WATER POLLUTION POTENTIAL OF SNOWFALL ON

SPENT OIL SHALE RESIDUES

by

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SECTION I

CONCLUSIONS

8. The dissolved solids concentration in snowmelt water is increased significantly by contact with oil shale residue, but not as much as in runoff from rainfall.
9. The chemical quality of surface runoff water from melting snow on oil shale residue may be estimated by procedures developed in this report.
10. The long contact period associated with snowmelt results in water percolation into a bed of oil shale residue and subsequent saturation.
11. Saturation eliminates compaction of oil shale residue.
12. Weathering of oil shale residue increases the tendency for percolation to occur.
13. Percolation caused by snowmelt may result in creep and slides.
14. Water which percolates through a bed of oil shale residue is very high in total dissolved solids.
15. Both the composition and concentration of dissolved solids in snowmelt runoff water from oil shale residue change with the cumulative volume of runoff.
16. Precipitation in the form of snow will not all appear as runoff.
17. The overland flow water quality model developed in this report is applicable to runoff from both rainfall and snowfall on oil shale residue.
18. Natural snow has a negligible dissolved solids concentration.
19. Compaction reduces the quality of runoff from rainfall and tends to be reduced by snowfall in at least the top few feet of depth.
20. The oil shale retorting residue need not be saturated for percolation from snowmelt to occur.

SECTION II

RECOMMENDATIONS

A complete soil mechanics study should be made to determine the physical properties of uncompacted, water saturated oil shale residue from above-ground retorting. The results of this soil mechanics study should be used to estimate the stability of oil shale residue piles that may be as high as 1,000 feet.

As far as water quality of the runoff is concerned, efforts to control the quality of the runoff from rainfall should have priority over efforts to control the quality of the runoff from snowfall. On the other hand, percolation water from snowfall should not be permitted to mingle with natural waters of better quality.

Research should be continued on applying the overland flow water quality model developed in this report to other high priority water quality research areas such as irrigation, runoff from cattle feedlots, and to natural precipitation on highly leachable natural soils. The results of this proposed research should be used to improve the quality of irrigation return flows, cattle feedlot runoff, as well as natural runoff from highly leachable natural soils.

Detailed information should be obtained in the oil shale areas with regard to the total precipitation and intensity (as a function of time) of each rainstorm. The same information should be obtained with regard to the total runoff and intensity of runoff of each snowstorm. This information should be used in conjunction with the equations in this report to predict the total water quality effect of oil shale development by surface retorting on all streams and rivers in the oil shale areas.

Additional research, similar to that reported herein, should be carried out on native surface soils in the oil shale area.

Finally, prediction of the environmental impact of oil shale development should be accomplished by the matrix methods illustrated in reference 2.

SECTION III

INTRODUCTION

Most of the information that would ordinarily go in this section has
already been covered in reference 1, pages 5-14. Accordingly, this
information will not be repeated here. As is evident from its title,
reference 1 dealt with the water pollution potential of rainfall on
spent oil shale residues from above ground retorting. Because more
than half the precipitation in the oil shale area falls as snow, the
effects of snowfall on the residue and the resulting changes in water
quality are considered in this report.

The largest untapped supply of oil in the United States is in
oil shale. 11 million acres of oil shale land in the Green River
formation of Colorado, Wyoming, and Utah will be increasingly called
upon to supply petroleum demands.

Above ground retorting of oil shale generates vast amounts of
residue which pose a disposal problem. If 60% of the residue (a
maximum figure) could be used as mine fill, 40,000 tons per day would
still have to be disposed of on the surface by an operation producing
50,000 barrels of oil per day. The effect upon water quality in the
area would depend upon how the residue is placed.

OIL SHALE RESIDUE

Properties of 3 oil shale residues are given in reference 1. The
residue used for the snowfall experimentation described in this report
was from the TOSCO (The Oil Shale Corporation) II process. This black
material is composed of fine particles whose surface characteristics
cause unusual behavior when contacted with water.

When saturated, the residue slides easily. The long water contact
period that occurs during a period of snow melt may cause water to
percolate into the residue and saturate it to a depth of at least a
few feet. Possibly the residue may even become somewhat fluidized.
Unless properly restrained the residue piles may be hazardous.

PURPOSE AND SCOPE OF REPORT

The purpose of this project was to investigate the effects of
snowfall on oil shale residue from the TOSCO process and the subsequent
effects on water quality.

This project consisted of determining the concentration and composi-
tion of runoff from a spent oil shale pile during a period of snow melt
and the properties of the shale before the application of snow and after
it disappearance.

SECTION IV

WATER POLLUTION CONSIDERATIONS

Both settleable and nonsettleable suspended solids are of importance when considering the quality of surface runoff water. Because the low rate of runoff due to melting snow causes negligible settleable solids transport as compared with that caused by rainfall, only nonsettleable solids were considered in this study.

CONCENTRATION OF DISSOLVED SOLIDS

The concentration of dissolved solids in the snowmelt runoff is a function of the pertinent parameters of hydrology and characteristics of the oil shale residue. During a snowmelt event one would expect concentration to decrease from an initial value as a function of cumulative volume of runoff.

From equation 18 on page 18 of reference 1, the rate at which the concentration of dissolved inorganic solids decreases is probably a function of several hydrologic parameters such as the following:

$$-\frac{dc}{dv} = f(i, \nu, s, L, v) \tag{1}$$

where
c = concentration, mg/ℓ
i = intensity of snowmelt, inches/hour
ν = kinematic viscosity, ft^2/sec
s = slope of residue surface, dimensionless
L = length of overland flow, feet
v = cumulative volume of runoff, inches.

It is apparent that all the independent parameters on the right side of equation 1 are approximately constant for a given snowmelt event except v and i. Because i is dependent upon temperature, wind speed, cloud cover, and several other parameters, it fluctuates during a period of snowmelt.

Several relations have been developed to predict snowmelt intensity. One such relation is Light's theoretical equation (reference 3). Light showed that the rate of snowmelt i, in inches per hour, was dependent on wind velocity, air temperature, humidity, and elevation above mean sea level as well as air density and atmospheric pressure.

If it is reasonable to assume that the concentration will decrease at a decreasing rate as cumulative volume increases, then perhaps

$$-\frac{dc}{dv} \propto \frac{1}{v} \tag{2}$$

Equation 2 states that as the cumulative volume of snowmelt runoff v increases, the rate of change in concentration decreases, and ultimately as $v \to \infty$, $dc/dv \to 0$.

With the exception of v, all the independent parameters in equation 1 are related as follows (equation 11 on page 17 of reference 1) for $s \leq 0.1$:

$$\bar{D} = (9.70 \times 10^{-3}) \left(\frac{v i L}{s}\right)^{1/3} \tag{3}$$

where $\bar{D}$ = mean depth of flow, ft. At $20^{\circ}C$ ($68^{\circ}F$),

$$\bar{D} = (10^{-4}) \left(\frac{10 i L}{s}\right)^{1/3} . \tag{3A}$$

Equation 20 on page 19 of reference 1 states that the concentration of inorganic dissolved solids c, in mg/ℓ, varies inversely with $\bar{D}$ to some power. Perhaps then one could state that

$$\frac{dc}{dv} \propto \frac{1}{(\bar{D})^n} . \tag{4}$$

Combining equations 2 and 4 and defining a constant of proportionality K_1, one obtains

$$\frac{dc}{dv} = \frac{K_1}{v \bar{D}^n} . \tag{5}$$

Integration of equation 5 between the limits $c = c_0$ when $v = v_0$ and $c = c$ when $v = v$ gives

$$c = c_0 - \frac{K_1}{\bar{D}^n} \ell n \left(\frac{v}{v_0}\right) . \tag{6}$$

Substituting equation 3A into equation 6 and changing to $\log_{10}$ gives

$$c = c_0 - K_2 \left(\frac{s}{iL}\right)^{n/3} \log_{10} \left(\frac{v}{v_0}\right) \tag{7}$$

where s is now in % and

$$K_2 \equiv \frac{2.3 \, K_1}{(10)^{n/3} (10^{-4})^n} \tag{8}$$

and c_0 is the concentration corresponding to v_0. From equation 7, it is clear that c_0 is the concentration in the snowmelt runoff when $v = v_0$. The value of c_0 should depend upon the mass of salt deposited (by capillary action and evaporation; see page 55 of reference 1) on the residue surface before the snowfall. Therefore (from page 54 of reference 1),

$$c_o = f(\Delta\omega, \rho, k) \tag{9}$$

where

$$\Delta\omega = \omega_s - \omega \tag{10}$$

ω = surface moisture content of the residue before snowfall, cm^3/g
ω_s = saturation moisture content of the residue, cm^3/g
ρ = residue bulk density, g/cm^3
k = residue permeability, cm^2

ω_s and ρ are related by

$$\epsilon = \rho\omega_s \tag{11}$$

where ϵ = residue porosity, dimensionless.

Equation 50 on page 54 of reference 1 is

$$c \propto \exp (K_3 \Delta\omega) \tag{12}$$

where $K_3 = 10.34$ g/cm^3 for rainfall. Equation 53 on page 54 of reference 1 is

$$c \propto \rho/k \tag{13}$$

Combining equations 9, 12, and 13, one obtains

$$c_o = K_4 \frac{\rho}{k} \exp (K_3 \Delta\omega) \tag{14}$$

where K_4 is a constant.

SECTION V

PROCEDURE AND EQUIPMENT

Pilot Studies

A pilot study program was undertaken at the Colorado State University Research Campus to investigate the effects produced by snow on oil shale residue from the TOSCO process. The objective of the study were:

1. To determine the quality and quantity of total runoff from spent shale piles following natural and artificial snowfall.
2. To determine the properties of the residue before application of snowfall, then during and after the process of snowmelt.

