predicated on continued government interference with the pricing structure; if such interference is removed—and it must be if any solution is to be reached—the demand would lessen. Only the free market can solve the complex problem of determining how much increased prices will decrease demand by improving efficiency of use; or how much such prices will bring new supplies—otherwise uneconomical to produce—into the market place. But we do know that under a free market the projected demand of figure 1 should be adjusted downward and the projected domestic supply of figure 2 upward. And yet these two adjustments do not in themselves seem capable of eliminating the 15 MBPD of imports shown as required by 1985. Where can such energy be obtained if not by imports?

FULFILLING PETROLEUM'S ROLE

Fortunately, the United States has ample petroleum resources to become essentially self-sufficient given proper economic, ecological and political conditions. Potential conventional oil resources in the United States exceed 500 billion barrels, a 75-year supply at current rates; the natural gas potential is over 2,000 TCF, more than 80 years supply at current rates. In addition, oil shale reserves exceed 1,200 billion barrels and coal conversion could supply even more.

The real problem is that the cost of developing these potential reserves
far exceeds historical U.S. energy prices which have been maintained by the federal government at an artificially low level for 20 years.

**Magnitude of Role**

Petroleum was projected to supply 36 MBPD of this nation's energy needs in 1985, of which 15 MBPD was to have been imports (fig. 2). The drastic change in the cost of overseas crude and the fact that not even the United States government can now prevent energy from commanding its true value mean that the 1970 demand projections are overstated. In addition, the domestic supply at higher prices will be greater . . . if equitable taxing policies are restored.

To analyze the domestic investment required to make the United States essentially energy self-sufficient, the projection as to the costs of relying on imports may be used as a starting point. As shown in figure 4, this would have required a $200 billion investment during the period 1975-85. Rearranging our supplies to where domestic conventional production and coal and shale conversions increase domestic supply by 7.9 MBPD would require an additional investment of $127 billion. The investments required for more U.S. refinery and transportation facilities would be partially offset by lesser tanker and port facilities costs so that the net result would be an increased investment of $130 billion.

Only by the sheerest coincidence could the petroleum supply mix and investments in 1985 resemble either the original projection or these adjustments. The free market alone can cope with the myriad changes that would result in energy demand and supply being balanced at a particular compositional mix of such demand and supply. This example is presented only to show that energy independence by 1985 was not an economically impossible goal for the United States until the 94th Congress put it beyond possibility.

As shown in figure 4, additional revenues of $460 billion of 1975 dollars would be required for the oil industry to accumulate after taxes the $220 billion more than the 1973 oil industry profits would generate during the period. Breaking this down one-half to gas revenues and one-half to oil would result in increases of 82¢/MCF and $4.40/bbl to average costs of about $1/MCF and $9/bbl. If all the oil increase were absorbed solely by increased gasoline prices, the pretax cost of gasoline would be 53¢ gal with total state and federal taxes ranging from 9 to 15¢ gal in the various states.

**Solving the Energy Crisis**

For petroleum and other energy industries to solve the energy crisis will require achieving the critical balance among economics, energy and
Energy Self-Sufficiency: The Goal for 1985

DOMESTIC OIL AND GAS CAPITAL REQUIREMENTS
1975-1985
BILLIONS OF 1975 DOLLARS

<table>
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<th>FACILITY</th>
<th>5 MBPD IMPORTS</th>
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<tr>
<td>ADDITIONAL REVENUES BEFORE TAXES</td>
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INCREASED PRICES NECESSARY

| PER MCF OF DOMESTIC GAS       | .39            | .82                       |
| PER BEL OF DOMESTIC OIL       | 2.11           | 4.40                      |
| PER GAL OF GASOLINE SOLD      | .09            | .21                       |

Figure 4.—Domestic oil and gas capital requirements from 1975 to 1985 (billions of 1975 dollars).

environment—a balance which does not exist today. Restoration of percentage depletion and the law of supply and demand without such counterproductive measures as "excess-profits" taxes would provide the proper economic climate. Removal of price and allocation controls on domestic crude oil and its products by the President, and on natural gas by Congress, would not only bring demand into balance with supply quickly, it would also allocate the currently available supplies to their highest value end uses. More importantly, it would provide the incentive to attract substantial new supplies of energy into the marketplace . . . supplies which cannot be economically produced at controlled lower price levels.

There is no one person, whether you label him Czar or color him bureaucrat or tycoon, who can solve the energy crisis. To really solve this crisis, we need to release and incite man's genius and creativity for solving problems. We need to realize that it is only the free market which can entice the geologist to find the energy, the landman to lease the property, the promoter to put the deal together, the driller to drill, the producer to produce, the transporter to ship, the purchaser to buy, the refiner to refine, the marketer to distribute, the service station to retail . . . and the banker to finance every stage . . . so that the American people can buy gasoline for 50¢/gal, one-third the price of milk, one-sixth the price of beer or coca cola, and one-twentieth the price of bourbon. On a weight
basis, crude oil and natural gas are cheaper than wheat, sugar, lead, zinc, aluminum, copper, tin, all precious metals and beef.

The free market can only exist where government fulfills its role to protect its citizens against fraud and coercion so that they have the three great freedoms to specialize, to transact and to exchange at an agreed price. Where such freedoms exist, the law of supply and demand reigns so that these two seemingly antithetical concepts are continually being brought into balance by price; price, a beacon which attracts or repels creativity and investment as necessary to balance supply and demand while also functioning as the most efficient allocation mechanism history has ever known.

But will it work with energy? Energy is primarily a fuel and fuel is a commodity. Look at another commodity that was in short supply not too long ago.

In 1963, sulphur was selling for $23.50/ton and experiencing a growth rate of 15 percent per year. As shown by figure 5, its inventory consumption ratio was decreasing sharply, much as are our energy inventories now. But being an unregulated commodity, the price of sulphur reflected this situation and rose to $50/ton by early 1968. Predictably, more sulphur began to come into the market at the higher price and by 1973, the inventory ratio was significantly higher than in 1963. More immediately, the demand as shown by the percentage growth rate fell from the 1963 high of 15 percent to 2 percent as the price increased. As the price began to decline

![Figure 5.-Free world brimstone.](image-url)
from the 1968 high, the growth rate began to pick up and by 1973 was at a healthy 11 percent.

More recently, and more dramatic resolutions of crises from the standpoint of quick solutions, the beef shortage of 1973 and the sugar shortage of 1974 demonstrated the efficacy of the free market. After government controls had over a 2-year period driven beef entirely out of our stores, restoration of the beef market returned beef to the supermarket faster than a bureaucracy could have printed up ration stamps. It is difficult to speculate on how chaotic the sugar situation would be if in the fall of 1974 the government’s “solution” to the sugar shortage would have been an increased import tax of $1/lb and a tax increase of $2 billion on the sugar industry.

A problem that the free market cannot overcome is with respect to the 1985 timeframe. The restrictions on energy prices dating from 1954 coupled with inflationary monetary policies and capital reducing tax policies have made it impossible for the energy industry to generate sufficient capital to have any significant shale or coal oil production by 1985. To expedite the development of these plentiful fuel sources would require a capital intensive program beyond the capacity of private industry. In addition, the estimated $20,000 investment per BPD capacity would require a $20 per barrel price of oil, a price which oil might well be commanding in 1985 but which no one can afford to risk considering the current situation in which prices are political rather than economic functions.

With such uncertainty, only an entity which can generate funds independent of economic and market conditions can afford to plunge into rapid development of shale and coal as petroleum liquids. This means that massive federal funds would have to be funneled into such developments in order to have a substantial synthetic liquids output by 1985.

**Necessary Conditions**

The first condition necessary for the free market to solve the energy crisis is for United States citizens and politicians to understand that the free market is not inflationary. Inflation is an increase in the volume of money and credit relative to available goods resulting in a substantial and continuing rise in the general price levels. Only the federal government can increase the volume of money and credit; historically, it has done so with such reckless abandon that inflation is truly a Frankenstein creation of Washington’s profligate printing presses. Although cartels can reduce the available goods, the only ones not prohibited by U.S. law are labor unions. Of course, foreign cartels are not under United States jurisdiction. The point is clear: there is nothing inflationary about any price paid by a willing buyer to a willing seller since such payment neither increases the volume of money or credit nor reduces the available goods.
The second understanding necessary is that "excess profits" is a demagogic term in a country where corporate income is taxed at 48 percent. "Excess" refers to that which exceeds some standard or proper norm. Comparing the petroleum industry to the cosmetics industry, on January 1, 1974, Forbes reported that during the prior 5-year period, Avon earned more than three times the return on equity that the 10 major integrated oil companies realized. Such earnings in an uncontrolled market is why cars are not lined up at the Avon Lady's house; she is making enough to utilize higher-priced cosmetic supplies and to continue to ring her customers' door bells. The oil industry, which for 20 years has been bearing the burden of the only price-controlled commodity in the country and is lagging behind 375 of the 720 reported companies, was not able to develop higher cost reserves and therefore, cars have been lined up at service stations.

As shown on figure 6, petroleum profits have generally been below the average of all manufacturing companies until 1973. On figure 6 we also show how gasoline prices prior to 1974 persistently lagged behind the consumer index for all items.

These first two understandings should pave the way for a free market. A third understanding is that to establish environmental conditions in which sufficient energy supplies can be developed to meet the nation's

![Figure 6](image-url)
needs will require revising radical ecology laws in order to permit working out cooperative, rational solutions to energy-environmental problems.

Above all, it is necessary that the American people reaffirm their personal confidence in the free enterprise system which made our country prosperous and great, and to unite in one cause to preserve not only our vital energy growth, but more importantly, the blessings of our liberty.
RESOURCE APPRAISAL OF OIL SHALE IN THE GREEN RIVER FORMATION, PICEANCE CREEK BASIN, COLORADO

C. William Keighin

ABSTRACT

The oil shale resource potential of the richer parts of seven oil shale zones in the Parachute Creek Member of the Eocene Green River Formation underlying much of the Piceance Creek Basin was evaluated. It is estimated that, in beds greater than 10 feet thick and yielding 25 gallons or more of oil per ton, there are 471 billion barrels (68 billion tonnes) of oil in place; of this total, 135 billion barrels (20 billion tonnes) are contained in the Mahogany Zone of the Parachute Creek Member. Included in these estimates are resources calculated for oil shale yielding 30, 35, and 40 gallons or more of oil per ton. If technology and economics permit use of lower grade resources, the total oil in place is significantly higher.

INTRODUCTION

The resource potential of the Green River Formation of Eocene age which underlies large areas of southwestern Wyoming, northeastern Utah, and northwestern Colorado has been of interest for many years (Donnell 1961). This report deals with the resource potential of richer oil shale zones of the Green River Formation in the Piceance Creek Basin in northwestern Colorado (fig. 1). Most of the rich oil shale beds are in the Parachute Creek Member, which is almost entirely oil shale.

Earlier estimates of the potential shale oil resources in the Green River Formation in the Piceance Creek Basin were made when fewer data were available (Donnell 1961) and these estimates often referred to selected intervals in the Green River Formation (Donnell and Austin 1971; Donnell and Blair 1970; Pitman and Donnell 1973); resources were also calculated for shale yielding less than 25 gallons of oil per ton. For the current appraisal a yield of 25 gallons of oil per ton was selected as a lower limit, because it is considered to be approximately the lowest grade oil shale...
which could now be treated economically. It was further assumed that beds less than 10 feet thick could not be mined economically. Thus, only units which yield at least 25 gallons or more of oil per ton, and are at least 10 feet thick were used to calculate the potential shale oil resources.

ACKNOWLEDGMENTS

The data for compilation of resource data were from computer programs generated by the U.S. Geological Survey. Some Fischer assay data were obtained from private companies and individuals, but most of these data
were from the U.S. Bureau of Mines Oil Shale Petroleum Research Center at Laramie, Wyo. (Belser 1951; Stanfield and others 1954, 1957, 1960, 1967). Guidance and assistance were provided by John Donnell and Janet Pitman of the U.S. Geological Survey.

**STRATIGRAPHY**

The Green River Formation was divided into four members—in ascending order, the Douglas Creek, Garden Gulch, Parachute Creek, and Evacuation Creek—by Bradley (1931). These members have been subsequently studied by many workers. The Evacuation Creek Member was abandoned; in the Piceance Creek Basin the name is replaced by the term "Uinta Formation" (Cashion and Donnell 1974).

Of primary interest here is the Parachute Creek Member which is almost entirely oil shale. The Parachute Creek contains, in addition to oil shale, thin analcime-rich tuff beds and thin sandstone beds, finely disseminated dawsonite, pods of nahcolite, and beds of halite and nahcolite (Donnell and Blair 1970; Pitman and Donnell 1973). The resource potential of dawsonite and nahcolite in the Green River Formation, which appears to be high, is discussed by Dyni (1974). The Parachute Creek Member can be subdivided into zones, persistent ledges, beds, and groups of beds, on the basis of weathering characteristics or on oil yield, many of which may be correlated throughout much of the basin (Cashion and Donnell 1972). The richest and most widespread of these is the Mahogany Zone (Mahogany ledge in surface exposures) (fig. 2).

The upper boundary of the Mahogany Zone is marked by "A" groove, a 10- to 15-foot-thick sequence of marlstone and lean oil shale. Within the Mahogany Zone is the Mahogany bed, a thin but rich oil shale bed which is a persistent marker over most of the basin. The oil shales above "A" groove are generally thinner and of lower grade than those below it (Pitman and Donnell 1973).

The lower limit of the Mahogany Zone is defined by "B" groove, a persistent lean oil shale zone. Below "B" groove, Donnell and Blair (1970) defined six rich oil shale zones, R-6 through R-1, on the basis of oil yield determined by Fischer assay (fig. 2). In the central part of the basin (core hole B, fig. 2) thick sequences and interbeds of nahcolite and halite complicate correlations of rich oil shale sequences (Donnell and Blair 1970, p. 77). Location of core holes is shown in figure 3.

**METHOD OF CALCULATION**

Fischer assay data from approximately 230 core holes were processed on the IBM 360-65 computer, which prepared histograms (fig. 2) and computed, for each core, all possible thicknesses of oil shale that main-
Figure 2.—Northwest-southeast cross section showing oil-yield histograms of lower part of the Parachute Creek Member of the Green River Formation, and correlation of rich oil shale zones labeled R-1 to R-6 and Mahogany Zone. Location of core holes is shown in figure 3.
Appraisal of Oil Shale in the Green River Formation

EXPLANATION

Area underlain by the Green River Formation

R-6

Approximate limit of rich oil-shale zone; dashed where formation removed by erosion. Zone boundary depths shown on Fig. 2

A Core hole

Figure 3.—Approximate limit of potentially valuable rich oil shale zones below the Mahogany Zone.

tained a specified average oil yield. Average yields of 25, 30, 35, and 40 gallons of oil per ton were used. The program excludes sequences of oil shale that exceed a specified maximum thickness—in this case, 10 feet—with an average oil yield less than a specified minimum. Thus, the program permits sequences of lean oil shale to be deleted from the averaging calculations (Pitman and others 1972), even when these lean zones may be within a rich zone, e.g., Mahogany Zone. From these data, the aggregate thickness of beds greater than 10 feet thick with yields equal to or greater than 25, 30, 35, and 40 gallons of oil per ton was calculated for each zone. The total for each grade includes the total of all resources of higher grade, that is, the totals for shale yielding 25 gallons of oil per ton include resources from shale yielding 30, 35, and 40 gallons of oil per ton. Isoresource maps were prepared of the oil yield in barrels per acre, the number of
acres were measured with a planimeter, and then the average oil yield per acre was multiplied by the area in acres to get the total resources (tables 1 through 3).

In order to convert the values obtained to metric units, the following conversion factors were used (World Energy Conference 1974)

\[
\begin{align*}
1 \text{ metric ton} &= 1 \text{ tonne} \\
1 \text{ gallon/ton} \times 0.29 &= 1 \text{ kg/tonne} \\
10^6 \text{ barrels} \times 0.145 &= 10^9 \text{ tonnes}
\end{align*}
\]

SHALE OIL RESOURCES

Of the seven zones the Mahogany Zone is, perhaps, of most immediate interest because it is the richest and shallowest; its potential shale oil content is given in figure 4. Approximately 29 percent of the shale oil contained in beds greater than 10 feet thick and assaying 25 or more gallons of oil per ton is contained in the Mahogany Zone, and this zone contains about the same proportion of shale oil in shales of higher grade (see table 1). The R-4 zone is the next richest zone, and contains between 18 and 25 percent of shale oil calculated to be in the richer zones of the Green River Formation in the Piceance Creek Basin. The potential shale oil resource of the zones below the Mahogany Zone generally parallels the trend outlined by the Mahogany Zone, but when the R-4 zone is reached, there seems to be only one rich center of deposition, in T. 1 S., R. 98 W. The potential maximum shale oil resource in this rich center of the R-4 zone is 700,000 barrels (101,500 tonnes) of oil per acre. Thickness and calculated shale oil content of the various rich oil shale zones for the three core holes are shown in table 2.

The total resources in all seven zones in the beds more than 10 feet thick that yield 25 gallons or more of oil per ton is 471 billion barrels (68 billion tonnes) of oil (table 1). Of this amount, 323 billion barrels (47 billion tonnes) are in beds that yield at least 30 gallons of oil per ton. Resources calculated for beds yielding 35 and 40 gallons per ton are, respectively, 175 billion barrels (25 billion tonnes) and 81 billion barrels (12 billion tonnes).

In figure 5, we show the aggregate thickness of beds, in all seven zones, greater than 10 feet thick and yielding 25 gallons or more of shale oil per ton. Two areas are defined which total more than 1,100 feet of oil shale yielding at least 25 gallons per ton. Total oil contained in these two areas is calculated at greater than 2 million barrels (290 thousand tonnes) of oil per acre.
TABLE 1.—Shale oil resources of the richer parts of seven oil shale zones in the lower part of the Parachute Creek Member of the Green River Formation in the Piceance Creek Basin (resources calculated from beds more than 10 feet thick with yields equal to or greater than that indicated. Resources are reported for oil in place as billions of barrels, and, parenthetically, billions of tonnes)

<table>
<thead>
<tr>
<th>Oil yield *</th>
<th>In place resource (billions of barrels)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mahogany</td>
</tr>
<tr>
<td>25 gpt (7.25 kg/tonne)</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>(20)</td>
</tr>
<tr>
<td>30 gpt (8.7 kg/tonne)</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>(14)</td>
</tr>
<tr>
<td>35 gpt (10.15 kg/tonne)</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>(9)</td>
</tr>
<tr>
<td>40 gpt (11.6 kg/tonne)</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>(4)</td>
</tr>
</tbody>
</table>

* Oil yield in gallons per ton (and kg/tonne), determined by Fischer assay.

** Between category totals are not additive; total for 25 gpt includes totals from 30, 35, and 40 gpt, 30 gpt total includes totals for 35, 40 gpt, etc.
### Table 2.—Thickness and calculated shale oil resource of oil shale in seven zones at three sites in the Piceance Creek Basin (data calculated for beds more than 10 feet thick and yielding 25 gallons or more of oil per ton (7.25 kg/tonne)

<table>
<thead>
<tr>
<th>Core hole</th>
<th>ZONE</th>
<th>Mahogany</th>
<th>R-6</th>
<th>R-5</th>
<th>R-4</th>
<th>R-3</th>
<th>R-2</th>
<th>R-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td></td>
<td>43</td>
<td>0</td>
<td>15</td>
<td>125</td>
<td>66</td>
<td>64</td>
<td>46</td>
</tr>
<tr>
<td>A</td>
<td>2.</td>
<td>76</td>
<td>0</td>
<td>28</td>
<td>221</td>
<td>118</td>
<td>115</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>3.</td>
<td>11</td>
<td>0</td>
<td>4</td>
<td>32</td>
<td>17</td>
<td>17</td>
<td>12</td>
</tr>
<tr>
<td>B</td>
<td>1.</td>
<td>190</td>
<td>194</td>
<td>225</td>
<td>232</td>
<td>128</td>
<td>86</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>2.</td>
<td>368</td>
<td>346</td>
<td>405</td>
<td>485</td>
<td>217</td>
<td>199</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>3.</td>
<td>53</td>
<td>50</td>
<td>59</td>
<td>70</td>
<td>31</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>C</td>
<td>1.</td>
<td>60</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2.</td>
<td>128</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>3.</td>
<td>19</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

1. Thickness, in feet.
2. Shale oil resource, thousands of barrels per acre, for thickness indicated.
3. Shale oil resource, thousands of tonnes per acre for thickness indicated. 

\(10^3 \text{ bbls } \times 0.145 = 10^3 \text{ tonnes}\).
Table 3.—Shale oil resources, by township, from seven zones in beds more than 10 feet thick and yielding 25 gallons or more of oil per ton (resources are given in billions of barrels, and, parenthetically, billions of tonnes: $10^9 \text{ bbl} \times 0.145 = 10^9 \text{ tonnes}$)

<table>
<thead>
<tr>
<th>Range (West)</th>
<th>95</th>
<th>96</th>
<th>97</th>
<th>98</th>
<th>99</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Twp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 N.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 N.</td>
<td>.8</td>
<td>16.8</td>
<td>30.3</td>
<td>14.8</td>
<td>.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(.12)</td>
<td>(2.4)</td>
<td>(4.4)</td>
<td>(2.2)</td>
<td>(.04)</td>
<td></td>
</tr>
<tr>
<td>1 S.</td>
<td>5.3</td>
<td>33.2</td>
<td>49.1</td>
<td>35.6</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(.8)</td>
<td>(4.8)</td>
<td>(7.1)</td>
<td>(5.2)</td>
<td>(.6)</td>
<td></td>
</tr>
<tr>
<td>2 S.</td>
<td>.5</td>
<td>11.9</td>
<td>39</td>
<td>43.8</td>
<td>23.2</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>(.07)</td>
<td>(1.7)</td>
<td>(5.7)</td>
<td>(6.4)</td>
<td>(3.4)</td>
<td>(.4)</td>
</tr>
<tr>
<td>3 S.</td>
<td>.1</td>
<td>5.3</td>
<td>19.8</td>
<td>31.4</td>
<td>20</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>(.01)</td>
<td>(.8)</td>
<td>(2.9)</td>
<td>(4.6)</td>
<td>(2.9)</td>
<td>(1.2)</td>
</tr>
<tr>
<td>4 S.</td>
<td>1.4</td>
<td>7.5</td>
<td>9.5</td>
<td>9.4</td>
<td>7</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>(.2)</td>
<td>(1.1)</td>
<td>(1.4)</td>
<td>(1.4)</td>
<td>(1)</td>
<td>(.5)</td>
</tr>
<tr>
<td>5 S.</td>
<td>2.7</td>
<td>4.4</td>
<td>4.1</td>
<td>4.4</td>
<td>2.4</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>(.4)</td>
<td>(.6)</td>
<td>(.6)</td>
<td>(.6)</td>
<td>(.4)</td>
<td>(.3)</td>
</tr>
<tr>
<td>6 S.</td>
<td>.1</td>
<td>1.5</td>
<td>1.7</td>
<td>2.9</td>
<td>1.1</td>
<td>.6</td>
</tr>
<tr>
<td></td>
<td>(.01)</td>
<td>(.2)</td>
<td>(.3)</td>
<td>(.4)</td>
<td>(.2)</td>
<td>(.09)</td>
</tr>
<tr>
<td>7 S.</td>
<td>.2</td>
<td>.5</td>
<td>.5</td>
<td>1</td>
<td>.1</td>
<td>.3</td>
</tr>
<tr>
<td></td>
<td>(.03)</td>
<td>(.07)</td>
<td>(.07)</td>
<td>(.2)</td>
<td>(.01)</td>
<td>(.04)</td>
</tr>
</tbody>
</table>
Figure 4.—Potential shale oil content, in thousands of barrels per acre, of beds greater than 10 ft (3 m) thick yielding 25 or more gallons of oil per ton (7.25 kg/tonne) in the Mahogany Zone.
Figure 5.—Aggregate thickness of oil shale beds greater than 10 ft (3 m) thick and yielding 25 or more gallons of oil (7.25 kg/tonne) per ton. Contour intervals 50 or 200 ft.
REFERENCES


DAWSONITE: ITS GEOCHEMISTRY, THERMAL BEHAVIOR, AND EXTRACTION FROM GREEN RIVER OIL SHALE

John Ward Smith and Neil B. Young

ABSTRACT

Dawsonite [NaAl(OH)₂CO₂], a rare mineral elsewhere, exists in huge amounts in Green River Formation oil shale of Colorado's Piceance Creek Basin. Occurring with the dawsonite is the aluminum trihydroxide, nordstrandite [Al(OH)₃]. Together these minerals represent a domestic resource of extractable alumina of over 6.5 billion tons. Analytical methods for determining dawsonite and nordstrandite in oil shale are described and evaluated. The geochemical conditions which produced these minerals in the oil shales are outlined. Thermal decomposition reactions of both minerals are described. With appropriate heat treatment dawsonite and nordstrandite both yield an alumina form readily and rapidly soluble in light base. A process based on extraction of alumina from properly prepared spent shale is compared with the Bayer process. Advantages in the extraction properties of spent shale may compensate adequately for the disadvantage of having to process ten times as much material to produce the same amount of alumina. Production techniques must be designed to exploit these advantages. Oil and soda ash are produced as coproducts with alumina. Electric energy generated by burning the shale oil is enough for aluminum metal production.

INTRODUCTION

Publications on dawsonite in Colorado oil shales have been appearing ever since 1966 when Smith and Milton showed that huge amounts of dawsonite existed in the Green River Formation oil shales of Colorado.

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The work upon which this report is based was done under a cooperative agreement between the U.S. Energy Research and Development Administration and the University of Wyoming.
and Nielsen (1969) emphasized the possibilities of this alumina resource in several presentations and papers. Factual information has been strongly exceeded by publicity and speculation, heavily colored by lack of understanding of the nature of oil shale and by an overpowering urge to produce alumina from oil shale by the Bayer process. However, a solid technical background exists. Published data are widely scattered, and each publication usually treats only a single facet of the multiple problems inherent in the mineral nature and in alumina \((\text{Al}_2\text{O}_3)\) production from dawsonite-bearing oil shale. Incorporating data developed at the Laramie Energy Research Center, this report assembles and evaluates the information now available on: the oil shale minerals yielding extractable alumina; the nature of the deposit; the alumina resource in oil shale and the analytical methods developed to evaluate it; the geochemistry which created this unique deposit; the thermal behavior of the aluminum-bearing minerals and the oil shale containing them; and the alumina extraction this behavior permits. Finally, procedures for the extraction of alumina from oil shale are compared to the Bayer alumina extraction procedures, and the energy balance for producing metallic alumina is evaluated.

The United States consumed 6.5 million tons of aluminum metal in 1973 with less than 8 percent produced from alumina extracted from domestic ores (Mineral Industries Surveys 1974). Our bauxite and alumina imports for 1973 were valued at more than $400,000,000, and we are completely dependent on foreign alumina supplies. The U.S. Bureau of Mines has evaluated processes for producing alumina from nonbauxite domestic ores, and has continuously concluded that these processes are not economic. The production of alumina from Colorado oil shale as a co-product with oil and sodium carbonates is an attractive prospect, spurring continued interest. Currently, however, development is blocked, because the federal government controls virtually all of the dawsonite resource and has refused to release any of its holdings to development.

MINERAL NATURE AND DISTRIBUTION

Extractable alumina arises from two minerals occurring together in oil shale. These minerals are dawsonite \((\text{NaAl(OH)}_2\text{CO}_3)\) and nordstrandite \((\text{Al(OH)}_3)\), and both minerals yield readily soluble alumina. Alumina also occurs in sodium and potassium feldspars and in illite clay in the dawsonite-bearing oil shale (Robb and Smith 1974), but like most forms of alumina in the world this is not readily soluble.

Before its discovery in oil shale, dawsonite was classed as an extremely rare mineral with only four known occurrences (Smith and Milton 1966). Dawsonite in the Green River Formation was noted first in 1959 by Milton and Eugster (1959), who reported its rare occurrence in vugs and fissures. In a 1963 study of changes in oil shale's organic matter with depth, Smith
Dawsonite: Its Extraction from Green River Oil Shale

indicated that large amounts of dawsonite existed in oil shales deep in Colorado's Green River Formation. Smith and Milton (1966) then collaborated to define the dawsonite occurrence, showing its presence in substantial amounts under a large area of the Piceance Creek Basin, stratigraphically located in the lower Parachute Creek Member in continuous sections to more than 700 feet thick. Subsequent study has shown two much less massive occurrences in Colorado oil shales, one just below the Mahogany Zone (Robb and Smith 1974) and the other in the Mahogany Zone (Smith and Robb 1973; Desborough and Pitman 1974), at specific locations in the Basin. However, the major dawsonite-bearing sequence is that initially described by Smith and Milton (1966). The geographic location and thickness of this major deposit is outlined in figure 1 (Beard, Tait and Smith 1974). Several subsequent publications show detail on the stratigraphic and geographic locations where dawsonite occurs in Colorado's oil shale (Robb and Smith 1974; Beard, Tait and Smith 1974; Smith and

![Figure 1](image-url)

_Figure 1._ Geographic location and thickness of Colorado's dawsonite deposits (Beard and others 1974).
Young 1969; Smith and Young 1970; Trudell, Beard and Smith 1970; Hite and Dyni 1967).

Dawsonite exists primarily as minute, discrete crystals disseminated in oil shale. Although Smith and Milton (1966) pictured several other modes of dawsonite occurrence, they carefully pointed out that most of it existed in tiny scattered crystals. Desborough and Pitman (1974) illustrated this in their microprobe study of oil shale minerals, saying "(Dawsonite) . . . is present as finely disseminated grains . . . most abundant in the (organic) rich layers."

Nordstrandite (Al(OH)₃) was recently identified by Milton and others (1975) as the crystal form of the other oil shale mineral yielding extractable alumina. In 1967 Smith and Johnson reported their thermal analysis detection of a mineral occurring with dawsonite. Decomposition of this mineral produced an endotherm on the differential thermal analysis (DTA) plot almost coincident with the primary dawsonite decomposition endotherm. Size relationship between the two peaks varied, and they could be separated by extraction with dilute acetic acid. All the dawsonite-bearing oil shales showed this extra DTA peak, while pure dawsonite did not.

Smith and Johnson (1967) concluded that the extra peak was produced by an unknown mineral, summarizing its observed characteristics as follows:

1. it dissolved in acid or alkali;
2. it contained aluminum but little or no sodium;
3. it was not detectable in oil shale by X-ray diffraction on powder samples;
4. it degraded thermally in two steps (as will be described later);
5. it coexisted in the shale with dawsonite.

They suggested it was a mineral form of Al(OH)₃, but could not identify it further. Schmidt-Collerus and Hollingshead (1968) subsequently detected this same pair of adjacent mineral decompositions by DTA on dawsonite-bearing oil shale. Although they managed some separation of the two minerals by sink-float techniques, they concluded that the two DTA peaks were produced by two forms of dawsonite. The Laramie Energy Research Center synthesized these two postulated dawsonite forms, finding that they behave identically in thermal analysis.

In developing and applying an analytical technique for determining dawsonite and the coincident nahcolite, Smith and Young (1969; 1970) consistently determined what they classed as "excess alumina." They defined this as acid-soluble alumina not associated with sodium. The proportion ranged from 0 to 31 percent, but an average of nearly 20 percent of the total extractable alumina was "excess alumina." The only mineral source for such alumina had to be an aluminum trihydroxide. Unable to identify it mineralogically, Smith and Young (1969; 1970) labelled this
mineral "gibbsite?". Goldberry and Loughnan (1970) then found nordstrandite with dawsonite in New South Wales, Australia. Milton and others (1975) identified nordstrandite in oil shales from the Piceance Creek Basin. Since the geochemistry forming the dawsonite creates the Al(OH)$_3$ form, nordstrandite, it appears probable that all of the Al(OH)$_3$ present with the dawsonite has this mineral form.

Nordstrandite occurs everywhere with dawsonite. Both thermal analysis (Smith and Johnson 1967) and chemical analysis (Smith and Young 1969; 1970) consistently demonstrate this. Consequently nordstrandite's distribution is similar to dawsonite's.

**ANALYTICAL METHODS**

Analysis of oil shale to determine its content of dawsonite and nordstrandite presents a formidable problem. Not only do these minerals share a common element (aluminum) but sodium-containing nahcolite (NaHCO$_3$) frequently occurs with them. Also always present in the oil shale are other minerals containing elements in common with dawsonite and nordstrandite: sodium feldspar, potassium feldspar, and illite clay. Still other Green River Formation minerals which might be present to furnish common elements are halite (NaCl) (Trudell and others 1970) and analcime (NaAlSi$_2$O$_6$·H$_2$O) (Smith and Young 1969). In addition dawsonite and nordstrandite are only a small part of any oil shale sample, rarely exceeding 15 weight percent.

The only analytical method capable of specifically determining both dawsonite and nordstrandite in oil shale was developed by Smith and Young (1969). They exploited the acid solubility of these minerals to separate them from the oil shale. Their method also determines nahcolite. In figure 2 we show a flow diagram of this analysis plan which separates nahcolite and then dawsonite and nordstrandite from the oil shale by successive leaches with water and hydrochloric acid. Analysis of the filtrates for sodium and aluminum yield values for quantities of the three minerals. Interference by halite is corrected where it occurs, and analcime does not occur significantly in the dawsonite-bearing oil shale. Two other successful methods for determining nahcolite have been described, but no other means is currently available for determining both of the extractable aluminum minerals in oil shale.

Intrumental methods investigated for these determinations include X-ray diffraction, thermal analysis, and infrared spectroscopy. Infrared spectroscopy did indicate the presence of Al(OH)$_3$ in oil shales (Huggins and others 1973) but did not provide satisfactory analytical resolution of the specific absorption bands. Thermal analysis which initially detected nordstrandite in oil shale gives responses suitable for analysis for both minerals. However, several specialized problems arise in the thermal
Figure 2.—Chemical analysis flow diagram for dawsonite, nordstrandite, and nahcolite in Colorado oil shale (Smith and Young 1969). Analysis of oil shale (Smith and Johnson 1967), and a procedure satisfactory for using this technique to determine these minerals has not yet appeared. Donald R. Johnson, thermal analysis specialist studying oil shales at the Laramie Energy Research Center, feels that combined differential thermal analysis and thermogravimetry (Smith and Johnson 1967) can measure both dawsonite and nordstrandite with accuracy better than the X-ray diffraction measurement of dawsonite.

X-ray diffraction initially detected dawsonite in oil shale and is extremely useful in defining dawsonite’s occurrence profile (Robb and Smith 1974). Both the diffraction peak height and peak area respond quantitatively to dawsonite. Quantitative analysis by X-ray diffraction has many inherent perils, but dawsonite adds two more. First, dawsonite’s primary diffraction response is sensitive to grinding. Extended or vigorous grinding sharply decreases the diffraction response (Huggins, Green and Turner 1973; Zen and Hammarstrom 1975). Because of this Zen and Hammarstrom (1975) concluded "that the X-ray diffraction method is not well adapted to the routine quantitative determination of dawsonite in oil shale.
of the Green River Formation." Huggins and others (1973) didn't quite agree, recommending the X-ray diffraction method to supplement the chemical analysis technique of Smith and Young (1969). The Laramie Energy Research Center attempted to avoid the grinding problem by minimizing and standardizing grinding time. This was successful enough to reveal the second difficulty Green River dawsonite presents to quantitative analysis by X-ray diffraction, namely, the degree of crystallinity of natural dawsonite appears to vary significantly. Both the peak height and the peak area of dawsonite's primary reflection change with this variation, making quantity calibration uncertain. We agree with Zen and Hammarstrom (1975) that X-ray diffraction, while very useful semiquantitatively, is not well adapted to routine quantitative determination of dawsonite. In addition, it fails to measure nordstrandite.

Two additional techniques deserve mention. Neither offers analytical quantity determination of dawsonite and nordstrandite but each has value. The Oil Shale Corporation uses a base extraction on spent shale from oil yield assay to measure alumina available for extraction. Their procedure has not been published before this symposium (Haas and Atwood 1975), but within the limits of thermal behavior of dawsonite and nordstrandite, to be discussed later, and the possibility of base attack on clay and feldspars, their measurement of extractable alumina appears sound.

The second method involves use of already available data from oil yield assay to estimate nahcolite and dawsonite. During oil-yield assay, nahcolite, dawsonite, and nordstrandite also degrade, contributing water and carbon dioxide which is measured with the assay products. A procedure for estimating nahcolite and dawsonite from assay data was developed statistically (Smith, Beard and Wade 1972). The resulting nahcolite estimates are sufficiently accurate to permit stratigraphic plotting and correlation. The individual estimates for dawsonite are less accurate, offering only a generalized average. However, if the individual dawsonite estimates are pooled by calculating a total or average dawsonite content for a stratigraphic section, accuracy of the estimated average is much higher. The values estimated too high or too low tend to compensate each other. The resulting estimates of average dawsonite content values for stratigraphic sections lie within ± 10 percent of the actual mineral content. Nordstrandite values were not incorporated in development of these estimates because of statistical difficulties, but water arising from nordstrandite will tend to raise the dawsonite estimates. Consequently, the resulting estimate of total extractable alumina in a stratigraphic section is a good approximation.

ALUMINA RESOURCE

Measuring the dawsonite-nordstrandite resource will be a massive job requiring accurate analysis of many samples. Although some accurate
analytical data is available (Smith and Young 1969; 1970), the job is barely begun. Consequently, an estimate of the resource based on the extensive assay data available cross the deposit furnishes the best current evaluation. Beard and others (1974), prepared such an estimate, the first based on deposit-wide analytical data. The thickness contours for the dawsonite-bearing interval and the limit of the significant dawsonite resource given in figure 1 came from that paper. The thickness decreases away from the center of deposition. So does the relative amount of dawsonite. The dawsonite reserves in the Piceance Creek Basin (Beard and others 1974) are mapped in figure 3.

Total alumina resource estimated from oil-yield assay data was 6.5 billion tons (Beard and others 1974). This estimate represents enough alumina to supply United States demand for hundreds of years, demonstrating the significance of this huge domestic resource.

Figure 3.—Dawsonite isoresources in the Piceance Creek Basin (Beard and others 1974).
Dawsonite: Its Extraction from Green River Oil Shale

GEOCHEMISTRY

The dawsonite-bearing oil shale deposit of Colorado is unique. No similar sedimentary deposit is known. Even the Green River Formation oil shales in Wyoming and Utah contain no dawsonite, although they are similar to the Colorado oil shale in most respects. Several features combine to emphasize the unusual nature of the deposit: (1) The occurrence of naturally formed dawsonite in huge quantities while this mineral is rare elsewhere; (2) its coexistence with nordstrandite, a combination known in only one other place (Goldberry and Leughnan 1970); (3) the presence of massive amounts of natural sodium bicarbonate (nahcolite) in the dawsonite-bearing oil shales while other natural nahcolite occurrences are minor; and (4) the incorporation of this remarkable group of minerals in oil shale with organic matter rich in hydrogen; and (5) a mineral assemblage that is predominantly authigenic (Smith 1974).

In his discussion of the chemistry of oil shale deposition in Colorado, Smith (1974) described conditions which led to the formation of dawsonite and nordstrandite. Oil shale genesis in the Green River Formation is shown to require a stratified lake kept permanently separated by the build-up of sodium carbonate in the bottom layer. The sodium carbonate accumulation in the bottom layer raised the water's pH to the level that the incoming fine particles of aluminosilicates largely dissolved and aluminite ion (AlO₃⁻) collected in solution. When organic matter from the lake's upper layer reached lake bottom, it trapped some sodium carbonate water containing aluminate ion. As CO₂ evolved from the organic matter, the pH of the trapped water was lowered from above 11 to about 9. This condition precipitated dawsonite. Bader and Esch (1944) used almost identical conditions to synthesize dawsonite, pointing out that dawsonite was obtained only when the initial sodium carbonate to aluminate ratio was higher than 15 to 1. This condition was naturally met in the sediment (Smith 1974).

Two interrelated events accompanied dawsonite formation. Both were generated by the CO₂ supply arising from the organic matter. As the pH of the water decreased, sodium bicarbonate formed from the sodium carbonate solution as indicated in the following equation:

\[ \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{ NaHCO}_3. \]  (1)

Smith (1974) explains how this triggered nahcolite crystallization. As the pH of the interstitial water decreased, aluminate ion precipitated as aluminum trihydroxide as in the following equation:

\[ \text{AlO}_2^- + \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3. \]  (2)

Formed in this manner the Al(OH)₃ either precipitated as in Papée, Tertian and Biais (1958) or altered to nordstrandite (Schoen and Rober-
These two products came to equilibrium with dawsonite according to the following equation:

$$\text{NaAl(OH)}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3 + \text{NaHCO}_3$$  \hspace{1cm} (3)

This equilibrium explains the persistent occurrence of nordstrandite with dawsonite. Because dawsonite predominates in the oil shales (Smith and Young 1969), the equilibrium of the equation was toward the left, explaining the difficulty of locating nordstrandite without dawsonite in Colorado oil shale.

**THERMAL BEHAVIOR**

The dawsonite and nordstrandite in oil shale yield readily extractable alumina if they receive appropriate thermal treatment. Consequently, knowledge of their thermal behavior is vital. Because these minerals exist as matrix minerals in the oil shale, the thermal behavior of the balance of the rock significantly influences alumina extractability. The organic matter and the nahcolite in dawsonite-bearing oil shale affect alumina extractability most, so their thermal behavior will be described with that of dawsonite and nordstrandite.

Dawsonite decomposes around 350°C according to the following equation (Smith 1972):

$$2 \text{NaAl(OH)}_2\text{CO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3 + 2 \text{H}_2\text{O} + \text{CO}_2.$$

Simultaneous DTA and weight loss curves for this decomposition are shown in figure 4. The dawsonite sample demonstrating this decomposition pattern was natural African dawsonite (Hay 1963), a well-crystallized specimen, containing no nordstrandite. The weight loss approximates that predicted in equation (4). Equation (4) is not quite accurate, however, because the alumina form appears to retain a small amount of water. The only reflections we detected from the product by X-ray diffraction over the interval from 370°C to nearly 700°C were faint reflections of sodium carbonate. The presence of sodium carbonate in this decomposition residue was verified by Huggins and Green (1973) using infrared absorption. The balance of the residue showed no significant crystallinity. Of the possible products only the chi-alumina form of $\text{Al}_2\text{O}_3$ produces X-ray diffraction patterns sufficiently diffuse to be difficult to detect (Tertian and Papée 1958). Brindley and Choe (1961) point out that chi alumina gradually loses water once it forms. The gradual water loss detected by Huggins and Green (1973) from artificial dawsonite supports the chi-alumina form. Because dawsonite has an aluminum-trihydroxide-type structure, symbolized by writing its formula in this manner,
Dawsonite: Its Extraction from Green River Oil Shale

and because it largely exists in fine particles in the oil shale, it probably produces chi alumina, as fine-grained gibbsite does (Brindley and Choe 1961). Tertian and Papée (1958) point out that the chi alumina produced from fine particles of gibbsite is highly susceptible to rehydration, generating its elevated solubility after its escape from the dawsonite structure.

The name “chi alumina” may not be completely accurate for the alumina form resulting from dawsonite degradation. Detailed study of dawsonite may eventually define the nature of the alumina product, but this is a horribly difficult task to attempt on a natural material. In the

Figure 4.—Simultaneous DTA and TG on nordstrandite-free natural dawsonite (Smith 1972).
meantime, many of the properties outlined for the dawsonite product resemble those of chi alumina prepared from fine-grained gibbsite (Tertian and Papée 1958), so we will call it "chi alumina."