The model had the following characteristics (see page 27 of reference 1):

1. Approximately 68 tons of TOSCO unweathered spent shale were placed in a pile 80 feet long, 8 feet wide at the bottom, and 12 feet wide at the top, with a maximum depth of 2 feet. The surface of the shale had a 0.75 percent slope.

2. A four-inch layer of sand was placed below the shale to serve as a drain for any percolation water.

3. An impermeable plastic barrier was placed below the sand filter and along the sides of the facility to insure that no percolation losses occurred.

4. A three-inch perforated plastic pipe was placed in the sand filter to collect any percolation water and divert it to a 42 gallon drum for storage.

5. Artificial snow was generated with a compressor and expansion nozzle of the type used on ski slopes. The position of the nozzle was changed at intervals during a snowfall event to equalize the depth of snow cover on the residue surface. (see Appendix A).

6. The depth and moisture content of the snow was measured after application. The rate and cumulative volume of surface runoff was measured during the period of snowmelt.

7. Three access tubes for use of a neutron moisture probe were installed in the middle of the shale at 20, 40, and 60 feet from the upstream end of the facility.

8. Three thermistors were installed 60 feet downstream from the upstream end to monitor the temperature of the air and the shale at depths of five inches and fifteen inches below the surface.

9. A trailer was located at the downstream end of the facility to
    serve as an on site laboratory.

Shown in Figures V-1 and V-2 are pictures taken during use of the
facility.

Chemical Analysis

The ions most prevalent in water which has contacted oil shale
residue are Na^+, Ca^{++}, Mg^{++}, HCO_3^-, and $SO_4^=$. The concentrations of
these ions were determined along with H^+, K^+, and Cl^-, which were
present in much smaller concentrations. Other ions that may appear
in water contacted with oil shale residue are given in Table XV on
page 69 of reference 1.

The concentrations of H^+, Na^+, Ca^{++}, and Cl^- were determined
using specific ion activity electrodes (see pages 89-94 of reference 1).
Na^+ and Ca^{++} concentrations were verified using atomic absorption
spectrophotometry. Mg^{++} concentrations were determined using atomic
absorption. K^+ concentration was determined using a flame photometer.
$SO_4^=$ concentration was determined using gravimetric analysis and HCO_3^-
concentration was determined with a recording titrator. The procedure
used for $SO_4^=$ and HCO_3^- is found in reference 4.

List of analytical instruments used:

1. Orion model 801 digital pH meter.
2. Orion specific ion electrodes.
3. Model 290 Perkins Elmer Atomic Absorption Unit.
4. Beckman Na^+ - K^+ Flame Photometer.
5. Sargent Welch recording titrator.
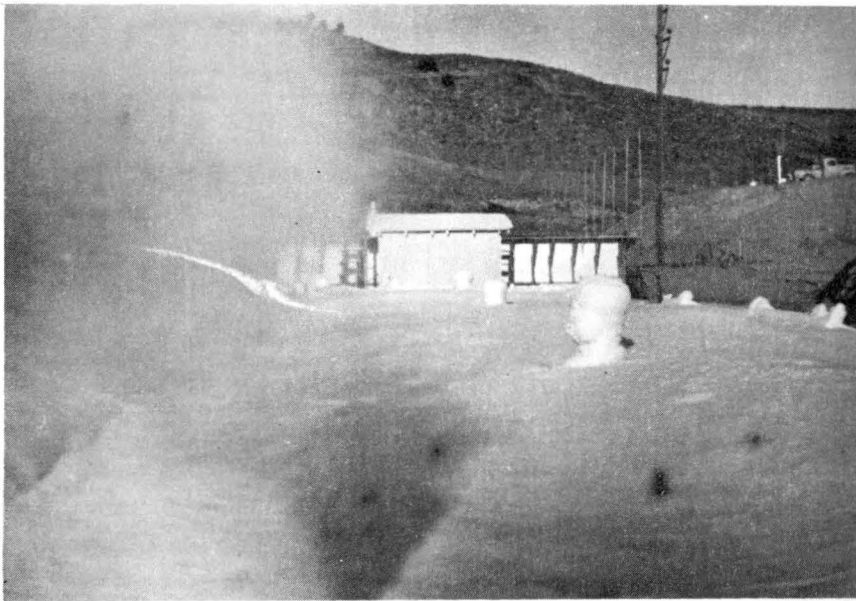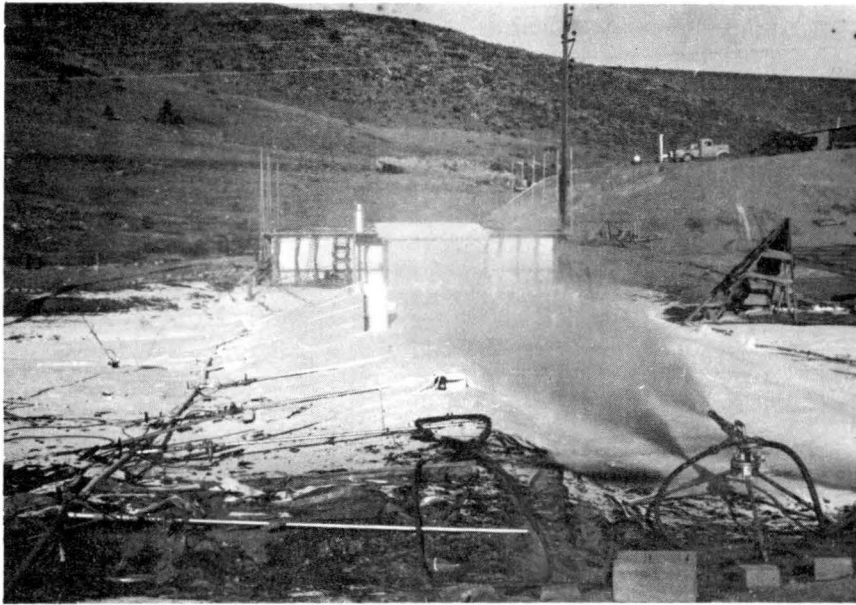
FIGURE V-1. Application of artificial snow.
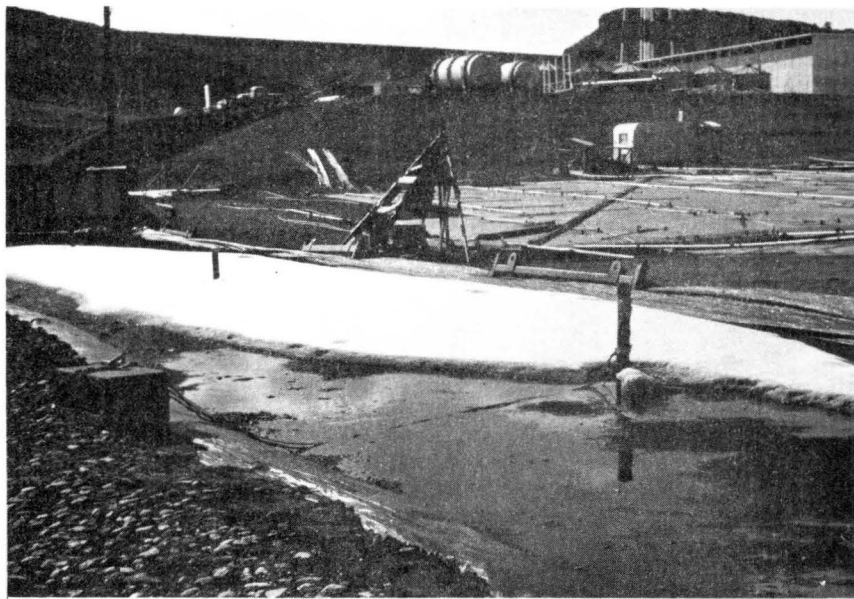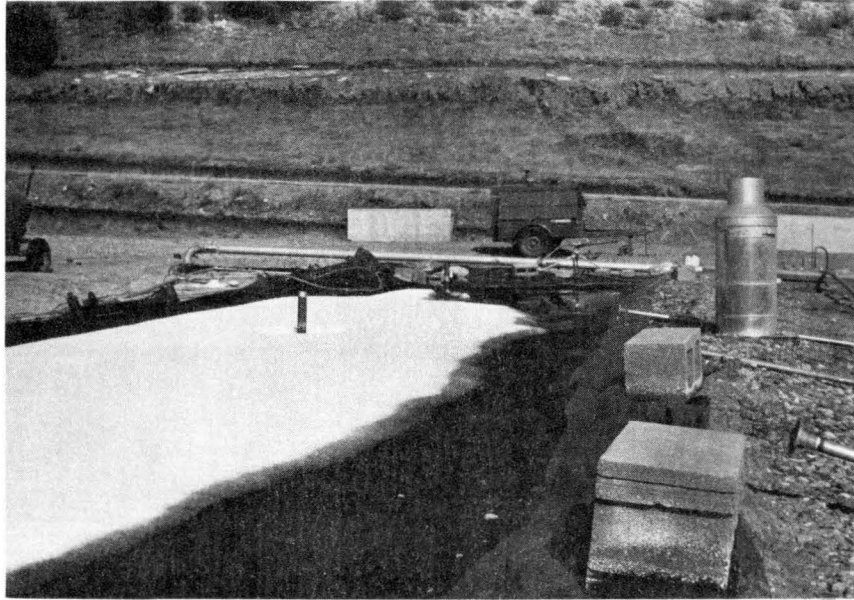
FIGURE V-2. Melting snow and resulting runoff.

SECTION VI

EXPERIMENTAL DATA AND RESULTS

Four experiments were conducted on the snowfall-runoff facility. Three of these were simulated snow storms and one was natural. Long periods of freezing weather followed by long periods of above freezing weather made it impossible to conduct any more experiments within the duration of the project.