As the dawsonite residue is heated to higher temperatures (fig. 4), the water from the chi alumina is gradually lost. In addition substantial amounts of CO₂ evolve as the product sodium carbonate attacks the alumina in a solid-state reaction. At about 700°C a burst of CO₂ is lost, and a crystallization exotherm appears. At this point crystalline sodium aluminate (NaAlO₂) is detectable in the product by X-ray diffraction (Smith 1972; Huggins and Green 1973). Production of sodium aluminate is not quantitative because of mobility problems inherent in solid-state reactions. In oil shale, this solid-state reaction would involve even less of the dawsonite products.

The thermal decompositions of nordstrandite and gibbsite are virtually identical (Milton 1975). Fine-grained gibbsite decomposes to chi alumina (Brindley and Choe 1961). Coarser-grained gibbsite can decompose by a different route, first losing part of its water to form the boehmite structure near 300°C, then losing the balance of its water near 500°C to form gamma alumina (Lodding 1969). In their paper describing their initial detection of nordstrandite, Smith and Johnson (1967) reported an unexplained DTA peak at about 500°C which appeared to be associated with the nordstrandite peak near 300°C. Pure dawsonite showed no such peak. This indicates that part of the nordstrandite has crystals sufficiently large to become gamma alumina. The amount of nordstrandite which will form gamma alumina varies with heating rate and reaction atmosphere as well as crystal size. Gamma alumina is much less soluble than chi alumina (Tertian and Papée 1958); consequently, this part of the nordstrandite alumina can’t be easily recovered from spent shale.

Oil shale is normally a nonwettable, nonporous rock. However, after oil shale is heated to produce oil, spent shale wets readily with water and is full of holes arising from the virtual disappearance of the organic matter. Volume percent of organic matter in the oil shale rock can be estimated from oil yield using equations developed by Smith (1969). Shale yielding 30 gallons of oil per ton contains organic matter occupying 35 volume percent of the rock. The organic matter is finely distributed throughout the oil shale and is the largest component by volume (Smith 1969). When the organic matter in the rock decomposes under normal retorting procedures, about 80 weight percent of it is driven off as oil, water, and non-condensable gas (Smith 1962). This leaves behind a high-carbon coke which has a density well above 2 instead of that near 1 of the original organic matter. This coke occupies only about 10 percent of the volume the organic material originally occupied, so about 90 percent of the original organic volume is now void space. This is true until the shale becomes rich enough (~ 40 gpt) to collapse. After retorting, nearly one-third (31.5
Dawsonite: Its Extraction from Green River Oil Shale

percent) the volume of 30 gallon per ton oil shale is pore space—interconnected, accessible, and water wettable. This porosity throughout the retorted shale provides access to the dawsonite and nordstrandite products.

Nahcolite in oil shale decomposes at low temperature (<130°C) as follows:

\[ 2 \text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2. \]

(5)

The nahcolite crystals don't change in size or shape during this reaction, but they lose nearly 37 percent of their weight. The resulting soda-ash pseudomorph is extremely porous but sturdy. This material is more readily dissolved than nahcolite, and water will contain much more soda ash in solution than nahcolite.

The sodium carbonate generated from dawsonite and from nahcolite by heating has one detrimental effect if temperatures above 600°C are reached. It reacts with the other oil shale minerals, serving as a flux to form glass. Because the alumina and the sodium carbonate from dawsonite are close together in the oil shale, the glass formation tends to prevent alumina extraction. Coupled with the decrease in readily dissolved alumina accompanying the loss of water at higher temperatures, this glass formation makes temperature control during retorting vital to alumina extraction from spent oil shale.

EXTRACTION

Obtaining aluminum in solution is the object of any extraction procedure. If this can be achieved, economic judgments can begin. Alumina in dawsonite and nordstrandite can be dissolved to some degree by either acid or base from either the untreated shale or the shale residue after heat treatment, so each possibility should be considered.

Acid treatment will extract the nordstrandite and dawsonite from raw oil shale as shown by the success of the analysis method based on acid extraction (Smith and Young 1969). Base extraction will also separate part of the alumina, but this is less efficient because of dawsonite's slow and limited base solubility.

Acid extraction of alumina from the raw shale presents some relatively expensive processing problems. The tough shale must be ground very fine, and because fine-ground shale is not water wettable, wetting agents are required for acid treatment. Because dawsonite is the least soluble in acid of the oil shale carbonates, alumina extraction with acid requires extracting all the carbonates in the ore. Acid is generally expensive, recovery of alumina from the calcium-, iron-, and magnesium-charged solution may be difficult, and for most acids regeneration is probably uneconomic. Suggestions for decreasing the cost of acid extraction of raw shale include treatment with CO₂ and water (carbonic acid) or with sulfurous acid.
obtained by solution of \( \text{SO}_2 \). The \( \text{CO}_2 \) in water is an inexpensive acid source, but it extracts dawsonite inefficiently. Sulfurous acid extraction (Peters and others 1962) may be feasible for recovering alumina from analcime in huge tuff beds like those occurring along the northern end of the Piceance Creek Basin, but is not strong enough to extract dawsonite. While strong acid extraction makes a good analytical procedure, it probably can't be an economic production method.

Base extraction of alumina from spent shale, the residue remaining after retorting for oil production, appears the best procedure. Acid extraction will also dissolve the alumina from spent shale, but its carbonate destruction and acid consumption problems still exist. Crushing and wettability problems are removed, but these are also simplified for base extraction. The spent shale is oil-free, porous, and water wettable. Its void space provides solvent access for alumina extraction. Each ore horizon will probably have an optimum particle size for extraction and separation. If size reduction is necessary, the spent shale crushes much more easily than raw oil shale.

The base extraction procedure used on spent shale should not be the Bayer process, now preparing virtually all the alumina consumed in this country. Its treatment is expensive, unnecessarily violent, and generally unsuited for extracting alumina from spent shale.

In the spent shale most of the alumina arising from dawsonite and nordstrandite is present in one form, chi alumina. It is much more easily dissolved in base than the gamma alumina (or boehmite at lower temperatures) arising from the balance of the nordstrandite. The amount of gamma alumina formed will vary with retorting conditions, but in any case base extraction will not recover all of the acid-extractable alumina found in the original shale.

Light base will extract the chi alumina from spent shale quite efficiently. In table 1 we illustrate the \( \text{Al}_2\text{O}_3 \) extracted by 0.5 M \( \text{Na}_2\text{CO}_3 \) from samples of nahcolite-free oil shale heated under nitrogen at temperatures of 450° and 600° for 30, 60, 90, and 120 minutes. The -100 mesh residue was extracted hot with stirring. Extraction time was 3 minutes, and longer times recovered no significant additional amounts of alumina. Shorter extraction times were not tested. Before heating, the specimen yielded 6.49 weight percent acid-extractable \( \text{Al}_2\text{O}_3 \), 5.15 percent in dawsonite and 1.34 percent in nordstrandite. About 94 percent of the acid-extractable \( \text{Al}_2\text{O}_3 \) was recovered at 450°C with heating times of 30 and 60 minutes. The high-carbon coke remaining on the shale did not interfere with the extraction.

Two factors which decrease alumina extractability are indicated in table 1. Significantly less alumina was available from the shale heated 600°C, and longer heating residence times appear to decrease the amount of extractable alumina. Similar decreases in alumina availability were
Dawsonite: Its Extraction from Green River Oil Shale

Table 1.—Alumina extracted by 0.5 M Na$_2$CO$_3$ from oil shale heated at 450°C or 600°C in a nitrogen atmosphere

<table>
<thead>
<tr>
<th>Shale heating time, min.</th>
<th>Alumina recovered wt pct raw shale*</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>450°C</td>
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<tr>
<td>30</td>
<td>6.12</td>
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<tr>
<td>60</td>
<td>6.12</td>
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<tr>
<td>90</td>
<td>6.08</td>
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<tr>
<td>120</td>
<td>5.73</td>
</tr>
</tbody>
</table>

*Extraction time 3 minutes.

noted when the samples were heated in air. At a temperature controlled to 450°C under air for 60 minutes, this same sample yielded only 5.4 weight percent Al$_2$O$_3$ to base extraction and a 600°C sample only 4.95 percent. Air over the sample undoubtedly burned part of the shale’s organic matter, heating the sample hotter than the controlled temperature.

These solubility reductions stemmed from the two effects mentioned earlier, glass formation and the loss of water from the chi alumina. Heating to higher temperatures under nitrogen gradually reduced the amount of available alumina, indicating the gradual loss of water. Apparently the glass formation had used up the available sodium carbonate by 600°C. To test this, shale samples intimately mixed with NaHCO$_3$ (analogous to crushed nahcolite) were heated. This treatment at 650°C reduced the extractable alumina to only 10 percent although more than 80 percent had been available after heating the nahcolite-free sample at this temperature. Apparently limiting the temperature to no more than 550°C is essential to prevent glass formation. Elimination of nahcolite from the sample can help, but Na$_2$CO$_3$ from the dawsonite will always be present. The loss of water from chi alumina can be minimized by short residence times and use of a limited temperature range. Oil evolution from the raw shale can be completed quickly at about 450°C, the most suitable temperature neighborhood for heating oil shale for both oil and alumina production.

Dissolving chi alumina consumes base. The solution equation with sodium carbonate might be represented as follows:

$$\text{Al}_2\text{O}_3 + 2 \text{CO}_3^- + \text{H}_2\text{O} \rightarrow 2 \text{HCO}_3^- + 2 \text{AlO}_2^-.$$

(6)

Production of the bicarbonate ion from the carbonate ion shows that one mole of hydroxyl ion was used up in dissolving one mole of aluminum. This equivalent reaction is

$$\text{Al}_2\text{O}_3 + 2 \text{(OH)}^- \rightarrow 2 \text{AlO}_2^- + \text{H}_2\text{O}.$$

(7)
The amount of aluminate ion which can be retained in solution depends on the amount of hydroxyl ion (pOH or the equivalent pH) in the solution (Pourbaix 1966). If the available base is consumed, the pH drops and solution of chi alumina will stop. This explains why water-leaching the retorted shale will not extract all of the available alumina. When dawsonite decomposes [eq. (4)], only one mole of carbonate is produced for two moles of aluminum in alumina. This is only half the base required [eq. (6)] to dissolve the alumina. In addition the nordstrandite product will require base to dissolve. If sodium aluminate were produced when dawsonite decomposes instead of the intimate sodium carbonate-chi alumina mixture indicated in equation (4), it would dissolve with little base consumption. Water extraction would then recover all of the dawsonitic alumina.

Enough base must be present in excess to maintain the aluminate ion in solution. If too much is consumed, the hydrolysis reaction

$$2 \text{AlO}_2^- + 4 \text{H}_2\text{O} \rightarrow 2 \text{Al(OH)}_3 + 2 \text{OH}^-$$

will buffer the solution. The reaction in equation (8) will limit alumina loss but the leach solution will dissolve no more alumina.

The other oil shale minerals are also exposed to light base when alumina is extracted from spent shale. The minerals include quartz, soda feldspar, potash feldspar, illite, iron-bearing dolomite, and pyrite (Robb and Smith 1974). These occur ubiquitously with dawsonite. All occur as very small particles and are usually well crystallized. Calcite will appear sporadically as will the siderite-magnesite cocrystal labeled “ferroan” (Young and others 1975). When oil shale is heated to 450°C in the inert atmosphere necessary for alumina recovery, quartz, the feldspars, illite, and calcite remain unaltered. Ferroan and dolomite will lose some CO₂ depending on residence time and CO₂ pressure in the retort. Extraction with soda ash will largely prevent solution of the carbonates and the residual oxides. Pyrite will become ferrous sulfide in the spent shale and will resist solution, although a small amount of soluble sulfide may appear because of H₂S attack on carbonates during retorting.

Only silica solution seems a possible problem. The tiny silicate particles present a huge contact surface but they are well crystallized and resist solution. Tests on silica solution at LERC indicate that relatively little can be dissolved. The small amounts will not interfere until aluminum trihydroxide is prepared for metal extraction. Here even tiny amounts are objectionable, so extraction conditions should be optimized to extract alumina and leave silica behind. Extracting with just enough base to dissolve the alumina and keep it in solution seems the best way to accomplish this. While this is easily done in a laboratory, commercial production will require continuous multiple extractions to raise the aluminate ion levels in the extract. Maintaining the most suitable base balance in such equipment may be a problem. The technique of successive base additions
described by MacMillan and Jackson (1972) coupled with the countercurrent decanter extractors described by Weichman (1974) seems to offer an attractive approach. If it can be accomplished, a desilication step in a production process should be unnecessary.

Analcime occurs peripheral to the major dawsonite deposits. Production of alumina from areas where analcime occurs should be avoided, because analcime yields silica readily dissolved by base extraction.

The base extraction of spent shale seems the most probable route to alumina production from oil shale. This procedure is the basis of three workable patents for such alumina production (MacMillan and Jackson 1972; Hall and Haas 1970; Van Nordstrand 1968). All three use both sodium carbonate and sodium hydroxide in their extraction processes. These are equivalent in aluminum extraction, but sodium hydroxide is more useful than soda ash for pH control. Soda ash can be readily obtained as a by-product, and sodium hydroxide can be readily manufactured from it using heated limestone or perhaps the dolomite remaining in the shale after extraction.

To summarize the optimum procedures for extracting alumina from oil shale, the raw shale should first be heated to drive out the organic matter and decompose the nordstrandite and dawsonite. Atmosphere over the shale should be inert or at least not oxidizing in order to achieve temperature control of the retorting step. The shale should be heated between 450°C to no more than 550°C for only as long as is necessary to evolve the organic matter as oil. Burning the residual carbon coke is neither necessary nor desirable. The resulting spent shale is porous, permeable, wettable, and easily crushed. Crushing should be limited to that necessary to facilitate fast and efficient extraction but permit easy separation of the spent shale residue. The extraction should be rapid and continuous, and it should minimize shale exposure to strong base. Control of the amount of nahcolite entering the retorting process will help prevent glass formation and will also help the solvent recovery processes. The recovery of alumina from sodium aluminate solutions will probably involve precipitation of Al(OH)₃ with CO₂. This works well, and the procedures are known. Sodium concentration in the aluminum-bearing liquor must be kept low enough to prevent dawsonite formation during Al(OH)₃ precipitation.

**COMPARISON WITH BAYER PROCESS**

To compete with the long established Bayer process, still in use more than 80 years after issuance of its primary patent (Bayer 1894), a new process applied to a new ore must have technologic and economic advantages. Extracting alumina from oil shale seems to have such advantages. The primary advantage is that Colorado’s dawsonite-bearing oil shale is
a huge domestic resource, irrefutably an asset.

The Bayer process requires ores high in alumina (~ 50 percent Al₂O₃) and low in silica (usually < 4 percent SiO₂) (Reese 1955). On this basis the oil shale is not a resource, so we need to evaluate what actually is available. In figure 5 we show the oil yield in gallons/ton and the dawsonite-nordstrandite alumina in weight percent of spent shale in a 277-foot interval selected from Bureau of Mines Colorado Corehole No. 2 (Smith and Young 1969). The corehole was drilled in sec 14, T 1 S, R 99 W, Rio Blanco County, Colorado. The interval selected for evaluation occurs at

![Figure 5](image_url)

*Missing

Figure 5.—Oil yield and extractable alumina in spent shale from Colorado corehole number 2 interval, 1903 to 2180 feet (Smith and Young 1970).
the bottom of the leached zone. To avoid the complication of small amounts of nahcolite in the section, the values are calculated nahcolite-free. Average oil yield for the 277-foot section is 32.4 gallons per ton, and average alumina from dawsonite and nordstrandite in the spent shale is 4.97 weight percent. A plant processing about 30,000 tons of raw shale per day of this section could yield about 1,000 tons of alumina per day at 90 percent recovery. Preparing the shale for alumina extraction would produce 23,000 barrels of oil, and associated nahcolite plus dawsonite will produce soda ash. The required development of coproducts with the alumina is a significant asset to alumina production from oil shale.

Technologies of the Bayer process and the oil shale extraction contrast sharply, and several processing advantages to the oil shale extraction may compensate for the relatively small amount of alumina available per ton of spent shale. For equal alumina production, processing spent shale requires handling 10 times as much 5 weight percent Al₂O₃ material as does 50 weight percent bauxite. To point out advantages in spent shale extraction this process must be compared with the Bayer process (Bayer 1894). Unfortunately, in the United States the Bayer process is proprietary, and we couldn't find a review on it prepared since 1955 (Reese 1955). In 1966 Peters and others outlined the Bayer process as part of their cost study on alumina production. They point out that although the original process has been modified, particularly to adapt it to different ores, it is still basically the original Bayer process.

The Bayer process is shown in figure 6 (Peters and others 1966). The major contrasts between the two processes lie in the pressure digestion, clarification, and precipitation steps. Specific differences between the two processes will be itemized and evaluated.

**Pressure Digestion**

**Bayer**

Ore ground to -20 mesh is digested at high pressure (commonly 200+ psig) and high temperature (to 400°F) in strong base (4 to 12 N) for periods of time ranging from 30 minutes to overnight (Reese 1955; Peters, Johnson and Kirby 1966).

**Oil Shale**

After inert atmosphere retorting to produce oil, alumina is dissolved from spent shale quickly and continuously in light base (~1N).

**Comparison**

The Bayer process is actually a batch process while oil shale retorting and extraction is a continuous process. The Bayer process is violent and
requires expensive specialized equipment for the extraction, including pressure and temperature control apparatus. It dissolves silica which precipitates with sodium and aluminum from the concentrated extract. Oil shale can be extracted under mild conditions using standard extraction.

**Figure 6.** Bayer process (Peters and others 1966).
equipment. Little silica will dissolve from the oil shale, eliminating the loss of caustic and alumina to the scale-forming sodium aluminum silicate precipitate which plagues the Bayer process. The moderate temperature and pressure conditions inherent in oil shale processing will minimize water requirements which are large in the Bayer process.

**Clarification**

*Bayer*

Separation of the undissolved residue from pressure digestion, called "red mud," is a complex procedure made difficult by the fine-particle product resulting from digestion. Many of the recently published improvements on the Bayer process center on speeding the settling rate of the red mud from the aluminum-bearing solution. Washing the red mud, now accomplished with large series multistage countercurrent mud washers (Reese 1955), is also a difficult procedure.

*Oil Shale*

The soluble alumina can be extracted efficiently from much larger spent shale particles. Particle size control to retorting and extraction can optimize both the extraction and the separation rate. Particles as small as those generated in the Bayer process [<1μ for some ores (Reese 1955)] need never appear in the spent shale.

**Comparison**

The spent shale settling equipment will have to handle many times the solids volume that the red mud from the Bayer process represents. However, the spent oil shale is easy to extract to wash and to filter and the possibility of using and maintaining larger particles, and the lower density of the liquor carrying the particles being separated all tend to make spent shale separation much easier than red mud separation.

**Precipitation**

*Bayer*

Aluminum trihydroxide is precipitated from the supersaturated "green liquor" by cooling, then seeding the liquor with as much additional aluminum trihydrate as is in the "green liquor." The precipitation is rapid at first, then slows. Total precipitation time is 65 hours, and only 50 percent of the alumina in the liquor is recovered (Peters and others 1966). After the Al(OH)_3 precipitate is removed, the spent liquor is reconditioned and recycled.
Oil Shale

Extracting alumina from spent shale requires only enough excess base to keep the low concentration of aluminate ion in solution. This limited base will neutralize readily on injecting CO₂, and the solution will shortly begin to precipitate Al(OH)₃. Seeding with about 25 percent of the liquor's Al(OH)₃ (Peters and others 1967) may be useful to provide particle size control. Hall and Haas (1970) found this precipitation both quick and nearly quantitative on a laboratory scale. The resulting sodium bicarbonate solution containing only a limited amount of alumina is reprocessed for soda ash recovery and recycling.

Comparison

Aluminum trihydroxide precipitation in the Bayer process is an art, according to Reese (1955). The required temperature control, the long storage time necessary for precipitation, and the density of the residual solution [making Al(OH)₃ separation difficult] indicate that it is also an expensive art. Chemical precipitation of Al(OH)₃ from the spent shale extract is much more likely to be a science.

Additional factors, which may provide alumina extraction from oil shale some economic advantage, include the availability of process materials from the processed ore. Soda ash will be produced routinely from dawsonite even in the absence of nahcolite. Co-occurring nahcolite can provide soda ash, if necessary. If not, the nahcolite may be mechanically separated for use as an SO₂ absorbent (Weichman 1974). The CO₂ required for the precipitation may be obtained from flue gas (Peters and others 1967) or might be recovered from processing the co-occurring nahcolite. Lime for generating the NaOH required could be obtained by firing some of the washed spent shale discard.

Aluminum Metal Production

Nielsen (1969) suggested producing aluminum metal from the oil shale products, burning the oil on site to generate the D.C. electric power required for electrolyzing the alumina. A test balance on energy available for electrolysis can be made using the specimen section described in figure 5. Aluminum metal production, including the heat-up of the molten salt bath, requires up to 13 kilowatt-hours of direct current energy per pound of aluminum metal produced (Shreve 1956). The 1,000-ton alumina yield indicated for 30,000 tons of dawsonite-bearing oil shale per day will yield 529 tons of aluminum metal. Consequently, production of aluminum metal will require 13.8 x 10⁶ kilowatt-hours of electrical energy daily.

The 23,000 barrels per day of shale oil represents 1.38 x 10¹¹ Btu of heat energy. On the basis that 3,412 Btu equal 1 kilowatt-hour, this repre-
sents $40.4 \times 10^6$ kilowatt-hours per day from oil combustion. Energy available from the oil appears adequate. However, thermal efficiency of electricity generation is a limiting factor. A thermal efficiency of 34 percent would be required to produce aluminum metal from all the oil produced. Additional energy would be available from the retort gas.

CONCLUSION

Production of alumina from oil shale bearing dawsonite and nordstrandite with simultaneous production of shale oil and sodium carbonates is technically feasible. Advantages in the extraction properties of spent shale may compensate adequately the disadvantage imposed by extracting large quantities of spent shale. Production techniques should be designed around the character of the oil shale, not applied directly from the Bayer process.

REFERENCES


Haas, F. C., and Atwood, M. T., 1975, Recovery of alumina from dawsonitic oil shales: Colorado School Mines Quart., v. 70, no. 3.


Dawsonite: Its Extraction from Green River Oil Shale


RECOVERY OF ALUMINA FROM DAWSONITIC OIL SHALES

Frank C. Haas and Mark T. Atwood

ABSTRACT

A process for the recovery of alumina from dawsonitic oil shales is outlined. A definitive assay procedure for determination of recoverable alumina in oil shale cores is described.

INTRODUCTION

The United States consumes about 13 million tons per year of alumina for the manufacture of aluminum metal. All but 1 million tons of the raw material, bauxite, is imported. Foreign suppliers of bauxite are continually exposed to the example of the Organization of Petroleum Exporting Countries (OPEC). There are vast reserves of recoverable alumina in the Piceance oil shale basin which must be removed in concert with oil recovery. Commercial development must proceed through the logical steps of: (1) resource evaluation, using an assay procedure for alumina which yields the maximum amount of recoverable alumina, and (2) the development of an alumina recovery process which can be interfaced with oil production.

RESOURCES

The first attempt to describe dawsonite reserves in the Piceance Creek Basin was published by Smith and Milton (1966). The wide distribution and vast magnitude of this mineral resource were delineated. Based on an examination of one oil shale core from the northern part of the Piceance Basin, Hite and Dyni (1967) estimated that the potential reserves of alumina, from contained dawsonite, amounted to about 42 million tons per square mile. This is a reserve greater than the known bauxite reserves of the United States. Beard, Tait and Smith (1974) espi-

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Frank C. Haas and Mark T. Atwood, The Oil Shale Corporation, Golden, Colorado 80401.
mated that the total reserves of dawsonitic alumina in the Parachute Creek Member of the Green River Formation of Colorado was about 6.5 billion tons. These reserves are associated with large deposits of nahcolite.

Finally, Ziemba (1974) reported the presence of about 500 feet of dawsonite bearing oil shale under federal lease tract C-a. This tract is being developed by Gulf Oil Corporation and Standard of Indiana.

An evaluation of the economics of recovery of these vast reserves requires precise determination of the alumina recoverable from oil shale core samples. The assay procedure must be in harmony with the anticipated oil and alumina recovery processes.

The alumina recovery process developed must be applicable to the processed shale produced from the shale oil recovery process, and the produced alumina must meet the rigid specifications of aluminum manufacturers. Finally, the proposed commercial plant must be environmentally sound.

Since there is little dawsonite in the oil rich Mahogany Zone, it is economically feasible to produce oil without recovering the inorganic minerals. In the deeper dawsonitic oil shale zones, the oil and alumina must be produced together.

**Assay Procedures**

The first analyses were for the mineral dawsonite and were conducted by X-ray diffraction (Smith and Milton 1966; Huggins, Green and Turner 1973). Later, a chemical method was developed for dawsonite determination in raw oil shale which involved, first, water extraction to remove nahcolite, and second, mineral acid extraction to remove acid soluble sodium minerals which are insoluble in water (Smith and Young 1969). Later, an ingenious method was developed for estimating the amounts of nahcolite and dawsonite in oil shale from Fischer assay data for water yield and “gas plus loss.” This is based on the fact that nahcolite yields, on Fischer assay retorting, one-half mole of carbon dioxide and one-half mole of water; and dawsonite yields one mole of water and one mole of carbon dioxide. This method is somewhat useful for nahcolite, but poor correlations were obtained on dawsonite. It is necessary that analcime (NaAlSi₃O₈ · H₂O) not be present, since it releases a mole of water during Fischer assay. This method was applied to determination of nahcolite and dawsonite reserves in the Piceance Basin (Smith and others 1972).

These procedures may provide realistic values for dawsonite, but dawsonite is not the only mineral which yields easily recoverable alumina (Smith and Johnson 1967; Desborough and Pitman 1974). There is need for an improved and more realistic assay procedure for total recoverable alumina.
Recovery Processes

There are a number of published or patented processes for the recovery of alumina from dawsonitic oil shale. These can be generally divided into schemes which recover alumina from oil shale ash residue, and those which recover alumina from a pyrolysis (retort) residue. Hall and Haas (1970) patented a process for recovery of sodium aluminate from spent shale which had been roasted at a temperature of 450 to 760°C. Nielsen (1969) described a process for leaching retorted shale with caustic and precipitation of alumina from the leach liquor with carbon dioxide. Dyni (1972) patented the recovery of alumina from spent shale by water leaching. Savage and Bailey (1968) also described caustic leaching of processed shale. Weichman (1974) outlined a process for “light caustic leach” of spent shale followed by carbonation or seeding to produce alumina trihydrate. Haas (1973) patented a process scheme for spent shale leaching, using a mixture of dilute aqueous soda ash and caustic soda.

Finally, Haas (1975) developed a process for alumina recovery from processed shale which involves leaching the processed shale with a dilute alkaline leach liquor at a low temperature, i.e., less than 40°C, and with a short contact time, followed by precipitation of product alumina trihydrate from the pregnant leach liquor, at an elevated temperature of 60 to 75°C, using alumina trihydrate seed to precipitate the product. The low temperature of leaching inhibits co-leaching of silica, and the precipitation of alumina trihydrate at an elevated temperature inhibits co-precipitation of silica. The specification for silica in cell grade alumina is very restrictive.

Analytical Procedures

Early in our research program, we investigated a variety of analytical procedures to determine the amount of recoverable alumina present in oil shale. These included analyzing both shale ash (roasted at various temperatures) and spent shale by leaching with water, various concentrations of sodium hydroxide, sodium carbonate and mixtures of caustic and soda ash. Other variables studied were time and temperature of leaching. After analyzing various samples from different parts of the Piceance Creek Basin, we found that the most reliable results were obtained analyzing spent shale by leaching with 0.5 N NaOH solution.

The procedure is simple and fast. One gram of Fischer assay residue (Goodfellow and Atwood 1974), ground to minus 65 mesh, is leached at room temperature for 10 minutes with 50 ml of 0.5 N NaOH solution. The solids are filtered off and the filtrate solution is then analyzed for alumina by conventional atomic absorption techniques.

*The retort residue is referred to as both spent and processed shale.
We have compared our results with the Bureau of Mines acid leach procedure (Smith and Young 1969). Results are given in tables 1 and 2. In table 1, the HCl extraction was done on raw shale and the NaOH extraction, as described above, was done on spent shale. The values obtained on spent shale were then corrected back to a raw shale basis, based on the Fischer assay weight loss. In table 2, both acid and base extractions were done on spent shale.

**Table 1.—Acid extraction vs. alkaline extraction (raw shale basis % Al₂O₃)**

<table>
<thead>
<tr>
<th>Sample (Ft)</th>
<th>HCl Extraction</th>
<th>NaOH Extraction</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004-2005</td>
<td>2.13</td>
<td>2.54</td>
<td>+19.2</td>
</tr>
<tr>
<td>2021-2022</td>
<td>5.48</td>
<td>5.68</td>
<td>+ 3.6</td>
</tr>
<tr>
<td>2023-2024</td>
<td>4.87</td>
<td>5.18</td>
<td>+ 6.4</td>
</tr>
<tr>
<td>2093-2094</td>
<td>6.61</td>
<td>6.61</td>
<td>0</td>
</tr>
<tr>
<td>2094-2095</td>
<td>7.93</td>
<td>7.81</td>
<td>- 1.5</td>
</tr>
<tr>
<td>2095-2096</td>
<td>4.30</td>
<td>5.21</td>
<td>+21.2</td>
</tr>
<tr>
<td>2069-2070</td>
<td>2.81</td>
<td>3.45</td>
<td>+22.8</td>
</tr>
<tr>
<td>2085-2086</td>
<td>2.68</td>
<td>3.14</td>
<td>+17.2</td>
</tr>
<tr>
<td>2089-2090</td>
<td>4.64</td>
<td>5.08</td>
<td>+ 9.5</td>
</tr>
<tr>
<td>2090-2091</td>
<td>3.87</td>
<td>4.09</td>
<td>+ 5.7</td>
</tr>
</tbody>
</table>

**Table 2.—Acid extraction vs. alkaline extraction on spent shale samples % Al₂O₃**

<table>
<thead>
<tr>
<th>Sample (Ft)</th>
<th>HCl Extraction</th>
<th>NaOH Extraction</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004-2005</td>
<td>2.42</td>
<td>2.82</td>
<td>+16.5</td>
</tr>
<tr>
<td>2021-2022</td>
<td>6.04</td>
<td>7.14</td>
<td>+18.2</td>
</tr>
<tr>
<td>2061-2062</td>
<td>5.13</td>
<td>4.48</td>
<td>-12.7</td>
</tr>
<tr>
<td>2093-2094</td>
<td>7.08</td>
<td>8.50</td>
<td>+20.0</td>
</tr>
<tr>
<td>2094-2095</td>
<td>8.21</td>
<td>9.18</td>
<td>+11.8</td>
</tr>
</tbody>
</table>

In both cases, the NaOH extraction tends to give somewhat higher recoverable alumina than does the HCl extraction.

There is one disadvantage in analyzing spent shale samples; samples should be analyzed as soon as possible after the Fischer assay is made. As spent shale ages, lower alumina values will result, especially if the spent shale is exposed to air or moisture. We have found that by storing samples in sample envelopes, the spent shale is stable for at least 3 to 4 weeks.

**DECOMPOSITION OF DAWSONITE**

Two equations have been proposed for the decomposition of dawsonite:
Recovery of Alumina from Dawsonitic Oil Shales

(A) \[ \text{NaAlCO}_3(\text{OH})_2 \rightarrow \text{NaAlO}_2 + \text{CO}_2 + \text{H}_2\text{O} \]

(B) \[ 2\text{NaAlCO}_3(\text{OH})_2 \rightarrow \text{Al}_2\text{O}_3 + \text{Na}_2\text{CO}_3 + \text{CO}_2 + 2\text{H}_2\text{O} \]

Previous investigators have not agreed as to which mechanism is involved in the decomposition of dawsonite. Savage and Bailey (1968), using differential thermal analysis, concluded that dawsonite decomposed at 370°C according to equation (A). Loughnan and See (1967), using thermogravimetric analysis, concluded that reaction (B) took place between 290 and 330°C. Smith and Johnson (1967) agreed with equation (B). Huggins and Green (1973) found that below 350°C, all of the water and two-thirds of the carbon dioxide was given off. The remaining carbon dioxide was then slowly evolved between 350 and 650°C.

Our studies have shown that about 90 percent of the carbon dioxide is evolved at 300°C, and the balance evolves slowly between 350 and 650°C. The procedure used for determining this is described below.

Samples of synthetic dawsonite were heated at various temperatures for 15 minutes, and then, portions leached with H\(_2\)O and 0.5 N NaOH solution at 2 percent solids. The water leach was then analyzed for carbonate ion. From the amount of carbonate ion present, the percentage of theoretical carbon dioxide evolved can be calculated. The caustic leach was analyzed for alumina and alumina extraction calculated. Results are given in table 3.

From the data presented in table 3, it appears that neither reaction (A) nor (B) represents the sole mechanism of dawsonite decomposition, however, reaction (A) seems to be the predominate one at the temperatures investigated. Both reactions occur at 300°C, but at 650°C, reaction (B) is almost nonexistent.

Optimum alumina extraction occurs after heating dawsonite in the temperature range of 450 to 650°C.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>%CO(_2) Evolved</th>
<th>%Al(_2)O(_3) Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>89.8</td>
<td>81</td>
</tr>
<tr>
<td>350</td>
<td>93.1</td>
<td>93</td>
</tr>
<tr>
<td>450</td>
<td>94.8</td>
<td>96</td>
</tr>
<tr>
<td>500</td>
<td>95.9</td>
<td>99</td>
</tr>
<tr>
<td>550</td>
<td>96.6</td>
<td>98</td>
</tr>
<tr>
<td>650</td>
<td>99.4</td>
<td>99</td>
</tr>
</tbody>
</table>

Table 3.—Decomposition of dawsonite vs. temperature
RECOVERY OF ALUMINA

Leaching

Alumina can be recovered from dawsonitic oil shales by first retorting the shale at about 500°C to decompose the kerogen. The spent shale is then rapidly leached at ambient temperatures and about 40 percent solids. After a liquid-solids separation, the pregnant leach liquor is heated to about 65°C and seeded with previously precipitated alumina trihydrate to precipitate the alumina. The precipitated alumina is then dried and calcined. One of the major problems associated with producing cell-grade alumina from shales has been silica contamination. By leaching cold and precipitating hot, this problem has been overcome.

Various parameters have been studied in the leaching step, e.g., time, temperature, percent solids and caustic concentration. It was found that conditions of 40 percent solids, 25°C, 20 g/l NaOH leach solution and one minute or less of leach time gave good alumina extractions with minimum silica dissolution. A summary of results is given in table 4. The spent shale used in these tests contained 3.8 percent Al₂O₃.

Precipitation

The sodium aluminate leach liquor is almost supersaturated with respect to sodium aluminate. If given enough time, the leach liquor will begin to decompose on its own according to the following reaction:

\[
\text{(C)} \quad 2\text{NaAlO}_2 + 4\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 2\text{NaOH}
\]

This reaction can be speeded up by the addition of an alumina trihydrate seed. In tables 5 and 6 we show the effect of time, temperature and seed ratio on alumina and silica precipitation. The data show that the best temperature range for precipitation is from 60 to 80°C with the optimum being at 65°C. Fifty percent of the alumina is precipitated in 1 to 2 hours, whereas, only 7 percent of the silica is precipitated. All the silica seems to precipitate in the first 30 minutes. Alumina precipitation is relatively slow at 30 and 90°C. Although alumina precipitates with seed ratios of 1:1 to 8:1, the rate is slower at a 1:1 ratio which is to be expected. The rate increases with seed ratio.

Recycle Leaching and Precipitation

Inspection of reaction (C) shows that caustic is generated from the decomposition of sodium aluminate leach liquors. This implies that once the leaching and precipitation cycle has been started, then the process is self-sufficient in caustic requirements. Test work has shown this to be the
## Table 4.—Alumina extraction from oil shale

<table>
<thead>
<tr>
<th>Leach Temp, °C</th>
<th>Leach Time, Min.</th>
<th>Leach Liquor g/1 NaOH</th>
<th>Pregnant Liquor g/1 Al₂O₃</th>
<th>% Al₂O₃ Ext'n</th>
<th>% Al₂O₃</th>
<th>g/1 SiO₂</th>
<th>% SiO₂</th>
<th>Ext'n</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>10</td>
<td>20</td>
<td>18.05</td>
<td>0.143</td>
<td>95</td>
<td>0.143</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>10</td>
<td>10</td>
<td>8.10</td>
<td>0.062</td>
<td>100</td>
<td>0.062</td>
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<tr>
<td>60</td>
<td>1</td>
<td>20</td>
<td>18.04</td>
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<td>0.090</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>10</td>
<td>15.83</td>
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<td>88</td>
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<tr>
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<td>19.11</td>
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<td>99</td>
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<tr>
<td>25</td>
<td>1*</td>
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<td>15.85</td>
<td>0.030</td>
<td>91</td>
<td>0.030</td>
<td>91</td>
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<td>20</td>
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<td>99</td>
<td>0.023</td>
<td>99</td>
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<td>10</td>
<td>8.38</td>
<td>0.015</td>
<td>99</td>
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<td>99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>20</td>
<td>7.13</td>
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<td>100</td>
<td>0.012</td>
<td>100</td>
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</tr>
<tr>
<td>25</td>
<td>0.5</td>
<td>20</td>
<td>19.26</td>
<td>0.027</td>
<td>92</td>
<td>0.027</td>
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<tr>
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<td>15</td>
<td>17.76</td>
<td>0.019</td>
<td>96</td>
<td>0.019</td>
<td>96</td>
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<td>10</td>
<td>16.96</td>
<td>0.016</td>
<td>83</td>
<td>0.016</td>
<td>83</td>
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<td>25</td>
<td>0.25</td>
<td>20</td>
<td>19.73</td>
<td>0.030</td>
<td>98</td>
<td>0.030</td>
<td>98</td>
<td></td>
</tr>
</tbody>
</table>

## Table 5.—Alumina and silica precipitation vs. time and temperature (5:1 seed ratio)

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Precip. Time, Hr.</th>
<th>Solution Analyses (g Al₂O₃/1 g SiO₂/1)</th>
<th>% Al₂O₃ Precip.</th>
<th>% SiO₂ Precip.</th>
<th>% SiO₂ in Prod. (Calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0</td>
<td>19.26 0.027</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>19.26 0.027</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>17.56 0.025</td>
<td>8.8</td>
<td>7.4</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>14.40 0.026</td>
<td>25.2</td>
<td>3.7</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>12.90 0.024</td>
<td>33.0</td>
<td>11.1</td>
<td>0.047</td>
</tr>
<tr>
<td>65</td>
<td>0</td>
<td>19.01 0.027</td>
<td>38.3</td>
<td>7.4</td>
<td>0.027</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>11.73 0.025</td>
<td>38.3</td>
<td>7.4</td>
<td>0.022</td>
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<tr>
<td></td>
<td>1</td>
<td>10.00 0.025</td>
<td>47.4</td>
<td>7.4</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.53 0.025</td>
<td>55.1</td>
<td>7.4</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>7.82 0.025</td>
<td>58.9</td>
<td>7.4</td>
<td>0.018</td>
</tr>
<tr>
<td>90</td>
<td>0</td>
<td>18.20 0.027</td>
<td>31.8</td>
<td>14.8</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>12.41 0.023</td>
<td>31.8</td>
<td>14.8</td>
<td>0.064</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>12.06 0.023</td>
<td>33.7</td>
<td>14.8</td>
<td>0.064</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>11.91 0.023</td>
<td>34.6</td>
<td>14.8</td>
<td>0.064</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>11.76 0.023</td>
<td>35.4</td>
<td>14.8</td>
<td>0.062</td>
</tr>
</tbody>
</table>
case; in fact, the process is a net producer of caustic and soda ash due to reactions (B) and (C). Instead of starting the cycle with 20 g/l NaOH solution, one could start with water. Alumina extraction in the first cycle would drop to about 60 percent from an expected 95+ percent, but sufficient caustic would be generated in the first and second precipitation cycles so that alumina extraction would increase rapidly to 95+ percent.

Data of a seven cycle leaching and precipitation test is summarized in table 7. In the first cycle, spent shale was leached at 40 percent solids for about one minute at 25°C with 20 g/l NaOH solution. After filtration, the leach liquor was heated from 70 to 80°C and seeded with alumina trihydrate at 5:1 seed ratio. After about half of the alumina precipitated, the product was filtered and the barren liquor was cooled to 25°C and was used to leach fresh spent shale under the same conditions as above. This procedure was followed for seven cycles.

After seven cycles, average alumina extraction was 95 percent, average alumina precipitation was 60 percent and average calculated silica content of the product was 0.026 percent SiO₂. Silica, in the product, was calculated from the solution analyses before and after precipitation.

All test work done so far was on dawsonitic oil shale that was free of nahcolite. In order to determine the effect of nahcolite containing shale,
the same shale used above was spiked with 4 percent NaHCO₃ prior to retorting. It was assumed that nahcolite in excess of 4 percent would be removed and recovered prior to retorting. The same procedure for leaching and precipitation was used as described above except all alumina precipitations were for 30 minutes, and the precipitation temperature for the first five cycles was 80°C, and then was lowered to 65°C for the remainder of the test. In addition, a 10 percent bleed of the barren liquor was taken to prevent excessive carbonate ion buildup. Results of the test are given in Table 8.

There appeared to be no adverse effect on the process or the product properties by adding the nahcolite. Average alumina precipitation was 53 percent. During the first five cycles with a precipitation temperature of 80°C, the calculated silica content of precipitated alumina averaged 0.045 percent. The temperature was lowered to 65°C for the last nine cycles.

**Table 7.—Direct precipitation at 70°C to 80°C; recycle leach liquor cooled to 25°C**

<table>
<thead>
<tr>
<th>Cycle and Liquor Type</th>
<th>Precip. Time, Hrs.</th>
<th>Solution Analyses</th>
<th>% Al₂O₃ Extrn</th>
<th>% Al₂O₃ Precip.</th>
<th>% SiO₂ in Prod. (Calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>g Al₂O₃/1</td>
<td>g SiO₂/1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>First Cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pregnant</td>
<td>4.0</td>
<td>20.76</td>
<td>0.045</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>Barren</td>
<td>19.5</td>
<td>8.95</td>
<td>0.044</td>
<td>57</td>
<td>0.008</td>
</tr>
<tr>
<td>Barren</td>
<td>19.5</td>
<td>7.95</td>
<td>0.044</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>Second Cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pregnant</td>
<td>4.0</td>
<td>24.75</td>
<td>0.041</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>Barren</td>
<td>4.0</td>
<td>9.79</td>
<td>0.039</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>Third Cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pregnant</td>
<td>0.5</td>
<td>26.98</td>
<td>0.043</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>Barren</td>
<td>0.5</td>
<td>11.67</td>
<td>0.041</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>Barren</td>
<td>1.0</td>
<td>11.67</td>
<td>0.041</td>
<td>57</td>
<td>0.013</td>
</tr>
<tr>
<td>Barren</td>
<td>2.0</td>
<td>11.51</td>
<td>0.041</td>
<td>60</td>
<td>0.013</td>
</tr>
<tr>
<td>Barren</td>
<td>3.0</td>
<td>11.11</td>
<td>0.039</td>
<td>57</td>
<td>0.025</td>
</tr>
<tr>
<td>Fourth Cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pregnant</td>
<td>0.5</td>
<td>26.05</td>
<td>0.043</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>Barren</td>
<td>0.5</td>
<td>10.33</td>
<td>0.038</td>
<td>60</td>
<td>0.032</td>
</tr>
<tr>
<td>Barren</td>
<td>1.0</td>
<td>9.37</td>
<td>0.038</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>Fifth Cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pregnant</td>
<td>0.5</td>
<td>23.70</td>
<td>0.034</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>Barren</td>
<td>0.5</td>
<td>10.08</td>
<td>0.029</td>
<td>54</td>
<td>0.037</td>
</tr>
<tr>
<td>Sixth Cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pregnant</td>
<td>0.6</td>
<td>25.91</td>
<td>0.030</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>Barren</td>
<td>0.6</td>
<td>9.58</td>
<td>0.026</td>
<td>63</td>
<td>0.024</td>
</tr>
<tr>
<td>Seventh Cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pregnant</td>
<td>0.5</td>
<td>23.27</td>
<td>0.032</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>Barren</td>
<td>0.5</td>
<td>9.59</td>
<td>0.028</td>
<td>59</td>
<td>0.029</td>
</tr>
</tbody>
</table>
cycles, and the silica content then averaged 0.014 percent.

**PROCESS DESCRIPTION**

A schematic of the flowsheet is given in figure 1.

Spent shale from a TOSCO II retort is cooled to 90°C by heat exchange. The spent shale is separated on a screen. The oversize goes to a ball mill for grinding, and the undersize to an attrition scrubber. Leach solution, composed of recycled barren liquor and makeup water, is introduced in both the ball mill and the scrubber. Attrition machines, rather than agitated tanks, are used in leaching because retention times are very short, and if retorting conditions are not just right, the spent shale can be difficult to wet. The slurry streams converge at rotary vacuum filters for separation of pregnant leach liquor from tailings.

Barren liquor is used for filter cake washing, and residual solution in the discarded tailings constitutes a circuit bleed stream to prevent excessive sodium buildup. The leach is conducted in the attrition scrubber at 25°C for a retention time of one minute or less. The slurry contains 40 percent solids.

Alumina is precipitated from the pregnant liquor by seeding with previously produced alumina trihydrate. Temperature of precipitation is about 65°C. Retention time is one-half hour. The product is separated in a hydroclassifier, with the fine portion being returned to the precipitation circuit for seeding and the remaining coarse fraction being filtered, washed and calcined to A12O3.

The recycled barren liquor must be cooled to 15°C to give a leach

**Table 8.—Recycle leach-precipitation test on nahcolite spiked shale**

<table>
<thead>
<tr>
<th>Cycle and Liquor Type</th>
<th>Solution Analyses</th>
<th>% Al₂O₃</th>
<th>% Al₂O₃</th>
<th>% SiO₂ in Prod. (Calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g Al₂O₃/1</td>
<td>g SiO₂/1</td>
<td>Ext’n.</td>
<td>Precip.</td>
</tr>
<tr>
<td>First Cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pregnant</td>
<td>21.35</td>
<td>0.069</td>
<td>97</td>
<td>22</td>
</tr>
<tr>
<td>Barren</td>
<td>16.58</td>
<td>0.066</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Third Cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pregnant</td>
<td>33.53</td>
<td>0.066</td>
<td>95</td>
<td>58</td>
</tr>
<tr>
<td>Barren</td>
<td>14.16</td>
<td>0.066</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seventh Cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pregnant</td>
<td>28.13</td>
<td>0.064</td>
<td>84</td>
<td>53</td>
</tr>
<tr>
<td>Barren</td>
<td>13.35</td>
<td>0.064</td>
<td></td>
<td></td>
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<tr>
<td>Twelfth Cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Pregnant</td>
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<td>0.060</td>
<td>97</td>
<td>56</td>
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<tr>
<td>Barren</td>
<td>13.69</td>
<td>0.056</td>
<td></td>
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<tr>
<td>Fourteenth Cycle</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pregnant</td>
<td>28.64</td>
<td>0.056</td>
<td>91</td>
<td>52</td>
</tr>
<tr>
<td>Barren</td>
<td>13.66</td>
<td>0.053</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. - Recovery of alumina from spent shale.
temperature of 25°C. This takes place in aerial coolers, cooling towers and refrigeration units.

A typical analysis of alumina produced from leaching dawsonitic spent shale is given in table 9. Wet chemical methods were used for silica analyses and emission spectroscopy for the remaining components.

REFERENCES


Desborough, G. A., and Pitman, J. K., 1974, Significance of applied mineralogy to oil shale in the upper part of the Parachute Creek Member of the Green River Formation, Piceance Creek Basin, Colorado: Rocky Mountain Assoc. Geologists Guidebook, p. 81-86.


Table 9.—Analysis of alumina produced from dawsonitic spent shale

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.026</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.007</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>0.01</td>
</tr>
<tr>
<td>Ga₂O₃</td>
<td>0.04</td>
</tr>
<tr>
<td>MnO</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>MgO</td>
<td>0.007</td>
</tr>
<tr>
<td>CuO</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>LiO</td>
<td>0.01</td>
</tr>
</tbody>
</table>


THE THERMO-OXIDIZING PYROLYSIS
OF OIL SHALES

Vladimir Kashirsky and Aleksandr Koval

When using high-ash and high-sulfur fuels in thermal electric power plants, we have a lot of problems with steam boilers. These problems are: great deposits on the heating surfaces, corrosion and abrasion of these surfaces, some difficulties in providing the nominal parameters of steam, and production of large quantities of air pollutants, such as sulfur oxides and particulate matter (Epik 1961).

In the future we will have some serious technical problems with burning solid fuels in modern power plants with gas turbines, with combined gas-steam units and magnetohydrodynamic generators. We will not be able to use original high-ash and high-sulfur solid fuels in these units, because all of these plants must be based only on clean fuels.

We will be able to get over these difficulties by using preliminary thermal preparation of solid fuels, and by burning clean fuels, like gas or oil.

For design and construction of large capacity units for thermal decomposition of fuels, a rapid heating rate of pulverized fuel with solid or gaseous or combined heat carrier is suggested (Chukanov 1961). Under these conditions, the process of thermal decomposition may be regulated.

It is known that raising of pyrolysis temperature increases gas yield. As a result, the yield of decomposition liquid products goes down, but concentration of aromatic hydrocarbons in liquid and gaseous products goes up (Chukanov 1961). However, the rise in temperature demands a big increase of solid heat-carrier consumption for processes of thermal decomposition of fuels.

Thermo-oxidizing pyrolysis of solid fuels has been suggested (Kashirsky 1966; Kashirsky, Koval and Sokolova 1969). In one stage the process provides deeper destruction of organic matter and produces large amounts of high heating value gas, olefins and aromatic hydrocarbons.
It was determined (Kashirsky 1966) that the supply of a small quantity of oxidizer in the pyrolysis zone intensifies the process of organic matter destruction and reduces heat-carrier consumption.

We studied the thermo-oxidizing pyrolysis of the Ukrainian Boltyshiski oil shales (Kashirsky, Koval and Sokolova 1969; Kashirsky, Koval and Igonkina 1969; Kashirsky and Koval 1969; Koval 1969; Koval 1971; Kashirsky and Koval 1972). The focus of our investigation was as follows: to get from oil shale fine fuel for thermal-electric power plants and the most interesting products for the chemical industry; to define influence of temperature, consumption of oxidizer by the gas evolution process, and quality and yields of obtained products.

The Boltyshiski oil shale is representative of high-ash, high-sulfur fuels and has typical characteristics for shales (fig. 1). In laboratory tests we used pulverized oil shale with size particles less than 0.25 mm. The heating rate of particles was 1,000 to 1,500°C/sec.

The principle of the experimental unit is shown on figure 2. The tube-reactor is the main element of this unit. Fine-ground oil shale was carried through a tube-reactor in a stream of air. The tube-reactor was heated in five tube-electro furnaces. Gas samples were removed for analysis at the

<table>
<thead>
<tr>
<th>Percentage of Dry Shale, Unless Otherwise Indicated</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASH -----------------------------------------------</td>
</tr>
<tr>
<td>KEROGEN CONTENT -----------------------------------</td>
</tr>
<tr>
<td>CARBON ---------------------------------------------</td>
</tr>
<tr>
<td>HYDROGEN -------------------------------------------</td>
</tr>
<tr>
<td>NITROGEN -------------------------------------------</td>
</tr>
<tr>
<td>SULFUR ---------------------------------------------</td>
</tr>
<tr>
<td>OXYGEN ---------------------------------------------</td>
</tr>
<tr>
<td>HEATING VALUE, Kcal/kg -----------------------------</td>
</tr>
</tbody>
</table>

Size of Particles, MM ------------------------------- <0.25
Heating Rate of Particles, °C/sec ------------------- (1000-1500)

FIGURE 1.—Ukrainian oil shale characteristics.
Figure 2—Experimental reactor.

1. Tube-reactor  
2. Feed-screw  
3. Electric motor  
4. Electric furnace tube  
5. System for gas sampling and thermocouple  
6. Temperature recorder  
7. Cyclone  
8. Drying tube  
9. Condenser  
10. Absorber  
11. Gas meter
end of each section. The product gas was separated from all solids by a cyclone at the end of the reactor and metered after removal of condensables. Aromatic hydrocarbons were absorbed by special coal char. Since we had precise separation of pyrolysis products, we had an opportunity to investigate all products and to make exact material balances for each test.

Variation of yields of the decomposition products with temperature is shown in figure 3. In these tests the consumption of carrier air was 150 liters/kg of oil shale. Eight to ten percent of theoretical air is required for the combustion of shale. The temperature varied in the range of 700 to 850°C. We can see with raising of the temperature that the rate of the decomposition of the oil (tar) products increases. In fact, at a temperature of 800°C we don't have oil (tar). The high temperature and the feeding in the pyrolysis zone of oxygen result in a deeper decomposition degree of organic matter macromolecules. This process, in combination with catalytic influence of mineral matter, produces conditions for synthesis of aromatic hydrocarbons. Maximum yield of pyrobenzene is at 800°C. Yield of pyro-gas increases with raising of temperature.

![Figure 3](image.png)

**Figure 3.** Variation of yields of the decomposition products with temperature.
The influence of pyrolysis temperature on yields and composition of pyrogas is shown in figure 4. Pyrogas is characterized by the large content of ballast component such as CO₂ and N₂. But the heating value of pyrogas is high, since pyrogas has a large percentage of olefins and methane.

An elementary mass balance of our test permitted us to study a distribution of elements of original oil shale between pyrolysis products. We determined that 55 to 60 percent of the organic carbon and 80 percent of the hydrogen in the original oil shale are contained in the pyrogas. In figure 5, we demonstrate that olefin hydrocarbons contain 50 percent of the total carbon and hydrogen of pyrogas. The maximum of carbon and hydrogen in the olefins is at 800°C and then the content of carbon and hydrogen in olefins is reduced. This means the carbon in olefins takes part in synthesis of high-molecular compounds, which form coke. The hydrogen in the olefins is used in the formation of aromatic hydrocarbons.

In fact, a minimum of carbon in the coke (fig. 6) has been at 800°C and then the percent of carbon, present as coke, increases. With an increase in the temperature we have secondary conversion reactions of volatile products, and high-molecular weight compounds are deposited on the pulverized particles of coke. The temperature of 800°C corresponds to the most complete conversion of oil shale organic matter to volatile products.

Consumption of oxygen, which has been fed to the pyrolysis zone, is a significant parameter for thermo-oxidizing pyrolysis. To determine the influence of oxygen consumption, we investigated the pyrolysis of oil shale in a stream of inert nitrogen and in an air stream. The consumption of oxygen has been changed from 16 to 138 gram/kg of oil shale.

We can see (fig. 7) that the process of gas evolution for pyrolysis in the nitrogen stream goes with less intensity than in the case of thermo-oxidizing pyrolysis. The supply, in the decomposition zone, of a small quantity of oxygen assists in the destruction and weakening of the most stable chemical structure in the organic molecules and increases the rate of decomposition.

The influence of oxygen consumption on the yields and composition of pyrogas is shown in figure 8. Upon raising oxygen consumption, the yield of pyrogas increases, but the heating value goes down as the content of inert components, such as N₂ and CO₂, goes up.

As is well known, the quality of gas as a raw material for the organic synthesis industry is dependent on the contents of olefins in gas. In choosing optimal pyrolysis conditions it is necessary to know the total weight yield of olefins and hydrocarbons in relation to oxygen consumption. The data of figure 9 shows that the maximum yield of olefins is at a consumption of 80 g oxygen/kg of oil shale. The total olefins yield is equal to 82 kg/ton of oil shale.

The fairly high yield of pyrobenzene is a great advantage for the in-
<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Yield of Pyrogas M³/kg Oil Shale</th>
<th>Gas Constituents (% by Vol)</th>
<th>Heating Value Kcal/N³</th>
<th>Heating Value Btu/cu ft</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>0.203</td>
<td>H₂S 0.7 CO₂ 11.6 C₄H₈ 0.8 C₃H₆ 7.4 C₂H₄ 6.4 CO 7.8 H₂ 4.1 CH₄ 9.1 N₂ 52.1</td>
<td>3,708</td>
<td>416</td>
</tr>
<tr>
<td>750</td>
<td>0.288</td>
<td>H₂S 0.7 CO₂ 11.1 C₄H₈ 0.6 C₃H₆ 6.7 C₂H₄ 10.9 CO 8.1 H₂ 9.6 CH₄ 13.5 N₂ 38.8</td>
<td>4,665</td>
<td>524</td>
</tr>
<tr>
<td>800</td>
<td>0.300</td>
<td>H₂S 0.6 CO₂ 10.4 C₄H₈ 0.3 C₃H₆ 5.1 C₂H₄ 12.1 CO 9.9 H₂ 11.9 CH₄ 13.8 N₂ 35.9</td>
<td>4,600</td>
<td>510</td>
</tr>
<tr>
<td>850</td>
<td>0.373</td>
<td>H₂S 0.6 CO₂ 9.7 C₄H₈ 0.4 C₃H₆ 2.9 C₂H₄ 11.5 CO 9.1 H₂ 13.4 CH₄ 12.8 N₂ 39.7</td>
<td>4,019</td>
<td>451</td>
</tr>
</tbody>
</table>

Figure 4.—Influence of temperature on yield and composition of pyrogas.
Figure 5.—Content of C and H of original oil shale in the components of pyrogas with temperature.
vestigated conditions of pyrolysis (fig. 10). Obtained pyrobenzene is a mixture of benzene hydrocarbons with a mixture of sulfur compounds. With an increase in temperature, percentage of benzene in the pyrobenzene goes up also. At 800 to 850°C we have in pyrobenzene 95 percent aromatic hydrocarbons. The use of pyrobenzene for extraction of individual chemical compounds such as benzene, thiophen, and toluene will improve the economical efficiency of combined power-chemical plants.

We propose that combined power-chemical plants with preliminary thermal treatment of high-ash and high-sulfur fuels, such as oil shale, will extend fuel resources for industry and power technology, and provide the chemical industry with fine raw materials.
The Thermo-Oxidizing Pyrolysis of Oil Shales

$\text{t}_{\text{pyr}} = 800^\circ \text{C}$

Influence of $O_2$ Consumption on Dynamics of Gas Evolution.

42: 80: 116: 138 - $O_2$ Consumption

\[ \frac{\text{g}}{\text{kg oil shale}} \]

--- Thermo-oxidizing Pyrolysis

--------- Pyrolysis in Nitrogen Stream

Figure 7.—Influence of $O_2$ consumption on dynamics of gas evolution.
<table>
<thead>
<tr>
<th>ITEM</th>
<th>$O_2$ Consumption, g/kg Oil Shale</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>16</td>
</tr>
<tr>
<td>Yield of Gas, M$^3$/kg Oil Shale</td>
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</tr>
<tr>
<td><strong>Constituents of Gas (%) by Vol</strong></td>
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</tr>
<tr>
<td>$H_2S$</td>
<td>0.5</td>
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<tr>
<td>$CO_2$</td>
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<tr>
<td>$C_4H_8$</td>
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<tr>
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<td>19.3</td>
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<td>6,507</td>
</tr>
<tr>
<td>Heating Value Btu/cu ft</td>
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</table>

**Figure 8.**—Influence of $O_2$ consumption on yields and constituents of pyroshou (t$_{pyr}$ = 800°C).
Figure 9.—Yields of olefins with $O_2$ consumption.
<table>
<thead>
<tr>
<th>Temperature or Pyrolysis Process, °C</th>
<th>Yield of Pyrobenzene g/kg Oil Shale</th>
<th>S Content in Pyrobenzene %</th>
<th>Components of Pyrobenzene</th>
<th>( \text{Low Boiling Hydrocarbons} )</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Thiophen</th>
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<tr>
<td>700</td>
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<td>1.63</td>
<td></td>
<td>6.6</td>
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<tr>
<td>850</td>
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<td></td>
<td>1.1</td>
<td>94.3</td>
<td>0.7</td>
<td>3.9</td>
</tr>
</tbody>
</table>

**Figure 10.**—Pyrobenzene characteristics for thermo-oxidizing pyrolysis.
REFERENCES

IN SITU OIL SHALE PROCESS DEVELOPMENT

Richard D. Ridley and R. T. Chew, III

It is a real pleasure to return here with another paper on the Garrett oil shale process. It is particularly interesting to attend what might be called the first symposium on in situ processing. It is a dramatic change from last year, when the only paper on in situ processing was about the Garrett process. Only one paper on today's program is not on in situ processing.

The intent is not to go into a large amount of technical detail on the Garrett process. We have said much on the process in the past and will not cover it in detail here. Basically, we mine out rooms underground. The first retorts were 30 feet on a side and 72 feet high. In the research phase we drilled vertical holes in the ceiling, loaded them with ammonium nitrate-fuel oil and blasted them. The result was a rubble pile, or underground chimney, 72 feet high. We then drilled down to the top of the retort for an entry way for air and recycle gas, lowered a burner in, started a fire at the top, and worked it down through the retort under controlled conditions. The process is essentially a modification of the NTU process.

Our first retort gave better than 60 percent yield according to Fischer assay.

Rather than a lot of details on processing, we will report on work underway, what has been accomplished during the past year, and give some idea of the sophistication in this process.

We have two mines. The original mine where we conducted our first three retorting experiments is now called the "Research Mine." Our second mine is the so-called "Commercial Mine." We began work in the summer of 1972 on the D. A. Shale/Callahan Trust Company property at the head of Logan Wash, outside of DeBeque, Colorado. We are on the outcrop of the Roan Cliffs along the southern edge of the Piceance Creek Basin. The surface plant is shown in figure 1. The drill rig in the foreground is close to a point directly above one of our retorts. The pipe extending down over the cliff brings the recycle gas and the air into the retort. An air blower is by the tent. Two stacks allow flexibility in venting the gas and locating scrubbing equipment.

Richard D. Ridley, Executive Vice President; R. T. Chew, III, Occidental Oil Shale, Inc., Grand Junction, Colorado.

123
We consider the original retorts to have been rather small. They are only 1/30th or 1/40th the size of commercial retorts, yet when compared with a conventional chemical reactor, this has been no pilot-plant size operation.

The research has been successful. The retorts contained from 6,000 to 10,000 tons. Work has been redirected in the Research Mine with most of the effort now concentrated on rock fragmentation research and with investigations there, and in the Commercial Mine, on rock mechanics.

There have been some novel problems. The cross-sectional area of a research retort is between 900 and 1,000 square feet and obtaining valid temperature measurements across that area has been difficult. We have learned how to control the flame front so that it moves in the direction we desire. We needed to place thermocouples in the vertical plane by drilling into the rubble pile from the surface and then placing the thermocouples using the drill pipe for the thermowell; but, this technique had not been tried. No one had drilled through rubble before us. We developed a technique that is reliable, and that problem is behind us now.

Oil and water run into the sump during the retorting process. The sump is behind the retort bulkhead in the gaseous atmosphere, and the oil and water are pumped from there to the surface where they are separated and analyzed. Gas coming off the retort also goes through the bulkhead in an 8-inch pipe, then through both a venturi scrubber and a Centrifix-type knockout.

Retort ignition is a relatively simple matter. We use propane for only
a few hours to start retorting and combustion, since only a small amount of heat is necessary. Propane is used as a matter of convenience.

Turning now to mining regulation, these regulations have traditionally developed around coal mine experience and they prohibit fires underground. The underground retort concept requires a fire, although it is in a mass of rock under low pressure, and is easily confined. Still a variance was required. We worked with the State Division of Mines, MESA, and U. S. Bureau of Mines to obtain the necessary permits which require adequate safety features and absolutely positive control. This safety system is now in effect.

All research retort operations are controlled from the surface plant. There is a satellite control room in the mine with direct communications to the surface but all valving is operated from the surface. Most of the gas analysis and monitoring is done from the surface. Instrumentation includes data logging of downhole temperatures, routine temperature recordings on many other points, and normal pressure measurement and control. Retorting is easily controlled by regulating gas. Oil production data can be related back to retort events but a time lag is involved that makes the relationship of oil properties to operating conditions rather ambiguous.

Continuous gas analyses are run on a number of components, including carbon monoxide and oxygen. Chromatographs have been installed for both individual components and complete gas analysis. A recent addition is a Varian mass spectrometer with capability to about 100 mass weight. It is doing a good job.

The success of the research program led to two decisions that changed the direction of the project. Research continues at an aggressive pace, but at the same time we have started development of a full-size commercial mine that will have the first commercial-size underground retort. The retort will be more than 100 feet square and more than 250 feet high. The decision to develop that room was made early last year.

The second decision was made at the end of 1974. The project was moved over to an operating arm of the company, and out of the research and development group, when Occidental Oil Shale, Inc., a subsidiary of the Occidental Oil & Gas Production Division, was set up. The change was made because so much of the work is now of a commercial, large-scale nature that it administratively overwhells the research aspect.

It was obvious to us that a full-size retort could not be developed in the existing mine. The Research Mine is just below the Mahogany Ledge, too high to recover the entire 250 to 300 foot ore horizon, and it was too small to permit operation of the size of equipment one needs to develop a commercial mine. There is insufficient room at the head of Logan Wash for a large mining operation.

The two entrances to the Commercial Mine, in a canyon off the north
side of Logan Wash about a quarter mile below the head, are shown in figure 2. On the lower level is a row of office and personnel trailers. We moved several thousand tons of muck to develop these platforms and the vertical face to mine into. Work started in mid-1974 on the lower level and a few months later on the upper level. Mining has progressed now into room 4, the first commercial room, and we will start burning it this summer.

Equipment was in short supply in 1974, and we had to improvise. We obtained an Ingersol-Rand two-boom jumbo built for use in a much smaller mine. We took the booms off, put an extension on to raise it 6 feet, reconditioned the jumbo and are using it on both levels. We now have an Atlas-Copco twin boom, electric hydraulic jumbo, excellent for drilling a 24 foot high face and capable of extending to drill a 30 foot high face, which we need in certain areas. We bought this jumbo off the floor at the American Mining Congress in Las Vegas. It is not full rotary, but is a vast improvement over the jumbo used initially. We have consistently drilled heading rounds 30 feet wide by 30 feet high using 12-foot steel, pulling about 10 feet, in less than 2½ hours, including setup time. We have another Atlas Copco jumbo on order. It will be full rotary, and we should have it by mid-1975. With it, we expect to drill the same size heading round in the same time, except that it will use about 24-foot steel and pull about 20 feet. We use a Gradall 1000 scaler to scale loose rock off the back and the ribs. We haul muck with EIMCO 920s with a 10-year bucket and CAT

Figure 2.—Commercial mine portals, Occidental Oil Shale, Inc.
In Situ Oil Shale Process Development

988s front-end loaders. We have developed a fair amount of availability and experience data with both. Underground mining is proceeding routinely.

By the end of 1975 we will have invested somewhere in the neighborhood of $25 million in our oil shale work.

Another area to be mentioned is our environmental work. We have developed a list of about 48 activities where environmental effects and permits must be considered. All environmental requirements must be met. To our thinking, most are legitimate, though some are not. At this time last year we had between 25 and 35 permits covering our operation. We have given up counting now but have a team of seven people spending about 90 percent of its time in the environmental area developing the information necessary to obtain permits needed now or in the future. We have a great deal of environmental baseline data gathering underway, including a meteorological study, fauna and flora studies, and others. We have completed paleontological and archaeological studies.

If we are fully satisfied with the results from room 4, we will make the decision to go into commercial production. If we are not fully satisfied, we will experiment with additional large rooms and perhaps more small rooms. Those of us on the project in Colorado anticipate a decision later this year to go commercial on the Logan Wash site.

More significant though, when we make the decision to go commercial, it will be on oil shale with a grade roughly half of that considered necessary for aboveground processing. The 300 foot thick seam that we are working in assays somewhere between 15 and 18 gpt. We are looking toward making a commercial oil shale venture on that seam. We do not have enough land to produce 100,000 barrels per day, but we see at least 30,000 barrels per day for 15 years. Much of the rock that we are using now is not ore by the conventional definition. In fact, it is not even resource. Our process is not selective. We process the entire height of the seam selected. By taking the full height, we take a major percentage of the resource for recovery.
THE USE OF THE LURGI-RUHRGAS PROCESS FOR THE DISTILLATION OF OIL SHALE

Dr. Ing. P. Schmalfeld

ABSTRACT

In the last few decades Lurgi was heavily engaged in the development of processes for the distillation of oil shale and built plants for retorting in tunnel kilns, in low-temperature carbonizers, in vertical retorts, on the inclined grate, in situ and in piles, for the recovery of oil and in fluid beds for power generation and cement raw material production.

The Lurgi-Ruhrgas process, which was developed originally for the carbonization of coal and the cracking of hydrocarbons, and which was applied frequently has now been modified and tested by Lurgi for the distillation of oil shale.

The features of the processes are discussed briefly and compared. In view of its specific advantages the Lurgi-Ruhrgas process is superior to all other processes.

The high worldwide increase in petroleum prices at the end of 1973 and the fact that the energy shortage will become greater in the next few decades have given new impetus to endeavors to recover oil and gas from oil shale. Even before the tremendous development in the petroleum industry in the 1950s there was a shale oil industry in Scotland, France, Germany, Sweden, Estonia, South Africa, Australia, Manchuria and Spain. Plants were built during the 1940s but after World War II almost all of them were shut down as petroleum became available at ever declining prices so that the recovery of shale oil was no longer competitive.

HISTORY OF OIL SHALE INDUSTRY

Originally, oil shale was distilled mainly in externally heated vertical Pumpherston retorts (Stewart 1968) which had, however, a low capacity

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and a high requirement of heating fuel. They were outrun by gas generators with distillation top where the carbon of the distillation residue was gasified and the resulting low-Btu gas used as circulating gas for distillation. Plants of that type (Yefimov and Piik 1968) were built primarily in Estonia and Manchuria. This process required an oil shale feed which had sufficient carbon in the residue, which did not plasticize during distillation, and which did not slag during gasification.

For the processing of the oil-rich Estonian oil shale, having an oil content of over 20 percent and, in some cases over 30 percent, the tunnel kiln (Sheloumov 1968) was developed. The plasticizing oil shale was kept in wagonettes which were pulled at short intervals through the kiln with lock systems. Circulating gases heated in heat exchangers were passed through the oil shale bed in the wagonettes which dried, preheated, and distilled the oil shale. The tunnel kiln furnished undiluted distillation gases and a high oil yield but required high investment costs and was expensive to operate due to the high power consumption of the circulating fans. The carbon in the distillation residue could not be utilized.

DISTILLATION PROCESSES HANDLED AND DEVELOPED
BY LURGI

TUNNEL KILN

Lurgi was among the first engineering companies engaged in the pyrolysis of oil shale, and after 1938 built two tunnel kilns according to a modified concept for the distillation of 800 tons per day of oil chalk in the north of Germany and after 1942 four tunnel kilns in Estonia of which only two were put on stream after World War II (Sheloumov 1968; Thau 1949). The kiln inlet side with a wagonette is shown in figure 1.

![Inlet side of a tunnel-kiln with a wagonette.](image-url)
LOW TEMPERATURE CARBONIZER

Lurgi was among the first engineering companies engaged in the pyrolysis of oil shale, and after 1938 built two tunnel kilns according to a modified number of plants between 1935 and 1945 to produce tar for hydrogenation to motor fuel and smokeless highly reactive lumpy char for a variety of uses. A plant with 10 carbonizers is shown in figure 2. In 1944 Lurgi supplied the engineering for a plant using that process for the distillation of 3,000 tons per day of Puertollano oil shale (Spain) (Thau 1949) but due to the disordered state after World War II the plant was not built. Instead, the Spanish installed the externally heated Pumpherston retorts which were, in fact, already outdistanced technically by the low temperature carbonization process.

In the low temperature carbonization process, the lumpy oil shale is first dried and preheated with circulating gases in a predrying zone and then distilled with hot circulating gases in the carbonization zone. These are a mixture of circulating gases treated in the cooling and condensation system and heated by cooling the distillation residue, plus hot combustion gases from an externally arranged combustion chamber.

In the normal low temperature carbonization process the carbon of the distillation residue is not used for heating. Merely the sensible heat of the distillation residue is recovered in part using the circulating gases as heat carrier. An additional fuel gas is required which cannot be fully covered from the distillation gas. Moreover, the oil vapors are diluted with circulating gas and have to be condensed by cooling the circulating gas, requiring substantial quantities of water and cooling equipment. The gasoline vapors can be recovered from the gases only by extensive washing with oil. In view of these circumstances the low temperature carbonization process is not an optimum solution for the distillation of oil shale.

Figure 2.—Plant comprising 10 LURGI-Spülgas carbonizers.
Attempts were made to avoid the dilution of the distillation gases with combustion gases by heating the circulating gases in a tube heater or in regenerators, but this would have caused higher costs for equipment and heating fuel which could not be compensated by the higher yield of undiluted distillation gas. Besides, the hazard existed that the heater tubes, which are heated to above 600°C, would be destroyed prematurely by the attack of the sulfur present in the distillation gases and the fuel gases. There is also the likelihood of cracking products depositing in the tubes.

Furthermore, it has to be considered that the low temperature carbonization process can handle only coarse-grained and lumpy raw material. The unavoidable undersizes have to be distributed uniformly over the entire cross-sectional area. The circulating gases must flow uniformly through the zones of the carbonizer, and the distillation residue has to be discharged uniformly over the entire cross-sectional area so that the oil shale can travel downwards through the drying and carbonizing zone at a uniform speed. Lurgi, therefore, divided the rectangular cross section of the large carbonizer into cells for the discharge of the distillation residue with distribution and collecting ducts for the circulating gases. With circular carbonizers having a large diameter, it is much more difficult to control the uniform flow of gas, shale, and residue.

Although these requirements have been largely considered in the Lurgi low temperature carbonizer, the oil yield is usually only 80 to 90 percent of that determined by the Fischer assay.

Improvements to the low temperature carbonization process were directed towards the utilization of the carbon in the distillation residue for heating. This could be realized by arranging a zone between carbonization and cooling zone into which air was uniformly distributed to burn the carbon so that the combustion gases could be used for the carbonization process. The carbonizers designed for the Puertollano oil shale already incorporated this improvement. In 1958 Lurgi built a carbonizer in Kisangani (formerly Stanleyville) in Zaire for the distillation of 400 tons of oil shale per day. The distillation residue from this carbonizer was used as cement raw material in which case the burning-off of the carbon in the carbonizer was a special advantage.

The construction of low temperature carbonizers with capacities of, say, 1,000 tons of oil shale per day involves considerable problems regarding the uniform distribution of the circulating gases and the solids, which increase the costs excessively.

**Batch Retorting**

Another variation of oil shale distillation is the process developed by Dr. Schweitzer in 1939 for treatment of the low-oil shale in Württemberg (West Germany) which was tried out in a pilot plant in 1940. Lurgi built the first commercial plant using that process after 1942 to process 1,000
tons of oil shale per day in 28 retorts. This plant is illustrated in figure 3 (Thau 1949; Hubmann and Lange 1954). The retorts are filled with lumpy oil shale and the charge is distilled by sucking air through it from top to bottom. The process proceeds similar to the sintering of ores: the air is heated to high temperature in contact with the hot shale residue and then burns the carbon in the residue so that the hot combustion gases heat up and distill the oil shale in the zone below.

The process has a favorable heat economy and requires less investment and operating costs since it operates without circulating gases. However, the oil vapors are recovered in diluted form, and the distillation gases cannot be utilized elsewhere due to their low calorific value and their dilution with a considerable quantity of combustion gases. The oil yield is usually 80 to 90 percent of that determined by Fischer assay.

The retorts had the great disadvantage that they could be operated only batchwise because the residue sintered into very large and solid lumps which could not be removed through a bottom discharge. The retorts had to be lifted by crane onto a support and unloaded by tilting. After filling with fresh oil shale they were placed back into operating position and re-ignited. These circumstances induced Lurgi to arrange the process for continuous operation.

**Continuous Retorting Process**

The original idea was to develop retorts with circulating grate but this operating method proved to be too complicated and too costly. This led to the development of the oblong "Hubofen" consisting of an inclined oscillating grate on which the shale travels constantly and slowly. Gases

**Figure 3.—LURGI-Schweitzer retorts.**
are withdrawn downward across the whole grate cross-sectional area so that the shale bed open at the top was passed through by air, which was preheated by the residue, which burnt the carbon in the residue and supplied hot combustion gases to heat and distill the oil shale. This continuous process created an ignition and a distillation zone starting in the uppermost layer of the shale bed at the beginning of the grate and extending in an inclined direction down to the lowermost layer of the shale bed at the grate end, similar to ore sintering on the continuous sinter belt but with a much lower bed depth.

This continuous retorting process is remarkable because of its simple setup, its substantially open construction, and its favorable heat economy. A disadvantage is that the distillation vapors and gases are strongly diluted so that the distillation gases can only be utilized for power generation. Two pilot plants (Hubmann and Lange 1954) using that process for a capacity of 60 tons per day of oil shale were built in 1944 at Dotternhausen, Württemberg (West Germany) (fig. 4), and in 1954 at Messel, near Darmstadt (West Germany). A third plant of same size for the gasification of washery refuse was constructed at Kohlscheid, near Aachen (West Germany).

**Distillation In Situ and In Piles**

During the Second World War Lurgi also participated in efforts towards the underground distillation of oil shale in situ without the use of retorts. In situ distillation of oil shale was tried out in Württemberg (West Germany). Chambers were formed in the shale seam by parallel adits. The lower layer of the seam was mined and the upper part of the seam was shattered by explosive charges. The distillation process was
initiated by suction in one adit and, after ignition of the full chamber length, distillation proceeded in the parallel adit. Due to a lot of infiltrated air, oil recovery was low and the hazard of detonation great. Furthermore, it was not possible to enter the adits later on as the hazards of poisoning and detonation could not be sufficiently suppressed.

Retorting in piles was also tried out where lumpy oil shale is piled above long, perforated exhaust pipes resting on the ground, and ignited. Due to side wind, distillation was not sufficiently uniform so that oil recovery was moderate. The experience from retorting in situ and in piles showed that economic distillation of oil shale is possible only in appropriately designed retorts.

**ROHRBACH-LURGI Process**

With the growing output of crude oil and the decreasing prices for crude oil in the 1950s, oil shale distillation lost in importance and was applied for oil recovery only in the USSR (Estonia) and in China (Manchuria). Lurgi developed in collaboration with Rohrbach the Rohrbach-Lurgi process where oil shale is retorted in a fluid bed retort at predetermined temperatures and the combustion heat is utilized for the generation of steam and electric power. The distillation residue is recovered as a valuable raw material for cement production. The process was applied in two plants with a total capacity of 720 tons of shale feed per day and a power generation of 6,000 kW at Dotternhausen, Württemberg (West Germany). The plants were built in 1960 and have been in operation since (Rohrbach 1968). The fluid bed retort is shown in figure 5. The process does not recover oil but the utilization of the residue for cement production and the simultaneous generation of power ensure satisfactory economics provided the oil shale is rich in limestone and inexpensive to mine, as is the case in Württemberg.

**THE LURGI-RUHRGAS PROCESS**

**Carbonization of Coal and Cracking of Naphtha and Crude Oil into Olefins**

In the 1950s Lurgi developed, in collaboration with Ruhrgas AG, a process for the devolatilization of coal fines for the principal production of high-Btu coal gases for piping. The coal fines to be used for firing in power plants were devolatilized first and only the residual coke fines fired in the steam boiler. Circulating solid heat carriers were used for devolatilization. In the first pilot plant heat carriers in the form of pebbles and Mullit balls of 10 to 12 mm size were tried out over a period of more than 2 years. A rotary drum was also used temporarily for intermixing the hot
heat carriers with the coal fines. Devolatilization and gasification of the coal fines were satisfactory. However, it was soon recognized that even moderately caking coal fines could not be processed without pretreatment to reduce the caking power, that heating of the heat carriers to about 1,000°C in industrial retorts was difficult and expensive, and that also the lifting of the large quantity of circulating heat carriers was difficult to perform. In 1951 the process was therefore modified to the devolatilization of coal fines using the char product as fine-grained heat carrier.

The Lurgi-Ruhrgas process was tried out in a 5 to 10 tons/day pilot plant in Herten (Ruhr District) over several years for the devolatilization and gasification of a variety of coals and for the cracking of hydrocarbons, ranging from heavy fuel oil through crude oil to naphtha, as well as butane and propane, to produce olefins and town gas. Large pilot plants for the devolatilization of coal fines and for the cracking of fuel oil and crude oil into olefins were built at Dorsten (Sommers 1974) and Leverkusen (Chem. Eng. 1959), respectively. The process was commercially applied for the devolatilization of lignite fines in Yugoslavia (Rammiler 1966) and for the production of char fines for hot briquetting from sub-bituminous coal at the Prosper coke oven plant of Ruhrkohle AG in Bottrop and in the Normanby Park Works of the British Steel Corporation in Scunthorpe, Lincolnshire (Schmalfeld and Rammiler 1974). The process was further used for the cracking of naphtha and crude oil to produce olefins, using sand as circulating heat carrier. Sand crackers were built in
The Use of the Lurgi-Ruhrgas Process

Dormagen (West Germany), Leuna (East Germany), Rosario (Argentina), Chiba (Japan) and Lanchow (China) (Schmalfeld 1968).

The LR process has found only limited use in the coal field because natural gas was available all over the world at lower prices so that coal gas was not competitive. In view of the low cost of crude oil, the production of tar was also not attractive and the demand for char fines rather limited. Due to the recent energy crisis, the much higher prices for crude oil and natural gas, and the anticipated shortage of energy during the next decades, this situation has changed so that the LR process will probably find increasing application for the devolatilization of coal (Döring and others 1974).

Retorting of Oil Shale

The processing of oil shale has regained interest. Efforts to distill domestic oil shale for the recovery of oil using own processes are being made by the Russians in Estonia, the Americans in Colorado, and the Brazilians in Sao Mateus do Sul. The LR process which is fully developed to commercial scale is superior to these processes for this application. Oil shale from Sweden, Colorado, and Württemberg, tar sand from California and asphalt rock from Africa have been distilled with good success in the LR pilot plant. These tests were discussed in previous papers (Rammler 1968; Sept. 1970). Commercial projects for oil shale distillation are under discussion in several countries.

Description of LR Process

The LR process for the distillation of oil shale is described hereinafter in conjunction with the flow sheet in figure 6.

The LR process mainly consists of the circulating system with lift pipe 1 to convey and heat the circulating fine-grained distillation residue, separating and collecting bin 2, mixer 3, and after-treatment unit 4. Arranged on the product gas side of the circulating system are the cooling and condensation facilities for the oil vapors, and on the offgas side the heat exchangers for preheating the combustion air and for steam generation as well as offgas dedusting. The oil shale, crushed to minus 6 mm sizes, is fed from bin 2 to mixer 3 where it is mixed with the 6- to 8-fold quantity of the hot residue from bin 2 and heated to about 500°C within a few seconds. The mixture is post distilled in unit 4 and passes through line 6 to the lower section of lift pipe 1 where combustion air at about 400°C is introduced, raising the mixture pneumatically and thereby burning the carbon contained in the residue. Combustion gas and residue are separated at about 650°C in collecting bin 2, the residue being supplied through line 5 to mixer 3, whereby the cycle is closed.
The volatile distillation products are freed of entrained dust in two series-connected cyclones 7 and 8 and then enter scrubbing coolers 9, 10, and 11. Scrubbing cooler 9 operates at higher temperature to remove residual dust from the vapors and gases by washing with circulating condensed heavy oil. Major condensation of the oil takes place dust-free in scrubbing cooler 10 above the water dew point to recover this oil water-free. Final cooling is by circulating condensate in scrubbing cooler 11, the condensate being recooled in air cooler 12 and water cooler 13. The condensate is separated into middle oil and process water in separator 14. Finally, the gas is treated with light oil in scrubber 15 for the recovery of naphtha. When compressing the gas and cooling it to lower temperatures, LPG is also recovered.

The offgases leaving collecting bin 2 are dedusted in cyclone 16 to return part of the entrained dust to the cycle, if necessary, and then routed through waste heat boiler 17, feed water preheater 18, cyclone 19, humidifier 20, and electrostatic precipitator 21. The dust withdrawn from the cycle and cyclone 16 passes through heat exchanger 22 where it exchanges its heat in countercurrent with the combustion air for lift pipe 1. The dust is then moistened with water in mixer 23 together with the dust from separators 20 and 21. The vapors and the offgases are jointly treated in humidifier 20 and electrostatic precipitator 21 before being discharged to atmosphere. If the distillation residue occurs as fine dust, as is the case with Colorado oil shale, heat exchanger 22 will be omitted and the air preheater will be arranged between cyclone 16 and waste heat boiler 17.

Typical hydrocarbon inspections are given in table 1. It should be noted that the yields, density, boiling range and all other properties of the individual hydrocarbon fractions depend on the temperatures set during the tests in the various cooling and scrubbing towers.
### Table 1.—Typical hydrocarbon inspections

<table>
<thead>
<tr>
<th></th>
<th>a) Heavy Oil (dust free):</th>
<th>b) Middle Oil:</th>
<th>c) Gas Naphtha:</th>
<th>d) Distillation Gas</th>
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</thead>
<tbody>
<tr>
<td>Density</td>
<td><strong>50°C</strong> kg/1</td>
<td><strong>20°C</strong> kg/1</td>
<td>Density</td>
<td>kg/Nm³</td>
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<tr>
<td>Viscosity</td>
<td><strong>50°C</strong> cP</td>
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<td>FIA analysis:</td>
<td></td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td></td>
<td>Aromatics and</td>
<td>vol %</td>
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<tr>
<td>(to Höffler)</td>
<td></td>
<td></td>
<td>diolefins</td>
<td>84.4</td>
</tr>
<tr>
<td>Settling point</td>
<td>°C</td>
<td></td>
<td>Olefins</td>
<td>1.7</td>
</tr>
<tr>
<td>(to DIN 51583)</td>
<td></td>
<td></td>
<td>Paraffins</td>
<td>13.9</td>
</tr>
<tr>
<td>Conradson test</td>
<td>wt %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial boiling point</td>
<td>°C</td>
<td></td>
<td>Initial boiling</td>
<td>°C</td>
</tr>
<tr>
<td>(at 760 Torr)</td>
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<td>point</td>
<td>36</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(at 738 Torr)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Final boiling</td>
<td>°C</td>
</tr>
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<td>point</td>
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</tr>
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<tr>
<td>Density</td>
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<td>0.699</td>
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<tr>
<td>Viscosity</td>
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<tr>
<td>(to Pensky Martens)</td>
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<td>diolefins</td>
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<td>Settling point</td>
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<td>(to DIN 51583)</td>
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<td>Conradson test</td>
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<td>(at 763 Torr)</td>
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<td></td>
</tr>
<tr>
<td>Final boiling point</td>
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<td></td>
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<tr>
<td>(at 763 Torr)</td>
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<td>H₂ vol %</td>
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<td>N₂ vol %</td>
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<td>C₂ vol %</td>
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<td>C₃ vol %</td>
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<td></td>
<td></td>
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<td>C₄⁺ vol %</td>
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<td></td>
<td></td>
<td></td>
<td>H₂S g/Nm³</td>
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<td></td>
<td></td>
<td></td>
<td>SO₂ g/Nm³</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Advantages of the LR Process

Undiluted Gases and High Yield of Hydrocarbons

One of the outstanding features of the LR process is that the oil vapors and the distillation gas are not diluted with combustion gases which simplifies condensation. The output of distillation gas is usually very low (only 10 to 30 Nm³/t oil shale) so that also the naphtha vapors and the C₃+ hydrocarbons are easy to condense. The rapid distillation of the oil within a few seconds at optimum temperatures ranging from 450 to 550°C and the short residence time of the oil vapors at that temperature ensure a high yield of hydrocarbons. The yield ranges from 95 to 110 weight percent of the oil content in the oil shale determined by Fischer assay, depending on the characteristics of the oil shale feed.