The in-place density of the surface layer of shale for these experiments was 1.20 g/cm^3. The overall in-place density was 1.36 g/cm^3. The permeability of the residue may be calculated using the following equation (equation 44 on page 38 of reference 1):

$$k = \frac{\phi^2 \, \varepsilon^3 \, M_g^2}{(36\kappa T)(1 - \varepsilon)^2 \, \sigma_g^{\ln \sigma_g}} \tag{1}$$

where

k = permeability, cm^2
36 = a pure number, dimensionless
T = tortuosity, ($T = 2$), dimensionless
κ = a dimensionless constant, ($\kappa = 2.36$)
ε = porosity, dimensionless
ϕ = shape factor, dimensionless
M_g = Geometric mean size, cm
σ_g = Geometric standard deviation of the particle size distribution, dimensionless

Porosity may be calculated with the relation,

$$\varepsilon = 1 - \frac{\rho}{\rho_s} \tag{2}$$

where

ρ = in-place density, g/cm^3
ρ_s = solids density, g/cm^3.

For the TOSCO oil shale retorting residue (see Table V on page 43 of reference 1):

ϕ = 0.097
M_g = 0.007 cm
σ_g = 3.27
ρ_s = 2.46 g/cm^3

Using the previously mentioned value of $\rho = 1.20$ g/cm^3, substitution of this value into equation 2 gives $\varepsilon = 0.512$. Substitution of this value of ε along with the above values for the other variables in equation 1 gives $k = 4 \times 10^{-10}$ cm^2.

Plots of total dissolved solids concentration versus cumulative volume of runoff were made for each snowfall run on semi-logarithmic paper. For each snowfall run, the experimental data plotted as a straight line of the form

$$c = \alpha_j - \beta_j \log_{10} (100v) \tag{3}$$

where α_j = constant for snowfall run j, mg/ℓ

β_j = constant for snowfall run j.

Equations 7 and 14 of Section IV can be combined to obtain,

$$c = K_4 \frac{\rho}{k} \exp (K_3 \Delta\omega)$$

$$- K_2 \left(\frac{s}{iL}\right)^{n/3} \log_{10} \left(\frac{v}{v_o}\right) . \tag{4}$$

Comparing equations 3 and 4, it appears that $v_o = 0.01$ inches and that

$$\alpha_j = K_4 \frac{\rho}{k} \exp (K_3 \Delta\omega_j) . \tag{5}$$

Also, apparently,

$$\beta_j = K_2 \left(\frac{s}{i_j L}\right)^{n/3} . \tag{6}$$

In order to obtain the values of K_4, K_3, K_2, and n in equations 5 and 6, it will be necessary to use the experimental results of snowfall tests 2 and 3 given in Appendix B. It will be noted that $\Delta\omega_2 = 0$ cm^3/g for all the data of snowfall test 2. Using the data of test 2 only, c was plotted versus $\log_{10}(100v)$ in order to evaluate α_2 and β_2. Therefore, when $v = 0.01$ inches, $100 v = 1$, and $\log (100v) = 0$, so that $\alpha_2 = K_4 \rho/k$ when $\Delta\omega_2 = 0$ cm^3/g. Knowing α_2, ρ and k, K_4 was calculated to be 7.24×10^{-8}. The slope of this plot was β_2.

Also $\Delta\omega_3 = 0.233$ cm^3/g for all the data of snowfall test 3 only. Using the data of test 3 only, c was plotted versus $\log (100v)$ in order to evaluate α_3 and β_3. Again, when $v = 0.01$ inches, $\alpha_3 = K_4 (\rho/k) \exp (K_3 \Delta\omega_3)$. Knowing α_3, K_4, ρ, k, and $\Delta\omega_3$, K_3 was determined to be 1.8 g/cm^3. The slope of this plot was β_3. From equation 6,

$$\beta_2 = K_2 \left(\frac{s}{i_2 L}\right)^{n/3} \quad \text{and}$$

$$\beta_3 = K_2 \left(\frac{s}{i_3 L}\right)^{n/3}. \text{ Knowing } \beta_2, \beta_3, s, L, i_2 \text{ and } i_3, \text{ these}$$

last 2 equations were solved simultaneously to obtain $K_2 = 3,720$ and $n/3 = 2.26$.

Substituting the above values of K_4, K_3, K_2, $n/3$, and v_o into equation 4 gives

$$c = 7.24 \times 10^{-8} \frac{\rho}{k} \exp (1.8\Delta\omega)$$

$$- 3{,}720 \left(\frac{s}{iL}\right)^{2.26} \log_{10} (100v) \quad . \tag{4A}$$

Equation 55 on page 55 of reference 1 is

$$c = 2.15 \times 10^{-2} \frac{\rho}{k} \frac{[\exp(10.33\Delta\omega)] (s/iL)^{2.3}}{\exp (2.3t^{1/3})} \tag{7}$$

where t is the time after rainfall starts in hours. Equation 7 is for rainfall. Also

$$v = it \quad . \tag{8}$$

Equations 4A and 7 show that for both snowfall and rainfall, c increases as ρ/k and $\Delta\omega$ increase, and that c decreases as v increases.

Equation 4A can be written

$$\log_{10} (100v) = \frac{7.24 \times 10^{-8} (\rho/k) \exp (1.8\Delta\omega) - c}{3{,}720 (s/iL)^{2.26}} \tag{4B}$$

so that a plot of $\log_{10}(100v)$ versus the quantity on the right hand side of equation 4B should be a straight line on semi-log graph paper for all the observed concentrations in the snowmelt runoff. Equation 4B is plotted in Figure VI-1 along with all the experimental snowmelt data. The correlation coefficient for Figure VI-1 is 0.996.

As an example of the use of Figure VI-1, consider the data for test 3 given in Appendix B. For this test, the various parameters had the following values:

$\rho = 1.2$ g/cm^3, $k = 4 \times 10^{-10}$ cm^2, $\Delta\omega = 0.233$ cm^3/g, $s = 0.75\%$, $i = 0.0318$ in/hr, and $L = 80$ ft.

Therefore the quantity

$$\frac{7.24 \times 10^{-8} \left(\frac{\rho}{k}\right) (\exp 1.8 \Delta\omega) - c}{3{,}720 \left(\frac{s}{iL}\right)^{2.26}} \quad \text{becomes}$$

$$= \frac{331 - c}{234} = \log_{10} (100v).$$
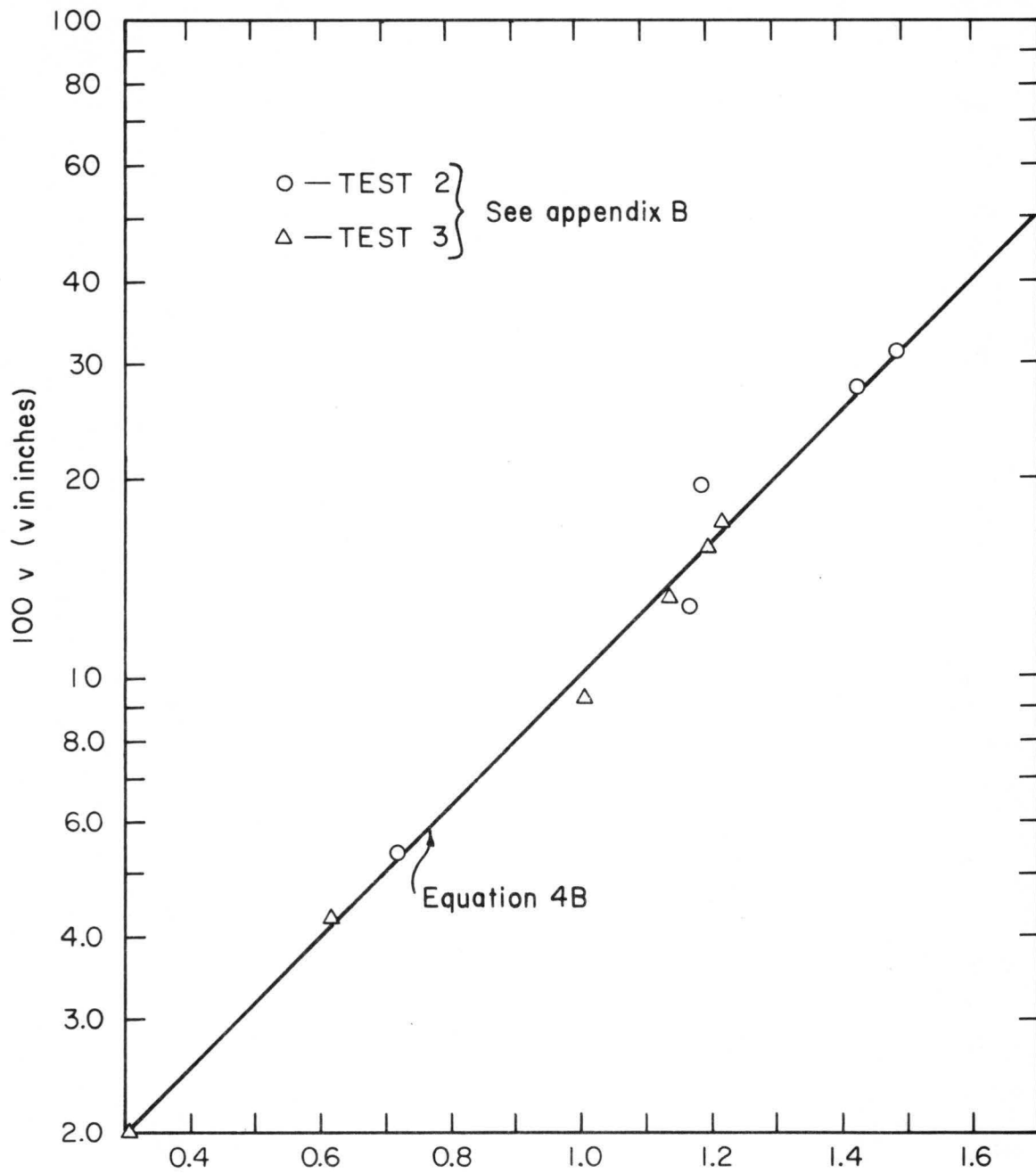
FIGURE VI-1. Plot of equation 4B with snowfall data.