When processing sub-bituminous coal, the LR process even furnishes yields of up to 170 weight percent of the tar content in the coal determined by Fischer assay (Peters 1958).

Favorable Heat Economy

Another major advantage is that the heat for distillation is covered from the combustion of the carbon in the distillation residue. The carbon is burnt with little surplus of air in conjunction with the pneumatic lifting of the oil shale residue serving as circulating heat carrier in the vertical lift pipe. If the residue does not contain sufficient carbon (about 3 percent carbon related to the shale input is adequate), dust-laden heavy oil or distillation gas is used as additional fuel in the lift pipe. A favorable heat economy is achieved by the fact that the offgases are utilized for combustion air preheating and that combustion can be performed without surplus of air and without recycling offgases to control hazardous over-temperatures. Surplus offgas heat is utilized for steam generation or for predrying shales with high water content. Pneumatic conveying of the circulating heat carrier is effected by the energy of the lift gases having a temperature of about 700°C requiring only the compression of cold air.

Processing of Fines

The LR process handles fines preferably below 6 mm but also up to 8 and 10 mm. This permits charging of the complete oil shale as mined to the process, which is a particular advantage versus shaft carbonizers which require coarse-grained or lumpy feed and which cannot handle the fines representing a proportion of 10 to 20 percent of the mined material. The processing of fines alone has, however, the disadvantage that all lumpy material has to be crushed, which increases the investment cost.
Distillation of Fines

The use of oil shale fines, which are rapidly and intimately mixed with large quantities of hot circulating fines in a mechanical mixer of special design and thereby heated and distilled, ensures uniform treatment and heating of the oil shale within a few seconds. The process is therefore very efficient and can be realized in large units.

LR units for the cracking of oils to produce olefins have already been built with large capacities.

The sand cracker in Chiba (Japan) shown in figure 7 would be suitable for the distillation of roughly 5,000 tons/day of oil shale. Units for the distillation of 8,000 tons/day oil shale can be built nowadays.

On the basis of a yield of 10 percent by weight of oil and naphtha

Figure 7.—LR sand cracker in Chiba, Japan, used to crack naphtha into olefins.
from oil shale, this unit would produce over 250,000 tons/year of liquid products.

**Dedusting of Heavy Oil**

Another disadvantage of the LR process is that when handling dust-containing fines the escaping vapors and gases from distillation carry a certain amount of dust. The bulk of this dust is separated in cyclones in dry condition and returned, but the very fine dust particles are only removed from the gases in the downstream condensation stage by the already condensed and circulating heavy oil. This dust-laden heavy oil is freed of dust by sedimentation and centrifuging, the viscosity of the heavy oil being sufficiently reduced by the addition of naphtha. Losses of heavy oil are thus kept low.

This was already found in the LR pilot plant when distilling Colorado oil shale which disintegrates into fine dust after burning of the carbon. Here again, suitable treatment was applied to the dust-laden heavy oil (Rammler, Sept. 1970). Therefore, the output of a dust-bearing heavy oil fraction is not a serious disadvantage. Moreover, the entrainment of a certain proportion of dust into the first condensation stage cannot be avoided in any process.

**Offgas Dedusting**

Also the offgases from the lift pipe entrain substantial quantities of dust. When processing Colorado oil shale it is to be expected that the very fine distillation residue is discharged with the offgases. These offgases are preferably routed through a shell-and-tube heat exchanger for preheating the combustion air and through a steam boiler before the dust is removed in cyclones and electrostatic precipitators.

**Sulfur Removal**

Some oil shales have a high content of calcium and magnesium carbonate which begins to calcine at temperatures of 600 to 700°C in the lift pipe. The oil shales frequently also contain a high proportion of sulfur compounds which may appear as hydrogen sulfide in the distillation gas and as organic sulfur compounds in the oil vapors but also as SO2 in the offgases during combustion. The SO2 is largely bonded by the CaO and MgO formed so that the discharged offgases are low in SO2 even when the oil shale is rich in sulfur.

**Little NOx Formation**

Combustion in the LR process proceeds at temperatures below 700°C
and with only very little surplus of air so that no NOₐ is formed with the atmospheric nitrogen. NOₓ can occur in the offgases only to the extent it is set free or formed from the nitrogen-containing distillation residue by decomposition of the residual organic substance on heating from about 500 to 650°C.

*Little Requirement of Process Water*

The oil shale deposits are frequently in dry areas so that a limited supply of water is available for the operation of large plants. In this connection the LR process has the advantage that the vapors and gases are not diluted with combustion gases and only little heat has to be removed to condense the oil vapors and to cool the gases. This can be largely done in air coolers. Water is required mainly for moistening the shale residue. The quantity is about 10 percent by weight of the quantity of residue to prevent the dry dust from being blown away by the wind. The process water at a quantity of 4 to 5 percent by weight related to the quantity of residue may also be used for this purpose unless it causes odor nuisance.

**UTILIZATION OF SHALE ASH**

The large quantities of distillation residue (shale ash) have to be transported away and deposited.

Some oil shale grdaes have a high content of lime so that the residue can be used for the manufacture of building bricks and cement. In the LR process part of the carbonates is decomposed on heating the circulating material in the lift pipe and the carbon is burnt. When it is desired to use the ash for building brick or cement production, it is advisable to withdraw the dust and the surplus circulating material at a temperature of 600 to 700°C, to post-treat in a separate fluid bed by the introduction of air and possibly fuel, to calcine completely at temperatures between 700 and 900°C, and to remove all the carbon.

**COMPARISON OF LR PROCESS WITH OTHER PROCESSES**

The LR process originally developed for the devolatilization of sub-bituminous coal is excellently suitable for the distillation of oil shale. It is superior to all other conventional processes, some of which have reached development stages which Lurgi already tried out on a pilot and commercial scale decades ago but which were found unsatisfactory and therefore abandoned. This applies to low temperature carbonization in externally and internally heated carbonizers with utilization of the carbon in the distillation residue as fuel and with indirect heating of the circulating gases, and to the retorting process which Lurgi tried out, batchwise and
continuously, in circular vertical retorts, on the inclined grate, in situ and in piles. Lurgi also abandoned, at an early stage, the use of coarse-grained heat carriers and of the rotary kiln as a mixing device. At the end of this experimental work Lurgi has available a process which can handle fines, which uses the distillation residue as circulating fine-grained heat carrier, which utilizes the carbon in the residue to cover the heat requirements, which can be realized in uniformly operating large capacity units and which furnishes a high yield of oil and even LPG as well as high-concentration gas. The process is nonpolluting and yields shale residue suitable for the production of building bricks and cement.

The LR process will, no doubt, find a wide application for oil recovery in the future. Apart from oil shale it can also handle tar sand (Rammler, Oct. 1970) and asphalt rock with equally good success.

ECONOMICS OF OIL RECOVERY

The properties of oil shale vary rather considerably regarding heating value, oil content, characteristics of product oil, composition of the distillation residue, as well as strength of the shale and its distillation residue. Other criteria are the natural deposits, thickness of the seams, purity of the seams, thickness of the top layers, sub-soil water conditions of the mine, etc., including the extent of the deposit and the general mining and environmental conditions. All these factors influence the mining cost of the oil shale and the oil production costs.

The mining cost can be kept at a reasonably low level when the oil shale can be won by open cast mining under favorable conditions or by the room-and-pillar system. At the current prices for crude oil, a commercial oil shale distillation plant can be operated economically when the oil shale contains more than 5 percent oil and when the mining costs are reasonable. The economics can be improved when the distillation residue is suitable for the production of building bricks and cement.

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ACCELERATED OIL SHALE IN SITU PROGRAM
OF THE U.S. GOVERNMENT

Andrew W. Decora and Harry R. Johnson

SUMMARY

Efforts to develop the nation's vast oil shale resources have largely focused on mining oil shale and retorting it in surface vessels. An alternative approach in situ (or in-place) retorting, has not been as actively pursued. Yet, development of a viable in situ technology offers the potential of both significant environmental advantages and an increase in the amount of recoverable resources.

The program described in this report is directed specifically at those federal actions recently announced that are directed towards overcoming the technical obstacles that have retarded the development of in situ processes. The program goal is to develop, by 1980, several commercially viable technologies for the in situ production of shale oil.

National in scope, the program is expected to be undertaken in part with private funds, in part with joint federal/private financing, and, in some research areas, wholly with federal funds. The federal government will provide overall program management to ensure that all parts of this highly interrelated program move forward harmoniously.

Although emphasis is directed toward the oil shales of Colorado, Utah, and Wyoming, research will also be initiated on the oil shale deposits that underlie much of the eastern United States. A number of feasible in situ technologies are planned for testing in various oil shale resource types.

INTRODUCTION

The Department of the Interior, in cooperation with the Energy Research and Development Administration (ERDA) and other government...
agencies, announced on March 19, 1975, a program designed to accelerate the development and application of in situ processes to recover oil from shale. Specifically, the objective of this program is:

To advance to the point of commercial application by 1980, alternative methods for in situ recovery of shale oil and, in so doing, extend the data base needed to form future policies for oil shale development on public lands.

The in situ program, to be administered by two federal agencies, involves two concurrent actions:

(1) By Interior: Initiate those steps that could lead to lease(s) of one or two prototype oil shale tracts for in situ development by private industry, and

(2) By ERDA: Initiate an accelerated program of in situ research designed to complement the Interior action.

The two actions are interrelated, with information developed under the first action used to program the second, that is, to determine industry interest, Interior will offer two oil shale tracts for in situ development. Industry will signal its interest (or lack thereof) by nominating tracts for development using a technology to be specified. This will then allow ERDA to program research to support—but not duplicate—what industry is willing to do. Also, technologies not of immediate interest will be pursued by cooperative ventures with industry or through in-house efforts. This accelerated program is planned for initiation by July 1975.

The conceptual framework for this in situ program has been presented, extensively reviewed, and approved for implementation. An updated schedule for the program is presented in figure 1. The upper line represents in situ research while the bottom two lines represent continuation of Interior’s prototype oil shale leasing program. The figure shows how information is expected to be developed and exchanged, the results of the leasing action providing the primary criterion to select the research to be conducted under government sponsorship.

In this report, we discuss the two federal actions announced March 19, 1975. Emphasis in the report will be devoted to summary description of the accelerated research and development activities that will be implemented by the government.

IN SITU LEASE TRACTS

With the final offering of oil shale lease tracts under the Department of the Interior’s Prototype Oil Shale Leasing Program on June 11, 1974, the
Figure 1.—Schedule for oil shale in situ program, including prototype leasing and research elements.
first stage of the Department's leasing program was completed. The prototype program, which evolved from an unsuccessful attempt to lease public oil shale lands in 1968, was this time successful and resulted in the sale of four oil shale lease tracts. Of the four tracts sold, Colorado tract C-a was expected to be developed by surface mining, Colorado tract C-b by underground mining in an area that will require mine de-watering prior to and during development, and Utah tracts U-a and U-b by underground mining in areas likely to contain only small amounts of water. These expectations will be realized as documented in the preliminary development plans for the four tracts as filed with the Department by the successful bidders. The two Wyoming tracts W-a and W-b were expected to be developed by in situ technology. Failure to sell these two tracts limits the amount of information sought under the prototype program, particularly regarding in situ technology.

In the mid-March announcement by the Department and by ERDA, the Department announced the intent to continue the prototype oil shale leasing program by re-offering for bonus bidding two tracts of public oil shale land of not more than 5,120 acres each. The two tracts will be specifically offered for testing in situ processing options.

The new call for nominations involves two related actions: (1) granting of permission for applications to conduct informational core drilling, and (2) the call for nomination of areas for oil shale leasing. Both of these actions are nearly similar to those announced at the initiation of the Prototype Oil Shale Leasing Program in 1971. The essential difference in the nomination process will be that a tract nomination shall be submitted together with a recommendation of the type of in situ technology that might be used to develop the tract using in situ means. Request for description of the recommended technology is to be brief (approximately 5 to 10 pages) and should include only such detail as is needed to provide the government with an accurate and unambiguous understanding of the recommended approach. The description of the recommended technology should indicate the general classification of the technology, i.e., "true in situ" (no mining), "modified in situ" (some mining), or variations thereof. It should indicate the mineral resources present on the nominated tract and preliminary plans with respect to maximum utilization of the resource, including associated minerals if present. If modified in situ is recommended, the probable proportion of the resource to be removed by mining and its disposition must be indicated.

Also to be addressed are preliminary plans to: (1) mitigate environmental degradation, (2) minimize water and power requirements, and (3) provide maximum protection for the health and safety of the workman. Submission of the recommendation will not obligate the nominator to apply that technology should be eventually win the right to develop the tract. The recommendation is expected to be made in good faith for the advice
of the government in decision making regarding future directions of government research programs and other such reasons as the government shall determine. Responses to the call for nominations shall be concluded by June 30, 1975. The nomination process will lead to the selection of two tracts that are for possible later lease sale.

After environmental evaluations, public hearings, and submission of Final Environmental Statements by the Department, a decision will be reached by the Interior Secretary on whether to proceed with the sale of the two tracts or not. If the Secretary decides to proceed, the two in situ tracts are expected to be offered for bonus bidding by midsummer of 1976.

ACCELERATED RESEARCH AND DEVELOPMENT PROGRAM*

The research and development program presented in this report represents the research necessary to achieve the in situ program objective. Some of this research is expected to be undertaken by private industry on private lands or in conjunction with the development of two in situ tracts on public lands. These efforts will not be duplicated under a federally sponsored program so that some of the research activities described below will probably not be undertaken with public funds. The plan will undergo some modification as additional information becomes available.

Specifically, the type of information to be developed includes:

- recovery efficiency (hydrocarbons and minerals),
- types of shale deposits to which process is applicable,
- compatibility of process with other processes which may ultimately be required to maximize recovery of total resource,
- guidelines to protect health and safety of workers,
- delineation of environmental effects,
- process demands on other resource bases (energy, water, equipment, and materials and manpower), and
- ability of process to contribute to national energy objectives, considering cost and rate of application.

Such information on surface and underground mine development followed by surface retorting will be available from development of four pro-


Figure 2.—Relation of in situ program to prototype oil shale leasing program.

totype tracts under Interior's 1974 leasing program.* The in situ program would complement this action as shown in figure 2.

Specifically, the in situ program is to develop, through leasing plus research, the ability by 1980 to:

(1) determine the technical and economic feasibility and environmen-

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tal costs of shale oil recovery by the true in situ or the modified in situ retorting method;

(2) determine the best fracturing or explosive rubblizing technique for the resource;

(3) determine the operating conditions necessary to obtain the desired retorting results, whether these results be maximum gas production, maximum oil production, or maximum resource recovery.

The development of the oil shale in situ research program considered four major types of oil shale resource targets and five distinct in situ technologies. The potential for application of in situ technology by resource target and technologic option is shown in table 1. As noted in table 1, there are 20 possible combinations of technology and resource type. However, present information indicates that only 7 of the 20 possible combinations are of potential commercial interest. These 7 combinations are marked with a + in table 1.

The variability of the oil shale deposits and the varying demands for hydrocarbon products (gasoline, fuel oil, or fuel gases) indicate that no one processing technique can be universally applicable to all types of oil shale resource targets. It follows that there is a need to develop several techniques to the point of commercial application to assure that efficient resource recovery is achieved at acceptable environmental costs.

OVERVIEW OF ACCELERATED IN SITU PROGRAM

Systematically planning a research program to test the feasibility of in situ technologies requires matching the projected potentials of the technologies with known needs or uses. Technical tradeoffs must be made to bring new technologies to fruition, and benefits versus detrimental effects must be determined. The accelerated program will develop this information. A generalized diagram of the major areas to be evaluated or considered in the accelerated program is presented in figure 3.

The accelerated in situ oil shale program is designed to evaluate both true in situ as well as modified in situ techniques. All these phases will be drawn together as shown in the overview PERT chart in figure 4.*

The PERT diagram shows that the accelerated oil shale in situ research needs to be conducted in three major areas. These areas are: (1) in situ production of liquids, and, in particular, the development of adequate fracturing techniques; (2) modified in situ production of liquids; and (3) in situ production of gases.

Both liquids and gaseous products will be made from oil shale in situ (fig. 4). Improvement in fracturing techniques is critical to employment of in situ methods as shown in the top part of the figure. The completion
of the fracturing research, along with the supporting activities could lead to the construction of a process demonstration unit (PDU) 2 years after the research is initiated. After PDU is operated for about 1 year, the decision for true in situ commercialization could come 4 years after the initiation of the fracturing program.

Modified in situ programs address the research problems associated with both horizontal and vertical retorting systems. Since industry is already actively engaged in the vertical retorting research, a cooperative program could rapidly advance the technology. For example, a cooperative program could lead to a decision for commercialization 2 years after such a program is initiated.

A horizontal retorting system will require a more gradual scale-up since little information is available from past accomplishments. Starting with a site capable of retorting 6,000 tons and scaling up to a site capable of retorting 24,000 tons will take at least 2 years after starting the program. Evaluation, construction, and operation of a PDU will require at least another 2 years. Therefore, a decision for commercialization will be at least 4 or perhaps 5 years from the start of the program.

Gasification of oil shale in situ (actually maximizing gas production in situ because both liquids and gases are produced) will offer yet another

Figure 3.—Diagram of major areas of research for accelerated oil shale in situ R&D.
Table 1.—Potential for application of in situ technology by resource target and technologic option* 

<table>
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<tr>
<th>Technologic options</th>
<th>Type I Deep 2,000 feet</th>
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<th>Type III Deep leached</th>
<th>Type IV Thin beds</th>
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<td>Inject hot fluids</td>
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<td>?</td>
<td>+</td>
</tr>
<tr>
<td>Inject hot gases</td>
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<td>?</td>
<td>N.A.</td>
<td>+</td>
</tr>
<tr>
<td>Direct combustion</td>
<td>N.A.</td>
<td>?</td>
<td>N.A.</td>
<td>+</td>
</tr>
</tbody>
</table>

*In addition to the + indications shown in this table, options listed under "in situ" and "type I" resource targets may also be appropriate. Data to support this conclusion is not publicly available, however.

Note:  
+ indicates promising application of a specific technology to a specific resource target.  
N.A. — not applicable.  
? — of questionable application.


option for development. This research is proposed to maximize the gas heating value as well as the gas produced from an underground oil shale operation. The construction of a 25- to 40-ton gasifier could lead to a decision to construct a PDU 2 to 3 years after initiation of the program. Results from the PDU would not be obtained for at least another 2 years.

The overall program is designed to assess many relevant in situ technologies in as short a time as practical. The accelerated research program concerns itself with a procedure for the measurement of the impacts of in situ oil shale development and the trade-off among these relevant technologies. This will be done in arriving at a final assessment of the technology for demonstrating the practicality of advancing the in situ oil shale research to the commercial phase.

Thus, a most important aspect of the accelerated research program is to extend the options available for process design. The results of this multiple approach research program will also allow decision-makers to clearly assess the technology’s relevance throughout the entire design program and not after the design has been completed. Although some assessments cannot be made until designs are formalized and pilot plants are built, the results
will provide a range of conditions within which the technology should operate.

Finally, the accelerated program will also include extensive supporting research, such as mathematical modeling, process evaluation from product characteristics, waste management, and environmental research. Specific research projects will be announced early in fiscal year 1976.
RESEARCH AND DEVELOPMENT ON RUBBLE IN-SITU EXTRACTION OF OIL SHALE (RISE) AT LAWRENCE LIVERMORE LABORATORY

Albert J. Rothman

ABSTRACT

A program for development of oil shale in situ has been active for almost 2 years. The process consists in forming a rubble chimney by the use of mining and high explosives and retorting in place using combustion in an air stream. The process is called RISE (Rubble In Situ Extraction). A proposed method of mining and rubble formation is described, and technical questions in the process are outlined. Field work is planned, but not yet funded. An experimental program is underway to answer these questions, and is presented. Recent experimental and calculational results related to retorting and rubblization are given.

INTRODUCTION

At the Lawrence Livermore Laboratory we have been working on a process for in situ recovery of oil from thick oil shale deposits of moderately low grade, namely, 20 gal/ton. Commercial above-ground retorting processes for oil shale typically use 30 to 35 gal/ton oil shale (National Petroleum Council 1972 and 1973). Deposits 400 or more feet thick within the Piceance Basin containing oil shale of 20 or more gal/ton hold 350 billion barrels of recoverable oil (Rothman 1975; Lewis and Rothman 1975). This is a substantial amount of oil, comparable in extent with recently quoted Middle East recoverable oil reserves of 316 billion barrels (DeGolyer and MacNaughton). We have proposed a vigorous field and laboratory program that would prove commercial scale operation in six years (Lewis and Rothman 1975) and permit rapid commercial expansion subsequently.

Albert J. Rothman, Lawrence Livermore Laboratory, University of California, Livermore, California. Work performed under the auspices of the Energy Research and Development Administration.
RISE (RUBBLE IN SITU EXTRACTION) PROCESS

Various in situ processes have been proposed and studied for oil shale including fracture of the rock using high explosives and massive hydraulic injection (hydrofracking) followed by combustion in place (Burwell and others 1973), leaching methods, use of hot gases in permeable oil shale regions (Dougan and others 1970), etc. Occidental Petroleum Corp. has reported field tests (Ridley 1974) on a modified in situ process in which a portion of the oil shale is mined underground and the remainder blasted into the void so created, resulting in a rubble-filled column that is then retorted in place using combustion. The terms “in situ,” “modified in situ,” “mining in situ process,” etc., have been used to refer to this general process.

To simplify the terminology, we have coined a term, “Rubble In Situ Extraction” (RISE) to refer to our version of this general procedure. In the RISE procedure, a rubble is created by a continuous mining process using a modified sublevel caving technique (fig. 1). Approximately 20 percent of the oil shale is removed to the surface, where it may be retorted in surface equipment and then discarded, or it may be discarded directly, depending on economic and environmental conditions at the particular site. We believe that this technique can produce large volumes of rubble with uniform and controlled void space, suitable for commercial scale retorting of the thick resources referred to above, namely, 400 or 600 feet to 2,000 feet, in blocks several hundred feet square. The rubble volume is then retorted in place using hot gas generated continuously from combustion of a portion of the oil shale, using an air stream. Alternatively an inert gas may be heated by external combustion, then circulated through the rubble.

A significant point here is the use of the continuous mining technique capable of preparing uniform rubble on a large scale, as opposed to mining out single or several larger cavities and blasting rubble into them. The latter procedure may be suitable for relatively thin accessible beds of oil shale or for experimental field tests, but is not expected to yield the control or uniformity of the modified sublevel caving technique, nor will it permit continual measurement of rubble size, which in turn permits modification of the rubble size by adjustment of explosives as mining proceeds. More details on the process, especially the proposed mining technique (Edey and others 1974) and its advantages (Lewis and Rothman 1975) are given elsewhere.

COMPARISON WITH OTHER PROCESSES

Comparisons of RISE with other processes are shown in tables 1 and 2. More detailed discussion of these comparisons, and evaluations of other in situ processes are given in another report (Lewis and Rothman 1975). The advantages of the RISE process are clear. Although the nuclear case shows
Figure 1—Rubble in situ extraction (RISE).
Table 1.—Estimated costs for various oil shale recovery methods

<table>
<thead>
<tr>
<th>METHOD</th>
<th>COST PER BARREL*</th>
<th>CAPITAL INVESTMENT 100,000 BARRELS/DAY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mining and surface retorting</td>
<td>$12</td>
<td>$1000-1500 million</td>
</tr>
<tr>
<td>Rubblization by mining and</td>
<td>$8</td>
<td>$600 million</td>
</tr>
<tr>
<td>in-situ retorting (RISE method)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nuclear fracturing and</td>
<td>$5</td>
<td>$300 million</td>
</tr>
<tr>
<td>in-situ retorting</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Cost includes upgrading to petroleum refinery feedstock standards.

Source: Lewis and Rothman 1975.

much potential, public acceptance at this time appears dubious.

The RISE concept was chosen for several reasons: (1) utilizes a very large thick resource compared to most other oil shale approaches (estimated 350 billion barrels recoverable, assuming 70 percent resource recovery, 60 percent oil yield for in situ operations and 95 percent oil yield for surface retorting of the mined shale). (2) Environmental impact is much smaller than for surface processes. Less shale needs to be dumped above ground, water requirements are less, and, compared with surface retorting, a smaller labor force is required. (3) Costs are difficult to compare in times of rapid inflation, but they appear to be significantly lower for RISE ($6-9/bbl) (Lewis and Rothman 1975) than for aboveground retorting processes. (4) Reasonable likelihood of technological success, based on experiments in the 150 ton Laramie retort (Harak and others 1975) and the encouraging reports on field tests by Occidental Petroleum Corp. (Ridley 1974). Other in situ processes do not appear to offer this likelihood. (5) Capital, equipment availability, and large-scale mining capability are in short supply. Requirements for these are much lower for the RISE than those for surface processes. For these and other reasons listed above, RISE offers greater likelihood of early commercial operation on a large scale within a decade. We estimate development to commercial scale demonstration could be accomplished by 1980 or 1981 (Lewis and Rothman 1975).

Of course, the RISE concept and surface retorting processes may complement each other, in that the latter most effectively employs richer oil shale closer to the surface, while the former utilizes deeper thicker deposits that are leaner in grade.

TECHNICAL AND ECONOMIC ISSUES

In table 3 we summarize a number of areas that need to be studied to
### Table 2. Comparison of the major methods that have been considered for recovering oil from oil shale for production of 1 million barrels/day

<table>
<thead>
<tr>
<th>RECOVERY METHOD</th>
<th>OIL SHALE RESOURCE</th>
<th>ENVIRONMENTAL IMPACT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grade (gal/ton)</td>
<td>Oil (billions of barrels)</td>
</tr>
<tr>
<td>Where Retorted</td>
<td>Shale Preparation</td>
<td>In Place</td>
</tr>
<tr>
<td>Surface</td>
<td>Underground mining, room and pillar</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Open pit mining</td>
<td>20</td>
</tr>
<tr>
<td>In Situ</td>
<td>Mining rubblization (RISE process)</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Nuclear fracturing</td>
<td>20</td>
</tr>
</tbody>
</table>
### Table 3.—Technical and economic issues

**TECHNICAL AND ECONOMIC ISSUES**

**RETOURING**
1. Choice between combustion process in-situ or circulation of non-oxidizing gas heated externally.
3. Optimum oxygen concentration. Possible steam addition.
4. Effect of retorting rate on yield and economics.
6. Oil yield and quality vs. heating rate.
7. Optimum fragment size and distribution.
8. Permeability changes of heated oil shale rubble.
9. Upgrading or utilizing low BTU content of large volumes of stack gas.

**RUBBLIZATION**
1. Mining system
2. Porosity and porous flow through rubble
3. Fragment size control
4. Subsidence
5. Economics and resource recovery
6. Mine safety including ventilation for possible retorting and mining in adjacent areas.

**MEASUREMENT AND CONTROL**
1. In-situ measurement of rubble size and void distribution
2. Temperature measurement
3. Flame location
4. Gas sampling and analysis

**ENVIRONMENTAL**
1. Leaching of spent shale into groundwater
2. Dewatering and salinity water management
3. Absorption of pollutants from off-gas

---

develop and optimize the RISE process. More details are given elsewhere (Rothman 1975). We have developed an experimental and calculational approach to the issues raised in this table. These are also discussed in more detail elsewhere (Lewis and Rothman 1975).

The culmination of the program is to be a series of successive field tests (Lewis and Rothman 1975) leading to one suitable for commercial scale operation (600 to 1,000 feet long rubble column, about 250 feet square in cross section). This scale is necessary to test some issues not resolvable by smaller scale operations, e.g., procedural details and effectiveness of a modified sublevel caving method for producing uniform void and rubble.
Also such large-scale tests are needed to study uniformity and control of combustion, retorting gas distribution and possible permeability loss due to weight of rubble in a long column.

EXPERIMENTAL WORK

The experimental program began late in 1973. Since then, progress has been made in a number of areas, and several completed works have been published (Lewis and Rothman 1975). Other work is proceeding and some of it is described below.

KINETICS

A number of analyses of the kinetics of kerogen decomposition have been made (Hubbard and Robinson 1950; Allred 1966; Fausett and others 1974) based on the data of Hubbard and Robinson's (1950) classic experimental study. These analyses have not explicitly taken into account the thermal induction period, i.e., the time to heat up the sample in the furnace in those experiments. Several of the analyses have instead implicitly assumed that the induction period arises from an autocatalytic mechanism. Braun and Rothman (1974) have proposed a kinetic model, using two first-order equations, which accounts for thermal induction time, and thereby gives a simple, yet accurate representation of the data.

The equations are given in table 4 and some typical results are shown in figures 2 and 3, demonstrating that our simple analysis fits the experi-

<table>
<thead>
<tr>
<th>Table 4.—Equations</th>
</tr>
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<tbody>
<tr>
<td>The pyrolysis of kerogen can be expressed as:</td>
</tr>
<tr>
<td>$K \xrightarrow{k_1} B + G_1 + C_1$</td>
</tr>
<tr>
<td>$B \xrightarrow{k_2} A + G_2 + C_2$</td>
</tr>
<tr>
<td>$K = \text{Mass of kerogen}$</td>
</tr>
<tr>
<td>$B = \text{Mass of bitumen}$</td>
</tr>
<tr>
<td>$A = \text{Mass of oil}$</td>
</tr>
<tr>
<td>$G_1 = \text{Mass of gas formed in reaction i}$</td>
</tr>
<tr>
<td>$C_1 = \text{Mass of carbonaceous residue formed in reaction i}$</td>
</tr>
<tr>
<td>$k_1 = \text{First-order rate constant for decomposition of kerogen}$</td>
</tr>
<tr>
<td>$k_2 = \text{First-order rate constant for decomposition of bitumen}$</td>
</tr>
</tbody>
</table>
mental data very well with only a few parameters which have reasonable physical significance, namely, thermal induction time $t_0$, i.e., the effective time required for the oil shale to reach temperature in the furnace; and oil yield when the reaction is allowed to go to completion, $f_A$.

**Retort Modeling**

A working numerical or computer model that takes into account the appropriate physical and chemical processes occurring in a rubble bed is a powerful tool that permits one to visualize more clearly what is taking place in the bed, what variables should be studied experimentally, and what precision is required in the physical and chemical properties used as input. Even more importantly, the model may help suggest basic process changes that would produce significant improvements in yields and costs. And of course a well-tested model permits extrapolation to large-scale commercial operation from small-scale laboratory and field tests.

Models of oil shale retorting have been developed by others, but a num-
Figure 3.—Temperature dependence of specific rate constants.

ber of the models are company proprietary. Nuttall and Curlee (1975) have summarized the characteristics of these models, but details have not been published, except for predictions made by the models (Nuttall and Curlee 1975; Johnson and Timmins 1975; Kondis and others 1975) or else the models have not been workable, according to Nuttall.

Our modeling studies are considered a keystone in this program. To date we have modeled the case of hot inert gas heating of a bed or uniformly size particles (Braun, private communication). Tables 5 and 6 show the conditions taken into account for this case. The basic differential equations have been solved numerically, and the computer output is shown
Table 5.—Model of inert gas flowing through a bed of reactive solid particles

**Model of Inert Gas Flowing Through a Bed of Reactive Solid Particles**

A. Axial heat and mass transport only  
B. Gas-solid heat transfer  
C. Reactions  
   1. Decomposition of kerogen  
   2. Decomposition of carbonate

Table 6.—Reactions used in current model of hot inert gas retorting

**Reactions Used in Current Model of Hot Inert Gas Retorting**

1. Chemical Reactions  
   A. Decomposition of kerogen to condensable organic vapor, noncondensable organic gas, and carbonaceous residue.  
   B. Reaction of dolomite with silica to produce diopside (CaMgSi$_2$O$_6$) and carbon dioxide.

2. Thermal Processes  
   A. Gas-solid heat transfer.  
   B. Thermal conduction within shale particles.  
   C. Endothermic heat of decomposition of the kerogen.  
   D. Exothermic heat of condensation of the condensable organic vapor.  
   E. Endothermic heat of reaction of dolomite.

In figures 4 and 5. Temperatures plotted are averages of the outermost one-third of the particle volume. In particular, figure 4 shows the development and broadening of two major changes of slope as the temperature front moves down the column, using 0.2 meter particles. The upper one near 500°C corresponds to the beginning of dolomite decomposition; at temperatures above 500°C decomposition is practically complete. The lower one near 300°C corresponds to the decomposition of oil, gas, and char; at temperatures above 350°C kerogen pyrolysis is virtually complete. Figure 5 shows the output when very large particles are used, namely, 2.0 meters. In this case the extensive broadening of the temperature vs.
distance is clearly seen, caused by the large thermal sink of these larger particles.

These figures of course are only representative of possible output from the model. The effect of gas rate, input temperature, bed height and particle size may be studied over broad ranges.

Work is underway, but not yet complete on the combustion model at LLL. Reactions are more complex, involving oxidation of gas, oil, and char to gaseous products. The combustion case has been solved for single particles (Braun and Mallon, private communication).

Another important step to be taken is the modeling of a bed having a size distribution of particles.

**RETOURING STUDIES**

Studies are underway in our laboratory to determine the effect on oil yield and product composition of heating rates and different atmospheres.
There is conflict in the literature and in unpublished discussions implying potentially severe losses in oil yield with increased heating time. An analysis of Cummins and Robinson's experimental data (1972; Cummins, Doolittle and Robinson 1974) by J. H. Raley (private communication) actually shows enhancement of oil yield by preheating at 300°C for times up to 4 days, the limit of the experiment. At 250 and 350°C the conclusions are less clear; but changes in yield due to preheating appear to be small. There does appear to be a significant loss in oil yield at 150 and 200°C for very long term heating (several months to a year). This appears to be confirmed by increases in the residual carbon content in the preheated oil shale. It is not clear at this time whether preheating times of many months at 150 to 200°C are realistic even in thick in situ retorts. However, confirmation of the above data is desirable because of conflicts in the literature and in unpublished experiment data of others.

The Bureau of Mines at Laramie has reported a number of experiments
in their large retorts, 10-ton and 150-ton capacities (Harak and others 1974; Carpenter and Sohns 1968; Sohns, Harak and Carpenter 1972; Dockter, Harak and Sohns 1972). The results are very useful guides to retorting of simulated rubble beds and have served as the basis for predicting yields in large-scale field operations. However, a number of points need to be explored further. Among them are the effect of adiabatic operation. Heat losses to the atmosphere in the Laramie 150-ton retort varied from 5 to 33 percent (typically about 15 percent) based on the total heating value of the input oil shale. Furthermore a number of runs showed unaccountable heat balance discrepancies up to 37 percent (typically about 15 percent). These losses calculated on the basis of the heating value of the oil recovered are even higher percentagewise (1.5 to 2 times higher). Furthermore, the percent loss increases with reduced retorting rates, since longer times are available for heat loss to take place to the surroundings. Thus the drop in yield at lower retorting rates in the Laramie work may be due primarily to larger heat losses. It is also desirable to utilize output retort data to test and improve models of retorting.

We have constructed a pilot retort 12 inches dia by 60 inches high and have made a number of exploratory runs. A simplified flow sheet of the equipment is shown in figure 6. The retort has a data acquisition system and will be operated adiabatically as soon as the computer control system is completed. Early results are displayed in figures 7 and 8 from an insulated column, but one whose heat losses to the atmosphere are appreciable. Thus, the temperature profiles will be different from those in a truly adiabatic column. Figure 8 shows an interesting feature, namely, the presence of two humps or peaks in temperature when gas recycle is used. The first peak is attributed to the combustion of components in the gas and the second to combustion of char lower in the retort. This effect is seen more clearly in figure 9 which shows the temperature plotted against time at a particular level of the column (about halfway down). This plot also shows that the temperature at the center of the retort cross section is higher than those 2 cm from the edge, confirming that the heat losses are significant.

A larger retort, 3 feet dia by 20 feet high is under construction. Its purpose will be to permit insertion of larger blocks in the rubble. It is planned to instrument the interior of these blocks as well as the bed as a whole.

**Single Blocks**

Anomalously rapid heating of single oil shale blocks has been reported by Laramie (Sohns, Harak and Carpenter 1972; Harak, Long and Carpenter 1970). We have studied this phenomenon in some detail and the results are presented in two companion papers in this symposium (Mallon and Miller 1975; Tyler 1975).
While not strictly an experimental program so far, this study has been important to determine pressure drop in rubble columns. A key issue here is that of characterizing the mean particle size of a bed having a broad particle size distribution. An analysis of data in the literature (McKee and Reynolds) has shown that the Ergun equation offers a good representation of pressure drop vs. flow rate if the mean particle diameter is taken as the harmonic or surface-area mean, i.e.,

$$\frac{1}{d_m} = \sum_i (W_i/d_i)$$

where $d_m$ is the proper mean diameter and $W_i$ is the weight fraction of the particles having diameter $d_i$.

Figure 10 shows pressure drop as a function of particle size for various porosities. The probable range of mean particle size is shown on the same figure, based on estimates of particle sizes of mine-run shale and those obtained from underground nuclear explosions in hard rock (McKee and Reynolds). Neither situation is truly applicable, but they give some idea
**Figure 7.** Retort temperature profile as a function of time after ignition (run 3).

**Figure 8.** Retort temperature profile (run 4).
of the range to be expected. These pressure drops were calculated for typical gas flow rates, based in part on pilot runs in the Laramie 150-ton retort (Harak and others 1974). We assumed 16,000 standard ft³/ton of air plus recycle gas, and an air velocity of 0.75 cm/s (89 ft/hr). These correspond to 2 to 2.5 ft/day retort rate, for 10 to 30 percent porosity. The air plus recycle rate is assumed proportional to the retort rate, and pressure drop is approximately proportional to the air plus recycle rate.

Figure 11 shows the effect of pressure drop on electrical costs for pumping, and illustrates the significant cost penalties of high pressure drops (Reynolds, internal communication). For this figure we assumed air plus recycle rate was 16,000 std cu ft/ton, and oil yield assumed was 60 percent of Fischer assay.

DEFORMATION AND LOSS OF PERMEABILITY

The only published works on this subject we are aware of are those of the Bureau of Mines (Burwell, Tihen and Sohns 1974; Tisot and Sohns 1971). From the Bureau's work, it appears that the permeability of 31 gal/ton and richer oil shale rubble beds decreases drastically when the oil shale is heated at a rate of about 70°C/hour under a stress of hundreds...
of pounds/square inch. Measurable, but much smaller losses in permeability are experienced in 20 gal/ton oil shale under the same conditions. There is also evidence of some recovery of permeability with prolonged heating.

We plan to study this phenomenon in some detail, including the effect of slower heating rates that correspond to those expected in an underground in situ case. Our equipment is constructed but runs have not yet begun.

CONCLUSION

We have summarized some recent experimental results in the Livermore in situ oil shale program. We anticipate that a number of detailed papers and reports from this program will be presented in the near future.
ACKNOWLEDGMENT

The results presented in this paper are those of a number of participants, whose work I hereby acknowledge. I especially wish to express appreciation for the assistance of R. L. Braun, C. R. McKee, W. J. Reynolds, and G. D. Snider during the preparation of this manuscript.

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THE NEW COLORADO ADMINISTRATION'S
THOUGHTS ON OIL SHALE

Harris D. Sherman

Let me begin my talk at this Eighth Annual Oil Shale Symposium with a quotation from a nationally respected magazine:

"Is the United States facing a gasoline famine? Shall we be required to forego automobiling except to meet the stern necessities of war and of utilitarian traffic? Are our petroleum fields showing signs of exhaustion? The output of petroleum has not yet begun to diminish; statistics show that it is still increasing; yet the downward trend of production from the present oil fields is plainly in sight.

Enormously increasing demands on the oil fields of America are being made and though the industry has never been so feverishly active as it is now and the output never so large, the truth is that the demand has not been entirely met.

It is just at this juncture that we have made a discovery that has disclosed what is undoubtedly one of our greatest mineral resources—oil shale—locked into mountain ranges of rock that will yield billions of barrels of oil.

For many years, travelers going through the Colorado River Valley of Colorado and into the Great Uinta Basin of eastern Utah have looked from the windows of their Pullman cars on the far stretching miles and miles of the Bookcliff Mountains, little realizing that in these and adjoining mountains, plainly exposed to view, lay the greatest oil reservoir in the country, the oil shales of Colorado, Utah, Wyoming, and Nevada."

Well, I am afraid as soon as I read this sentence about Pullman cars, you realize that this quotation is not from a current publication, but one out of our past. It was a major article in the February 1918 edition of

Harris D. Sherman, Executive Director, Department of Natural Resources, Colorado.
National Geographic. It tells us a lot of things we are repeating everyday in our present oil shale discussions.

I don't need to tell this audience that the oil shale industry has been on the brink of development in spurs and starts for more than 100 years. The boom was to start in the 1850s only to see Colonel Drake drill his famous oil well near Titusville, Pennsylvania. In 1915, the boom was on again only to collapse as cheaper crude oil sources of Eastern Texas were found. We know that oil shale development will always hinge on the economic incentives available to industry. But, we have added to that the political realities of our modern world, and a particular national need to become less dependent upon the whims of the oil exporting nations.

When I was asked to give this speech some two months ago, the proposed title was "The Lamm Administration's Policies on Oil Shale Development." I, of course, assumed that two full months on the job would produce clear policies and directions by the new administration. Perhaps it comes as no surprise to you that we have found that this topic is immensely complex, a puzzle with a thousand pieces, many of which are unfortunately outside of our control. So, we are moving cautiously and carefully—trying to weigh and understand each of the parts and their relationship to the whole.

So I come today less to spell out Colorado's oil shale policy which we are in the process of formulating, but rather to give you our clearest thoughts, concerns, and questions about oil shale and spell out some of the procedures and ground rules by which we will operate. I should preface my comments by saying that we are highly cognizant that we are dealing with irreplaceable, nonrenewable resources and that we serve as the caretaker of these resources, not only for ourselves but for future generations. Our allegiance must be without question to Colorado and the nation; the social and economic well being of our people, lands, water, and our other natural resources.

To that end, within the limited time I have today, I would like to briefly comment on some of our concerns.

**DIALOGUE AND COMMUNICATION**

Let me assure you that we have much to share with each other. There is no question that the facts, research and perspectives arrived at by government, industry, universities, civic and environmental organizations should be shared as fully and widely as possible. I am convinced that reasonable people generally agree after a full airing of the facts. We need maximum input from all sectors before we can properly understand the subject. Dialogue is essential.

In addition, we must be candid and tell it like it is—with all the attendant possibilities, pitfalls, and problems. I must confess that the lack
of candor on occasion does provide us moments of comic relief. If I can
digress for a moment, I would like to share with you a recent letter that
Governor Lamm received from the president of a mining company which
I shall leave unnamed. This gentleman was introducing his latest mining
device, which, of course, was patented, and which, of course, was held out
to be the most important breakthrough in the oil shale industry. After
explaining how the mining device worked the gentleman then stated:

"Does this mean great gaping open pits and mountainous piles of debri?
No it does not. This extraordinary method of mining gently subsides
the surface overburden and as the oil shale is removed, the surface in-
dication can only be detected by surveying instruments. Cattle and
wildlife can continue to use the surface without being aware that the
removal of oil shale is going on.

The shale from which the oil has been removed will be fed into the
subsidence. There will be no retaining dams and piles of tailings. The
total activity at any one time will be confined to a small area. Within
a week, grass and shrubs will be growing on it. It will be far better
land than the original surface.

Water for processing will be entirely that water pumped out of the
mine workings. It will be used after processing to irrigate the surface to
insure growth. Not a single gallon will be taken from the Colorado,
White, or other rivers, and not a gallon will be discharged into these
rivers.

The United States could be completely independent of the Arabs and
their oil. The United States could be independent of the 'blue-eyed
Arabs' of Alberta, Canada, too. We are prepared to make it work. Your
support in the right places is necessary to get it working.

Sincerely"

Now, if we only had such candor from all of you, no doubt our prob-
lems would be resolved overnight.

Returning to dialogue, we must learn together. Just as you have never
before put together a viable, high production oil shale development, we in
state government have never before been faced to respond so quickly to
such profound questions of deep public concern.

The Secretary of the Interior recognized this when he so wisely insti-
tuted the prototype program. He said, in effect, "Let's see what happens,
let's see what our problems are," and "let's see what kinds of solutions we
can arrive at before we proceed at top speed into what might be an irre-
versible venture."

My door is open. I ask you to keep the dialogue going so that we
formulate our responses to your plans within a time framework that allows
mutuality. Don't place us in the position of responding to mining and
operational plans after they are set in concrete and major issues are cast in
THE NEED FOR A RATIONAL FEDERAL ENERGY POLICY

For those of you in industry, you have been waiting patiently for national direction. We in state government feel the same frustration. How Colorado responds to demand and supply energy questions is largely dependent upon what the federal government does.

Just where does the oil shale industry fit into the national plan? What part of our energy shortages will be taken up by oil shale? By coal? By imports? By natural and synthetic gas? And nuclear energy? What will oil shale cost? How critical is oil shale to our national well-being and in what time framework?

Let's not forget conservation and how it might fit into the national energy picture. I won't elaborate on the dearth of conservation programs. Colorado's government is going to do its best to demand intelligent, far-reaching national conservation measures. The state should also enact its own measures. Our nonrenewable natural resources should not be spent to satisfy wasteful habits. Conservation demands more than lip service and ineffectual programs.

So, too, the national government must insure that all sectors of this country contribute to the supply side of the energy question. Certainly this state and region must contribute but it must be a genuine nationwide program.

Energy programs must also be sound, guaranteeing energy payoffs as opposed to energy standoffs. I believe the oil shale industry will have to demonstrate a viable energy input-output ratio to justify full-scale development. Colorado is anxious to work with industry in making such determinations as witnessed by the pending studies to be undertaken by the Colorado Energy Research Institute on this very question.

THE RULES OF THE GAME MUST BE ESTABLISHED AS EARLY AS POSSIBLE TO ALLOW ALL PARTICIPANTS TO UNDERSTAND WHAT IS EXPECTED OF THEM

Never ending changes in policies, laws, regulations, and requirements will frustrate and work hardships on all of us. We are endeavoring to formulate such rules for legislative and administrative review and enactment. We would urge the federal government to do likewise. Our rules will respond to your plans and proposed activities. Back to the dialogue again.
COLORADO MUST PLAY THE ESSENTIAL, CRITICAL ROLE IN DETERMINING ITS OWN FUTURE, AND NOT BE PREEMPTED BY THE FEDERAL GOVERNMENT

Administration of water rights, water quality, air quality, environmental controls, mined land reclamation, land-use decisions, growth rates, taxation matters, and socioeconomic factors are in large part areas of state and local concern.

In many ways, the exploratory-planning stages of oil shale have served as a catalyst in raising jurisdictional questions with the federal government over where decision-making power lies. With 84 percent of the high-grade oil shale reserves found in Colorado and 80 percent of that reserve belonging to the federal government, Colorado must continue to work in a cooperative, close manner with the Department of the Interior and other federal agencies. But Colorado does not want to abdicate its responsibilities; we are confident we can manage our own future.

I should say that we have been fortunate in enjoying a completely open and candid relationship with our federal counterparts. At the working level particularly, our people have had the benefit of knowing the thinking of federal people and have had a chance for meaningful input on some important issues. We expect this air of cooperation to be even more prevalent as details of plans unfold.

THE NEW ADMINISTRATION SUPPORTS A PROTOTYPE OIL SHALE PROJECT, SO THAT WE CAN TEST ECONOMIC, ENVIRONMENTAL, AND SOCIAL IMPACTS OF SUCH DEVELOPMENT

We do not come with preconceived notions. We concur that many answers to important questions will be found in the analysis of a prototype project. But we stress that this experimental stage is only experimental. It is not an open ticket to full- or medium-scale development until all critical questions are answered. The monitoring process must be thorough and the testing complete before the necessary endorsements will be given.

I've heard that some of the required predevelopment testing and monitoring are overly extensive; possibly, but once the program gets into high gear, the opportunity for obtaining valuable ambient data is lost forever.

THIS ADMINISTRATION IS COMMITTED TO MAINTAINING AND STRENGTHENING OUR AGRICULTURAL ECONOMY

Agriculture has long been Colorado's most stable economic resource and it represents an important way of life for many of our citizens. Yet this industry has faced a serious challenge and deterioration because of
pressures on its waters and lands. On the one hand, municipalities have successfully condemned irrigators' water rights because of constitutional preferences, e.g., Thornton. On the other hand, industry, particularly in the energy sector, has successfully purchased agricultural water rights. Caught between these two forces, agriculture cannot compete at the marketplace. The result has been a steady erosion of irrigation waters.

So, too, have agricultural farm lands declined. Pressed by urban expansion and energy development, these lands have steadily diminished. The Lamm Administration is committed to reversing this trend. Colorado can play an important role in easing the world food crisis. We feel strongly that oil shale and coal development should not further erode this important economic and social resource within our state.

In sum, this administration must actively oppose any conversion of critically needed agricultural water or land to heavy industry use.

THE LAMM ADMINISTRATION WILL PUSH FOR STRONGER RECLAMATION AND ENVIRONMENTAL LAWS, AND THEIR ACCOMPANYING REGULATIONS, TO PRESERVE THE BEAUTY AND UTILITY OF OUR LAND

We will insist that the land be restored to full and productive use. We are particularly hopeful that in situ research will produce new, less environmentally damaging mining and processing techniques. We will also push for full compliance with our air and water quality standards. The Governor has said much on this subject and I don't feel that it is necessary to elaborate on his often mentioned concerns.

THE BENEFICIARIES OF OIL SHALE DEVELOPMENT—THAT IS, INDUSTRY, LAND SPECULATORS, GROWTH BUSINESSES, AND THE CONSUMER—MUST PAY THE DIRECT AND INDIRECT COST OF OIL SHALE DEVELOPMENT

These costs cannot be borne by the innocent bystanders or persons on fixed incomes, such as the elderly.

It is not easy to assess precisely what these costs are. To an extent the direct costs are measurable, but how do we assess the true cost, for instance, of placing an electric generation plant in Craig which may provide the power that is necessary to operate oil shale retorts in counties to the south with all of the attendant roads, sewers, schools, hospitals, law enforcement agencies, and social services?

How do we measure and pay the cost of urban expansion attributable to oil shale in those communities outside the development area, such as Grand Junction and Glenwood Springs? We need to put a price tag on areas lost to recreational hunting and fishing; we need to put a price tag
on the eventual disruption of the tourist trade and a price tag on the changes in life style that full development will bring. Cost accounting in these areas is not an exact science.

Even if the beneficiaries are to pay, what is the vehicle for accomplishing this? And the timing problem—local governments without question need front-end money to tide them over until the proposed plants become tax producing. In addition, the financing system should protect local communities if the bottom drops out of the oil market and prices go down, spelling an end to the industry. The boom-bust cycle should be a phenomenon of the past. Hopefully, when industry commences full-scale development, it will be one of long standing and provide a stable, reliable, economic and social base for the communities in which it is located.

I have intentionally not commented on a variety of issues which I know are of direct concern to you. Questions of federal price supports, federal construction loans, the size and pace at which the prototype program grows, and off-site disposal are of equal concern to us. The complexity of these issues requires more time on our part so that we can intelligently and fairly respond. We clearly want your input on such questions.

In summary, this administration intends to work hard at getting the creative and best ideas from industry, government and the local persons affected by this development; we intend to firm up the state regulations which will affect this industry; and we hope that industry will make our job easier by sharing their plans soon so that we can plan together.
SIMULATED IN SITU RETORTING OF OIL SHALE IN A CONTROLLED-STATE RETORT

J. J. Duvall and H. B. Jensen

ABSTRACT

Oil shale has been retorted at heating rates and at retorting zone velocities simulating those of in situ retorting with nitrogen as the retorting gas. This retort is heated externally by electricity and allows the taking of oil and shale samples at various stages of the retorting process. Data obtained so far show new information about the dynamics of the product shale oil.

INTRODUCTION

Oil shale exists in several conditions: from outcroppings to buried under hundreds of feet of overburden; from very rich to very lean in organic components; in beds hundreds of feet thick to thin seams; and, in opposition to the way it is thought to have been formed, most of this country's oil shale lies in regions that are semiarid. For these and other reasons, in situ retorting is being considered as a method of extracting energy from oil shale, especially as the only economical method for using the shales that are deep in the ground, or too lean for mining and above-ground retorting, or exist in seams too thin to be economically mined.

In situ retorting of oil shale basically involves (fig. 1) fracturing the shale in place, starting a fire in the fractured shale, feeding the fire air for combustion, and pumping out the product shale oil which moves away from the combustion and retorting zones. In figure 1 we show horizontal in situ retorting as in the Bureau of Mines' demonstrations (Burwell and others 1973), but it has also been demonstrated in the vertical mode by Occidental Oil Shale, Inc. (Ridley 1974). There are several advantages in favor of in situ retorting in addition to making use of otherwise unrecoverable energy sources. Water is not necessary for retorting, mining is held to a minimum, and spent shale disposal is averted or at least minimized.

Figure 1.—Schematic of an in situ oil shale retorting process.
There are also several questions that need attention. For example, how to fracture the shale efficiently and effectively? What are the effects on ground water? How efficient is the shale oil production process? How does the product oil move from the retorting zone to the collection point? How does the product oil differ from other crude oils? How do the retorting conditions change the quality of the product oil? How can the product oil be upgraded to be compatible to conventional refinery techniques? These questions and others have been or are being investigated both by industry and by the ERDA Energy Research Centers, in particular the Laramie Energy Research Center.

Because of the problems in extracting representative oil samples from an actual in situ operation and the difficulty involved with channeling of air streams through the shale bed, aboveground retorts were built to simulate in situ retorting. The first of these had a nominal capacity of 10 tons of oil shale and a later one was constructed with a nominal capacity of 150 tons of oil shale. Pieces as large as 4 ft x 4 ft x 7 ft have been retorted in the larger retort (Harak and others 1974). However, even in these retorts, control of gas flow, control of heating rate, and control of the rate of movement of the retorting zone through the shale bed are difficult. Therefore, to gain better control of retorting variables, we designed and built what we call the controlled-state retort (fig. 2). This retort is heated electrically with the movement of the retorting zone going from top to bottom. Gas flow rate, heating rate, maximum temperature, and isothermal advance rate are easily controlled.

Because the retort is easily controlled and because the retorting process can be stopped at any time during an experiment, the amount and quality of the product oil, the amount of bitumen in the shale, and the amount of combined unconverted kerogen and carbon residue can be determined at any point in the retort. These data can be used to study the kinetics of the pyrolysis of oil shale and also mechanisms of product movement.

For the purposes of this report the following definitions apply:

Kerogen (K) is that organic material in oil shale that is not soluble in cyclohexane.

Bitumen (B) is that organic material in oil shale that is soluble in cyclohexane and may be present naturally or be formed by the action of heat on kerogen (pyrobitumen).

Oil (O) is that liquid organic material that exudes from the shale on heating.

Gas (G) is the noncondensed material that forms from the shale during heating.

Carbon residue (CR) is that insoluble organic material that remains in the shale after retorting.

Oil shale kerogen and bitumen are complicated materials and therefore
Figure 2.—Controlled state retort facility.
any study of the kinetics of their pyrolysis must be short of perfect. However, attempts have been and are being made to understand the kinetics because of their usefulness in understanding what has happened and thereby predicting what will probably happen when oil shale is pyrolyzed. Earlier reports on the kinetics of oil shale pyrolysis have included treating the process as two consecutive first-order reactions (Allred 1966; Hubbard and Robinson 1950), as in line 1 of table 1. Fausett and coworkers (1974) treated the process as a combination of two first- and three second-order reactions, as shown in lines 1 through 4 of table 1. The three second-order reactions postulate the catalysis by bitumen of the breakdown of kerogen to products. The process has also been treated as a combination of 17 first-order reactions (Shul'men and Proskuryakov 1968); however, a simpler system will probably be more useful.

Several experiments have been conducted with the controlled-state retort, and the oils produced have been analyzed for amount of oil per distillation range for five distillation ranges. The results obtained have been compared with data from the mathematical model of Fausett and others (1974). We have also tried to discover how the product oil moves from the retorting zone over the increasingly cooler shale to the receiver vessel.

**EXPERIMENTAL**

A retort facility (fig. 2) has been constructed that consists of a vertically hinged electric heater, 13 feet long that encloses a 3-inch stainless steel pipe. The heater contains pairs of elements 6 inches long, and each pair of elements is controlled by an autotransformer. The retort has a 1-inch concentric tube that is used for a thermocouple well, with the thermocouples placed opposite the center of each heater element, and also for cooling

<table>
<thead>
<tr>
<th>Table 1.—Proposed reactions in the pyrolysis of oil shale</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( K \rightarrow B \rightarrow OG )</td>
</tr>
<tr>
<td>2. ( K + B_1 \rightarrow B_1 + B_2 )</td>
</tr>
<tr>
<td>3. ( K + B \rightarrow B + OG )</td>
</tr>
<tr>
<td>4. ( K + B \rightarrow B + CR )</td>
</tr>
</tbody>
</table>

\( K = \) kerogen, \( B = \) bitumen, \( OG = \) oil and gas, \( CR = \) carbon residue
\( k's = \) reaction rate constants
water when desired. Crushed raw shale, assaying 30 to 35 gpt and screened to ¼ inch to ½ inch, is placed in the annulus between the two pipes. A receiver is fitted to the bottom of the retort to collect the product oil. The retort is also fitted to allow a gas to flow down through it during operation.

In table 2 we show four parameters—rate of temperature increase, isothermal advance rate, maximum temperature, and rate of flow of carrier gas through the retort—that we have been studying so far. The results reported here are from experiments using nitrogen as the carrier gas, although in the latest experiments gas containing oxygen was used as the carrier gas. The conditions used were selected to simulate conditions used in the 150-ton retort.

Each experiment is started by commencing heating in the top heater-element zone at the selected rate, and after the predetermined time the next zone is started heating at the same rate, and so on. When each zone gets to the maximum temperature, it is held there for 8 hours and then allowed to cool. Thus there are some zones cooling down, some lower zones being held at temperature, and even lower zones heating up, and the lowest zones are still at room temperature. When the heated region has reached about halfway down the retort, heating is stopped, the heater is opened, and water is passed up through the 1-inch pipe and down over the outside pipe. This cooling in effect stops both the production of oil and gas and the flow of oil through the retort. When the retort is cooled, it is laid down and cut into 24 sections corresponding to the heater-element zones.

As observed from the top zones down, the upper zones have been fully retorted; and the retorted oil has been transported to or through lower zones. Then one gets to a region three to four zones long where the shale

<table>
<thead>
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<th>Table 2.—Variables investigated with CS retort</th>
</tr>
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<tbody>
<tr>
<td>Run No.</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>1</td>
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<tr>
<td>2</td>
</tr>
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<td>3</td>
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<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
</tbody>
</table>
has not been fully retorted, and the shale is oil wet. Further down the retort, the sections contain unretorted shale that is oil wet from the retorted oil.

The shale in each section is individually bottled. Those shales that are oil wet are washed with cyclohexane to recover the surface oil. A portion of the washed shale of each oil-wet section is ground to 100 mesh or less, and the bitumen in the shale is recovered by Soxhlet extraction with cyclohexane. Solvent is removed from aliquots of the oil and bitumen solutions to determine the amount of oil or bitumen present. The oil and bitumen solutions are then analyzed by an internal standard-simulated distillation method (Poulson and others 1972) that determines the percentage of oil or bitumen by distillation range and the milligrams of oil or bitumen per gram of shale by distillation range.

The extracted shales are analyzed for carbon, hydrogen, mineral carbon dioxide, and ash. The gas leaving the retort is sampled periodically and analyzed by mass spectroscopy.

RESULTS AND DISCUSSION

An example of the analysis of the oil washed from the shale in our retort is shown in table 3. The conditions of this particular experiment are: a heating rate of 2°F/min, an isothermal advance rate of 3 in./hr, a nitrogen sweep gas flow of 24 scf/h/ft², and a maximum temperature of 1,500°F.

On this table and on succeeding tables like it, zone number zero is the last zone from the top of the retort that has neither oil on the shale nor bitumen extractable from the shale. In other words, the retorting is complete and the oil has been completely removed from the shale in that zone. The next zone, zone No. 1, is the first zone that has either oil on the shale or extractable bitumen in the shale. Zones below these two zones are numbered in succeeding order. The temperature listed here is the temperature of the zone at the time the experiment was stopped and the reactor cooled.

In table 3 we list the composition of the oil washed from the shale that is in the five distillation fractions. The naphtha has an endpoint of 400°F; the light distillate, 600°F; the light gas oil, 800°F; the heavy gas oil, 1,000°F; and residue is that material boiling over 1,000°F. Note that there is no naphtha in those zones which have been heated above ambient; and also that in the oil washed from the shale, the concentration of the light distillate and light gas oil fraction increases from zone 1 to a rather constant concentration.

Notice that in the shale in zone No. zero, there was no oil to be washed from the shale, not even that material boiling above 1,000°F, even though the maximum temperature of the zone was only 900°F. Notice too that in zone No. 2 there is a relatively large percentage of material in the 800 to 1,000°F range. This would indicate that some distillation of lower boiling
<table>
<thead>
<tr>
<th>Zone</th>
<th>Max. temp., °F</th>
<th>Composition, wt-pct</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Naphtha (amb-400° F)</td>
</tr>
<tr>
<td>0</td>
<td>990</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>750</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>460</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>amb</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>amb</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>amb</td>
<td>3</td>
</tr>
<tr>
<td>Product</td>
<td>amb</td>
<td>4</td>
</tr>
</tbody>
</table>
point material is taking place from that zone. The type of distillation displayed here can be related to that found in gas chromatography. That is, material is transferred at temperatures below its boiling point because sufficient vapor pressure occurs for the material to be transported with the sweep gas.

These percentages are typical of the results that we have obtained from all of our experiments. Individual percentages change somewhat, but the trends are the same. Distillation fractions are essentially missing if the temperature of the shale in that zone was above that fraction's boiling point. There are oils that have a relatively large amount of material of a particular fraction in them if that zone is the first or second that has a lower temperature than the boiling point of that fraction. An example of this is the percentage of heavy gas oil (table 3) which increases from 25 percent in zone 1 to 39 percent in zone 2 and then decreases to an average of 24 percent in the zones at ambient temperature. The percentage composition of the oils from zones at ambient temperature becomes essentially constant with the first sample at ambient temperature. This fact indicates that most of the oil is simply flowing over the unheated shale to the receiver and is essentially not volatilized except for small amounts in those samples that are heated.

The results of converting the percentages of table 3 into milligrams of oil per gram of shale, again by distillation fraction, are shown in table 4. Notice that the amount of oil increases and then decreases slightly even though, as mentioned previously, the percent composition remained essentially constant from zone 4 on down. The largest amount of oil per gram of shale is in zone 4, the first zone below the heated region. This indicates that our cooling of the retort was not fast enough to keep some oil from continuing to flow from the heated zones to the first unheated zone as the amounts of oil in the lowest two distillation ranges have increased while amounts of residue have dropped off from zone 3 to zone 4. As temperature drops, higher boiling point material should become more viscous than lower boiling material and would be less likely to continue to flow.

The bitumen composition by distillation range of the five distillation fractions for the same run is shown in table 5. One can see, as with the oil, the percentage of a particular fraction increases as one goes from the hotter samples to cooler samples and how the percentage stabilizes in the samples at ambient temperature.

The compositions of the oil on the shale (table 3) and the bitumen in the shale (table 5) in zone 1 are very similar. For example, the oil is 64 percent residue and the bitumen is 70 percent residue. This indicates that the oil that had been on the shale of zone 1 from above zones has now moved down the retort and that the oil on the shale of zone 1 is that which has just emerged from within the shale.
<table>
<thead>
<tr>
<th>Zone No.</th>
<th>Max. temp., °F</th>
<th>Naphtha (amb-400° F)</th>
<th>Light distillate (400-600° F)</th>
<th>Light gas oil (600-800° F)</th>
<th>Heavy gas oil (800-1,000° F)</th>
<th>Residue (above 1,000° F)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>950</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>1</td>
<td>750</td>
<td>0</td>
<td>0.1</td>
<td>0.5</td>
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<td>3.9</td>
<td>6.1</td>
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<tr>
<td>2</td>
<td>400</td>
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<td>2.1</td>
<td>8.8</td>
<td>12.7</td>
<td>8.7</td>
<td>32.3</td>
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<tr>
<td>3</td>
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<td>7.6</td>
<td>13.2</td>
<td>9.8</td>
<td>13.9</td>
<td>44.5</td>
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<tr>
<td>4</td>
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<td>18.6</td>
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<td>amb</td>
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<td>11.8</td>
<td>18.8</td>
<td>13.8</td>
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</tr>
<tr>
<td>9</td>
<td>amb</td>
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<td>11.1</td>
<td>17.8</td>
<td>12.6</td>
<td>6.1</td>
<td>49.3</td>
</tr>
</tbody>
</table>

Table 4.—Distribution of oil on shale
<table>
<thead>
<tr>
<th>Zone</th>
<th>Max. temp., °F</th>
<th>No.</th>
<th>Compostion, wt-%</th>
<th>Light Naphtha (400–600° F)</th>
<th>Light distillate (600–800° F)</th>
<th>Heavy gas oil (800–1,000° F)</th>
<th>Heavy gas oil (above 1,000° F)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
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<tr>
<td></td>
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<td>750</td>
<td>460</td>
<td>200</td>
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<td>6</td>
<td>1</td>
<td>8</td>
<td>13</td>
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<tr>
<td></td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</tr>
</tbody>
</table>
In the lower zones, the bitumens are about 50 percent residue; however, the oils are about 12 percent residue. This shows that the bitumens are higher boiling materials than the oils. Also, because the lower zones have not been heated, the composition of the bitumen in those zones can be taken as that for the naturally occurring bitumen.

In table 6 we show milligrams bitumen/gram shale. A comparison of the total amounts of bitumen between zones shows that zone 2 has the most bitumen, but the composition of the bitumen of zone 2 is not much different from the composition of the unheated zones. This shows that kerogen has been converted to bitumen (pyrobitumen) and that the composition of the pyrobitumen is not much different from the composition of the natural bitumen in zone 2.

A plot of total gram bitumen per gram shale versus final sample temperature for all experiments is shown in figure 3. This graph shows clearly the relationship between the temperature to which shale has been heated and the amount of bitumen present. As the temperature is increased up to about 650 to 700°F, more and more bitumen is formed; but as the temperature is further increased, the amount of bitumen decreases because it leaves the shale as oil and gas. These results are in contrast to those for the oil on the outside of the shale, which are shown in figure 4. The amount of oil present is inversely related to the temperature, that is, the lower the temperature, the more oil present.

The gas analysis for the same experiment as the results given in tables 3 to 6 is shown in table 7. The gas fed into the retort was pure nitrogen at 24 scfh/ft²; and by the time zone 1 had reached 620°F, small amounts of other gases were being produced. Between the time that zone 1 reached 1,020°F and it reached 1,500°F, the gas analysis changed dramatically due mostly to the breakdown of carbonates but also due to products of the pyrolysis of the kerogen. Once the retorting zone has fully entered the column of shale, the gas analysis stabilized and remained more or less constant throughout the rest of the experiment. The row at the bottom of table 7 gives an approximation of the total gases that were produced during the experiment. In addition to the gases shown in the table, small amounts of other gases were produced, such as other low-molecular-weight hydrocarbons and H₂S to a total of about 2.5 ft³.

A comparison of experimental data with a mathematically derived set of results that we calculated using Fausett’s model (Fausett and others 1974) is shown in figure 5. The data, total oil and gas and total bitumen, are from an experiment that had a heating rate of 1°F/min, an isothermal advance rate of 1 in./hr, and a gas flow of 48 scfh/ft². The experimental work provided only the few points shown, and unfortunately the points were too far apart to show much in the region where concentrations were changing the most rapidly. The data show that the retorting takes place at a higher temperature than that predicted by Fausett’s mathematical
### Table 6.—Bitumen extracted from shale

<table>
<thead>
<tr>
<th>Zone</th>
<th>Max. temp., °F</th>
<th>Naphtha (amb-400° F)</th>
<th>Light distillate (400-600° F)</th>
<th>Light gas oil (600-800° F)</th>
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<th>Residue (above 1,000° F)</th>
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<tr>
<td>0</td>
<td>950</td>
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<td>5.7</td>
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</table>
Figure 3.—Bitumen vs. temperature of zone.

Figure 4.—Oil vs. temperature of zone.
Table 7.—Composition of retort gas

<table>
<thead>
<tr>
<th>Hrs into run</th>
<th>Temp. zone, °F</th>
<th>Gas, vol pct*</th>
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<tr>
<td></td>
<td>N₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>4</td>
<td>620</td>
<td>98.6</td>
</tr>
<tr>
<td>8</td>
<td>1020</td>
<td>96.8</td>
</tr>
<tr>
<td>12</td>
<td>1500</td>
<td>37.1</td>
</tr>
<tr>
<td>Rest (34.5 hrs total)</td>
<td>Cooling</td>
<td>30.5</td>
</tr>
<tr>
<td>Total gas (ft³)</td>
<td></td>
<td>51.8</td>
</tr>
</tbody>
</table>

*Note: other low-molecular weight hydrocarbons, such as ethane, ethylene, propane, and propylene were found in quantities of less than 1 percent.
model. For example, in the model, kerogen is completely converted by the time a temperature of 760°F is reached; but our experimental data show that 70 percent of the kerogen is still present at a temperature of 780°F. Our data also show that kerogen decomposition starts at a lower temperature than predicted by the model. At 400°F, where the experimental data show that around 10 percent of the kerogen has decomposed, the model suggests that the kerogen is essentially unchanged.

Experimental and calculated data are compared in figure 6; but for experiments where the heating rate was 2°F/min, the retorting zone velocity was 3 in./hr, and the gas flow was 24 scfh/ft². Again we have few experimental points, but they show that kerogen is being converted to bitumen at lower temperatures than predicted by the model. However, in this experiment the retorting seems to be complete, that is, all the kerogen has been converted to products at about the time predicted by the model.

In figure 7 we compare experimental and calculated data for experiments with a heating rate of 4°F/min, an isothermal advance rate of 6 in./hr, and a gas flow of 224 scfh/ft². The experimental data in this case show clearly that the retorting is done before the model predicts.
Some possible explanations for the differences between the experimental data and Fausett's mathematical model predictions are: (1) that the model was derived from the results of isothermal experiments and our experiments involve increasing the temperature at certain rates; (2) that the model was derived from experiments in which the naturally occurring bitumen had been removed prior to retorting, whereas the shale we used still contained the natural bitumen; and (3) the complicated nature of kerogen and bitumen precludes a perfect mathematical model. The model is, however, an extension and improvement over earlier work in that it includes catalysis of the breakdown of kerogen by bitumen.

That bitumen catalyzes the pyrolysis is shown in two ways. The first is that our experimental data show that the conversion of kerogen into pyrobitumen occurs in a shorter time than predicted by the mathematical model. The second is that our data show that at least 10 percent of the kerogen is converted into pyrobitumen in the 17.5 hours it took for the temperature to reach 400°F (table 6, zone 2, having reached 400°F, has 90 percent more bitumen than the zones at ambient temperature and the organic material in our starting shale was about 10 percent natural bitumen). In the work of Cummins and Robinson (1972), it was shown that in an oil shale with the natural bitumen removed, it took 90 days to convert 3 percent of the kerogen into pyrolytic products.
SUMMARY

In summary, we have constructed a retort in order to simulate conditions occurring during in situ retorting. This controlled-state retort allows us to control heating rate, gas flow, maximum temperature, and rate of movement of the isothermal zones through a bed of shale.

The oils produced have been analyzed by gas chromatography for composition by distillation range. The results show that the composition of the oil of zones near the retorting zone varies according to the temperature of that zone; normally a zone will have little or no oil whose boiling point is below the temperature of that zone. This indicates that some distillation does occur in the heated zones. However, the composition of the oils does not change from the first zone at ambient temperature on down the retort, indicating that the vapors have condensed in the first zone whose temperature is below their boiling point and that the oil is flowing over the shale at ambient temperature rather than vapors passing through the shale.

The bitumens extracted from the shales have also been analyzed for composition by distillation range. The results show that no material whose boiling point is below the temperature of a particular zone is present in the bitumen of that zone. The bitumens contain materials of higher boiling point than the oil washed from the same shale. The zones that had the
most bitumen in them were those that were at the highest temperature and that still had bitumen present. This is in contrast to the oils where the higher the temperature the less amount of oil present.

The comparing of our experimental data with the data from Fausett's mathematical model for retorting of oil shale indicated that while the model probably uses correct chemical equations for the pyrolysis of oil shale, some additional work is necessary in the area of specific rate constants to make it useful in a dynamic system.

REFERENCES

EXCESS HEAT GENERATION IN RETORTING OIL SHALE IN AIR

A. Lamont Tyler

ABSTRACT

The phenomenon of anomalously high heating rates observed when single blocks of oil shale are retorted in air was studied. Single blocks of oil shale were cut into hollow, thick-walled cylinders 0.20 m OD x 0.038 m ID and were heated along the inside surface with hot gases. The temperatures were recorded as a function of time at 24 points at 4 radii within the block of oil shale. Similar blocks were heated with air and with nitrogen, and the previously observed result of a significantly higher heating rate deep inside the oil shale was seen when air was used.

The rate of heat generation within the oil shale which is required to explain the experimentally observed heating rates was calculated numerically from the one-dimensional heat conduction equation. When nitrogen was used as the heating medium, the calculated rate of heat generation was zero. For 45 gpt oil shale heated in air, the calculated rate of heat generation was about 1.2 Mw/m³ at the heated surface and fell to near zero at approximately 1 cm from the surface. If heat generation of 1.2 Mw/m³ is attributed to the oxidation of hydrocarbons of the molecular form (CH₂)ₙ, 0.028 kg/m³/sec of hydrocarbons must be oxidized, requiring 3.4 x 10⁻⁴ standard m³/sec of air per cubic meter of oil shale.

The heating rate curves for oil shale blocks heated in air and in nitrogen as well as the calculated rates of heat generation are shown.

A. Lamont Tyler, Department of Chemical Engineering, University of Utah, Salt Lake City, Utah 84112. Work on this paper was performed at Lawrence Livermore Laboratory, Livermore, California, under the auspices of the Energy Research and Development Administration.
NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
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<tr>
<td>$C_p$</td>
<td>heat capacity</td>
<td>joule/kg K</td>
</tr>
<tr>
<td>$G$</td>
<td>rate of heat generation</td>
<td>watt/m³</td>
</tr>
<tr>
<td>$h$</td>
<td>increment in radial direction</td>
<td>m</td>
</tr>
<tr>
<td>$k$</td>
<td>thermal conductivity</td>
<td>watt/m K</td>
</tr>
<tr>
<td>$s$</td>
<td>increment in time</td>
<td>sec</td>
</tr>
<tr>
<td>$r$</td>
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</tr>
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<td>$t$</td>
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<td>sec</td>
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<tr>
<td>$\rho$</td>
<td>density</td>
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SUBSCRIPTS

- $i$: index for radial position
- $j$: index for time

INTRODUCTION

Large single blocks of oil shale, when retorted in air, are heated much more rapidly than would be predicted by considering the heating mechanism to be one of simple conduction (Harak and others 1971; Lesser and others 1967; Mallon and Miller 1975). The ability to heat the interior of large blocks of oil shale rapidly in in situ retorting may permit oil to be recovered efficiently from blocks too large to be heated to retorting temperatures by conduction alone. In the work reported here, cylindrical blocks of oil shale with a concentric hole along the axis of the cylinder were instrumented and heated along the inside surface with hot gases. Blocks of nearly identical grade were heated with nitrogen and with air in an effort to determine quantitatively the amount of anomalous heating which occurs due to the presence of oxygen in the air.

When cylinders are heated along the internal surfaces, as in these experiments, both the area normal to heat flow and the volume of oil shale being heated increase with increasing distance from the heated surface. In the U.S. Bureau of Mines experiments (Harak and others 1971), where anomalous heating was first observed, and in subsequent experiments at Lawrence Livermore Laboratories (Mallon and Miller 1975), nearly spherical blocks were heated from the exterior surface and the converse
was true. This different configuration seems to have led to a different mechanism for the observed anomalous heating rates.

Experiments were performed with two blocks of oil shale which were lean (12 gallons/ton Fischer assay as predicted from the density) and with two blocks which were fairly rich (45 and 48 gal/ton, respectively). The anomalous heating was pronounced in the rich oil shale. Data showing the heating rates at various radii in the block and calculations of the rate of heat generation (most likely from the oxidation of hydrocarbons) within the oil shale are presented. The results of chemical analyses which were performed on samples taken from the block of oil shale after retorting will be presented in a separate paper (Tyler 1975).

APPARATUS AND PROCEDURE

The blocks of oil shale used in this work were selected from the LLL inventory of large blocks of mine run oil shale obtained from the U. S. Bureau of Mines at Anvil Points, Colorado. The samples were prepared by coring the oil shale to obtain 0.203 m (8 inches) diameter cylinders with axes at right angles to the bedding planes. An 0.038 m (1½ inches) diameter hole was then cored along the axis of each cylinder to form an inner surface from which the sample was heated with hot gases. The blocks, shown in figure 1, were from 0.178 m to 0.254 m (7 to 10 inches) long.

Thermocouples were placed in the blocks along 3 radii at each of two levels. The radii were 120 degrees apart and the two levels were 0.051 m (2 inches) apart—the upper level or plane containing thermocouples being 0.051 m (2 inches) from the top surface of the block. One thermocouple of each row was attached at the inner surface of the cylinder and the other three were spaced on 0.02 m (13/16 inch) centers along the radius of the block. In each block, six such groups of four thermocouples were imbedded in the block (three groups at 120 degrees on each of two levels), making a total of 24 thermocouples per block. The thermocouples were placed by drilling holes from the top surface and potting the thermocouple in place with Sauereisen. The Sauereisen was allowed to dry at least 24 hours before heating the oil shale block.

After a block of oil shale was instrumented with thermocouples, gas inlet and outlet lines were mounted to permit the introduction of hot gases into the center hole. The block was placed in a chamber and enclosed in vermiculite insulation to reduce heat losses. Hot gases, heated by passing them alongside three 500-watt Calrod heaters in a preheater section of piping, were introduced into the center hole to heat each block along its inner surface. The Calrod heaters were powered with conventional Variac power supplies at approximately 4.5 amperes at 110 volts per heater. The volume surrounding the Calrod heaters was packed with stainless steel
wool to provide increased area for heat transfer to the gas. During each run, gases entered the cavity in the oil shale block at a rate of 0.03 standard cubic meters per minute which enabled a maximum inlet gas temperature of approximately $1035\,^\circ\text{K}$ to be attained.

After the gases passed through the block, they entered an oil collection tank and were then vented to the atmosphere. A diagram of the sample as it was held in the apparatus during heating is shown in figure 2.

Readings from all the thermocouples in the block plus those from additional thermocouples placed in the inlet and exit gas streams were recorded on magnetic tape with a Dymac digital data acquisition system. The temperatures were also recorded with a multipoint recorder to provide a back-up record of the temperatures. Each of the thermocouples were read approximately every 2 minutes during the rapid heat-up time and at 5-minute intervals thereafter.

The hot gas was applied to each oil shale block until the temperature
Excess Heat Generation in Retorting Oil Shale in Air

Figure 2.—Schematic of apparatus.

at approximately 0.03 m (1½ inches) from the inner surface reached 670°C or approximately the temperature at which oil production commences. The power to the heaters was then turned off and the flow rate of unheated gas was increased to about double the value used during the heating cycle. The block was cooled to ambient temperatures in approximately 3 hours.
in each case. The rates of heating as a function of position and time were read from the thermocouple records.

THEORY OF HEAT TRANSPORT

The theoretical analysis of the heat transport and heating rates in blocks of oil shale was undertaken to obtain a quantitative method for evaluating the rate at which heat is generated in the oil shale when it is heated with air. This heat generation has been attributed to the oxidation of hydrocarbons within the block of oil shale. Inasmuch as the heating value of saturated hydrocarbons per unit weight is nearly independent of the species (Perry and Chilton 1973), it is possible to calculate the amount of oxygen or air which must migrate into the oil shale to account for the heat generation by the oxidation of hydrocarbons.

The energy conservation equation can be written in cylindrical coordinates to describe the heating of the samples. Temperature gradients in the axial direction were considerably smaller than those in the radial direction and were neglected in the analysis. Heat transport was thought to occur only by conduction, and the generation of heat from all sources within the oil shale blocks was lumped into a single term. The resultant differential equation is shown in equation (1). All the symbols are defined in the section on Nomenclature.

\[
\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{G}{K \alpha} \frac{\partial T}{\partial t} = 0
\]  

(1)

If the term representing the generation of heat \( G \) is zero in equation (1), the equation reduces to the simple one-dimensional radial heat conduction equation in cylindrical coordinates (Carslaw and Jeager 1959). In order to obtain the heat generation term as a function of the position and time for each of the blocks for which time-temperature data were obtained, equation (1) was rewritten in difference form. A form analogous to the Crank-Nicholson (Lapidus 1962) form for parabolic partial differential equations was used, and the result is shown in equation (2).

\[
\frac{T_{i+1,j+1} - 2T_{i,j+1} + T_{i-1,j+1}}{h^2} + \frac{1}{r} \frac{T_{i+1,j+1} - T_{i,j+1}}{h} + \frac{G_{i,j+1}}{k} = \frac{1}{\alpha} \left( \frac{T_{i,j+1} - T_{i,j}}{s} \right)
\]  

(2)

The rate of heat generation can be obtained directly from equation (2) as follows:
EXCESS HEAT GENERATION IN RETORTING OIL SHALE IN AIR

\[ G_{i,j+l} = -T_{i+1,j+1} \left[ \frac{k}{h^2} + \frac{k}{rh} \right] + T_{i,j+1} \left[ \frac{k}{\alpha s} + \frac{k}{rh} + \frac{2k}{h^2} \right] \]

\[ -T_{i-1,j+l} \left[ \frac{k}{h^2} \right] - T_{i,j} \left[ \frac{k}{\alpha s} \right] \] (3)

Inasmuch as only four thermocouples were placed in the blocks along any radius, a direct application of the data to calculate the heat generation from equation (3) is not practical. In order to obtain values of the temperature at additional radii, the data were interpolated by fitting them with a cubic spline at each value of time for which measurements were made. The boundary conditions used for the cubic spline were: (a) a zero temperature gradient at the exterior surface of the block, and (b) a second derivative at the inner surface which was obtained from a linear extrapolation of the second derivative from the interior points. The boundary condition of a zero temperature gradient at the exterior surface can be defended because the blocks were insulated during the experiment. However, the boundary condition for the second derivative at the inner surface was used without firm justification to be able to fit the data with a cubic spline.

In each of the runs, 28 increments (29 total points from the inner to the outer surface) were used across the radius and the heat generation was calculated from equation (3) at each of the 27 interior points at each time for which temperature data were measured. The values of the thermal conductivity used in the calculation were taken from the empirical equation developed by Tihen, Carpenter and Sohns (1968); and the values of heat capacity were calculated from the empirical equation of Shaw (1971). The measured values of density were used. The effect of the retorting reactions on the values of these physical properties was accommodated by considering that the values proceed linearly with temperature from those for raw shale at 600°F to those for spent shale at 750°F. Below 600°F, values for raw shale were used; and above 750°F, values for spent shale were used.

The results of these calculations, discussed in detail later, show, as expected, nonzero values of the heat generation term occur only when air was used as the heating gas. It was possible to predict the observed temperatures for the sample heated in air only by postulating the existence of a heat source within the oil shale.

RESULTS AND DISCUSSION OF RESULTS

The measured values of the interior temperatures for the blocks of rich oil shale heated with air and with nitrogen are shown in figures 3, 4, and 5. In figure 3, the measured temperatures are presented for the thermocouples
which were placed at a radius of 0.04 m (13/16 inch) from the inner surface of the blocks. The two lines for each of the runs shown in figure 3 represent the thermocouple readings at the two axial positions (separated by 2 inches) and provide an indication of the magnitude of the axial temperature gradient. Similar plots of the temperatures at radii of 0.06 m (1/8 inches) and 0.08 m (2-7/16 inches) from the inner surface are shown in figures 4 and 5, respectively.

The results shown in figures 3, 4, and 5 indicate that the assumption of one-dimensional heat flow is reasonable inasmuch as the differences in the temperatures between the two levels at which thermocouples were placed are small. Typical axial temperature gradients were less than one-tenth the radial gradients. It can further be noted that the time-temperature histories for the two cases were nearly identical during the initial parts of the runs. At a time of 125 minutes, however, hydrocarbons produced in the block heated with air were ignited; and the interior tempera-
Excess Heat Generation in Retorting Oil Shale in Air

Figure 4.—Time-temperature history (45 gpt oil shale) (radius = 0.06 m).

The calculated values of the rate of heat generation required to produce the observed anomalous rise in the temperature are plotted in figure 6. The upper four lines in figure 6 represent the calculated values of the generation of heat at radii of 0.022, 0.025, 0.028, and 0.031 meters. (The radius at the inner surface of the block was 0.019 m.) At radii greater than about 0.031 meters, the generation term was essentially zero, and a typical result is shown, also in figure 6, for a radius of 0.08 meters. The results of identical calculations for the block of oil shale which was heated in nitrogen are shown in figure 7 and indicate that no heat generation need be postulated to predict the observed temperature profiles. The positive and negative fluctuations near 200 minutes (500 minutes in fig. 7) result from trying to
approximate the abrupt change in the first and second partial derivatives of the temperature by finite differences and do not represent a real affect.