The major constituents in the surface runoff from melting snow were Ca^{++}, Mg^{++}, Na^+, $SO_4^=$, and HCO_3^-. The composition of the runoff water varied with cumulative volume of runoff. The percentage of Na^+ and Mg^{++} decreased as the percentage of Ca^{++} increased during a snow melt event. The major part of the anion concentration was $SO_4^=$ with HCO_3^- variable between 0.2 and 1.5 me/ℓ, depending upon contact time. The longer contact time of the snowmelt water on the residue surface, the greater the HCO_3^- concentration. $SO_4^=$ concentration steadily decreased with increasing cumulative volume.

A plot of cation composition of snowmelt runoff is shown in Figure VI-2. Also shown, for comparison, is the cation composition of runoff from rainfall on oil shale retorting residue (Figure 26 on page 60 of reference 1). Arrows indicate direction of increasing cumulative volume. It will be noted that the composition of runoff from rainfall and snowfall is quite different, but tends to become less different as the cumulative volume of runoff increases.

Water Balance data are given in Table VI-1.

TABLE VI-1. WATER BALANCE DATA

Snowmelt event (test #)	Applied water, inches (applied as snow)	Water appearing as runoff, inches	Water which percolated and/or evaporated, inches
1	1.0	0.02	0.98
2	2.0	0.317	1.683
3	1.75	0.178	1.572

As shown in Table VI-1, only a fraction of the applied snow appeared as runoff. In the case of event 1, a significant part of the applied water may have been lost by sublimation during a three week period of cold, windy weather. In events 2 and 3, however, most of the difference between the volume of applied and runoff water could be attributed to percolation into the residue bed.

The total amount of water applied as snow was 4.75 inches, but 10.37 inches would have been required to completely saturate the bed if it had been initially dry. The saturation moisture content required to completely saturate the residue is 0.431 cm^3/g. At the beginning of test 3, the moisture content was 0.233 cm^3/g, so that the residue was 54.1% saturated. Still, (0.541 x 10.37 inches =) 5.6 inches would have been required to completely saturate the residue whereas only 1.75 inches was applied (as snow) during test 3. Yet, percolation occurred during test 3 which indicates that the residue need not be saturated with water for percolation to occur.

Ultimately, most of the percolated water returned to the surface via capillary action during subsequent periods of drying. In the case of event 3, however, 44 gallons of water percolated entirely through

NOTES:

Concentration decreases in
    direction of **arrows**

Cumulative volume increases
in direction of arrows

Shift in run 3 is due to a
long water-surface contact
period during an over-
night freeze

① — Test 1

② — Test 2

③ — Test 3, 1st day

④ — Test 3, 2nd day

⑤ — Runoff from natural snow

⑥ — Percolated water sample
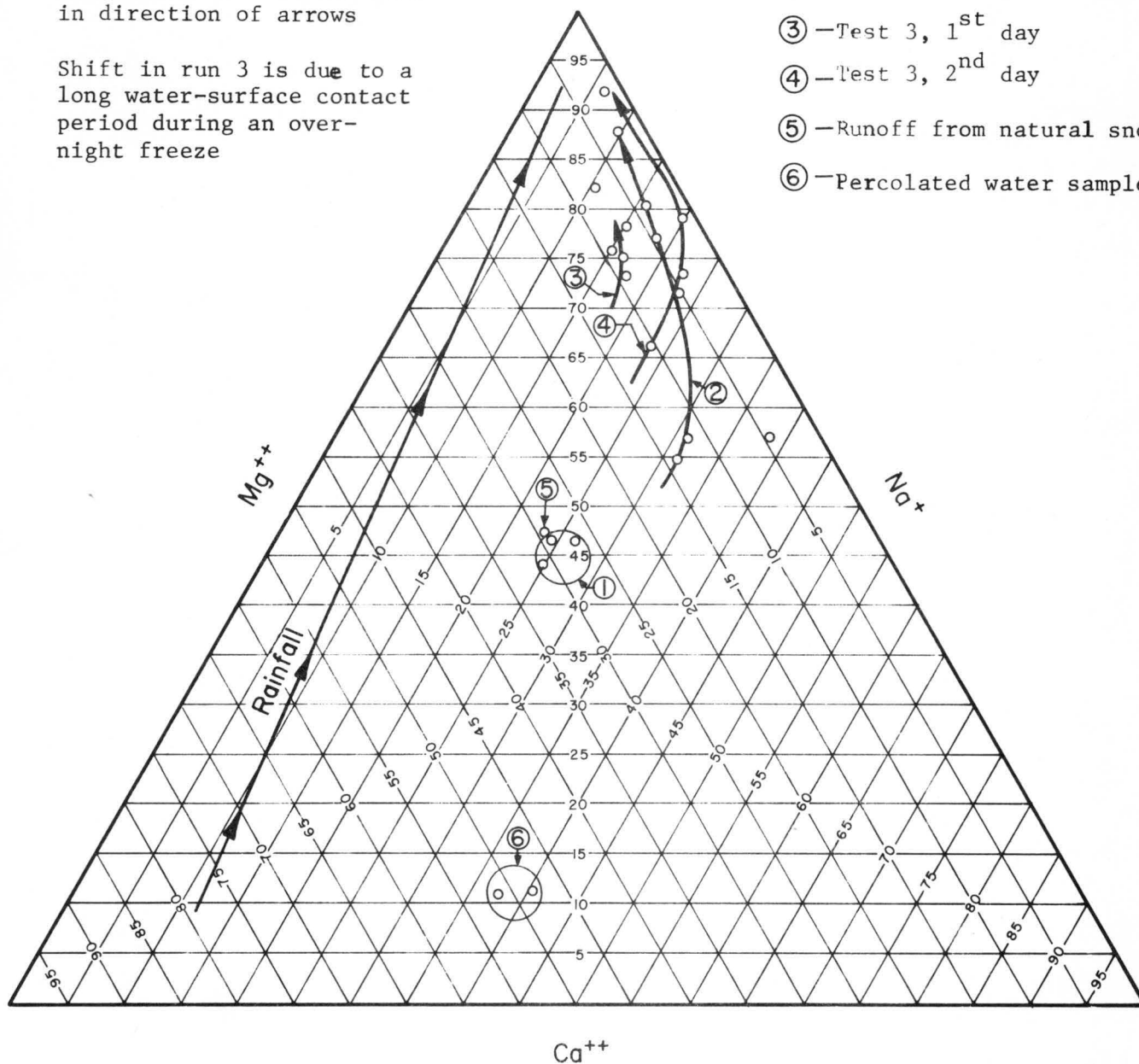
FIGURE VI-2. Trends in percentage composition of cations in
              runoff from melting snow on oil shale retorting
              residue.

the bed. When analyzed this water gave a dissolved solids concentration of ~20,000 mg/ℓ (see Appendix B).

The long water contact time occurring during a period of thawing greatly increases the tendency for water to percolate into the residue. The effect of this water on water quality in a spent shale disposal area could be significant.

Experiments show that the first water to percolate through a 4 foot depth of residue has a salinity of about 140,000 mg/ℓ. However, this concentration decreases rapidly and eventually appears to approach roughly 1,000 mg/ℓ (see Table VIII on page 48 of reference 1).

SECTION VII

DISCUSSION OF RESULTS

The first water to appear as runoff from precipitation on the oil shale residue surface carries the highest concentration of dissolved solids. The magnitude of this initial concentration is largely dependent upon the mass of salts deposited on the surface by capillary action and evaporation prior to the precipitation event. This mass of salts is in turn dependent on the mass of water which has percolated into the residue pile and the subsequent evaporation that returns the salt laden water to the surface. Thus the process of snowmelt increases the potential for capillary transport of salts by causing percolation into the shale piles. On the other hand, cold winter weather postpones drying of the residue bed. Probably the greatest mass of salts will appear on the surface in late spring after the residue bed has had time to dry to a considerable depth. Therefore, the first summer rainfalls will cause the greatest impact on water quality as far as precipitation runoff is concerned.

As developed in Section VI, equation 4A predicts the dissolved solids concentration as a function of various parameters. Given estimates of snowmelt intensity and the physical properties of the inplace residue, one can predict dissolved solids concentration as a function of the estimated cumulative volume of runoff, v.

By taking a simple conductance measurement of the runoff water, one can arrive at a reasonable estimate of TDS (total dissolved solids) by referring to the empirical relation shown in Figure VII-1. With this value of TDS one can arrive at an estimate of total cation concentration by referring to Figure VII-2. In general, for both rainfall and snowfall on oil shale retorting residue,

$$TDS = a + b \text{ (me/}\ell \text{ cations)}$$

$$= a' + b' \text{ (conductance at } 25^{\circ}C, \frac{\mu \text{ mho}}{cm}) \tag{1}$$

where values of a, b, a', and b' are given in Table VII-1.

TABLE VII-1. VALUES OF a, b, a', and b'

Type of precipitation	mg/ℓ		b, $\frac{mg/\ell}{me/\ell}$	b', $\frac{mg/\ell}{\mu \text{ mho/cm @}25^{\circ}C}$
	a	a'		
rainfall	1.7	-48.6	70.5	0.973
snowfall	0	0	77.5	0.725

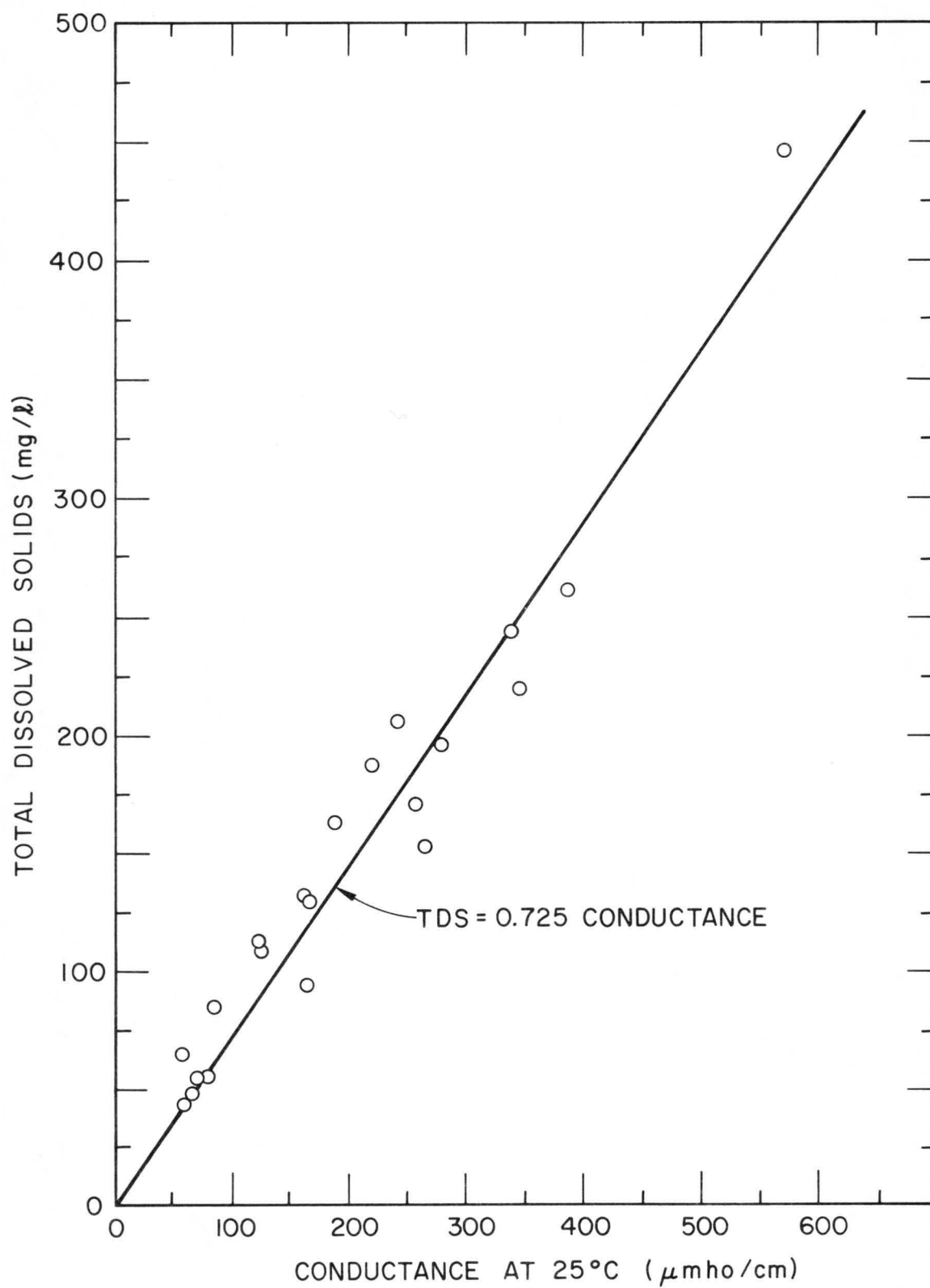(values for rainfall obtained from Figures 30 and 31 on pages 74 and 75 respectively of reference 1).

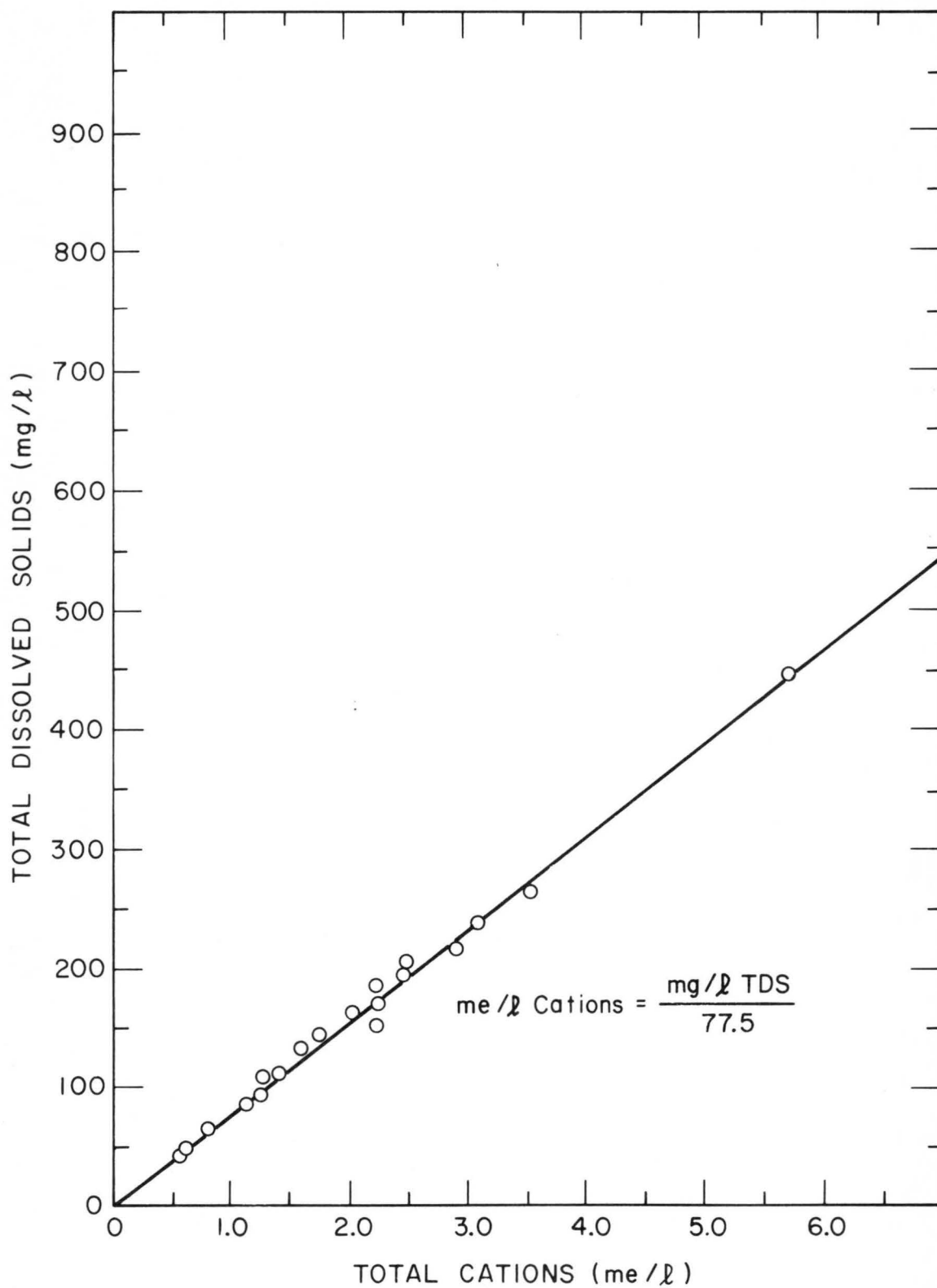FIGURE VII-1. Conductance vs total dissolved solids for
snowmelt runoff.

FIGURE VII-2. Total dissolved solids vs total cations for
snowmelt runoff.

Percolation Effects

It should be noted that freshly placed oil shale residue is fairly hydrophobic. When contacted with water for a long period of time however, percolation into the residue bed will begin to occur. Once saturated and redried, it will immediately become saturated again when contacted with water unless its capillary structure is disturbed. If the capillary structure is disturbed, it will again be hydrophobic. Thus if the residue bed is left undisturbed, each application of water will tend to increase the depth of saturation.

Hydrophobicity of the disturbed oil shale residue is probably due to a combination of physical phenomena. The residue particles are small and irregular and form a microscopically rough surface. This contributes to hydrophobicity by supporting water on millions of tiny projections, leaving the valleys between filled with nonwettable air capillaries. The low contact area minimizes adhesion between water and the surface. Residual hydrocarbons remaining on the particle surfaces also contribute to hydrophobicity by replacing hygroscopic hydroxl groups which are normally present on soil particles.

Saturation followed by drying causes the appearance of a capillary structure which, if undisturbed, facilitates water percolation into the residue. The capillary structure, however, does not cause total wetting of the residue. Hydrophobicity remains on a microscopic level and tiny bubbles remain occluded to the residue particles. Thus when saturation occurs on a macroscopic level, fluidization may occur via particle flotation.

As the above considerations would indicate, saturation tends to reduce the compaction of oil shale residue. The top three inches of the CSU rainfall-runoff facility had been mechanically compacted during the previous rainfall experiments to an in place density of 1.63 g/cm^3. Saturation, caused by snowmelt, reduced the density of this surface layer to 1.20 g/cm^3.