If it is assumed that all the heat generated is produced from the oxidation of hydrocarbons liberated from the retorting of kerogen in the oil shale, it is possible to calculate the amount of oxygen (as air) which would have to diffuse into the block against the outward flow of oil and gases in order to provide the required heat generation. The heat of combustion of saturated hydrocarbons to H₂O gas and CO₂ is approximately 44.4 M joule/kg (Mallon and Miller 1975) (10.6 Kcal/gram) independent of the molecular species involved. This datum leads to the conclusion that air must be supplied at a rate of 3.4 x 10⁻⁴ standard m³/sec per cubic meter of oil shale at a radius of 0.022 m (0.11 inches from the heated surface) where the generation term reached 1.2 Mw/m³, and at a rate of 1 x 10⁻⁴ standard m³/sec per cubic meter of oil shale at a radius of 0.031 meters (0.46 inches from the heated surface). Crude calculations in which average values of diffusivities and gas flow rates during retorting were used indicate it is not
Excess Heat Generation in Retorting Oil Shale in Air

unreasonable to expect air flows of that magnitude to occur by molecular diffusion.

The heat generation term calculated by the methods described falls to zero when the local temperature reaches approximately 750°K—the temperature considered to be that above which no further hydrocarbons are evolved.

CONCLUSIONS

Results of the experiments discussed here indicate that the anomalous heating of the cylindrical blocks of oil shale employed during retorting in air can be explained by postulating the generation of heat from the oxidation of hydrocarbons near the heated surface of the block. Significant rates of heat generation occurred only at distances less than 0.012 m (0.46 inches) from the heated surface, and then only for the few minutes that hydrocarbons were being evolved from that thin surface layer. The amount of material consumed to account for the heat generated is modest, and the air

![Figure 6.—Heat generation rate (air heated block).](image)

\[ r = 0.022 \text{ m} \]
\[ r = 0.025 \text{ m} \]
\[ r = 0.028 \text{ m} \]
\[ r = 0.031 \text{ m} \]
\[ r = 0.081 \text{ m} \]
requirements are sufficiently small that they could be supplied by diffusion against the outward flow of retorting products. The oxidation need not occur deep inside the block to explain the heating rates which were observed.

The phenomenon seemed to occur with lean oil shale with a Fischer assay of about 12 gal/ton, but it is not nearly as pronounced as with the richer (45 gal/ton) material.

ACKNOWLEDGMENTS

The author is deeply indebted to A. J. Rothman and Don Snider of Lawrence Livermore Laboratory for suggestions and counsel. The assistance of Neil Madsen was invaluable in determining how to calculate the rate of heat generation from the data. The author also wishes to thank Calvin Hall and Randy Dunham for the work in preparing the oil shale blocks and Gary Kortan who assisted in reducing the data.
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Tyler, A. L., 1975, Partial retorting of simple oil shale blocks: Part 2, UCID Rept. (no. to be assigned), Livermore, Calif., Lawrence Livermore Labs.
THERMAL BEHAVIOR OF OIL SHALE BLOCKS
HEATED IN AIR

Richard G. Mallon and William C. Miller

ABSTRACT

Anomalously high rates of temperature increase have been observed near the center of large blocks of shale being retorted in air. Because of the potential importance of this behavior for in situ processing, an investigation of possible mechanisms of the temperature increase has been performed. Known mechanisms for which the conditions in the shale block are slowly varying have been shown to be unsatisfactory in explaining the observed behavior. For example, transport of oxygen by diffusion from the block surface to the interior is too slow to produce the rapid temperature increase by oxidation of hydrocarbons. A rapidly varying or oscillatory phenomenon was therefore sought. Pressure-sensing capillary tubes were sealed into a block of shale so that interior pressure could be observed. During retorting of the block, pressure pulses occurred periodically. During a portion of each pulse, the interior pressure was below the pressure at the block surface. Since a shale block develops numerous small cracks during the early part of the retorting process, the pressure pulses result in transport of thermal energy and oxygen to the interior of the block along these cracks. The pulsing behavior has been observed in a range of block sizes and shale grades.

INTRODUCTION

The Lawrence Livermore Laboratory is undertaking the development of an economical in situ process for production of oil from oil shale. A part of this development is the study of the behavior of individual blocks of shale which are being retorted by hot gases. Some interesting data on this subject has been reported by the Laramie Research Center of the Bureau

Richard G. Mallon and William C. Miller, Lawrence Livermore Laboratory, Livermore, California. Work performed at Lawrence Livermore Laboratory under the auspices of the Energy Research and Development Administration.
of Mines (Harak and Carpenter 1970; Harak and others 1971; Sohns and others 1972).

In several runs in the Laramie 150-ton retort a large block of oil shale was included in the column packing, and internal and external temperatures of the block were measured as a function of time. On figure 1, the solid lines represent temperature data taken on a 7000 pound block of shale in run 4 as reported by Laramie (Sohns and others 1972). The dashed lines on this figure represent analytical temperature distributions for comparison. For simplicity in analysis, we assume a step function for the surface temperature, as shown on the upper portion of the figure. The dashed line on the lower portion shows the resulting center temperature as a function of time based on the assumed surface temperature if the only heating mechanism in the interior were conduction of heat from the surface. For this calculation, values of thermal diffusivity were taken from Tihen and

![Figure 1: Comparison of measured and calculated temperatures in a large-scale block (measured temperatures from Sohns, Harak and Carpenter 1972).](image-url)
others (1968). As figure 1 shows, the surface temperature rise used in the analysis is more rapid than the actual rise; the computed internal temperature rise is much slower than the actual temperature rise. Thus, it appears from this comparison that some mechanism other than thermal conduction was producing a rapid increase in internal temperature of the large block during retorting. According to the Laramie report, all runs in the 150-ton retort which included a large, temperature instrumented block of shale showed this type of behavior (Sohns and others 1972).

This internal heating effect might be of considerable value to in situ retorting processes. From the Laramie data, it appears that the interior of very large blocks will increase in temperature about as rapidly as small blocks; therefore, a steep and fast-moving temperature front in shale being retorted would leave little unretorted shale behind the front even if the distribution of size of the broken shale is very wide. This anomalous thermal behavior of large blocks must be considered in optimizing the overall process, whether or not the effect is strongly beneficial.

To better understand the phenomenon of rapid internal heating, experiments on shale blocks were begun at the Livermore Laboratory. In these experiments, a single block is placed in an insulated vessel, and gas continuously flows over the block. The gas composition and temperature are controlled. The block is heated by the gas and by radiant heaters. The assumption in this experimentation is that the thermal behavior of a single block will be similar to the behavior of the block in a region of rubblized shale, provided the atmosphere around the single block is the same as that around the block in the rubble. Comment on this assumption is made near the end of this report. In early single block experiments at Livermore, Doggett (1975) showed that blocks retorted in air have anomalously high rates of internal temperature rise. The observed temperature behavior resembled that reported by Laramie for large blocks in the 150-ton retort. When Doggett repeated the experiments using nitrogen instead of air, the internal temperatures rose more slowly. The observed internal temperatures of blocks heated in nitrogen are in good agreement with temperatures calculated on the basis that thermal conductivity is the only effective mechanism for heating the interior.

From Doggett's results, we conclude that the anomalous internal heating is due to the internal combustion of hydrocarbons supported by oxygen transported from the block surface to the interior. An understanding of the mechanism of this transport is therefore necessary to describe the internal heating phenomenon. One possible transport mechanism is molecular diffusion of oxygen through gas along pores and cracks in the shale. An approximate calculation of transport by diffusion showed that this mechanism could not account for the observed heating, even if the effective cross-sectional area for diffusion was taken to be 10 percent of the block surface area.
Because the observed behavior cannot be explained by diffusion, a model involving rapidly varying processes was considered. One possible variable in such a model is internal gas pressure. Accordingly, a measurement was made of gas pressure in a shale block during retorting. The measurement showed rapid, periodic pressure variation. In subsequent tests, pressure pulses have been observed in a range of block sizes and shale grades. Following is a description of the apparatus used in these tests.

EXPERIMENT DESCRIPTION

Samples

Five shale blocks have been retorted with interior pressure measurement. Three of these, the small blocks, weighed about 15 pounds each. The weights of the two large blocks were 190 and 287 pounds. The Fischer assay oil yield of the samples ranged from 18 to 45 gallons per ton. All of the samples were from the Bureau of Mines installation at Anvil Points, Colorado. The two large blocks were selected on the basis of size, uniformity of dimensions, oil yield, and minimal cracks. The small blocks were cored with a 6-inch diamond drill. Their selection was based on oil yield and minimal cracks. Determination of oil yield was based on the correlation of yield to specific gravity (Smith 1969). In each case the yield was based on overall rock specific gravity, not chip sample specific gravity. The yield for each sample is shown in table 1.

Retort Vessels

For these experiments, two different apparatus assemblies were used. A large retort with associated equipment was used for the two large blocks.

<table>
<thead>
<tr>
<th>Block Weight</th>
<th>Fischer Assay Oil Yield (Gal. Per Ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14 lb</td>
<td>6.3</td>
</tr>
<tr>
<td>17 lb</td>
<td>7.7</td>
</tr>
<tr>
<td>18 lb</td>
<td>8.2</td>
</tr>
<tr>
<td>190 lb</td>
<td>36.0</td>
</tr>
<tr>
<td>287 lb</td>
<td>130.0</td>
</tr>
</tbody>
</table>
Much smaller apparatus was used for the small blocks. Figure 2 is a schematic of the general arrangement of both assemblies. Table 2 provides detailed information on the retorts.

**Data Recording**

Data taken during each run were as follows:

- Inlet gas composition
- Inlet and discharge gas temperature
- Inlet gas flow rate
- Gas preheater power
- Radiant heater power
- Surface and internal block temperature
- Internal block gas pressure

The same type of diagnostic apparatus was used for both large and small blocks. In each block except that weighing 190 pounds, two pressure measurements were made. In figure 3 we show the connections to the pressure sensing cavities. In one cavity, the absolute pressure was measured. The other cavity was used to measure the difference in pressure between the interior of the rock and the annular region between the rock and the vessel. There was no connection between the two cavities. The 190-pound block had only an absolute pressure measurement.

Each block was drilled perpendicular to the bedding planes for pressure sensing. The cavities were created by inserting the stainless steel pressure tubes part way in the drilled holes and then cementing the tubes in place with Sauereisen ceramic cement. The cavity size for the large blocks, 0.07 in.³, was designed to be ten times larger than the gas volume in the connecting tubing. The cavity size for the small blocks, 0.02 in.³, was three times larger than the gas volume in the connecting tubing. In each case, part of the tubing and all of the pressure transducer chamber was filled with oil to reduce the size requirement of the sensing cavity. The pressures were continuously recorded with a two-pen strip-chart recorder.

Temperatures were measured by unsheathed chrome-alumel thermocouples. The internal thermocouples were cemented into holes drilled perpendicular to the bedding planes. The surface thermocouples were held in place by stainless steel tabs attached to the rock by screws in tapped holes. The temperatures were sequentially read by a multipoint recorder.

Details of the diagnostic equipment are given in table 3.

**Operating Procedure**

Each sample was supported in the retort vessel from the bottom. The large blocks were set on firebrick. The small blocks were set on alumina
insulators, 1 inch in diameter and 3 inches long. In heating the block, the power to the gas preheater and the radiant heaters was varied to try to maintain uniform surface temperature of the blocks; this was only partially successful. The time during which pressure pulses were observed varied widely between samples. Heating of the block continued until pressure pulsing stopped.

### Table 2.—Retort data

<table>
<thead>
<tr>
<th>System Details</th>
<th>Large Block Retort</th>
<th>Small Block Retort</th>
</tr>
</thead>
<tbody>
<tr>
<td>vessel material</td>
<td>stainless steel</td>
<td>stainless steel</td>
</tr>
<tr>
<td>chamber size</td>
<td>24&quot; dia x 46&quot; high</td>
<td>8-3/8&quot; dia x 18&quot; high</td>
</tr>
<tr>
<td>insulation</td>
<td>4&quot; fiberglass blanket</td>
<td>4&quot; loose vermiculite</td>
</tr>
<tr>
<td>air inlet</td>
<td>1-1/2&quot; dia top center</td>
<td>1/4&quot; dia top center</td>
</tr>
<tr>
<td>gas discharge</td>
<td>2&quot; dia side near bottom</td>
<td>1&quot; dia bottom center</td>
</tr>
<tr>
<td>radiant heaters</td>
<td>3 top. 0.75 KW ea.</td>
<td>8 side, 1 KW ea.</td>
</tr>
<tr>
<td>pre-heater</td>
<td>5 clam shell, 1.5 KW ea.</td>
<td>0.5 KW</td>
</tr>
<tr>
<td>maximum input power</td>
<td>16.5 KW</td>
<td>8.5 KW</td>
</tr>
<tr>
<td>diagnostic access</td>
<td>thru side port</td>
<td>thru bottom flange</td>
</tr>
<tr>
<td>oil sump capacity</td>
<td>5 gallons</td>
<td>1 gallon</td>
</tr>
<tr>
<td>demister volume</td>
<td>0.7 ft³</td>
<td>0.15 ft³</td>
</tr>
</tbody>
</table>
Figure 3—Diagnostic equipment schematic.
Table 3.—Diagnostic equipment data

<table>
<thead>
<tr>
<th>Item</th>
<th>Large Block</th>
<th>Small Block</th>
</tr>
</thead>
<tbody>
<tr>
<td>pressure cavity size</td>
<td>7/32&quot; dia x 1-3/4&quot; Lg</td>
<td>3/16&quot; dia x 3/4&quot; Lg</td>
</tr>
<tr>
<td>tubing size</td>
<td>1/16&quot; od x .020&quot; id</td>
<td>1/16&quot; od x .020&quot; id</td>
</tr>
<tr>
<td>transducer, differential</td>
<td>Tavis ± 2 psi</td>
<td>Validyne ± 1 psi</td>
</tr>
<tr>
<td>transducer, absolute</td>
<td>Taber 0-50 psia</td>
<td>Validyne ± 1 psi</td>
</tr>
<tr>
<td>thermocouples</td>
<td>type K, 24 gage</td>
<td>type K, 24 gage</td>
</tr>
<tr>
<td>flowmeter</td>
<td>Fisher Porter</td>
<td>Matheson, 605 Lube</td>
</tr>
<tr>
<td>recorder, pressure</td>
<td>HP 17505A, 2 pen</td>
<td>HP 7132A, 2 pen</td>
</tr>
<tr>
<td>recorder, temp.</td>
<td>Brown 24 point</td>
<td>Brown 12 point</td>
</tr>
</tbody>
</table>

RESULTS OF PRESSURE INVESTIGATION

General Characteristics

The general characteristics of the pressure pulses were the same for all of the blocks. The pressure recorder shows sharp pulses separated by periods during which the pressure is constant. In figure 4 we show the pressure behavior for the 287-pound block shortly after pulsing started. The lower trace shows the absolute pressure in the block interior. The upper trace shows the pressure difference between the block interior and the annulus between block and vessel. The first thing to note is that the pressure pulses start at the same time in the two sensing cavities even though the cavities were not connected when the sample was prepared. Evidently cracking between the cavities provides pressure communication between them.

After completion of a run, many interconnected cracks can be observed during removal of a block from the vessel. These cracks are both parallel and perpendicular to the bedding planes, although the cracks parallel to bedding are generally wider. Presumably, these cracks serve as channels for gas flow during the pulsing.

In figure 4, the upper trace, showing differential pressure, deflects downward for interior pressure higher than annulus pressure; upward deflection indicates that annulus pressure exceeds block interior pressure. From the figure, it is seen that during the first part of a pulse, the interior pressure exceeds the annulus pressure. Therefore, gas flow in the cracks in the block is outward initially. After about a third of the time duration of a pulse, the pressure differential reverses and gas flow in the block is inward. The duration of the pulses is almost constant. If the gas flow
Thermal Behavior of Oil Shale Blocks Heated in Air

Figure 4.—Pressure pulses in the 287-pound block.
rate is constant, the time between successive pulses varies about 20 percent during any one run.

Usually, the heights of the pressure pulses gradually increase, pass through a broad maximum, and slowly decrease until they can no longer be observed. In the block for which the pressure is shown on figure 4, the pulsing stopped abruptly about one-half hour after it started. Later, when the vessel was opened, it was found that the block had split in two along a bedding plane, with the split passing through the pressure-sensing cavities.

The interior and surface temperatures for the 287-pound block are shown on figure 5. At the time that pulsing started, the central temperature was about 100°C and the maximum surface temperature was about 350°C. Figure 5 does not show a sudden increase in the slope of the central temperature curve when pulsing started. Probably, this is due to the low frequency of the pulsing, as shown in figure 4. A higher air injection rate would have resulted in higher pulse frequency, as described below.

**Effect of Gas Flow on Frequency**

The effect of variation of the oxygen content and the flow rate of the inlet gas was investigated during the run with the 14-pound block. After

![Figure 5](attachment:image.png)

**Figure 5**—Temperature history of the 287-pound block.
the pulsing was well established with air as the injected gas, the inlet flow was changed to nitrogen. The pulsing immediately stopped. When the air flow was restored, the pulsing restarted. Gas mixtures consisting of equal parts of air and nitrogen, and of three parts of air to one part nitrogen were tried. Neither of these would support pulsing. The pulsing again started when the inlet flow was changed back to air.

With air as the gas, the inlet flow rate was gradually varied, and the variation in pulse frequency was noted. The duration of each pulse was independent of flow rate. In figure 6 we show the time between the start of successive pulses as a function of air flow rate. This behavior can be explained as follows. When a pulse is complete, essentially all of the oxygen in the vessel has been consumed by combustion. The oxygen concentration gradually increases as air enters the vessel. When the oxygen concentration reaches a certain critical level, ignition occurs and another pressure pulse takes place. One would then expect that the product of the inlet flow rate \( F \) and the quiescent time between pulses \( t \) is a constant.

\[
F \cdot t = \text{constant}
\]

The quiescent time is obtained by subtracting the pulse duration, 5\( \frac{1}{2} \) seconds, from the time between the start of successive pulses. In figure 7 we show quiescent time as a function of air flow rate. The dashed line on figure 7 represents a constant value of \( F \cdot t \). The agreement between the data points and the line is satisfactory.

By using an estimated value for the effective mixing volume in the vessel, a calculation can be made of the critical oxygen concentration at which ignition occurs. In all of the runs, the horizontal distance from the block to the vessel wall was much less than the vertical distance to the top cover. Therefore, there was a narrow flow channel around the block and a relatively large free volume above the block. Since the gas was probably stagnant in the vessel corners, the effective volume \( V \) is taken as a fraction of the free volume above the block. In the absence of detailed information, this fraction is arbitrarily taken to be one-half. The fraction \( f \) of the gas mixture which is air when ignition occurs is given by:

\[
f = 1 - \exp \left[ - \frac{F \cdot t}{V} \right]
\]

For the 14-pound block, the value found for \( f \) is 0.76, or an oxygen concentration of 16 percent. This result is consistant with the previous observation that pulsing did not occur with three parts of air to one part of nitrogen, but did occur with air alone. Making the same assumptions, the calculation was performed for two other blocks of about the same oil yield. Observed values and calculated results are shown in table 4.

The duration of individual pulses showed little variation. The duration
Figure 6—Dependence of period on air flow rate.
Figure 7.—Dependence of quiescent time on air flow rate.
appears to be essentially independent of block size, oil yield, and gas flow rate.

**PRESSURE-PULSE AMPLITUDE**

The amplitude of the pressure pulses is strongly dependent on the Fischer assay oil yield of the shale and on the size of the block. In order to correlate this data, we define a characteristic distance for release of pressure. This distance is the shortest distance, along a bedding plane, from the center of the block to the surface. In table 5 we show the maximum value of the amplitude of pressure pulses observed on the absolute pressure transducer as a function of this characteristic distance and oil yield.

**TABLE 5.—Maximum value of the amplitude of pressure pulses**

<table>
<thead>
<tr>
<th>Block Weight lbs.</th>
<th>Oil Yield Gal/Ton</th>
<th>Pressure Release Distance - in.</th>
<th>Pulse Ht. Psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>41</td>
<td>2.9</td>
<td>0.20</td>
</tr>
<tr>
<td>17</td>
<td>18</td>
<td>2.9</td>
<td>0.027</td>
</tr>
<tr>
<td>18</td>
<td>45</td>
<td>2.9</td>
<td>0.32</td>
</tr>
<tr>
<td>190</td>
<td>35</td>
<td>5.7</td>
<td>0.81</td>
</tr>
<tr>
<td>287</td>
<td>42</td>
<td>7.5</td>
<td>4.5</td>
</tr>
</tbody>
</table>

This data can be correlated with an accuracy of about 25 percent by the expression
\[ \Delta P = K L^5 G^{2.5} \]

where

- \( \Delta P \) = pressure pulse amplitude
- \( L \) = pressure release distance
- \( G \) = Fischer assay oil yield
- \( K \) = empirical constant

For \( L \) in inches, \( G \) in gallons per ton, and \( \Delta P \) in pounds per in.\(^2\),

\[ K = 0.764 \times 10^{-6} \]

CONCLUSIONS AND FUTURE WORK

From results obtained in the single block experiments, we conclude that pressure pulsing causes an enhanced transport to the block interior in these experiments. The material transported could be very hot gas produced by combustion or could be oxygen which would support combustion in the interior. In either case, the transport results in rapid internal temperature increase. The pressure pulses are caused by rapid combustion of hydrocarbon gases which quickly exhaust the available oxygen.

Some insight into the nature of the combustion can be gained from the pressure and temperature data, figures 4 and 5. Because of the low internal temperature at the time pulsing starts, it is unlikely that ignition occurs in the interior. More likely, ignition occurs at or near the block surface where the temperature is high. Since hydrocarbon gases will flow to the surface primarily through cracks, the intersection of such a crack with the block surface is the probable location for ignition. After ignition, the combustion proceeds into the gas around the block and probably a short distance up the crack.

As mentioned near the beginning of this report, it has been assumed that the anomalous thermal behavior of large blocks in the large Laramie retort and the similar behavior of single blocks in the smaller Livermore retorts are both due to the same cause. This has not yet been experimentally verified. At present, apparatus is being assembled at Livermore to retort a column of crushed shale. Capacity of this retort is about 7 tons. After this equipment becomes operational, we intend to place a large block in a retort, loading in a way which is equivalent to loading in the Laramie retort. The large block will be instrumented to observe the internal gas pressure during retorting. This will then establish the extent by which pressure variation contributes to internal heating of a block in a rubblized column of shale.
ACKNOWLEDGMENTS

Several of our colleagues have contributed valuable discussion to this work. Particularly to be recognized are R. L. Braun, J. H. Raley, A. J. Rothman, and G. D. Snider.

We thank Calvin W. Hall for his careful workmanship in preparing the samples and assembling the apparatus, and for his assistance in performing the experiments.

REFERENCES

IN SITU RETORTING OF OIL SHALE RUBBLE: A MODEL OF HEAT TRANSFER AND PRODUCT FORMATION IN OIL SHALE PARTICLES

W. F. Johnson, D. K. Walton, H. H. Keller and E. J. Couch

ABSTRACT

A mathematical model of the pyrolysis of an oil shale particle, represented as an equivalent sphere, has been developed. The quantities of oil, gas, and carbonaceous residue formed from the kerogen initially present in the shale can be determined as a function of time for any specified heating cycle. Thermal decomposition of kerogen is represented by a kinetic scheme of 10 endothermic irreversible first-order reactions whose temperature dependencies are formulated as Arrhenius equations. The calculated fraction of kerogen converted to shale oil is determined by this kinetic scheme, and the development of the scheme is presented in some detail. Inorganic carbonate decomposition and water loss are included, since these endothermic reactions significantly alter the temperature profile in the particle and indirectly influence the quantity of oil formed. The thermal conductivity, heat capacity, and density at a given radius in the particle are determined by the temperature and degree of kerogen conversion at this radius, as well as the initial organic content of the shale. The density is also a function of the water-loss, carbonate decomposition, thermal expansion, and swelling of the particle. Extension of the model to include organic burn-off can be readily accomplished by the addition of appropriate equations for combustion reactions and oxygen diffusion.

Matches between calculated and measured product yield have been obtained using a wide variety of laboratory data obtained over the temperature range 302 to 977°F. Both isothermal and nonisothermal conversions were studied. The largest particles investigated in the laboratory were spheres 4 inches in diameter.

W. F. Johnson, D. K. Walton, H. H. Keller, and E. J. Couch, Mobil Research and Development Corporation, Research Department, Field Research Laboratory, Dallas, Texas.
The model predicts that, for a given surface temperature, the shale oil yield can be expected to decrease as the particle size increases. A decrease in the surface temperature also results in a decreased oil yield. These factors are not significant contributors to any reductions in oil yield in aboveground retorts of recent design, which are charged with small sized particles rapidly heated to retorting temperature. However, most in situ shale oil production schemes are based on the retorting of beds of shale rubble, where the average particle size is much larger and the size distribution broader than for the shale charged to aboveground retorts. Heating rates for in situ processes are expected to be much slower than those typically used in surface retorts. Reduction in oil yields as a result of the lowered heating rate should be expected for in situ retorts. Oil yields obtained by the U.S. Bureau of Mines in their 150-ton retort are in agreement with this prediction.

INTRODUCTION

The principal part of the organic content of oil shales is an insoluble solid polymeric material normally referred to as "kerogen." A small amount of a soluble organic material, bitumen, is usually found associated with the insoluble kerogen. To generate usable organic products from the shale, the most common process is the thermal decomposition of the initial organic fraction of the rock. At the temperatures usually employed, organic material vaporizes from the shale, leaving a solid organic residue on the inorganic fraction of the shale. The condensable portion of the volatile material is shale oil.

In general, the initial stage of the thermal decomposition of organic polymers approximately conforms to a first-order rate law. This is true for synthetic and natural polymers having a wide range of molecular structures. The kerogen of oil shale is no exception. A first-order rate equation has been employed in nearly all studies of oil shale pyrolysis in which a quantitative rate expression has been used. The equation describes an irreversible reaction of kerogen to yield products, which are lumped together as an entity.

In retorting processes intended for commercial application the quantity of oil produced and the rate at which it is produced will determine its commercial success. These may be different from the amount and rate of kerogen decomposition. Any kinetic scheme used to model commercial retorting processes should also predict the amount of oil formed when the kerogen pyrolysis occurs under nonisothermal conditions. It is not necessary to depict all the actual molecular processes. The kinetics only need to represent the quantities of major products formed during the decomposition of kerogen.

In any discussion of kerogen pyrolysis it must be emphasized that the
molecular structure is not well defined. Pyrolysis products possess a wide spectrum of molecular structures with a broad distribution of molecular weights. A detailed mechanism providing for the formation of individual chemical species is clearly an impossible task. However, it has been demonstrated in many petroleum process models that the products can be lumped together into large groups whose compositions are determined by condensation temperature, molecular type, and other empirical criteria. Cook (1974) has recently discussed the empirical nature of product definitions for oil shale retorting.

Comparison of the retorting behavior of the Colorado shale with that of Estonian shales, Australian torbanites, and coals having a high content of sapropelic macerals showed that the structural complexity of the polymeric organic of all of these materials results in a very similar thermal degradation behavior. Therefore, concepts arising from studies of the pyrolysis of all of these materials have been used to develop the generalized retorting mechanism presented in this paper.

The product groups considered are those commonly identified as gas, oil, bitumen, and coke, with the addition of various postulated intermediates. These product groups are defined as:

- Gas is that portion of the volatile products remaining uncondensed at a temperature of about 35°F.
- Oil is defined as the portion of the volatile material condensable at 35°F.
- Bitumen is the nonvolatile material which can be readily extracted from the shale, using an organic solvent, e.g., benzene. No distinction is made between the bitumen initially present in the shale and that formed by pyrolysis.
- Coke is the nonvolatile, insoluble carbonaceous residue left as a matrix or cement on the inorganic constituents of the shale.

The kinetic scheme discussed above requires that the temperature of the kerogen and all of its intermediate decomposition products can be specified as a function of time and position in the shale particle. For such a specification, the kinetic decomposition scheme has been coupled with a heat transfer model for spherical particles. Heat sinks, generated by the endothermic kerogen decomposition, inorganic carbonate decomposition, and dehydration reactions, result in significant alteration in the temperature profile within the particle and are included in the model. The physical properties of raw shale are functions of its organic content and during the retorting process are functions of temperature, degree of kerogen conversion, water loss, and carbonate decomposition. The effects of these variations in physical properties are also included in the retorting model. Heat transfer to the spherical shale particle during retorting occurs by convection from an inert gas stream in which the particle is immersed.
Mass transport within the shale is represented as occurring by diffusion. This representation allows the model to be readily extended to the burn-off of organic residue by incorporating combustion reactions and oxygen diffusion.

**SCHEMES FOR DESCRIBING KEROGEN PYROLYSIS**

McKee and Lyder (1921) demonstrated that, during the decomposition of kerogen, a benzene-soluble intermediate of low volatility was formed. The formation of this intermediate, now commonly referred to as "bitumen," was confirmed by Franks and Goodier (1922) and somewhat later by Maier and Zimmerly (1924). The latter authors established that it formed in abundance at temperatures as low as 527°F. In his studies of Australian torbanites, Cane (1951; 1963) observed measurable kerogen decomposition at temperatures as low as 392°F. Cummins and Robinson (1972) have reported a measurable rate of kerogen decomposition at 302°F by extending the duration of their heating cycle to 12 months.

Cane pointed out that no theoretical lower temperature limit for the decomposition of kerogen has been established. The probable formation of an intermediate product, other than bitumen, was also demonstrated. The second step in the decomposition was shown to be a softening to an insoluble intermediate, which Cane called "rubberoid." This step involves the rupture of cross-linkages and the generation of a more nearly linear elastomeric polymer. For pyrolysis in an inert atmosphere, Cane's mechanism can be written as

\[
\text{Kerogen 1} \rightarrow \text{Kerogen 2} \rightarrow \text{Rubberoid} \rightarrow \text{Bitumen} \rightarrow \text{Oil} \\
\text{Gas} \qquad \text{H}_2\text{S} \qquad \text{Coke} \\
\text{(H}_2\text{S + CO}_2) \quad \text{H}_2\text{S}
\]

He commented that his sequence resembles somewhat the one suggested by Fitzgerald (1952) for the pyrolysis of coking coal, which can be written:

\[
\text{Coal} \rightarrow \text{Plastic Coal} \rightarrow \text{Semi-Coke} \\
\text{Volatile} \quad \text{Volatile}
\]

Schnackenberg and Prien (1953) reduced the secondary cracking of primary decomposition products by using the thermal solution process to study the conversion. On the basis of their experimental results, they proposed that the decomposition followed the sequence:
The principal difference between this mechanism and Cane's [eq. (1)] is the long sequence prior to the evolution of any gases and the formation of coke from oil.

The kinetics of the decomposition of Baltic oil shales were investigated by Aarna (1956), who observed that a linear relation was obtained when a first-order rate constant for kerogen decomposition was plotted against the degree of decomposition of the kerogen. On the basis of this observation and the rate of evolution of low boiling components, he proposed that the pyrolysis of kerogen could be represented by:

\[
\text{Kerogen} \rightarrow \text{Pyrolytic Bitumen} \rightarrow \text{Residue} \rightarrow \text{Volatile Oil} \rightarrow \text{Oil} \rightarrow \text{Coke}
\]

This scheme essentially duplicates Fitzgerald's scheme [eq. (2)] for the pyrolysis of coking coals.

As a part of an extensive investigation of the physical properties and chemical constitution of coal by van Krevelen and his students, Chermin and van Krevelen (1957) developed a mathematical model of coal pyrolysis. Their scheme may be represented by:

\[
\text{Coal} \rightarrow \text{Metaplast} \rightarrow \text{Semi-Coke} \rightarrow \text{Coke}
\]

This scheme differs from that of Fitzgerald (1952) in the points of origin of the volatiles. In both of these mechanisms for coal pyrolysis, the formation of a semi-coke is proposed, which in the Chermin and van Krevelen scheme undergoes further reaction to form coke and volatiles. This latter step has also been used in mechanisms proposed for the formation of petroleum cokes, as in the mechanism of Catry (1968).

An elaborate kerogen decomposition product generation scheme has been proposed by Shul'man and Proskuryakov (1968), which may be written as:
They successfully assigned numerical values to the rate constants of their scheme, which produced good agreement between measured and calculated product yield data. This matching was accomplished for isothermal pyrolyses conducted at temperatures of 662°F, 700°F, and 727°F. The agreement with experimental data obtained at 700°F, the only case they exhibit, is excellent. Activation energies for the pseudo-reactions were evaluated, but these authors did not extend their results beyond the 662 to 727°F range, nor did they consider nonisothermal pyrolysis.

Two first-order reactions and three second-order reactions are combined in the scheme recently proposed by Fausett and others (1974). In effect, the bitumen formed by kerogen decomposition is presumed to promote the rate of formation of bitumen, volatiles, and carbonaceous residue from kerogen. Gas and oil products are lumped together as volatiles. This scheme provides a reasonable match between calculated and experimentally observed rates of volatiles production at temperatures in the neighborhood of 800°F.

The mechanisms given above were used to explain certain features of the pyrolysis of oil shales and coals. In general, these authors attempted to explain qualitative or quantitative aspects of the pyrolysis observed in the experiments they had conducted. As a result, their interpretations were limited in scope to a fairly small set of data. By considering all of the materials to have the same pyrolysis behavior, insofar as a gross scheme is concerned, most of the best features of these mechanisms can be combined into a general mechanism for the decomposition of kerogen and formation of products:
This general reaction scheme allows for variation in ultimate product distribution with different time-temperature histories. The selection of reactions is based on qualitative considerations and quantitative matching of calculated product yields to those experimentally measured for all available data. The intermediate species, heavy oil, arising from semi-coke decomposition, has been incorporated on the basis of kinetic data.

DEVELOPMENT OF THE PYROLYSIS SCHEME

An examination of our scheme for the thermal conversion of kerogen given above, equation (7), shows that if products arising from different precursors are considered different products, we have two gases, three oils, two soluble intermediates and, including the kerogen, four insolubles. There are a total of 11 product groups. Experimentally there are four readily distinguished product groups, i.e., gas, oil, solubles and insolubles. This discrepancy between the number of product groups is a good indication of the empirical nature of kerogen decomposition schemes in general.

The scheme proposed in this paper was developed and justified on the basis of the following list of primary and secondary requirements:

- **Primary requirements:**
  1. It must predict the amounts of all experimentally identified product groups at all times during the conversion.
  2. It must predict the amounts of products for any specified time-temperature history experienced by the kerogen.
  3. It must be of minimal complexity.

- **Secondary requirements:**
  4. It must be capable of predicting a minimum, if one exists, in a plot of the insolubles concentration versus time. Insolubles are defined as the initial total organic concentration minus the sum of the concentrations of the volatiles and solubles.
  5. It must be capable, with the proper initial concentrations of kerogen and bitumen, of predicting a minimum in a plot of the relative yield of volatiles versus time of conversion. The relative yield of volatiles is defined as the ratio of volatiles to volatiles
plus solubles. This criterion was proposed by Mityurev (1962).

(6) It should provide a means by which the properties of the shale oil produced can vary with retorting conditions.

(7) It should provide a basis for calculating the concentration of combustible organic material remaining in shale particles as a function of time, temperature, and position, to allow its incorporation into an overall model of retorting and burning.

With the assignment of proper values for the kinetic parameters, the decomposition scheme proposed here, equation (7), meets all of these requirements.

The most comprehensive experimental study of the thermal decomposition of oil shale which has been published is that of Hubbard and Robinson (1950). They investigated the pyrolysis of oil shales having Fischer assay oil yields of 26.7, 52.6, and 75.0 gal/ton over a temperature range of 662 to 977°F. The quantities of gas, oil, and bitumen formed, as well as organic material remaining on the shale, were measured as a function of time at each temperature used. The reaction times used were such that the decomposition did not proceed beyond the formation of semi-coke. For the initial evaluation of rate constants, Hubbard's data for pyrolysis at 752 and 797°F were used.

The decomposition of kerogen has been most frequently described by a single irreversible first-order reaction; however, the formation and disappearance of bitumen during the retorting process obviously requires the use of at least two reactions. A set of consecutive reactions, such as,

\[ C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow C_4 \]  

(8)
does provide for the production and disappearance of bitumen, but there is only one final product, and requirements 1 and 2 cannot be met. Mechanisms of this type also fail to satisfy requirements 4 and 5. To meet requirement 4, at least one branch point must be added to the scheme. This addition provides for two final products, which is still inadequate, and a chain of consecutive reactions with a single branch point can be rejected.

By adding two branch points, a scheme is produced which meets requirement 4 and has the necessary three final products. The simplest two branch point scheme is

\[ K_1 \quad K_2 \]
\[ C_1 \rightarrow C_2 \rightarrow C_3 \]
\[ K_4 \quad K_3 \]
\[ C_5 \rightarrow C_4 \]  

(9)
This four constant representation of the kinetics was found to produce good agreement between the calculated and measured product yields. Braun and Rothman (1974) have recently studied the two branch point scheme as a method of representing the oil formation data of Hubbard and Robinson over the temperature range 752 to 977°F. They obtain a good fit to the experimental data for oil production, using as a parameter an "induction time" evaluated from the experimental data.

We obtained the best fit to experimentally measured product yields using the branched decomposition scheme:

\[
\begin{align*}
\text{Kerogen} & \xrightarrow{K_1} \text{Rubberoid} \xrightarrow{K_2} \text{Bitumen} \xrightarrow{K_5} \text{Semi-Coke} \\
\text{Gas} & \xrightarrow{K_4} \text{Oil 1} & \text{Oil 2} & \xrightarrow{K_6}
\end{align*}
\]

This scheme not only gave the best data match but also has two sources from which oil arises. Requirement 6 can thus be met. The other 5 criteria which are not temperature dependent are met, subject to the restriction that the residue left in the shale corresponds to the semi-coke stage of reaction. As mentioned earlier, the experiments of Hubbard and Robinson appear to conform to this requirement.

Since at this point only isothermal retorting at two temperatures had been considered, no test of requirements 2 or 7 was possible. To test these latter two requirements, some form of temperature dependence of the rate constants was required. To evaluate the rate constants, the method employed by Chermin and van Krevelen (1957) was employed after some modification and extension, which adapted it to our rather more complex scheme. These preliminary estimates were modified by trial and error procedures. The best fit was judged by visual comparison of calculated curves with the empirical data points. The best estimate values so obtained were then used as input for a nonlinear regression routine to obtain optimum values for the rate constants for isothermal retorting at temperatures of 752 and 797°F. Data for product formation for the three shale grades used by Hubbard and Robinson were analyzed. A single set of rate constants, independent of shale richness, appeared to provide an adequate fit to the retorting data.

The temperature dependence of the rate constants was assumed to be given by the Arrhenius equation. Values of frequency factors and activation energies were determined from the fit to applicable pyrolysis data, obtained by a large number of investigators and spanning a large temperature range. During the course of the investigation, it was found necessary to extend the scheme from that given by equation (10) to the full scheme as given by equation (7). Estimates of the frequency factors and activation
energies for the decomposition of semi-coke were made using long-term linear heat-up data, data of Aarna (1955), and data of Hill and co-workers (1967). The activation energies for the entire scheme are listed in table 1.

PYROLYSIS OF LARGE PARTICLES, HEAT TRANSFER, AND KINETICS

The kinetics scheme presented above can only be used for finely divided shale, or heating rates which are sufficiently small to ensure uniform temperature throughout shale particles. In most retorts proposed for commercial retorting operations, the particle size and heating rates are well outside the range of conditions over which uniform shale temperature can be assumed. Therefore, the kinetic schemes presented above were incorporated into a model of heat transfer in a sphere. Allowing for diffusion of each component within the sphere, the conservation equation for the kth component is:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_k \frac{\partial c_k}{\partial r} \right) + B_k = \frac{\partial c_k}{\partial t}$$

where

- $D_k$ = mass diffusion coefficient, $L^2 \theta^{-1}$
- $c_k$ = concentration of kth component in shale, $ML^{-3}$
- $K_k$ = reaction rate constant for kth reaction, $\theta^{-1}$
- $r$ = radial position, $L$
- $t$ = time, $\theta$

The net reaction rates $B_k$ are given by:

- $B_1 = -R_1 - R_4$ (12a)
- $B_2 = R_1 - R_2 - R_3$ (12b)
- $B_3 = R_2 - R_5 - R_6$ (12c)
- $B_4 = R_3$ (12d)
- $B_5 = R_4$ (12e)
- $B_6 = R_5 - R_7 - R_8$ (12f)
- $B_7 = R_6$ (12g)
- $B_8 = R_7$ (12h)
- $B_9 = R_8 - R_9 - R_{10}$ (12i)
- $B_{10} = R_9$ (12j)
- $B_{11} = R_{10}$ (12k)

and the $R_k$'s are defined in table 1. Water vapor is formed at the rate:

$$B_{11} = R_{11} = K_{11} C_{21}$$

where $C_{21}$ = concentration of water in the shale, $ML^{-3}$.