Comment

Equations 4A (snowfall) and 7 (rainfall) in Section VI both fit the observed precipitation data extremely well, as is commonly the case with empirical equations. However, it will be noted that the behavior of c with respect to the ratio s/iL is unexpectedly contradictory. Therefore, in order to resolve this conflict, a more fundamental approach has been attempted in the following Section VIII. While the resulting equations in Section VIII do not fit all the observed precipitation data as well as the aforementioned 2 empirical equations, it is believed that the development in Section VIII provides a better understanding of the effect of overland flow on water quality as well as providing a more general framework where more diverse types of overland flow water quality problems may be resolved. Finally, it is believed that more accurate predictions can be made using the results of the following Section VIII than the aforementioned 2 empirical equations, especially where the values of s and L are quite different.

In any event, the results of the following Section VIII provide an independent means of checking predictions made by equations 4A and 7 of Section VI.

SECTION VIII

AN OVERLAND FLOW WATER QUALITY MODEL

All of the equation numbers referred to in this section are equations in this section.

The following quantities are shown in the definition sketch (Figure VIII-1):

Q = water volume flow rate per unit time, ft^3/hour
M = rate of mass transfer across the oil shale residue—water interface per unit horizontal area per unit time, $mg/(ft^2)(hr)$
θ = slope of oil shale surface, degrees
$\Delta x \cos \theta$ = horizontal distance between sections i and i+1, feet
D = depth of flow, feet

Subscripts P, S, and E refer to precipitation, seepage (infiltration), and evaporation, respectively.

A water volume (per unit time) balance results in the following equation:

$$Q_i + Q_P = Q_S + Q_{i+1} + Q_E \qquad (1)$$

In order to develop a mass salt balance (per unit time), additional terms must be defined:

C = concentration, mg/ft^3
W = width, perpendicular to direction of flow, feet

$$C_i Q_i + C_P Q_P + M W \Delta x \cos \theta = C_{Si} Q_S + C_{i+1} Q_{i+1} \qquad (2)$$

If P is the intensity of precipitation in ft/hour, then

$$Q_P = P W \Delta x \cos \theta \qquad (3)$$

If S is the intensity of seepage in ft/hour, then

$$Q_S = S W \Delta x \cos\theta \qquad (4)$$

If E is the intensity of evaporation in ft/hour, then

$$Q_E = E W \Delta x \cos \theta \qquad (5)$$

For the total length of overland flow, L, in feet, then

$$R = P - S - E \qquad (6)$$
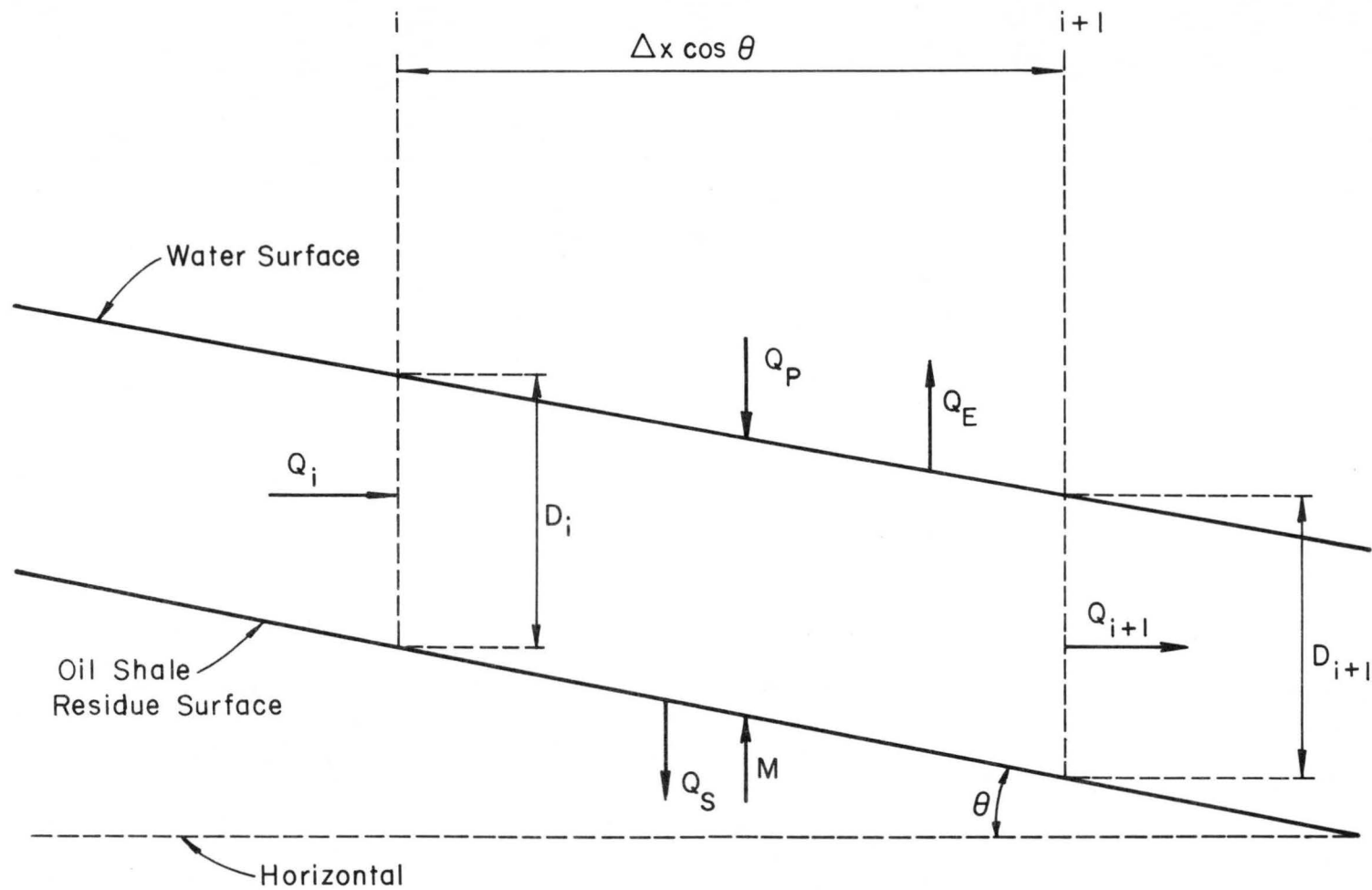
Figure $\underline{VIII}$ – 1. Definition Sketch for Overland Flow Water Quality Model

where R = intensity of runoff, ft/hour. Making stepwise calculations using equation 1, and substituting in equations 3, 4, 5, and 6, one obtains

$$Q_x = R \, W \, x \, \cos \theta \tag{7}$$

where Q_x is the runoff rate in ft^3/hour at a horizontal distance $x \cos \theta$ downstream from the beginning of overland flow.

Rainfall

For rainfall, a permissible approximation is that $Q_S = Q_E = S = E = 0$, so that combining equations 1, 2, 3, and 6 gives (for steady-state conditions)

$$C_{i+1} - C_i \simeq \frac{R \, W \, \Delta x \, (\cos \theta)(C_p - C_i)}{Q_{i+1}} +$$

$$+ \frac{M \, W \, \Delta x \, \cos \theta}{Q_{i+1}} \tag{8}$$

However, in general, $Q_{i+1} = Q_x$, so substitution of equation 7 into equation 8 gives

$$C_{i+1} = \frac{\Delta x}{x} \left(C_p + \frac{M}{R} \right) + C_i \left(1 - \frac{\Delta x}{x} \right) \tag{9}$$

Defining

$$X \equiv \frac{\Delta x}{x} \left(C_p + \frac{M}{R} \right) \tag{10}$$

and

$$Y \equiv (1 - \Delta x / x), \tag{11}$$

then

$$C_{i+1} = X + Y \, C_i \tag{12}$$

Because $C_0 = C_p$,

$$C_1 = X + Y \, C_p \tag{13}$$

Also

$$C_2 = X + Y \, X + Y^2 \, C_p \tag{14}$$

In addition,

$$C_3 = X + Y X + Y^2 X + Y^3 C_P \tag{15}$$

Finally,

$$C_4 = X + Y X + Y^2 X + Y^3 X + Y^4 C_P \tag{16}$$

In general, for $n \geq 1$,

$$C_n = X \sum_{j=0}^{j=n-1} Y^j + Y^n C_P \tag{17}$$

From equation 11 it is clear that $Y < 1$. Therefore, as n becomes large, $Y^n \rightarrow 0$. It is also true that

$$(1 - Y)^{-1} = 1 + Y + Y^2 + Y^3 + Y^4 + Y^5 + \cdots$$

if $Y^2 < 1$. Hence, equation 17 becomes, when n is very large,

$$C = X (1 - Y)^{-1} \tag{18}$$

Therefore,

$$C = C_P + M/R. \tag{19}$$

The total volume, V_P, of precipitation (in ft^3) at time t (for constant P) is

$$V_P = P W L t \tag{20}$$

where t is the time in hours.

Equation 19 could have also been obtained based on an overall volume and mass balance. However, one of the assumptions involved in the derivation of equation 19 is that M is constant (at a given time for a given slope) along the length L. The data from the simulated rainfall experiments show that this is true. M would not be expected to change with width. Therefore, it seems reasonable to assume that

$$\frac{dM}{d(V/W)} = \frac{-K}{(V/W)} \tag{21}$$

where K is a constant mass transfer coefficient for a given storm, $mg/(ft^2)(hr)$, and V is the volume of runoff for a given storm, in ft^3, at time t.

For rainfall, M appears to decrease to a constant value of M_0 corresponding to a total volume per unit width of V_0/W. Integrating equation 21 between the lower (initial) limits M = M at V = V and the upper (final) limits $M = M_0$ at $V = V_0$, one obtains

$$M = M_0 + K \ln (V_0/W) - K \ln (V/W) \qquad (22)$$

Substituting equation 22 into equation 19 gives

$$(C - C_P) R = M_0 + K \ln (V_0/W) - K \ln (V/W) \qquad (23)$$

K is given by the following empirical equation for a horizontal surface:

$$\log_{10} K = \frac{0.754}{\varepsilon} + 3 \left(\frac{\Delta\omega}{\omega_s}\right) \qquad (24)$$

where

ε = porosity, dimensionless,

$\Delta\omega$ = $\omega_s - \omega$

ω_s = ε/ρ = saturation moisture content, cm^3/g

ω = moisture content, cm^3/g

ρ = bulk density of the residue, g/cm^3

For oil shale retorting residue, $M_0 = 0$, and $V_0/W = 8.3$ ft^3/ft width. In other words, the upper limit of validity for equation 23 is $V/W = 8.3$ ft^2. For values of $V/W \geq 8.3$ ft^2, $(C - C_P) P = 0$.

Clearly the maximum possible range for $\Delta\omega/\omega_s$ is $0 \leq \Delta\omega/\omega_s \leq 1$, so that the maximum possible range for K is $0.754/\varepsilon \leq \log_{10} K \leq 3 + 0.754/\varepsilon$ for a horizontal surface, so that the ratio of the maximum possible value of K to its minimum possible value is 1,000 for rainfall.

While the product $(C - C_P) P$ eventually decreases to zero, in practice this would not be a common occurrence unless the length of overland flow was extremely long, the rainfall intensity was very high, and the duration of the storm was very long. Moreover, the average volume-weighted concentration even where these 3 conditions are satisfied would be $\overline{C}_{V_0} - C_P = K/R$. In fact, the average volume-weighted concentration for $V/W \leq V_0/W$ is

$$\overline{C}_V - C_P = \frac{K}{R} \{1 + [\ln (V_0/W)] - [\ln (V/W)]\} \qquad (25)$$

The value of K obtained from equation 24 must be divided by cos θ to obtain the value of K to be used in equations 21, 22, 23, and 25.

Equation 23 can be rewritten in the following dimensionless form:

$$\frac{(C - C_P) R}{K} = \ln \left(\frac{V_0/W}{V/W}\right) \qquad (26)$$

In practice, it is probably more convenient to deal with the quantities in the above equation in the following units:

c = concentration, mg/ℓ

i = runoff intensity, in/hr

Therefore,

$$C = 28.3 \; c \tag{27}$$

$$P = i/12 \tag{28}$$

and equation 20 becomes

$$V/W = i \, L \, t/12. \tag{29}$$

Substituting equations 27, 28, and 29 into equation 26, using the experimentally determined value of V_0/W, and converting to $\log_{10}$ for graphical purposes, one obtains:

$$\frac{(c - c_p) \, i}{K} = 0.975 \log_{10} \left(\frac{99.5}{i \, L \, t}\right)$$

$$\simeq 2 - \log_{10} (i \, L \, t) \tag{30}$$

If the foregoing development is correct, then the ratio $\dfrac{(c - c_p)i}{K}$ should be a straight line function of $\log_{10} (i \, L \, t)$ with intercept 2 and slope -1. 11 observed experimental values representing the widest possible variation in all the parameters of interest are listed in Table VIII-1, and are plotted in Figure VIII-2 along with equation 30. It should be noted that equation 30 is valid for all values of $i \, L \, t \leq 100$ inch-feet. When $i \, L \, t > 100$ inch-feet, the concentration in the runoff, c, is equal to the rainfall (precipitation) concentration, c_p. It should be noted that the maximum deviation from the predicted values occurs for very small values of t, and also that this deviation rapidly becomes very small as t becomes larger. This is probably due to the fact that some finite time is necessary in order to reach the steady state conditions assumed in the previous development.

It is of interest to note the values of the average volume-weighted concentration for a storm of such duration that $i \, L \, t = 100$ inch-feet. In order to present these results in familiar terms, it is necessary to substitute equations 27 and 28 into equation 25 to obtain (for $V/W = V_0/W$)

$$\overline{c}_{V_0} - c_p = 0.424 \; K/i \tag{31}$$

TABLE VIII-1. OBSERVED EXPERIMENTAL DATA FOR SIMULATED RAINFALL EXPERIMENTS

							Observed				Calculated	
Test	ε	ω_s, $\dfrac{cm^3}{g}$	$\Delta\omega$, $\dfrac{cm^3}{g}$	L, ft	i, $\dfrac{in}{hr}$	t, hr	mg/ℓ		K, $\dfrac{mg}{(ft^2)(hr)}$	$\overline{c}_{V_0} - c_P$
							runoff c	$c - c_P$		
1	0.442	0.317	0.061	80	0.54	1.75	93.4	50.6	190	149
2	0.442	0.317	0.106	80	0.46	0.317	1,049	1,006	510	470
3	0.442	0.317	0.087	80	1.00	0.0833	660	617	335	142
4	0.442	0.317	0.156	30	1.70	1.33	158	115	1,510	377
4	0.442	0.317	0.156	50	1.70	0.853	287	244	1,510	377
5	0.442	0.317	0.202	80	2.25	0.35	397	354	4,100	772
6	0.442	0.317	0.13	80	0.94	1.25	118	75	860	389
7	0.345	0.212	0.058	80	0.40	3.08	201	158	980	1,040
8	0.345	0.212	0.102	80	1.20	0.367	663	620	4,100	1,450
9	0.345	0.212	0.80	80	2.12	0.58	223	180	2,000	400
10	0.345	0.212	0.047	80	1.72	0.15	545	502	680	168

simulated rainfall dissolved solids concentration = 42.8 mg/ℓ for all runs = c_P
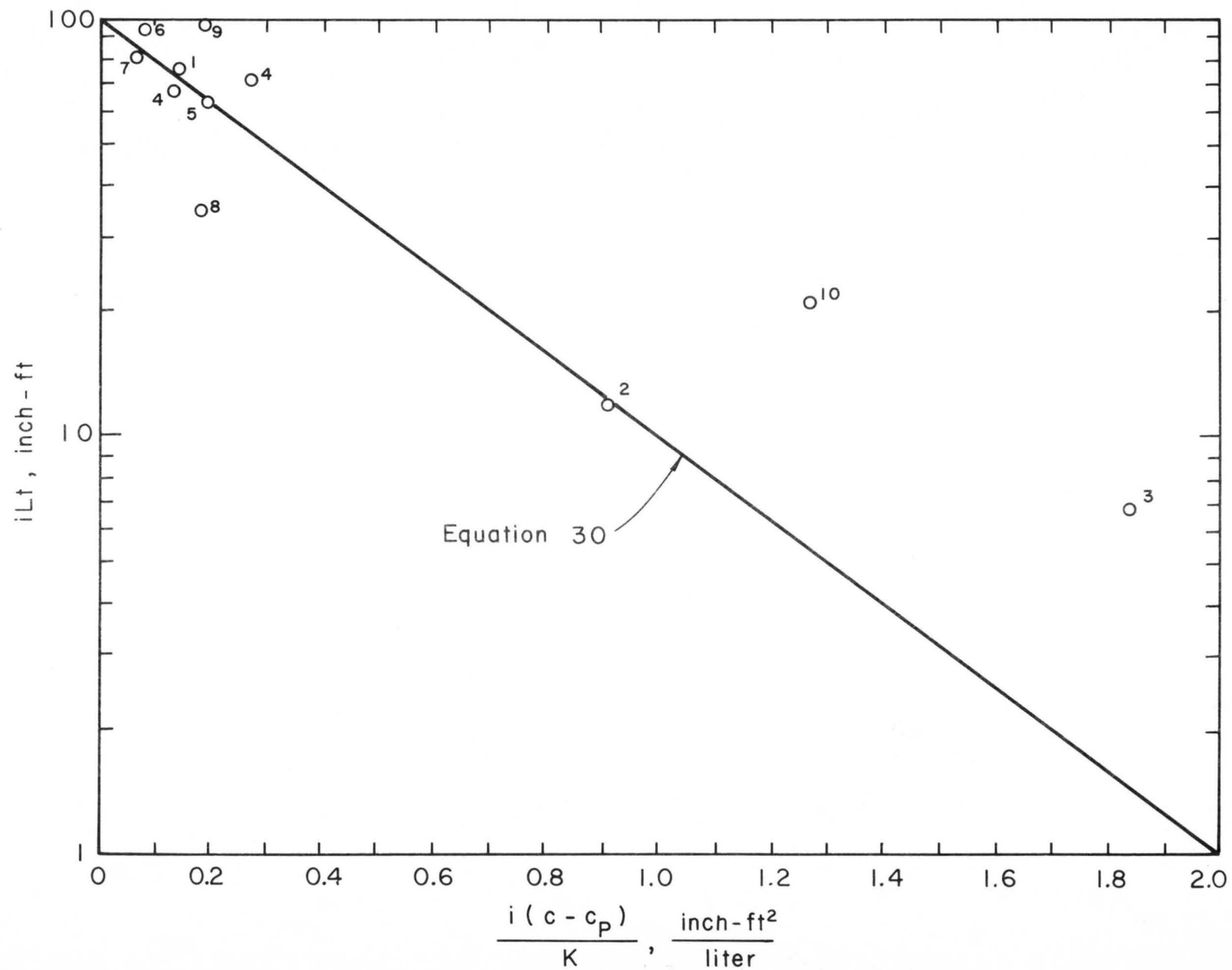
Figure VIII - 2. Comparison of Experimental Data with Prediction Equation for Rainfall

Observed values of $\bar{c}_{V_0} - c_P$ are plotted in Figure VIII-3 versus values calculated by equations 31 and 24. It should be noted that there may be considerable error in the underlined observed values of $\bar{c}_{V_0} - c_P$ because the underlined observed values are based on volume weighted averages calculated from as few as only 2 observations and at most 7 observations (average 4 observations). At any rate, the calculated values of $\bar{c}_{V_0} - c_P$ using equations 31 and 24 appear to give an unbiased estimate, in that there seems to be no consistent over or under estimate of the value of $\bar{c}_{V_0} - c_P$. In fact, the predicted average value of $\bar{c}_{V_0} - c_P$ for all 10 tests is the same as the observed average value of $\bar{c}_{V_0} - c_P$, namely 540 mg/ℓ.