Carbon dioxide is formed by carbonate decomposition at the rate:

$$B_{12} = R_{12} = -K_{12} n^{-1} C_{03}^{-n} C_{31}^{(1-n)}$$

where
Table 1.—Activation energies and frequency factors for the first-order pseudo-reactions of the kerogen pyrolysis scheme (equation 7)

\[ K_k = A_k \exp \left[ -\frac{E_k}{RT_F + 160} \right], \text{s}^{-1} \]

\[ C_k = \text{concentration of } k^{th} \text{ component in shale, } \text{ML}^{-3} \]

<table>
<thead>
<tr>
<th>Rate Constant, ( K_k )</th>
<th>(Reaction)</th>
<th>(Precursor) ( \rightarrow ) (Product)</th>
<th>Rate of Product Formation, ( R_k ), ( \text{ML}^{-3} \text{s}^{-1} )</th>
<th>Activation Energy, ( E_k ), BTU/( \text{lb})-mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_1 )</td>
<td>( C_1 ) (kerogen) ( \rightarrow ) ( C_2 ) (rubberoid)</td>
<td>( R_1 = K_1 C_1 )</td>
<td>77,900</td>
<td></td>
</tr>
<tr>
<td>( K_2 )</td>
<td>( C_2 ) (rubberoid) ( \rightarrow ) ( C_3 ) (bitumen)</td>
<td>( R_2 = K_2 C_2 )</td>
<td>61,400</td>
<td></td>
</tr>
<tr>
<td>( K_3 )</td>
<td>( C_2 ) (rubberoid) ( \rightarrow ) ( C_4 ) (oil)</td>
<td>( R_3 = K_3 C_2 )</td>
<td>82,100</td>
<td></td>
</tr>
<tr>
<td>( K_4 )</td>
<td>( C_1 ) (kerogen) ( \rightarrow ) ( C_5 ) (gas)</td>
<td>( R_4 = K_4 C_1 )</td>
<td>85,900</td>
<td></td>
</tr>
<tr>
<td>( K_5 )</td>
<td>( C_3 ) (bitumen) ( \rightarrow ) ( C_6 ) (semi-coke)</td>
<td>( R_5 = K_5 C_3 )</td>
<td>60,100</td>
<td></td>
</tr>
<tr>
<td>( K_6 )</td>
<td>( C_3 ) (bitumen) ( \rightarrow ) ( C_7 ) (oil)</td>
<td>( R_6 = K_6 C_3 )</td>
<td>83,200</td>
<td></td>
</tr>
<tr>
<td>( K_7 )</td>
<td>( C_6 ) (semi-coke) ( \rightarrow ) ( C_8 ) (coke)</td>
<td>( R_7 = K_7 C_6 )</td>
<td>94,700</td>
<td></td>
</tr>
<tr>
<td>( K_8 )</td>
<td>( C_6 ) (semi-coke) ( \rightarrow ) ( C_9 ) (heavy-oil)</td>
<td>( R_8 = K_8 C_6 )</td>
<td>91,000</td>
<td></td>
</tr>
<tr>
<td>( K_9 )</td>
<td>( C_9 ) (heavy-oil) ( \rightarrow ) ( C_{10} ) (oil)</td>
<td>( R_9 = K_9 C_9 )</td>
<td>31,030</td>
<td></td>
</tr>
<tr>
<td>( K_{10} )</td>
<td>( C_9 ) (heavy-oil) ( \rightarrow ) ( C_{11} ) (gas)</td>
<td>( R_{10} = K_{10} C_9 )</td>
<td>61,000</td>
<td></td>
</tr>
</tbody>
</table>
\[ C_{31} = \text{concentration, } ML^{-3}, \text{ of mineral carbonate (as CO}_2\text{) in shale at time, } t \]
\[ C_{031} = \text{initial concentration of mineral carbonate (as CO}_2\text{), } ML^{-3} \]
\[ n = \text{reaction order, negative, and a function of temperature.} \]

The diffusion coefficients are given by:
\[ D_k = D_{kB} \frac{T_R^{3/2}}{P_R} \tag{15} \]

where
\[ D_{kB} = \text{diffusion coefficient, } L^2\theta^{-1}, \text{ at reference temperature, } T_B, \text{ and reference pressure, } P_B \]
\[ T_R = \frac{(T + 460)}{(T_B + 460)} \tag{16} \]
\[ P_R = \frac{P}{P_B} \tag{17} \]

The temperature distribution in the shale sphere is described by the energy balance:
\[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 n \frac{\partial T}{\partial r} \right) + S = \rho C_q \frac{\partial T}{\partial t} \tag{18} \]

where
\[ S = \sum_{k=1}^{12} R_k \Delta H_k \tag{19} \]
\[ \Delta H_k = \text{heat of reaction, } L^2\theta^{-2} \]
\[ T = \text{temperature, } T \]
\[ \rho = \text{density of shale, } ML^{-3}, \text{ at time, } t \]
\[ C_q = \text{heat capacity, } L^2\theta^{-2}T^{-1} \]
\[ n = \text{thermal conductivity, } ML\theta^{-2}T^{-1} \]

As the shale is heated, thermal expansion occurs, and when kerogen conversion begins, the shale swells. The expanded radius of the sphere which results is described by:
\[ R_s = R_0 \left[ 1 + \eta (T_s - T_0) + \zeta (1 - C_{15}/C_T) \right] \tag{20} \]

where
\[ R_s = \text{radius of sphere, } L, \text{ at specified time} \]
\[ R_0 = \text{initial radius of sphere, } L \]
\[ \eta = \text{coefficient of linear expansion, } T^{-1} \]
\[ \zeta = \text{coefficient of swelling} \]

with
\[ C_{15} = C_1 + C_2 + C_3 + C_6 + C_8 + C_9 \]
and

\[ C_T = \sum_{k=1}^{11} C_k, \text{ at } t = 0. \]

The density of the shale is a function of the change in radius and the weight lost through evolution of products. The density after heating has started is given by:

\[ \rho(t) = \rho_R S (R_o/R_s)^3 - W_L \quad (21) \]

where

\[ W_L = (C_T - C_{15}) + (C_{021} - C_{21}) + (C_{031} - C_{31}). \]

The mass balance, equation (11), and heat balance, equation (18), are solved simultaneously with the following boundary conditions specified:

\[ C_k(r, 0) = C_{ok}(r) \quad k = 1, 2, \ldots, 13 \quad (22a) \]

\[ T(r, 0) = T_o(r) \quad (22b) \]

\[ \frac{\partial T}{\partial r} \bigg|_{r=0} = 0 \quad (22c) \]

\[ \frac{\partial C_k}{\partial r} \bigg|_{r=0} = 0 \quad (22d) \]

\[ -n \frac{\partial T}{\partial r} \bigg|_{r=R_s} = h (T - T_g) \bigg|_{r=R_s} \quad (22e) \]

\[ -D_k \frac{\partial C_k}{\partial r} \bigg|_{r=R_s} = K_{gk} (C_k - C_{k2}) \bigg|_{r=R_s} \quad (22f) \]

where

\[ h = \text{heat transfer coefficient, } M^0 \theta^{-1} T^{-1} \]

and \[ K_g = \text{mass transfer coefficient, } L^0 \theta^{-1}. \]

These conditions correspond to a sphere initially having uniform distributions of composition and temperature. There is symmetry at the center of the sphere. In addition to these conditions, the temperature of the gas surrounding the sphere is known as a function of time, \( T_g(t) \). The shale is assumed to be isotropic. A finite difference formulation was used with an iterative algorithm to effect a solution to the difference equations.

**THERMAL PROPERTIES OF OIL SHALE**

Approximate values of thermal conductivity at various temperatures were extracted from early laboratory and field data. These results were
combined with the data of Gavin and Sharp (1920) and those of Thomas (1966) to obtain a preliminary estimate of the thermal conductivity and its variation with temperature. It was found that the inverse temperature function of Kingary and McQuarrie (1954) gave a good approximation to these data. Using the model described here, the parameters of the thermal conductivity functions were modified until agreement with experimental temperature profiles, observed during the heating and retorting of 4.00 inch diameter oil shale spheres, were obtained. Parameters for the thermal conductivity equations for spent shale and burned shale were obtained from data for the same set of spheres. The temperature range covered in these experiments was 80 to 1,100°F. Colorado oil shale having a Fischer assay oil yield of approximately 30 gal/ton was used. The thermal conductivities obtained in this manner are corrected for heats of reaction, change in dimension of the sample, change in heat capacity, and change in density resulting from weight loss, since these factors were independently incorporated in the model.

It was observed that the thermal conductivity for spent 30 gal/ton shale, as given by the equations of Tihen, Carpenter and Sohns (1968), agreed quite well with the results obtained from our correlation. On the basis of the agreement for the spent shale, the variation of thermal conductivity with shale richness obtained by Tihen, Carpenter and Sohns was incorporated into our thermal conductivity equations to obtain equations of the following form with different coefficients for raw, spent, and burned shale:

$$n = \frac{a + b (GPT) + d (GPT)^2}{\alpha + \beta T + \gamma T^2}$$

(23)

where

$$(GPT) = \text{Fischer assay of shale, gal/ton.}$$

The thermal conductivity at time, t, during retorting was obtained from equation (23) in the following manner:

$$n = n_{RS} - \frac{\nu}{0.87} (n_{RS} - n_{SS}), \quad \text{for } \nu < 0.87$$

(24)

where

$$\nu = \frac{1 - C_{15}/C_T}{n_{RS}}$$

$n_{RS} = \text{thermal conductivity raw shale}$

$n_{SS} = \text{thermal conductivity spent shale}.$

Oil shale is anisotropic and, as Sladek (1970) has shown, the thermal conductivities parallel and perpendicular to the bedding planes are not identical. The values calculated from equation (24) are average values for a
hypothetical isotropic shale. These are the appropriate values for our model.

The heat capacity equation used for raw shale is

\[ C_{RS} = 0.172 + (0.001)[0.067 + 0.00162(GPT)](T + 460), \]  

(25)

and that for spent shale is

\[ C_{SS} = 0.174 + 0.000051(T + 460) \]  

(26)

As the shale loses water and organic matter during heating, the heat capacity changes. This change is represented in the model as:

\[ C_q = (1 - \nu)\left[C_{RS} - 0.4/\rho_{RS}\left(C_{o21} - C_{21}\right)\right] + C_{SS}. \]  

(27)

It was assumed that the heat capacity of spent shale and burned shale are identical. Equations (25) and (26) are those given by Sohns and others (1951). Some improvement in the model might result if the more recent correlations of Wise, Miller and Sohns (1971) for the heat capacity were used. We have not investigated this possibility, since most of our work was completed before these later correlations were available; the differences in the final results should be minor.

The complete model was designed to model both retorting and burning of oil shale spheres. To achieve this overall utility, heat and mass transfer, to and from the gas phase surrounding the particle, were incorporated in the model. However, in the present instance, our only interest is in modeling of the retorting phase of oil shale conversion. For this purpose, a modification of the model was useful. In this version the surface temperature of the shale particle as a function of time was used as input data. This “surface temperature version” was further modified to include cylindrical particle geometry for fitting Hubbard and Robinson’s (1950) data at temperatures in excess of 797°F.

APPLICATION TO MATCHING OF EXPERIMENTAL PRODUCT YIELD DATA

In the first section a general similarity of pyrolysis behavior for all sapropelic shales was suggested. This can be substantiated to some degree by comparing the overall initial first-order rate constants obtained for many shales by many investigators with the overall first-order rate constants obtained from our pyrolysis scheme. (See Maier and Zimmerly 1924; Cane 1951; Cane 1963; Cummins and Robinson 1972; Aarna 1956; Hubbard and Robinson 1950; Hill and others 1967; Allred 1966; DiRicco 1955; Aarna and Kask 1956; Luts 1934.) Such a comparison is made in figure 1, where experimental data covering the temperature range 302 to 977°F are shown as points, and the calculated results, by a solid line. The calcu-
lated initial first-order rate constants give a constant activation energy of 84,100 Btu/lb mole over the entire temperature range. The experimental points are rather uniformly distributed about the calculated line, except at the upper end of the temperature range. The low values for the experimental rate constants in this high temperature region have been found to be a result of the long times for the sample to reach temperature, relative to the time required for retorting.

Using rate constants which have been optimized to fit a particular set of isothermal data, the calculated product yield curves closely approximate

![Graph showing overall initial first-order rate constant for kerogen decomposition.](image)

**Figure 1.**—Overall initial first-order rate constant for kerogen decomposition.
In Situ Retorting of Oil Shale Rubble

Figure 2—Formation of products during the pyrolysis of 26.7 gpt oil shale at 752°F (Hubbard and Robinson 1950).

Product's wt. % initial organic

Time, minutes

OIL, EXPT.
BITUMEN, EXPT.
GAS, EXPT.
CALCULATED
the measured values. Such a fit is shown in figure 2, which presents a comparison of Hubbard and Robinson's data for 26.7 gal/ton at 752°F (shown as points) with the calculated curves (shown as solid lines). The relative yield of volatiles curves, requirement 5 above, indicated that the presence of some bitumen in the sample was likely, but the indicated amount was dependent on the elapsed time required for the sample to reach temperature. Similar results were obtained using the criteria of requirement 4. Based on these results, no definite conclusions could be reached as to the initial bitumen content of the samples, but it appeared likely that a small amount of bitumen was initially present. Such a view coincides with Cook's (1974) view that some bitumen which is not readily accessible to solvents may be present in the shale. The curves shown in figure 2 were calculated assuming the samples reached the final temperature instantaneously and that the organic material consisted of 7.5 weight percent bitumen and 92.5 weight percent kerogen.

Low temperature isothermal pyrolysis data are not plentiful. Aarna (1956) obtained some results, using a Baltic oil shale having an estimated assay oil yield of 150 gal/ton. He lists oil yield data for isothermal retorting temperatures of 527, 572, 617, and 662°F. A comparison of the calculated oil yield versus time curves with the measured yields is shown in figure 3. The calculated curves lie somewhat below the experimentally determined values at all temperatures. Considering the extreme richness of this shale, the results are considered acceptable.

Another comparison for "isothermal" conditions can be made using the final oil yields obtained by Aarna (1956; 1955) and Aarna and Kask (1956). These results were obtained using samples of Baltic shales having assay oil yields ranging from 80 to 150 gal/ton. The measured and calculated yields are compared in figure 4. In view of the scatter in the experimental data the calculated curve is in reasonable agreement. One of the sets of data plotted in figure 4 was not obtained under strictly isothermal conditions. Aarna (1955) states that the shale samples were heated to the final temperature at a rate of 2.7°F/min. Our estimates of the duration of the heat-up period (assumed to be linear) and isothermal periods for these experiments are presented in table 2, along with the experimentally measured oil and gas yields. Product yields calculated using the full kinetic scheme of equation (7) for nonisothermal conditions are also given in this table. If the overall scatter in the experimental data is considered, the calculated yield values are in good agreement with those observed.

Some long-term heating experiments using Colorado oil shale have been reported by Hill and others (1967). The shale samples used by these investigators had Fischer assays in the range 21 to 31 gal/ton. The particle size range was about 0.5 to 1.0 inch. Hill's oil yield data are plotted in figure 5 where they are compared to the calculated oil yields obtained using the pyrolysis scheme of equation (10) and setting the final time as
Figure 3—Calculated oil formation compared with Aarni's (1956) experimental values for Baltic bituminous shale.
Figure 4.—Oil formed in long-term isothermal heating experiments of Aarna and Kask (1956) and Aarna (1955; 1956).
**Table 2.**—Observed and calculated (equation 7) product yields for Baltic oil shale (Aarna 1955)

<table>
<thead>
<tr>
<th>Final Temp, °F</th>
<th>572</th>
<th>626</th>
<th>680</th>
<th>716</th>
<th>752</th>
<th>788</th>
<th>824</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hours to Attain Final Temp.</td>
<td>3.05</td>
<td>3.38</td>
<td>3.88</td>
<td>3.93</td>
<td>4.17</td>
<td>4.38</td>
<td>4.60</td>
</tr>
<tr>
<td>Hours at Final Temp.</td>
<td>741</td>
<td>129</td>
<td>10.3</td>
<td>4.57</td>
<td>3.33</td>
<td>0.62</td>
<td>1.40</td>
</tr>
<tr>
<td>Obs. Oil Yield a)</td>
<td>15.2</td>
<td>37.4</td>
<td>33.2</td>
<td>44.9</td>
<td>51.8</td>
<td>57.8</td>
<td>58.4</td>
</tr>
<tr>
<td>Calc. Oil Yield a)</td>
<td>21.4</td>
<td>31.5</td>
<td>32.5</td>
<td>40.9</td>
<td>53.7</td>
<td>53.6</td>
<td>61.6</td>
</tr>
<tr>
<td>Obs. Gas Yield a)</td>
<td>5.7</td>
<td>8.0</td>
<td>6.7</td>
<td>6.8</td>
<td>8.4</td>
<td>11.1</td>
<td>12.2</td>
</tr>
<tr>
<td>Calc. Gas Yield a)</td>
<td>9.1</td>
<td>10.9</td>
<td>11.6</td>
<td>13.2</td>
<td>14.7</td>
<td>15.1</td>
<td>15.4</td>
</tr>
<tr>
<td>Obs. Residue a)</td>
<td>79.1</td>
<td>54.6</td>
<td>60.1</td>
<td>48.3</td>
<td>39.8</td>
<td>31.1</td>
<td>29.4</td>
</tr>
<tr>
<td>Calc. Residue a)</td>
<td>69.5</td>
<td>57.6</td>
<td>55.9</td>
<td>45.9</td>
<td>31.6</td>
<td>31.3</td>
<td>23.0</td>
</tr>
</tbody>
</table>

*Yield given as weight percent initial organic*.

infinity \( t_{\text{final}} = \infty \). These calculated results are shown as the continuous curve in the figure. The dashed curve was obtained in a similar manner, using the kinetic scheme of equation (7). Calculated oil yields are presented in this manner, since the data of Hill and others are probably not truly isothermal data, and insufficient information is available to allow a nonisothermal calculation. The dashed curve represents an upper limit to the oil yields that can be expected, while the solid curve represents the upper limit if the final residue is semi-coke. Also plotted in figure 5 are the oil yield data given in table 2. At temperatures greater than 650°F, the data of Aarna are in excellent agreement with the data of Hill. This cannot be considered as any kind of “proof,” but it tends to lend some credibility to our earlier hypothesis that the mechanisms of kerogen decomposition are essentially the same for Baltic and Green River oil shales. With the exception of Aarna’s data point for 626°F, all of the measured yields are seen to be somewhat below the solid curve calculated with the abbreviated mechanism. The rate of product evolution was very slow under the conditions prevailing, and the products remained in the retort vessel for appreciable times after their formation. Some of the oil formed could have undergone cracking and polymerization in the retort, resulting in a reduction in the measured oil yield to a value less than its true value. Hill and co-workers expressed some concern that such polymerization oc-
Figure 5.—Oil yields obtained in long-term isothermal oil shale retorting.
In their experiments and demonstrated experimentally that it can occur readily under appropriate conditions.

We conducted a series of retorting experiments in which the temperature was increased linearly with time from 77 to 880°F. Following the linear heat-up period, the temperature was held at 880°F for a time period equal to one-third that of the heat-up time. Colorado shale of 30 gal/ton oil yield and a nominal particle size of % inch was used in all experiments. The retort, product collection equipment, and a gas circulation pump formed a closed-loop through which oxygen-free gas was continuously circulated. Only the final product yield was measured. Measured and calculated product yields are given in table 3. Both the measured and calculated oil yields decrease, as the rate of heating decreases, and are in good quantitative agreement.

Cummins and Robinson (1972) have published the results of isothermal retorting of 65 gal/ton Colorado oil shale at 90°F temperature increments over the temperature range 302 to 662°F. At the two lowest temperatures, 302 and 392°F, the calculated oil production is 0.00 weight percent at 302°F and 0.01 weight percent at 392°F. These results are in agreement with the experimental data. Comparisons of calculated and experimental product yields for temperatures of 482, 572, and 662°F are shown in figure 6. The data of Hubbard and Robinson (1950) for 52.6 gal/ton shale at 662°F are also plotted.

For temperatures of 572 and 662°F, the oil yield is plotted in figure 6. As shown in this figure, good agreement between the calculated and measured oil yields was obtained at 572°F. At 662°F the calculated oil yield is shown.

Table 3.—Calculated and observed yields obtained in linear heat-up retorting experiments

<table>
<thead>
<tr>
<th>Time to reach 880°F</th>
<th>Residue, Weight % of Initial Organic</th>
<th>Oil, Weight % of Initial Organic</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.68</td>
<td>12.2</td>
<td>15.5</td>
</tr>
<tr>
<td>4.5</td>
<td>17.5</td>
<td>18.5</td>
</tr>
<tr>
<td>6.0</td>
<td>17.2</td>
<td>18.8</td>
</tr>
<tr>
<td>11.5</td>
<td>18.2</td>
<td>21.5</td>
</tr>
<tr>
<td>24.0</td>
<td>17.8</td>
<td>22.5</td>
</tr>
<tr>
<td>68.0</td>
<td>20.0</td>
<td>23.0</td>
</tr>
<tr>
<td>168.0</td>
<td>20.2</td>
<td>24.2</td>
</tr>
<tr>
<td>340.0</td>
<td>21.5</td>
<td>19.7</td>
</tr>
</tbody>
</table>
yield rises rather steeply to a value in the neighborhood of 50 weight percent, then bends rather sharply and levels off. With the exception of the point at a time of 4 days, \( t/t_{\text{max}} = 1 \), the experimental yields obtained by Cummins and Robinson are lower than the calculated yields. These
measured oil yield data approximately conform to a zero-order rate law. If one ignores the oil yield point at 1 day \( t/t_{\text{max}} = 0.25 \), the combined 662°F oil yield data can be approximated by two straight lines, intersecting at an oil yield of 15 percent and \( t/t_{\text{max}} = 0.073 \) \( (t = 0.29 \text{ days}) \). These results might then be interpreted as showing a rather abrupt change from one zero-order mechanism to another zero-order mechanism at 15 percent oil yield. As might be expected, our calculated curve, though showing a higher rate of oil formation than measured by Hubbard and Robinson, is in much better agreement with these earlier results than with the later data of Cummins and Robinson. We may also note that, as shown in figure 3, our calculated rate of oil formation is less than that measured by Aarna at this temperature.

Hubbard and Robinson used shale samples in the form of cylinders, having a diameter of 1 centimeter and length of 6 centimeters. Therefore, the model was modified to correspond to cylindrical, rather than spherical geometry. In this version, the surface temperatures of the shale surface as a function of time were independently evaluated for use as input data. In order to fit the product yield data of these investigators, the surface temperatures were estimated as functions of time from the charts of Heisler (1947).

The greatest effect of the time to reach temperature is present in the experiments conducted at the highest furnace temperature employed, which was 977°F. Our estimate of sample temperatures indicate that at a time of 7 minutes, the longest heating time recorded for this temperature, the sample reached a nearly uniform temperature of about 945°F, or some 30°F lower than the furnace temperature. Oil yields calculated at a furnace temperature of 977°F are compared with experimental values in figure 7. The oil yield versus time curve, calculated for true isothermal, uniform sample temperature retorting, is also shown in figure 7. No large increase in oil yield is indicated, but, as can be seen, the rate of oil formation is much greater. Comparisons of calculated nonsothermal, nonuniform temperature yield curves with the experimental data at 932, 887, 842, and 797°F show similar behavior, with the isothermal and nonsothermal results coming closer together at the lower furnace temperatures. Actually, our calculations indicate that, even at 752°F, a small temperature gradient existed in the sample, and retorting was not quite isothermal.

Braun and Rothman (1974) give similar indications of a departure from isothermal retorting in the Hubbard and Robinson experiments. In their treatment, they assume a thermal induction time, which, though its absolute magnitude decreases nearly linearly with increasing furnace temperature, becomes a larger fraction of the total retorting time as the furnace temperature increases.

Both our model and that of Braun and Rothman confirm that the low activation energy obtained at temperatures greater than 800°F by Hubbard and Robinson is probably a result of neglecting the finite time required to
heat the sample. The extension of a constant activation energy into the high temperature region, as was done in constructing figure 1, is thus justified.

A thermo-gravimetric technique was used by Allred (1964) to study the retorting behavior of oil shale. In the experiment considered here, his samples were cylinders whose length was equal to their diameter of 0.75 inch. It was not possible to measure temperatures of the sample and the weight loss simultaneously. The technique adopted by Allred was to use
two samples of shale, which were as nearly identical as possible. One sample was used to measure the weight loss and the other for the measurements of the surface and center temperatures. The shape of the sample made it difficult to determine whether the spherical or cylindrical version of the model should be used. On the basis of some trial calculations, the cylindrical version was adopted. Agreement between the measured and calculated center temperatures was taken to be the proper criterion for heat transfer matching, even though some departure from the measured surface temperature was required. The calculated weight loss and center temperatures are compared with the measured values in figure 8. The agreement shown in figure 8 was considered adequate for evaluating decomposition mechanisms.

At times in excess of about 5 minutes, the calculated weight loss curve is in good agreement with the measured curve. Weight loss during the first 5 minutes was largely the result of water loss.

Basing our conclusions on the results obtained with our model, organic decomposition started at about 750°F and was essentially complete at about 950°F. Very little mineral carbonate decomposition is indicated during the short time that the sample was at high temperature. The excellent agreement between the calculated and observed weight loss during the period of kerogen conversion is another measure of the ability of the model to simulate nonisothermal retorting of shale particles in which a temperature gradient exists.

Thermo-gravimetric data for the retorting of accurately machined oil shale spheres of 0.5 and 1.0 inch diameter have been obtained in Mobil's laboratories. The technique was the same as Allred's, in that the temperature measurements and weight loss measurements were made on different spheres. Good agreement was obtained between the calculated and measured weight loss curves for these experiments. An example of the agreement obtained is shown in figure 9, in which the results of a one-half inch diameter sphere are presented. In this case, the rate of heating is so great that a large temperature gradient was established in the particle. As a result, an overlap of the weight loss resulting from water loss and that resulting from organic decomposition occurred, and no well-defined water loss portion of the curve exists.

Perhaps our most elaborate set of experiments was a series of thermo-gravimetric retorting runs conducted using accurately machined oil shale spheres 4 inches in diameter. A special large thermo-gravimetric apparatus was built to accommodate samples of this size. During the retorting portions of our experiments, the spheres were heated by a rapidly flowing oxygen-free gas stream. A constant mass flow rate was maintained. The temperature of the gas stream was controlled by a programmable controller. The weight loss and shale temperatures were measured simultaneously on the same sample. Shale temperatures were measured at sphere radii corresponding to 0, 25, 50, 75, and 100 volume percent of the sphere,
Figure 8.—Pyrolysis of 0.75-inch diameter oil shale cylinder (Allred 1964).

the first of these positions being the center and the last the surface of the sphere. In all the runs made using this equipment, the gas temperature was increased linearly with time to a preselected temperature, and then held constant for a period deemed sufficient to achieve conversion of the organic material, at least as far as the semi-coke stage. Typical results
In Situ Retorting of Oil Shale Rubble

Figure 9.—Pyrolysis of 0.5-inch diameter oil shale sphere.
obtained using a sphere of 30.5 gal/ton shale are shown in figure 10. The measured surface temperature is shown as a dashed curve, since it was used as input data for calculations shown in this figure. Using an appropriate film coefficient, the same results can be obtained using the gas temperature versus time curve.

The temperature curve for the center of the sphere shows a rather strong "dip," the midpoint of which is at about 100 minutes. Such dips occurred in all of the runs and are similar to the "dips" shown in the curves of Meelk (1959) for the retorting of 100 mm long blocks of Estonian oil shale, having an 80 x 80 mm cross section. This dip in the temperature curve is the result of a combination of factors, including changes in thermal conductivity, dimensional changes, and endothermic reactions. The flattening of the knee in the 50 volume percent temperature curve corresponds to the dip at this latter radius. It will also be noted that at long times the three temperature curves remain separated and become nearly parallel. This persistent temperature gradient in the shale sphere results from the heat sinks provided by the slow endothermic semi-coke and dolomite decomposition reactions. By using the model with the heats of semi-coke and mineral carbonate decomposition set at zero, the calculated temperature curves show the expected asymptotic approach to the surface temperature and a nearly uniform temperature throughout the sphere at long times. The nearly linear, slow weight loss at times in excess of about 130 minutes, shown in figure 11, is another manifestation of these decomposition reactions.

The initial weight loss, shown in figure 11, is the result of water loss from the shale. This provides a heat sink, which slows the rate of heating of interior parts of the shale at early times. Verification was obtained by making calculations with the heat of reaction for water evolution set to zero. No adjustment in the thermal conductivity was capable of providing an adequate match between the calculated and observed temperatures during the early part of the sphere heating, with the heat sink eliminated. The water content of the shale is thus seen to have a significant effect on the rate of heat transfer in massive oil shale.

For the conditions prevailing in this experiment, active kerogen decomposition began at the time the center temperature had reached about 730°F and just prior to the cessation of water evolution. Conversion of the kerogen to semi-coke was essentially complete by the time the center of the sphere reached 900°F. At all points in the sphere, the rate of heating was large enough that the retorting reactions occurred at temperatures sufficient to produce an amount of oil only slightly less than Fischer assay. At the inverted knee in the weight loss curve, occurring in the vicinity of 100 minutes, the calculated and observed values are not in complete agreement. Better agreement in this region was obtained in some of the other runs. Regions showing this degree of mismatch were observed in all of the runs, with the position of these regions along the weight loss curve varying
Figure 10.—Temperature profiles for retorting of 4-inch diameter sphere of 30.5 g/s oil shale.
Figure 11.—Weight loss during retorting of 4-inch diameter sphere of 30.5 gpt oil shale.
between runs. Physical parameter values used in the model are average values, which gave the best overall representation to the data for all of the runs.

**USE OF MODEL AS AN INTERPRETIVE AND PREDICTIVE TOOL**

In the model described in this paper, the relative yields of gas, oil, and solid organic residue formed are determined by the temperature time cycle to which the organic matter of the shale (kerogen and bitumen) is subjected. Our representation of this dependence of the yields on temperature history has been derived from data obtained in laboratory experiments. We have also examined data obtained on pilot plant scale equipment to confirm the validity of the model. At least two processes have been tested at the pilot plant level of development. These processes heat the organic fraction of the shale very rapidly to temperatures of the order of 900 to 950°F in an inert atmosphere. These are the Tosco II and Lurgi Ruhrgas processes. According to Hendrickson (1974), oil yields as high as 107.6 volume percent Fischer assay have been reported for the Tosco II retort, and Rammler (1970) reports yields of the order of 102 weight percent of Fischer assay for the Lurgi process. In both of these processes the oil shale is comminuted during retorting, eliminating any significant heat transfer time. At the other ends of the scales of particle size and heating rates is the 150-ton retort of the U.S. Bureau of Mines. This retort is an experimental above ground unit in which mine-run shale having an average particle size of about 6 inches has been charged. Carpenter and Sohns (1974) have reported that in the first series of runs in this retort, the maximum oil yield obtained was 65.8 volume percent Fischer assay. Heating rates are at least two orders of magnitude less in the 150-ton retort, than in the Tosco II and Lurgi retorts.

Using the model, we predict that by instantaneous heating of the organic material to 970°F, an oil yield equivalent to 73.0 weight percent of total organic could be obtained, or about 110 weight percent of Fischer assay by Smith (1966) correlation. If the shale is allowed to remain at retorting temperature for an adequate length of time, oil yields in excess of 100 weight percent Fischer assay, as measured in the Tosco II and Lurgi retorts, should be obtained by instantaneous heating to temperature over the rather broad range of 772 to 1,377°F. The agreement between the model and the pilot plant data from Tosco II and Lurgi retorts is quite good. High oil yield when heating small shale particles rapidly to temperatures in excess of 800°F is thus confirmed.

At the other extreme of retort design are those retorts in which a large fraction of the shale particles exceed 6 inches in size, and the rate of temperature increase is low. The size distribution of mine-run shale is broad,
with appreciable quantities of material less than 0.5 inch and greater than 20 inches. As a result, oil was generated in the 150-ton retort runs over a broad range of organic heating rates, and calculations of oil yield using the model must be made and compared with the experimentally measured yield. Information adequately detailed to allow us to make such calculations has been published by Harak and others (1971), for run #2 made in this retort. Assuming that the gas phase is inert and all of the oil generated in the shale particles is recovered as product from the retort, the calculated oil yield for this run is in the range of 67.5 to 71.7 weight percent Fischer assay. The range given results from the range of values reported for the conversion of oil yield, expressed as weight percent total organic to oil yield as percent Fischer assay. If the assumption is made that all oil produced into the gas stream after its temperature reaches 1,200°F is lost as a result of burning or cracking, the calculated yield drops to the range 62.7 to 66.6 weight percent Fischer assay, which is in good agreement with the measured yield of 62.2 volume percent Fischer assay. The value of 1,200°F as the cutoff point was chosen on the basis of previous studies. These calculations indicated that this cutoff would provide a reasonable approximation to the fraction of oil generated which would be produced from the retort.

As a result of the low rate of temperature rise in the gas stream, the calculated maximum oil production in small particles was in the range 70 to 74 weight percent Fischer assay. The low rate of heat transfer to interior portions of large particles, 28 inch diameter, resulted in a decrease in oil production to the range of 60 to 64 percent Fischer assay. The calculations were extended to include a particle size equivalent to the 7,500 lb block, included in the retort charge. These calculations indicated that this block would completely retort, as was observed, even under the assumption that it was heated only by convective transfer from an inert gas stream and that no surface combustion occurred.

At the 1974 NSF Workshop on “In Situ Oil Shale Retorting,” a paper (Snyder and others 1974) was presented showing calculated yields for in situ retorts, in which void volume was generated by partial mining, followed by rubblizing. An in situ combustion case and a hot gas injection case were considered as alternate methods to provide the required heat. The calculations were made assuming the particle size distribution in the retort was the same as that for mine-run shale which was used for run #2 in the Bureau of Mines 150-ton retort. Oil yields were found to decrease with decreasing gas flux and increasing retort height, or length, for inert gas heating.

Caution should be exercised in using any of the reported data or retorting models for shales containing appreciable amounts of inorganic carbonates other than dolomite and calcite. Such shales are those underlying the Mahogany Zone of the Piceance Basin, which contain dawsonite, and some sections of the shales of Wyoming and Utah, which contain shortite.
The temperature profile is very dependent on the amounts and reactivities of these inorganics.

The Mobil yield model was originally developed to estimate the oil yields that might be obtained from an oil shale retort formed by a nuclear device. It has proved useful in estimating oil yields from retorts in which large pieces of shale are retorted.

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A MATHEMATICAL MODEL OF AN OIL SHALE RETORT

Donald W. Fausett

Editor's note: the paper, "A Mathematical Model of an Oil Shale Retort," by Donald W. Fausett, was not presented at the Eighth Oil Shale Symposium, but is included in the Proceedings because of its relevance.

ABSTRACT

A mathematical model has been developed that can serve as an analytical tool to study operating procedures for an oil shale retort. Such a model naturally separates into two principal components: a model of the kinetics of oil shale pyrolysis and a model of the retorting combustion process.

A system of thermal decompositions is presented that provides a description of the mechanism of oil shale pyrolysis. Specific rate constants for that system have been determined by a least squares procedure, and are shown to exhibit a temperature dependence that is in good agreement with the Arrhenius equation.

The quasi steady-state approximation from classical flame propagation theory has been adopted to describe the propagation of the high temperature (combustion) reaction through the retort. Analytical expressions for temperature distribution and oxygen concentration in the retort are presented. A numerical method for solving those equations is presented.

A procedure is given for combining the kinetics model and the temperature profile model to produce a mathematical model of the oil shale retort. An example of a simulated retort run is discussed, using values for the parameters in the model that are based on physical data from an experimental retort run.

INTRODUCTION

The possibility of economically exploiting the energy potential stored in known oil shale deposits has attracted interest for many years (Clarkson...
1919; Sladek 1974). The importance of oil shale reserves has increased in recent years because energy production has fallen behind energy consumption in the United States (Cameron 1973; Glenn 1974; Ritzma 1973). Most investigations into methods of extracting hydrocarbons from oil shale have been based on some idea for retorting the oil shale (Hendrickson 1974; Matzick and others 1966). Retorting may be performed on the surface above ground (ex situ retorting), which requires mining of the oil shale rock. An alternate method is to retort the shale in place in the formation where it occurs (in situ retorting) (Carpenter and Sohns 1974; Sohns and Carpenter 1966).

It is desirable to be able to predict the behavior of retorting processes under various conditions. Oil shale pyrolysis is an essential feature of any retorting process. An investigation of possible systems of thermal decompositions comprising the mechanism by which pyrolysis of oil shale takes place has been reported by Fausett, George, and Carpenter (1974). The nature of this mechanism has been the subject of several previous investigations (Allred 1967; Blackburn 1924; Cane 1943; Cane 1951; Carlson 1937; Cummins and Robinson 1972; DiRicco and Barrick 1956; Engler 1913; Franks and Goodier 1922; Hill and Dougan 1967; Hubbard and Robinson 1950; Maier and Zimmerley 1924; McKee and Lyder, July 1921; McKee and Lyder, August 1921; Shul'man and Proskuryakov 1968; Snyder, Timmins, and Johnson 1974; Tissot 1969; Weitkamp and Gutberlet 1970). A mathematical model that generates a good fit to experimental data is based on a thermal decomposition system consisting of two first-order reactions and three second-order reactions. Values computed for the specific rate constants corresponding to that system are shown in the following to exhibit a temperature dependence that is in good agreement with the Arrhenius equation, over the temperature range of the data used in the study.

In order to be able to apply the kinetics model to oil shale retorting problems, one must know something about how the temperature distribution in the retort behaves as a function of time and position. An investigation of this problem has been reported by Fausett (1974). The retort studied is of the forward combustion type, that is, a high temperature (combustion) reaction is propagated through the retort in the same direction as an injected oxidant gas stream. The equations describing this process are closely related to those occurring in classical flame propagation theory; those equations have been the subject of several investigations (Berman and Riazanov 1972; Bledjian 1973; Evans 1952; Frank-Kamenetskii 1969; Friedrichs 1946; Gel'fand 1963; Johnson 1963; Johnson and Nachbar 1963; Klein 1967; Spalding 1956; Spalding, Stephenson, and Taylor 1971; von Kármán 1956; von Kármán and Penner 1954; Vulis 1961; Wilde 1972; Williams 1965; Zeldovich and Barenblatt 1959). Gel'fand (1963) has given a good discussion concerning questions of existence, uniqueness, and stability of solutions. We have adopted for our purposes
A procedure originally developed for the investigation of steady-state propagation of flat flames. This procedure, which is known as the "quasi steady-state approximation," is based on the hypothesis that definite temperature and concentration profiles are established early in a retort run and move uniformly thereafter. The problem is transformed to a moving coordinate system in which the shapes of the temperature and concentration profiles are unchanged with respect to an observer moving at the same (constant) velocity as the combustion zone. Analytical expressions for temperature distribution and oxygen concentration are obtained by Lagrange's method of variation of parameters. The resulting nonlinear integral equations are evaluated by a numerical procedure.

The kinetics model and the temperature profile model can be amalgamated to produce a mathematical model of an oil shale retort. A procedure for combining the two models is described in the sequel. An example of a simulated retort run is presented using values for the parameters in the mathematical model that are based on physical data from an experimental retort run.

THE KINETICS MODEL

INTRODUCTION

The potential oil content of oil shale is not a free oil. It is an organic material embedded in an inorganic matrix of compact, laminated, sedimentary rocks. Following Hubbard and Robinson (1950), we make the following definitions:

Kerogen. The portion of the organic material in oil shale that is insoluble in ordinary solvents for petroleum and that, upon the application of heat, may yield some or all of the following products: pyrolytic bitumen, gas, oil, and a carbon residue.

Natural bitumen. The soluble organic material naturally present in oil shale.

Pyrolytic bitumen. The soluble organic material that forms during heating of an oil shale.

Gas. The noncondensed vapors that form from the organic matter during heating of an oil shale.

Oil. The hydrocarbons and other organic compounds that form as a vapor during heating of an oil shale and that subsequently condense.

Carbon residue. The insoluble portion of kerogen remaining in the spent shale after destructive distillation; this residue is similar to fixed carbon in coal.

Previous investigators generally have assumed a thermal decomposition system for oil shale pyrolysis consisting of two successive first-order reac-
tions: kerogen decomposes into bitumen; bitumen in turn decomposes into the final products of oil, gas, and carbon residue. Allred (1967) has demonstrated that this system does not provide an adequate description of the mechanism of oil shale pyrolysis. Allred presents curves representing the experimental data of Hubbard and Robinson (1950) (see also figs. 1 and 2). Comparison of those curves with curves of consecutive reactions (see also fig. 3) leads Allred to remark that "...it may indicate that the rate of decomposition of kerogen is dependent upon the amount of bitumen present. If so, this would be very significant since it would imply that the bitumen has a catalytic or solvent action on kerogen decomposition."

Our investigation has been into possible second-order effects in the mechanism of oil shale pyrolysis, such as that of bitumen acting as a catalyst in the decomposition of kerogen. The general procedure is as follows: for a fixed temperature, we assume a possible system of decompositions, which includes the relevant substances of kerogen, bitumen, oil and gas, and carbon residue. The corresponding differential equations for the kinetics are written according to the mass action law. Reaction rate constants are then obtained from experimental data via a least squares procedure. With the reaction rate constants thus determined, the system of differential equations may be solved numerically for the concentrations of the substances.

**Theoretical Considerations**

We now consider a method for finding a system of thermal decomposition reactions to represent the mechanism of oil shale pyrolysis. The criterion for evaluating the adequacy of a system of reactions is taken to be goodness of fit to experimental data of Hubbard and Robinson (1950).

**Components of the Pyrolysis Mechanism**

Before one can attempt to determine numerical values for reaction rate constants, it is necessary to formulate a hypothetical system of thermal decompositions to comprise a possible mechanism by which oil shale pyrolysis might occur. Due to the complex nature of the organic material in oil shale, "...the unraveling of these kinetics has not been a straightforward matter" (Allred 1967).

As mentioned in the introduction, Allred (1967) has shown that the pyrolysis reactions are not adequately described by simple first-order kinetics. Our study has been especially concerned with investigation of possible second-order effects.
Figure 1. Experimental data of Hubbard and Robinson (1950) at T = 425°C.
Figure 2.—Experimental data of Hubbard and Robinson (1950) at T = 475°C.
Figure 3—Curves generated by model based on system I at $T = 475^\circ C$. 

Data modified to account for production of carbon residue.
Types of Thermal Decomposition Systems Studied

For notational convenience, the following nomenclature will be used:

\[ A_1 = \text{kerogen}, \]
\[ A_2 = \text{pyrolytic bitumen}, \]
\[ A_3 = \text{oil and gas}, \]
\[ A_4 = \text{carbon residue}, \]

\[ x_i(t) = \text{concentration of substance } A_i, \quad 1 \leq i \leq 4, \text{ at time } t, \text{ expressed as a fraction of total insoluble organic material initially contained in the oil shale.} \]

By virtue of our definition of concentration, any proposed system of reactions must satisfy the constraint

\[ x_1(t) + x_2(t) + x_3(t) + x_4(t) = 1 \text{ for } t \geq 0. \]

The temperature \( T \) is considered to be constant, and the initial conditions for all systems studied are

\[ x_1(0) = 1, \quad x_2(0) = x_3(0) = x_4(0) = 0. \]

These conditions are consistent with experimental data of Hubbard and Robinson (1950) in which the natural bitumen was extracted from the oil shale with benzene before pyrolysis.

Concentration of the carbon residue was not measured by Hubbard and Robinson at each time of observation; however, production of carbon residue may be estimated by a material balance procedure suggested by Allred (1967). This procedure is based on the assumption that disappearance of kerogen and appearance of carbon residue are represented by the same type of function. In a laboratory carbon analysis, it is difficult to distinguish carbon residue from unconverted kerogen. This difficulty accounts for the absence of carbon residue concentrations in the data of Hubbard and Robinson. Lack of such data leaves unverified the procedure adopted for calculating values of carbon residue concentrations. Since the rate of production of carbon residue is an important consideration in the design and operation of an oil shale retort, any contribution to knowledge in this area would be of interest to many people.

The types of thermal decomposition reactions considered are the following:

1. First-order reactions include decomposition of kerogen into bitumen, oil and gas, and carbon residue; decomposition of bitumen into oil and gas and carbon residue; and decomposition of oil and gas into carbon residue.

2. Second-order reactions include decomposition of kerogen with bitumen acting as a catalyst into bitumen, oil and gas (as suggested by Allred 1967), and carbon residue; decomposition of kerogen with oil and gas acting as a catalyst into bitumen, oil and gas, and carbon residue; and
decomposition of bitumen with oil and gas acting as a catalyst into oil and gas and carbon residue.

The most complex system possible consisting of types of reactions considered would be one in which each substance present reacted in every possible manner. It is not seriously considered that all of these reactions occur, nor is this list exhaustive of all hypothetically possible types of reactions; for example, we could consider a second-order reaction with kerogen acting as a catalyst in the decomposition of bitumen into oil and gas.

A great many combinations of these reactions were studied. Some systems studied consisted of as many as nine reactions, some consisted of as few as two reactions. Most systems studied consisted of five, six, or seven reactions.

**Form of the Differential Equations for a Kinetic System**

Differential equations are written for the kinetic system studied in the following manner. Suppose that a first-order reaction is governed by the reaction equation $A_i \rightarrow A_j$, then mathematical statements for disappearance of $A_i$ and appearance of $A_j$ are

$$-\frac{dx_i}{dt} = kx_i \text{ and } \frac{dx_j}{dt} = kx_i.$$  

If a second-order reaction is governed by the equation

$$A_i + A_j \rightarrow A_m + A_j,$$

then mathematical statements for disappearance of $A_i$ and appearance of $A_m$ are

$$-\frac{dx_i}{dt} = kx_ix_j \text{ and } \frac{dx_m}{dt} = kx_ix_j.$$  

The concentration $x_j$ of the catalyst is unchanged by this last reaction. These differential equations are special cases of the mass action law (Ben-son 1969).

Suppose that a kinetic system of $m$ reactions involving the four substances $A_i$, $1 \leq i \leq 4$, has been chosen for study. The corresponding system of differential equations is of the form

$$x' = X(x)K, \quad (1)$$
where

\[
\begin{bmatrix}
    x_1 \\
    x_2 \\
    x_3 \\
    x_4
\end{bmatrix}
= \begin{bmatrix}
    \frac{dx_1}{dt} \\
    \frac{dx_2}{dt} \\
    \frac{dx_3}{dt} \\
    \frac{dx_4}{dt}
\end{bmatrix},
\]

\[
K = \begin{bmatrix}
    k_1 \\
    k_2 \\
    \vdots \\
    k_m
\end{bmatrix},
\]

and \( X(x) \) is a 4 x m matrix with elements as determined by the mass action law for the particular system of reactions under study. Explicit expressions for \( X(x) \) are presented in the section on examples of systems studied.

**Determination of Specific Rate Constants**

Assume that the experimental data available for estimating specific rate constants corresponding to a hypothetical system of thermal decompositions consist of measured concentration values at \( n \) values of time (at constant temperature). Let the set of time values be denoted by \( t_j, 1 \leq j \leq n \).

At a particular value of time, say \( t_j \), the matrix equation (1) has the form

\[
x'(t_j) = X(x(t_j))K.
\]

The use of this equation to solve for \( K \) has the disadvantage that it requires the values of the derivatives of the concentrations at time \( t_j \). Since the given data only include concentration values, it would be necessary to differentiate numerically to obtain values for \( x'(t_j) \). In general, numerical differentiation is unreliable in the sense that it exaggerates errors in data. Bellman (1953) has termed it a "coarsening" process. Numerical integration, on the other hand, is a smoothing process. We can transform our problem into one involving numerical integration rather than numerical differentiation.

Starting with equation (1), we integrate both sides to obtain
A Mathematical Model of an Oil Shale Retort

\[ x(t_j) - x(0) = \left\{ \int_0^{t_j} X(x(t)) \, dt \right\} K. \]

If we define
\[ x_j = x(t_j) - x(0) \]
and
\[ U_j = \int_0^{t_j} X(x(t)) \, dt, \]
then in place of equation (1), we have the equivalent expression
\[ x_j = U_j K. \] (2)

The matrix \( U_j \) requires numerical integration of the concentration values. There are a variety of methods available for performing numerical integration of discrete data. The method which we employed is that of fitting a least squares cubic spline function (Anselone and Laurent 1968; Klaus and Van Ness 1967) to the concentration values and then integrating analytically the resulting spline function.

We solve for \( K \) from equation (2) by a standard least squares procedure (Fox 1965).

Once least squares estimates for the specific rate constants have been computed, we have a mathematical model of the thermal decomposition system under study. Comparison of concentration values generated by that model with experimentally observed values provides a basis for evaluating the accuracy of the model.

**Measurement of Accuracy of a Model**

The measure that we used to determine how well a particular mathematical model describes the behavior of the true (but unknown) thermal decomposition system is the sum of the squares of the differences between observed values of concentrations and computed concentration values, using the right-hand side of equation (2) with the least squares solution for \( K \) corresponding to that model. In other words, we computed

\[ \sum_{j=1}^{n} (x_j - U_j K)^T(x_j - U_j K), \] (3)

where the superscript \( T \) denotes the matrix transpose. There is no theoretical point of demarcation between values of the summation (3) indicating a "good fit" as opposed to values indicating a "poor fit." For a given set of experimental data, the model which corresponds to a minimum value of
(3) is considered to provide a good fit to those data relative to other models which correspond to larger values of (3).

**Examples of Thermal Decomposition Systems**

For each system of thermal decompositions studied, we computed the least squares solution for the specific rate constants. Experimental data used to obtain solutions were those of Hubbard and Robinson (1950) with modification as suggested by Allred (1967) to account for production of carbon residue.

Among the many thermal decomposition systems that we studied are the following of special interest and significance.

**Thermal Decomposition System I**

Allred (1967) suggests that if one considers only that portion of kerogen that goes to form bitumen, then the pyrolysis reaction may be simplified by supposing it to be represented by the equations

\[
\begin{align*}
A_1 & \rightarrow A_2, \\
A_2 & \rightarrow A_3.
\end{align*}
\]

The differential equations for concentrations for this decomposition system can be written in the matrix notation of equation (1) as

\[
x' = \begin{bmatrix}
x_1 \\
x_2
\end{bmatrix} = \begin{bmatrix}
-x_1 & 0 \\
0 & -x_2
\end{bmatrix} \begin{bmatrix}
x_1 \\
x_2
\end{bmatrix} + \begin{bmatrix}
k_1 \\
k_2
\end{bmatrix}.
\]

Concentration curves generated by this system with least squares estimates for the specific rate constants based on data for \( T = 475^\circ C \) are shown in figure 3. The curves were generated by numerically solving equation (1) for this system by the Runge-Kutta-Gill method (Romanelli 1960).

In figure 2 we show curves representing experimental data of Hubbard and Robinson with Allred's modification at \( T = 475^\circ C \). Comparison of the curves shown in figures 2 and 3 reveals a fundamental difference in the character of the two sets of curves. That difference indicates (as observed by Allred) that the pyrolysis mechanism cannot be adequately represented by simple first-order kinetics.
**A Mathematical Model of an Oil Shale Retort**

*Thermal Decomposition System II*

A model that generates a good fit to observed concentration values in comparison with other models studied is based on the following assumed system of thermal decompositions:

\[ \begin{align*}
    k_1 & : A_1 \rightarrow A_2, \\
    k_2 & : A_2 \rightarrow A_3, \\
    k_3 & : A_1 + A_2 \rightarrow A_2 + A_2, \\
    k_4 & : A_1 + A_2 \rightarrow A_3 + A_2, \\
    k_5 & : A_1 + A_2 \rightarrow A_4 + A_2.
\end{align*} \]

The differential equations for concentrations for this decomposition system can be expressed as

\[
x' = \begin{bmatrix}
-x_1 & 0 & -x_1x_2 & -x_1x_2 & -x_1x_2 \\
x_1 & -x_2 & x_1x_2 & 0 & 0 \\
0 & x_2 & 0 & x_1x_2 & 0 \\
0 & 0 & 0 & 0 & x_1x_2 \\
0 & 0 & 0 & 0 & x_1x_2
\end{bmatrix} \begin{bmatrix}
k_1 \\
k_2 \\
k_3 \\
k_4 \\
k_5
\end{bmatrix}
\]

Concentration curves generated by this system with least squares estimates for the specific rate constants based on data for \( T = 425 \)°C and \( T = 475 \)°C are shown in figures 4 and 5.

Figures 1 and 2 show curves representing experimental data of Hubbard and Robinson with Allred's modification at \( T = 425 \)°C and \( T = 475 \)°C. Comparison of the curves shown in figures 1 and 2 with those shown in figures 4 and 5 reveals a general similarity in the character of the curves. This similarity indicates that a more adequate description of the pyrolysis mechanism is obtained by consideration of second-order kinetics in addition to simple first-order kinetics. In particular, this similarity lends support to Allred's conjecture (1967) that the rate of decomposition of kerogen may be dependent upon the amount of bitumen present.

We remark here that Hubbard and Robinson (1950) have pointed out that their experimental data may be somewhat shifted with respect to time because of "... the time required to bring the temperature of the sample from its initial temperature to the desired temperature. This heating lag is relatively insignificant at low temperatures where the heating periods are long, but as it remains fairly constant it becomes increasingly significant..."
Figure 4.—Curves generated by model based on system II at $T = 425^\circ$C.

Data modified to account for production of carbon residue

Kerogen

Oil and gas

Bitumen

Carbon residue on shale

Concentrations of substances

Time, min
Figure 5.—Curves generated by model based on system II at $T = 475^\circ\text{C}$. 

Data modified to account for production of carbon residue

Kerogen

Oil and gas

Bitumen

Carbon residue on shale

CONCENTRATIONS OF SUBSTANCES

TIME, min
at high temperatures where the heating periods are short.” It appears that this time lag can be observed in comparison of the numerically generated curves with the experimental curves.

**Thermal Decomposition System III**

A model that is closely related to that of system II is based on the following assumed thermal decomposition system:

\[
\begin{align*}
&k_1 \\
A_1 &\rightarrow A_2, \\
&k_2 \\
A_2 &\rightarrow A_3, \\
&k_3 \\
A_1 + A_2 &\rightarrow A_2 + A_2, \\
&k_4 \\
A_1 + A_2 &\rightarrow A_3 + A_2, \\
&k_5 \\
A_1 + A_2 &\rightarrow A_4 + A_2, \\
&k_6 \\
A_1 &\rightarrow A_3, \\
&k_7 \\
A_1 &\rightarrow A_4.
\end{align*}
\]

This decomposition system is represented by the following matrix differential equation for concentrations:

\[
\begin{bmatrix}
-x_1 & 0 & -x_1x_2 & -x_1x_2 & -x_1x_2 & -x_1 & -x_1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-x_1 & -x_2 & x_1x_2 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & x_1x_2 & 0 & x_1 & 0 \\
0 & 0 & 0 & 0 & x_1x_2 & 0 & x_1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix}
\begin{bmatrix}
x' \\
k_1 \\
k_2 \\
k_3 \\
k_4 \\
k_5 \\
k_6 \\
k_7
\end{bmatrix}
\]

Concentration curves generated by this system with least squares estimates for the specific rate constants based on date for \( T = 475^\circ C \) are shown in figure 6.

Comparison of the curves generated by this system with those generated by system II for \( T = 475^\circ C \) (fig. 5) shows essentially no difference in the two sets of curves. Apparently, at this temperature, the model based on system II is not improved appreciably by adding the reactions

\[
\begin{align*}
&k_6 \\
A_1 &\rightarrow A_3, \\
&k_7 \\
A_1 &\rightarrow A_4.
\end{align*}
\]
A Mathematical Model of an Oil Shale Retort

Figure 6—Curves generated by model based on system III at \( T = 475^\circ \text{C} \).
TEMPERATURE DEPENDENCE OF SPECIFIC RATE CONSTANTS

The Arrhenius equation (Benson 1969) states that the specific rate constants are dependent upon temperature according to the relation

$$\ln k = a + \frac{b}{T}, \quad (4)$$

where $T$ is the absolute temperature ($^\circ$K) and $a$ and $b$ are empirical constants. Sometimes equation (4) is written with the constant $b$ replaced by $E/R$, where $R$ is the universal gas constant. In that form, it is possible to give a theoretical interpretation to the constants $a$ and $E$ (Benson 1969). In this interpretation, $E$ is called the activation energy for the equation and $a$ is called the frequency factor. Benson (1969) suggests that a more appropriate nomenclature for $a$ would be to call it the Arrhenius factor.

Values computed for the specific rate constants for thermal decomposition system II at $T = 425^\circ$C and $T = 475^\circ$C can be used to determine values for the empirical constants in equation (4) for each specific rate constant $k_i$, $1 \leq i \leq 5$. Values thus obtained are shown in table 1.

The numbers shown in table 1 are of the same general magnitude as those given by other investigators for the empirical constants describing the influence of temperature on the thermal decomposition of kerogen. Maier and Zimmerley (1924) studied the rate of formation of bitumen from kerogen over the temperature range of 275 to 365°C. Based on data for a Utah oil shale, they obtained as values for the empirical constants $a = 30.99$ and $b = -20,896$. Hubbard and Robinson (1950) studied the rate of thermal decomposition of kerogen into gas, oil, and bitumen. Based on data for three Colorado oil shales, they obtained two sets of values for the empirical constants for different ranges of temperature. For temperatures in the range of $437^\circ$C and below, they obtained $a = 47.09$ and $b = -31,251$. For temperatures in the range of $437^\circ$C and above, they obtained $a = 21.05$ and $b = -12,777$. The values obtained by Maier and Zimmerley and Hubbard and Robinson cannot be compared directly with those shown in table 1 because their values are based on different systems of thermal decompositions.

Values of the specific rate constants computed by the least squares procedure for thermal decomposition system II using data for $T = 425^\circ$C and $T = 475^\circ$C are shown in table 2. Those values were used to determine the values of the empirical constants shown in table 1. Also shown in table 2 are values of specific rate constants computed by the least squares procedure for system II using data for $T = 450^\circ$C and values for specific rate constants at $T = 450^\circ$C calculated from equation (4) using values of the empirical constants from table 1.
A MATHEMATICAL MODEL OF AN OIL SHALE RETORT

Table 1.—Values of empirical constants in the Arrhenius equation \( \ln k = a + b/t \) for thermal decomposition system II determined from experimental data at \( T = 425^\circ C \) and \( T = 475^\circ C \)

<table>
<thead>
<tr>
<th>METHOD</th>
<th>COST PER BARREL*</th>
<th>CAPITAL INVESTMENT FOR 100,000 BARRELS/DAY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mining and surface retorting</td>
<td>$12</td>
<td>$1000-1500 million</td>
</tr>
<tr>
<td>Rubblization by mining and in-situ retorting (RISE method)</td>
<td>8</td>
<td>600 million</td>
</tr>
<tr>
<td>Nuclear fracturing and in-situ retorting</td>
<td>5</td>
<td>300 million</td>
</tr>
</tbody>
</table>

*Cost includes upgrading to petroleum refinery feedstock standards
Source: Lewis and Rothman 1975.

Table 2.—Values of specific rate constants for thermal decomposition systems II*

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Specific rate constants, min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>°K</td>
</tr>
<tr>
<td>-----</td>
<td>-----------</td>
</tr>
<tr>
<td>425</td>
<td>698</td>
</tr>
<tr>
<td>450</td>
<td>723</td>
</tr>
<tr>
<td></td>
<td>(0.005)</td>
</tr>
<tr>
<td>475</td>
<td>748</td>
</tr>
</tbody>
</table>

*Values shown in parentheses are obtained from the Arrhenius equation.
**In general, \( k_i \) will have the units of a frequency (time\(^{-1}\)) only if \( k_i \) represents the specific rate constant for a first-order reaction. For a second-order reaction, the units for \( k_i \) generally will include a concentration term, for example, liters per mole per minute (1. mole\(^{-1}\) min\(^{-1}\)). Since we are expressing concentration as a fraction of total insoluble organic material initially present, the concentration term in the units for \( k_3 \), \( k_4 \), and \( k_5 \) is unity.

THE TEMPERATURE PROFILE MODEL

Introduction

The oil shale retort under study in this investigation is a 150-ton capacity batch retort designed, constructed, and operated by the U.S. Bureau of Mines (now Energy Research and Development Administration) at the
Laramie Energy Research Center (Harak, Dockter, and Carpenter 1971; Harak, Dockter, Long, and Sohns 1971). The retort vessel is 45 feet high and 11½ feet in inside diameter [see fig. 7, reproduced from Harak, Dockter, and Carpenter (1971) by permission]. It is supported by a 92 feet high steel superstructure. The retort is a refractory lined carbon steel cylinder with an opening at the top for loading shale and a hinged grate at the bottom for supporting the shale bed. The hinged grate is opened by a hydraulic mechanism to discharge spent shale from the vessel after termination of an experimental run.

A flow diagram of the retort is shown in figure 8 [also reproduced from Harak, Dockter, and Carpenter (1971) by permission]. The shale vessel is charged with crushed mine-run shale. A natural gas burner mounted on the retort lid is used to initiate combustion of the shale bed. An oil tank collects liquid products from the retort outlet. Gaseous products from the retort, which contain some oil and water mist, are passed through a packed tower and a demist tank to remove most of the entrained material. After passing through another blower, the gas stream is split. Some of the gas can be recycled back into the retort; the remainder vents to the stack and is burned. Thermocouples are placed in horizontal planes (typically eight thermocouples per plane) at regular intervals throughout the shale bed. The thermocouples are wired to temperature recorders to log bed temperatures.

The combustion process used in the retort is of the type known as "forward combustion," that is, the high temperature (combustion) reaction is propagated through the retort in the same direction as the injected oxidant gas stream. The combustion zone is a relatively narrow region of the retort. Residual fuel deposited ahead of the combustion zone is all consumed in this region (provided that the combustion temperature is sufficiently high). The combustion zone advances seeking new fuel. Heating by conduction and convection occurs ahead of the combustion zone. This heating causes pyrolysis of the oil shale to occur. The carbon residue formed during that pyrolysis is thought to be the principal source of fuel for the combustion process. The oil and gas products formed ahead of the combustion zone are driven forward and recovered. The carbon residue formed remains in place and undergoes combustion. Cooling, also by conduction and convection, occurs behind the combustion zone. A comprehensive discussion of the forward combustion process is presented by Thomas (1963).

The other basic type of combustion process is known as "reverse combustion." In such a process, the combustion zone is propagated in a direction opposite to the flow of oxidant gas. All oxygen is consumed in the combustion zone; the combustion zone moves toward the oxygen supply. Combustion thus takes place with an excess of fuel. A thorough discussion of the reverse combustion process is given by Warren (1960).
We assume linear heat flow in a homogeneous system that we consider to be represented by a one dimensional, infinitely long, constant pressure system in which the temperatures of the shale, oil, and gas are the same.
at any given spatial point, $x$, and temporal point, $t$. All physical parameters are assumed to be temperature invariant; the parameters are assigned values that are appropriate for the ranges of temperature involved.

**Temperature Distribution Equation**

Conservation of energy, accounting for conduction, convection, heat generation, and heat loss, gives the following partial differential equation for the distribution of temperature with respect to space and time (Berry and Parrish 1960):

$$k \frac{\partial^2 T}{\partial x^2} - \dot{m}_g C_g \frac{\partial T}{\partial x} + g(T) - L(T) = (\phi_g \xi_g C_g + \xi_s C_u) \frac{\partial T}{\partial t},$$

where:

- $T = \text{temperature, } ^\circ\text{F}$,
- $x = \text{distance, feet}$,
- $t = \text{time, hours}$,
- $k = \text{gross thermal conductivity, Btu/hour - foot - } ^\circ\text{F}$,
- $\dot{m}_g = \text{mass gas flux, lb/hour - sq foot}$,
- $C_g = \text{heat capacity of gas, Btu/lb - } ^\circ\text{F}$,
- $\xi_g = \text{density of gas, lb/cu foot}$,
A Mathematical Model of an Oil Shale Retort

\[ C_s = \text{heat capacity of solid, Btu/lb} - \degree F, \]
\[ \zeta_s = \text{density of solid, lb/cu foot}, \]
\[ \phi_g = \text{gas space porosity, dimensionless}, \]
\[ g(T) = \text{heat generation function, Btu/hour} - \text{cu foot}, \]
\[ L(T) = \text{heat loss function, Btu hour} - \text{cu foot}. \]

Oxygen Concentration Equation

Conservation of mass, accounting for convection and reaction, gives the following partial differential equation for the oxygen concentration with respect to space and time (Berry and Parrish 1960):

\[ \frac{\partial \eta}{\partial x} + \phi_g \zeta_g \frac{\partial \eta}{\partial t} + \frac{\phi_g}{N_o} G(T) = 0, \]

where (in addition to the above nomenclature):

\[ \eta = \text{fraction of original oxygen remaining unreacted, dimensionless}, \]
\[ N_o = \text{original oxygen concentration, weight fraction of the injected gas}, \]
\[ G(T) = \text{reaction rate function, lb oxygen consumed/hour} - \text{cu foot of gas space}. \]

Fuel Concentration

As mentioned in the introduction, it is believed that the principal combustion mechanism involves a reaction between oxygen and the carbon residue formed during pyrolysis of the oil shale. Conservation of mass considerations lead to a partial differential equation for the concentration of carbon residue analogous to that for oxygen concentration (Thomas 1963).

For the case of reverse combustion, such an equation is not needed in order to model the combustion process since all of the oxygen is consumed in the combustion zone in the presence of excess fuel (Berry and Parrish 1960). Thomas (1963) has shown that in the case of forward combustion, however, it is possible that unreacted oxygen can pass through the combustion zone at high rates of gas injection. The fuel concentration equation is thus needed to provide a comprehensive model of the forward combustion process. The addition of such an equation greatly increases the mathematical complexity of the problem. Thomas simplifies his model by considering only a single element of time, \( \Delta t \), chosen sufficiently small so that it may be supposed that

\[ \frac{\partial \tau}{\partial t} = \frac{\partial \eta}{\partial t} = \frac{\partial F}{\partial t} \approx 0 \]

where \( F \) denotes the concentration of fuel. He says, "Solution of such a
system in essence amounts to taking a snapshot of the temperature and concentration profiles at a given instant in time."

We shall simplify our model by ignoring the equation for fuel concentration, as is done in the case of reverse combustion (hence the procedure that we shall develop in the sequel should also be applicable to reverse combustion problems). However, we shall allow for the situation in which unreacted oxygen passes through the combustion zone by introducing a parameter, \( \epsilon \), to represent the value of relative oxygen concentration beyond the combustion zone. This artifice permits us to retain a time dependency in our solutions for temperature distribution and oxygen concentration.

**Heat Loss Function**

If heat is lost to surroundings that are at a constant external temperature, then the heat loss function is given by (Berry and Parrish 1960):

\[
L(T) = hp(T - T_e),
\]

where:

- \( T_e \) = external temperature, °F,
- \( h \) = heat transfer coefficient, Btu/hour - sq foot of surface area - °F,
- \( p \) = perimeter shape factor (ratio of heat loss surface area to volume), sq feet/cu feet.

**Heat Generation Function**

The rate of heat generation in a unit volume of the system is assumed to be proportional to the gas space volume, the heat liberated by reaction per unit weight of oxygen, and the reaction rate function, \( G(T) \). The heat generation function is thus of the form (Berry and Parrish 1960):

\[
g(T) = \phi_\sigma G(T),
\]

where:

- \( \sigma \) = heat generation constant, Btu/lb of oxygen.

**Reaction Rate Function**

The reaction rate is assumed initially to be a first-order Arrhenius reaction of the following form (Thomas 1963):

\[
G(T) = \eta \bar{A} e^{-B/\left(T+460\right)},
\]

where:

- \( \bar{A} \) = reaction rate coefficient, lb of oxygen reacted/hour - cu foot of gas space,
\( \bar{B} = \text{reaction rate exponent, } ^\circ R. \)

(Absolute temperature in \( ^\circ R \) equals temperature in \( ^\circ F \) plus 460.) Later we shall modify somewhat the form of the reaction rate function to be used in the oxygen concentration equation.

**Quasi Steady-State Approximation**

Adopting a procedure originally developed for the investigation of steady-state propagation of flat flames (Zeldovich and Barenblatt 1959), we shall transform our problem from the fixed coordinate system \((x,t)\) to a moving coordinate system \((y,z)\). To do so, we must assume that the shapes of the temperature and concentration profiles are unchanged with respect to an observer moving at the same velocity as the combustion zone, and that the velocity of the combustion zone is constant (these are the "steady-state" hypotheses). This procedure has been applied to reverse combustion problems (Berry and Parrish 1960; Warren 1960; Warren, Reed, and Price 1960). Thomas (1963) discusses the possibility of using a quasi steady-state model to describe the forward combustion process. He states, "Particular difficulty is attached to this scheme, however, in fitting appropriate boundary conditions. . . . numerical integration of the pertinent equations must be necessarily carried out from right to left along the spatial coordinate rather than the usual, opposite direction. This requires that initial conditions be stipulated for the downstream side of the wave." All of these observations have held true with regard to the present investigation as well.

Let \( v \) denote the velocity of the combustion zone (feet/hour). Assume that steady-state has been attained, and introduce the variables \( y \) and \( z \) by making the definitions:

\[
y = x - vt \quad \text{and} \quad z = vt. \tag{7}
\]

*Transformation of the Temperature Equation*

Under the transformation \((7)\), we have that

\[
\frac{\partial T}{\partial x} = \frac{\partial T}{\partial y} \frac{\partial y}{\partial x} + \frac{\partial T}{\partial z} \frac{\partial z}{\partial x} = \frac{\partial T}{\partial y},
\]

and similarly

\[
\frac{\partial^2 T}{\partial x^2} = \frac{\partial^2 T}{\partial y^2}.
\]
Also
\[
\frac{\partial T}{\partial t} = \frac{\partial T}{\partial y} \frac{\partial y}{\partial t} + \frac{\partial T}{\partial z} \frac{\partial z}{\partial t} = v \left( \frac{\partial T}{\partial z} - \frac{\partial T}{\partial y} \right) = -v \frac{\partial T}{\partial y},
\]

since \( \frac{\partial T}{\partial z} = 0 \) by the steady-state hypotheses. All derivatives are now with respect to \( y \), so we may write equation (5) as an ordinary differential equation in \( y \):
\[
\frac{d^2T}{dy^2} + \alpha \frac{dT}{dy} - \beta T = -\Omega \eta e^{-B/(T+460)} - \beta T_e,
\]
where we have grouped constants as follows:
\[
\alpha = \frac{v(\phi_g \xi g C_g + \xi_g C_u) - \bar{m}_g C_g}{k},
\]
\[
\beta = \frac{hp}{k},
\]
\[
\Omega = \frac{\phi_g \bar{A}}{k}
\]

Transformation of the Oxygen Equation

Under the transformation (7), equation (6) becomes:
\[
\frac{d\eta}{dy} = -\rho \eta e^{-B/(T+460)}
\]
where:
\[
\rho = \frac{\phi_g \bar{A}}{(N_0(\bar{m}_g - v\phi_g \xi g))}.
\]

Traveling Waves

Let us examine (8) and (9) briefly to get a clearer understanding of the implications of the transformation (7). We have differential equations that describe the behavior of the function \( T(x,t) \) as \( T(x-vt) \) and the function \( \eta(x,t) \) as \( \eta(x-vt) \). Consider the function \( T(x,t) = T(x-vt) \). The graph of \( T(x-vt) \) is the same as the graph of \( T(x) \) translated to the right by a distance equal to \( vt \). This means that as \( t \) increases, \( T(x-vt) \) represents a profile of the form \( T(x) \) traveling to the right with velocity \( v \). If
(8) were the wave equation instead of the temperature equation, \( T(x-\nu t) \) would be called a forward wave (Young 1972). The term "forward wave" may be considered as synonymous with forward profile for our problem. Similar comments apply to \( \eta(x,t) = \eta(x-\nu t) \). A backward wave is one of the form \( T(x+\nu t) \); it would be the corresponding conceptualization for a reverse combustion problem. Forward and backward waves are both known as "traveling waves."

**Statement of the Problem**

We consider three thermal regimes to be associated with the combustion process.

Zone I is ahead of the combustion region. In this zone, the temperature rises from its initial value to that necessary to initiate combustion under the existing conditions of oxygen and fuel concentrations. Since combustion does not occur in this zone, the heat generation term is set equal to zero throughout zone I. The heat loss function is written as \( L(T) = h(T-T_0) \), where \( T_0 \) is the initial temperature, in zone I since the system "loses" heat with receding time relative to its initial temperature. Hence in zone I, equation (8) takes the form:

\[
\frac{d^2T}{dy^2} + \alpha \frac{dT}{dy} - \beta T = -\beta T_0, \quad y > 0;
\]

where we assume the leading edge of the combustion zone to be at the point \( y = 0 \). The relative oxygen concentration in zone I is assumed to maintain the constant value \( \epsilon \):

\( \eta(y) = \epsilon, \quad y > 0. \)

Zone II is the combustion region in which the high temperature reaction between oxygen and the carbon residue takes place. Heat loss is assumed to be negligible in this zone, so that \( L(T) = 0 \) throughout zone II. We assume that the trailing edge of the combustion zone is at \( y = \hat{y} \), the value of which must be determined. Hence in zone II, we have:

\[
\frac{d^2T}{dy^2} + \alpha \frac{dT}{dy} = -\frac{\beta}{(T+460)} , \quad \hat{y} < y < 0,
\]

and

\[
\frac{d\eta}{dy} = -\frac{\beta}{(T+460)} , \quad \hat{y} < y < 0.
\]

Note that these two equations are coupled by the reaction rate function. Later the reaction rate for the oxygen equation will have to be modified.

Zone III is behind the combustion region. In this zone, the temperature
decreases to that of the external surroundings. The heat generation term is set equal to zero throughout zone III. Hence equation (8) takes the form:

\[
\frac{d^2T}{dy^2} + \alpha \frac{dT}{dy} - \beta T = - \beta T_e, \quad y < \hat{y}.
\]

Relative oxygen concentration has the constant value 1:

\[
\eta(y) = 1, \quad y < \hat{y}.
\]

Let \( T_j \) denote the solution to the temperature equation in the \( j \)-th zone for \( j = I, II, III \). The conditions that we want the solutions to satisfy are the following:

(i) \( \lim_{y \to \infty} T_I(y) = T_I, \)

(ii) \( \lim_{y \to \infty} T_{II}(y) = T_e, \)

(iii) \[
\frac{dT_{II}}{dy} \bigg|_{y=0} = \delta \quad (\delta = 0 \text{ when the fuel concentration has reached its maximum value for some value of } y \geq 0),
\]

(iv) \( T_I(0) = T_{II}(0), \)

(v) \( T_{II}(\hat{y}) = T_{III}(\hat{y}), \)

(vi) \[
\frac{dT_{II}}{dy} \bigg|_{y=\hat{y}} = \frac{dT_{III}}{dy} \bigg|_{y=\hat{y}} \quad (\text{this condition cannot be satisfied automatically; it allows an iterative procedure to be employed for the determination of } T_{II}(0), \text{ the maximum temperature then becomes self-determinative}).
\]

Let \( \eta_j \) denote the solution to the oxygen equation in the \( j \)-th zone for \( j = I, II, III \). The conditions that we want the solution in zone II to satisfy are:

a) \( \eta_{II}(0) = \varepsilon \) [this condition cannot be satisfied for equation (9); it will necessitate a modification of the reaction rate for the oxygen equation],

b) \( \eta_{II}(\hat{y}) = 1 \) (this condition will be used to determine the value of \( \hat{y} \)).

**Solutions to the Problem**

Because of the nonlinear nature of the reaction rate function, we shall
eventually have to resort to numerical approximations to our solutions in zone II. Before doing so, we shall present analytical expressions for the solutions there in the form of nonlinear integral equations obtained by Lagrange's method of variation of parameters (Saaty and Bram 1964).

**Solutions to the Temperature Equation**

Let $\gamma = \sqrt{\alpha^2 + 4\beta}$.

The general solution of the temperature equation in zone I is

$$T_1(y) = Ce^{-((\alpha+\gamma)/2)y} + De^{((\gamma-\alpha)/2)y} + T_i,$$

where $C$ and $D$ are arbitrary constants.

For zone II, the general solution of the temperature equation is

$$T_{II}(y) = Ae^{-\alpha y} + B + \frac{\Omega}{\alpha} e^{-\alpha y} \int_0^y \eta(\xi) e^{\alpha \xi} - \frac{\beta}{T(\xi)+460} d\xi$$

$$- \frac{\Omega}{\alpha} \int_0^y \eta(\xi) e^{-\frac{\beta}{T(\xi)+460}} d\xi,$$

where $A$ and $B$ are arbitrary constants, and the lower limits of integration in both integrals are taken to be zero since we shall be imposing conditions at the fixed boundary $y = 0$ of zone II.

The general solution of the temperature equation in zone III is

$$T_{III}(y) = Ee^{-((\alpha+\gamma)/2)y} + Fe^{((\gamma-\alpha)/2)y} + T_e,$$

where $E$ and $F$ are arbitrary constants.

We now see what the implications are of conditions (i) - (vi) on the above solutions.

Condition (i) implies that $D = 0$.

Condition (ii) implies that $E = 0$.

Condition (iii) implies that $A = -\delta/\alpha$.

Condition (iv) implies that $C = B - T_i - \delta/\alpha$.

Condition (v) implies that

$$F = e^{-((\alpha-\gamma)/2)y} \left( B - T_e - \frac{\Omega}{\alpha} e^{\frac{\gamma}{2}} - \frac{\beta}{T(\xi)+460} d\xi \right)$$

$$+ e^{-((\alpha+\gamma)/2)y} \left( \frac{\Omega}{\alpha} \int_0^y \eta(\xi) e^{\alpha \xi} - \frac{\beta}{T(\xi)+460} d\xi - \frac{\delta}{\alpha} \right).$$
Condition (vi) implies that

\[ F = \frac{2}{\gamma - \alpha} e^{-((\alpha + \gamma)/2)y} \left( \delta - \Omega \int_0^y \eta(t) e^{\alpha \xi - \tilde{B}/(T(\xi)+460)} d\xi \right) \]

After imposing conditions (i) − (iii), the solutions take the forms:

\[ T_I(y) = C e^{-((\alpha + \gamma)/2)y} + T_i, \]

\[ T_{II}(y) = -\frac{\delta}{\alpha} e^{-\alpha y} + B + \frac{\Omega}{\alpha} e^{-\alpha y} \int_0^y \eta(t) e^{\alpha \xi - \tilde{B}/(T(\xi)+460)} d\xi, \]

\[ T_{III}(y) = F e^{((\gamma - \alpha)/2)y} + T_e. \]

The procedure that we used to impose conditions (iv) − (vi) is to guess an initial value for B, compute the temperature and oxygen profiles using the corresponding values for C from condition (iv) and F from condition (v), then use condition (vi) to generate a new estimate for B. This can be done by considering the difference between the two values of F obtained from conditions (v) and (vi) corresponding to each estimate for B, that is, by considering the function

\[ f(B) = e^{((\alpha - \gamma)/2)y} \left( B - T_e - \frac{\Omega}{\alpha} \int_0^y \eta(t) e^{-\tilde{B}/(T(t)+460)} d\xi \right) \]

\[ + e^{-(\alpha + \gamma)/2)y} \left( \frac{\Omega(\gamma + \alpha)}{\alpha(\gamma - \alpha)} \int_0^y \eta(t) e^{\alpha \xi - \tilde{B}/(T(\xi)+460)} d\xi - \frac{2\delta}{\gamma - \alpha} \right). \]

The desired value of B is the zero (if any) of f(B). It is possible to choose values for the parameters \( \delta, \alpha, \gamma, \Omega, \) and \( T_e \) so that f(B) has no zero. Since \( T_{II}(0) = B - \delta/\alpha \), a reasonable initial guess for B is to set B equal to the anticipated maximum temperature for the combustion process (assuming that \( |\delta/\alpha| \) is small). We have found the bisection method to be satisfactory for locating zeros of f(B).
Modification of the Oxygen Equation, and the Resulting Solution

If we solve the equation \( \frac{d\eta}{dy} = -\rho \eta e^{-B/(T+460)} \) for the oxygen concentration in zone II, we obtain the solution

\[ \eta(y) = e^{-\rho \int_0^y e^{-B/(T(\xi)+460)} d\xi}. \]

Hence \( \eta(0) = 1 \), and it is impossible to satisfy condition (a).

Following a procedure analogous to that of Warren (1960), we modify the oxygen concentration function by simply subtracting a constant so that condition (a) is satisfied, that is, we set

\[ \eta_\Pi(y) = e^{-\rho \int_0^y e^{-B/(T(\xi)+460)} d\xi} (1 - \epsilon). \]

Thus the continuity of \( \eta_I \) and \( \eta_\Pi \) at \( y = 0 \) is achieved. The function \( \eta_\Pi \) differs from the original function \( \eta \) only by the subtraction of a constant, hence the derivatives of both functions are the same although the two functions satisfy different differential equations. The differential equation for oxygen concentration corresponding to the modified oxygen concentration function \( \eta_\Pi \) is

\[ \frac{d\eta}{dy} = -\rho(\eta + 1 - \epsilon) e^{-B/(T+460)}. \]

The value of \( \dot{y} \) is determined by condition (b).

Numerical Approximation

The numerical integration of \( \eta_\Pi \) and \( T_\Pi \) proceeds from right to left, starting at \( y = 0 \). Values for \( \eta_\Pi \) and \( T_\Pi \) are computed on a discrete set of points \( y_j \): \( \ldots < y_n < \ldots < y_2 < y_1 < y_0 = 0 \).

The general formulas used for computing \( \eta_\Pi(y_n) \) and \( T_\Pi(y_n) \) are:

\[ \eta_\Pi(y_n) = e^{-\rho \sum_{j=1}^n (y_j - y_{j-1})} e^{-B/(T(y_{j-1})+460)} (1 - \epsilon), \]

and

\[ T_\Pi(y_n) = B - \frac{\delta}{\alpha} e^{-\alpha y_n} + \frac{\Omega}{2\alpha^2} e^{-\alpha y_n} \sum_{j=1}^n (\eta(y_j)) \]
\[ + \eta(y_{j-1}) (e^{\alpha y_j} - e^{\alpha y_{j-1}}) \left( \frac{-B}{(T(y_{j-1})+460)} \right) \]

\[ - \frac{\Omega}{2\alpha} \sum_{j=1}^{n} (\eta(y_j)) \]

\[ + \eta(y_{j-1}) (y_j - y_{j-1}) \left( \frac{-B}{(T(y_{j-1})+460)} \right) . \]

The values of \( \eta_\Pi(0) = \epsilon \) and \( T_\Pi(0) = B - \frac{\delta}{\alpha} \) are assumed to be given initially.

A step size of \( \Delta y = y_j - y_{j-1} = .01 \) has been found to be satisfactory for the above numerical integration procedure for temperatures in the range encountered in the oil shale retorting process. The procedure continues until a value of \( y_n \) is reached so that \( \eta_\Pi(y_n) \equiv 1 \). An iterative procedure, such as Newton’s method, can then be used to obtain a refined estimate of \( \hat{y} \) so that \( \eta_\Pi(\hat{y}) \approx 1 \).

**Example**

An example of a temperature profile generated by the temperature and oxygen equations in zones I, II, and II is shown in figure 9. The values used for the parameters in this example are: \( \alpha = .5405, \gamma = 1.2835, \delta = 0, \Omega = 1,162,075,000, B = 1,200, B = 25,000, T_i = 26, T_e = 26, \rho = 2,000,000, \epsilon = .1 \).

After the iteration for the value of \( B \) based on condition (vi) converged, the new value for \( B \) and the corresponding values for \( y, C \) and \( F \) are: \( B = 1,199.27, \hat{y} = -1.88956, C = 1,173.27, F = 1,817.39 \).

The temperature profile shown in figure 9 is of the same general shape as the schematic temperature distribution presented by Thomas (1963); however, it differs somewhat from temperature profiles that are typical for the 150-ton oil shale retort. A temperature profile based on actual data corresponding to an experimental run on the 150-ton retort is presented in the next section.

**THE OIL SHALE RETORT MODEL**

The kinetics model can be combined with the temperature profile model to construct a mathematical model of an oil shale retort. The procedure for combining the two models previously discussed is as follows.

We first obtain a temperature profile that is representative of the physical data for the situation that we wish to simulate. The retort is con-
Figure 9—Example of temperature profile generated by model.
sidered to be subdivided into uniform subintervals, say $\Delta x$ feet per subinterval. The temperature profile is initially positioned so that the leading edge of the combustion zone, $y = 0$, is at the top of the retort, $x = 0$, at the beginning of the simulated run, $t = 0$. As simulation time advances in increments of $\Delta t$, the temperature profile advances down the retort in distance increments of $v\Delta t$. The average temperature (ahead of the combustion zone) for each subinterval is computed for each step. Values of the specific rate constants for thermal decomposition system II are then calculated using the values of empirical constants in the Arrhenius equation shown in table 1. Those rate constants are used to compute concentration values of kerogen, bitumen, oil and gas, and carbon residue for each time step using the differential equations for thermal decomposition system II. (At higher temperatures, it is necessary to take smaller time steps to maintain numerical stability.) Only the gas and oil products that are produced ahead of the combustion zone are recovered, hence we need use only the zone I portion of the temperature profile for simulating the retorting process.

**Example**

Using values for the parameters in the temperature and oxygen equations based on physical data corresponding to an experimental run on the 150-ton retort, we can simulate the retort run with the mathematical model. The data used in this example correspond to experimental run number 2 on the 150-ton retort (Harak, Dockter, and Carpenter 1971; Harak, Dockter, Long, and Sohns 1971). Data values were taken from Harak, Dockter, and Carpenter (1971), Harak, Dockter, Long, and Sohns (1971), and additional unpublished information provided by personnel at the Laramie Energy Research Center. Values of the reaction rate coefficient $\hat{A}$ and exponent $B$ were assigned arbitrarily to produce a temperature profile with maximum temperature and combustion zone width of the general magnitudes observed in the experimental data. The resulting values for the parameters are: $\alpha = 5.195$, $\gamma = 5.272$, $\delta = 0$, $\Omega = 11,943,300,000$, $B = 1,200$, $\overline{B} = 25,000$, $T_i = 26$, $T_e = 26$, $\rho = 2,000,000$, $\epsilon = .1$.

After the iteration for the value of $B$ based on condition (vi) converged, the new value for $B$ and the corresponding values for $y$, $C$, and $F$ are: $B = 1,199.69$, $\hat{y} = -1.13012$, $C = 1,173.69$, $F = 1,217.20$.

The corresponding temperature profile is presented in figure 10. A comparison of this profile with the one shown in figure 9 reveals that pre-combustion heating occurs more abruptly and post-combustion cooling occurs more gradually in the latter example than in the previous one. Such behavior is more typical of temperature profiles observed during experimental runs on the 150-ton retort [see fig. 11, reproduced from Harak and others (1971) by permission].
Figure 10—Temperature profile generated by model with parameters based on physical data for retort.
Figure 11.—Thermocouple arrangement and temperature history of level 4, run 9, 150-ton retort.
The above coefficients for $T_1$ were used in the mathematical model to simulate experimental run 2. The model run resulted in a computed estimation that 78.44 percent of the total organic material initially present should be recovered as oil and gas produced during the retorting run. The experimental run actually produced 62.2 percent of the organic material in the form of oil (Harak, Dockter, and Carpenter 1971; Harak, Dockter, Long, and Sohns 1971); gas produced was either recycled or vented to the stack (see fig. 8). Hubbard and Robinson's data (1950) indicate that 10 to 20 percent (depending upon temperature) of the organic material should be produced as gas, hence the model's production estimate is not incompatible with the experimental value.

**Utility of the Model**

Once the model's estimates have been brought into fair agreement with experimental results for a run on the retort, the model can be used to study the effects of varying the retorting parameters. In this way, the model can serve as an analytical tool to study operating procedures for the 150-ton retort.

The model is limited in that (among other things) it does not account for the effects of carbonate decomposition during pyrolysis of oil shale (Jukkola and others 1953) or low-temperature oxidation of hydrocarbons occurring in the retort ahead of the combustion zone (Cummins and Robinson 1972; Dabbous 1971).

**SUMMARY**

A mathematical model of a 150-ton oil shale retort has been developed. The model naturally separated into two principal components: a model of the kinetics of oil shale pyrolysis and a model of the retorting combustion process.

A system of thermal decompositions has been presented that provides a description of the mechanism of oil shale pyrolysis. That system consists of two first-order reactions and three second-order reactions. Values computed for the specific rate constants were found to exhibit a temperature dependence that is in good agreement with the Arrhenius equation, over the temperature range of the data used in the study.

A mathematical model of the combustion process is described by a pair of nonlinear differential equations for temperature distribution and oxygen concentration, coupled by a reaction rate function of the Arrhenius type. Analytical expressions for the solutions of those equations were given in the form of nonlinear integral equations. A numerical method for evaluation of the analytical expressions was presented.
An example of a simulated retort run was presented using values for the parameters in the model that are based on physical data for an experimental retort run. The simulation estimates obtained were in generally good agreement with the experimentally observed results for that run.

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A Mathematical Model of an Oil Shale Retort


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