Having demonstrated the validity of the overland flow water quality model for rainfall, it now remains to apply this model to the snowfall data obtained in this project.

Snowfall

Referring back to equation 2, it is clear that one of the difficulties in dealing with snowfall arises from evaluation of C_{si}. However, if Δx is chosen small enough, then it can be assumed that $C_{si} = C_{i+1}$. Combining equations 1, 2, 3, 4, 5, 6, and 7, one obtains

$$C_{i+1} = \frac{C_i [(S + E) \Delta x + Rx] + P \Delta x (C_P - C_i) + M \Delta x}{S \Delta x + R x} \tag{32}$$

If Δx is chosen small enough, then $S \Delta x \ll R x$, and equation 32 becomes

$$C_{i+1} = \frac{\Delta x}{x} \left(\frac{P C_P + M}{R} \right) + C_i \left(1 - \frac{\Delta x}{x} \right) \tag{33}$$

Defining

$$X_s \equiv \frac{\Delta x}{x} \left(\frac{P C_P + M}{R} \right) \tag{34}$$

then

$$C_{i+1} = X_s + Y C_i \tag{35}$$

which has the same form as equation 12. Therefore,

$$C = X_s (1 - Y)^{-1} \tag{36}$$

and

$$C = \frac{P}{R} C_P + \frac{M}{R} \tag{37}$$

For snowfall, P is the rate at which the snow melts to water. Clearly $P \geq R$, so that the ratio $P/R \geq 1$.
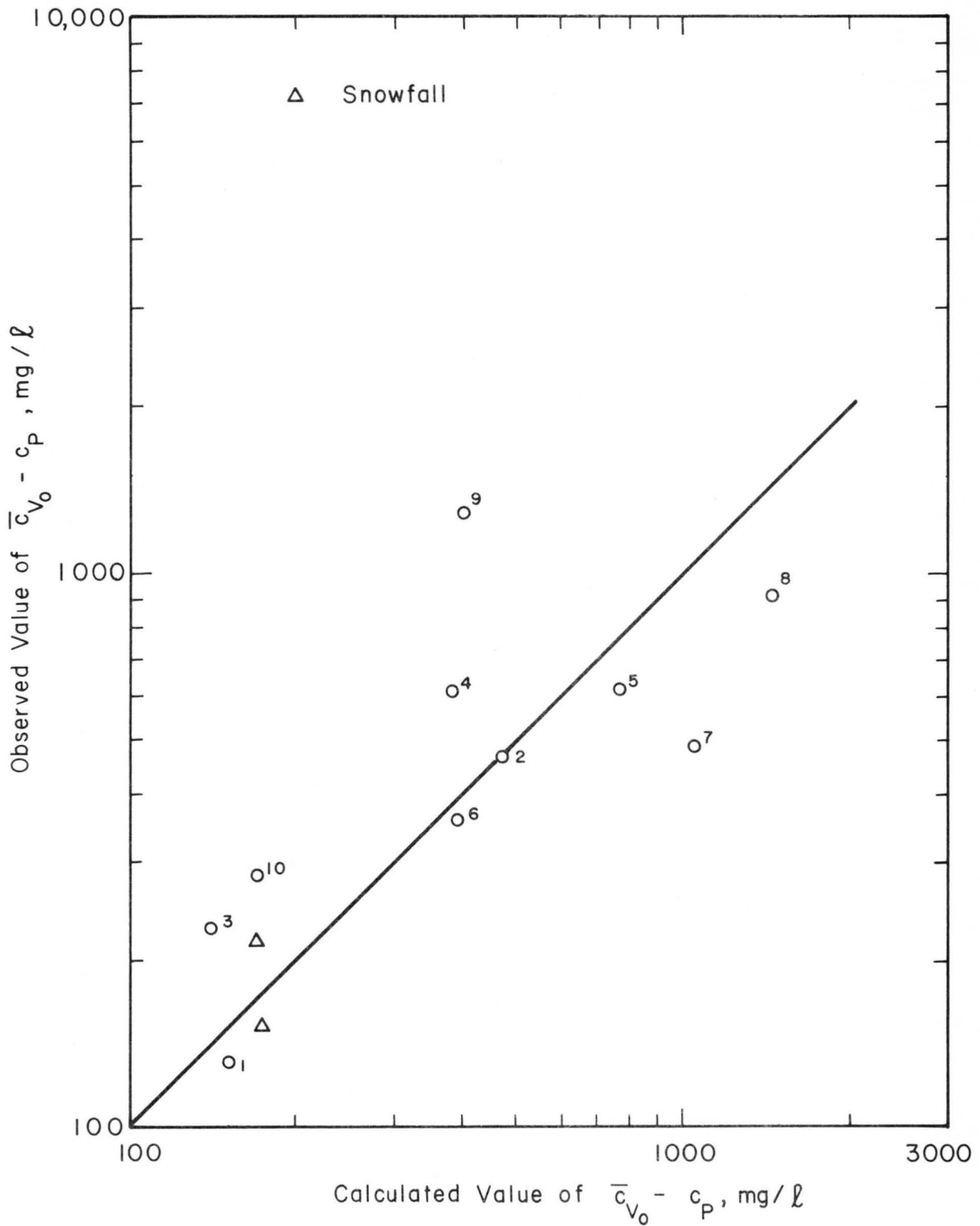
Figure VIII - 3. Observed Versus Calculated Values of the Quantity $\overline{c}_{V_0} - c_P$ for Rainfall

The total volume, V, of runoff (in ft^3) at time t (for constant R) is

$$V = R\ W\ L\ t \tag{38}$$

where t is the time in hours. Assuming that equation 21 is also valid for snowfall, and that $M_0 = 0$ for snowfall too, then equation 22 can be substituted into equation 37 to give

$$(C - \frac{P}{R}\ C_P)\ R = K\ \ln\ (V_0/W) - K\ \ln\ (V/W) \tag{39}$$

For snowfall, P (and therefore R) will usually vary from 0 up during a 24 hour period, and it may take several days to melt all the snow. The left hand side of equation (39) can be rewritten as follows:

$$C\ R - P\ C_P = R\ (C - C_P) + C_P\ (\ R - P) \tag{40}$$

In order to use equation 39 to interpret the snowfall data obtained in this project, it will be necessary to assume that the difference $R - P = - (S + E)$ is a constant. With this assumption, equation 39 can be rewritten as follows:

$$R\ (C - C_P) = [C_P\ (P - R) + K\ \ln\ (V_0/W)] - K\ \ln\ (V/W) \tag{41}$$

Defining

$$I \equiv [C_P\ (P - R) + K\ \ln\ (V_0/W)] \tag{42}$$

equation 41 becomes

$$R\ (C - C_P) = I - K\ \ln\ (V/W) \tag{43}$$

Because R varies from 0 up during a 24 hour period, the total volume of runoff at time t is

$$\frac{V}{W} = L\ \sum_{j=1}^{j=N} R_j\ \Delta t_j \tag{44}$$

where

$$\sum_{j=1}^{j=N} \Delta t_j = t.$$

Using the fact that $R = i/12$, equation 27 can be substituted into equation 43 to obtain

$$i\ (c - c_p) = 0.424\ I - 1.183\ K\ \log_{10}\ (V/W) \tag{45}$$

For a given run then, a plot of the product $i(c - c_p)$ versus $\log_{10} (V/W)$ should be a straight line with slope - 1.183 K and intercept 0.424 I. After determining K from the slope, the average value of P - R and V_0/W can be obtained from the intercept.

For snowfall runs 2 and 3, the value of ε was 0.518. In snowfall run 2, $\Delta\omega/\omega_s$ was 0, and in snowfall run 3, $\Delta\omega/\omega_s$ was 0.541. Therefore the equation equivalent to equation 24 for rainfall is

$$\log_{10} K = \frac{0.256}{\varepsilon} + 0.477 \left(\frac{\Delta\omega}{\omega_s}\right) \tag{46}$$

where equation 46 is for snowfall. Comparison of equations 24 and 46 shows that, for the same values of ε and $\Delta\omega/\omega_s$, the value of K for rainfall is much greater than the corresponding value of K for snowfall.

With only 2 snowfall runs yielding useful data, it is clear that if the 2 unknowns in equation 42 (namely P-R and V_0/W) are to be evaluated, they must be assumed to be constant for both snowfall runs. With this assumption, P-R = 0.0193 ft/hr for both snowfall runs. For run 2, the time-weighted average value of R was 0.00419 ft/hr, the value of R/P was 0.158, and therefore the value of P was 0.0265 ft/hr, and the corresponding value of P-R was 0.0223 ft/hr. For run 3, the time-weighted average value of R was 0.00240 ft/hr, the value of R/P was 0.102, and therefore the value of P was 0.0235 ft/hr, and the corresponding value of P-R was 0.0211 ft/hr. Therefore, the assumption that P-R was the same for both snowfall runs is accurate within ± 6%, and the calculated value of P-R is within 12% of observed values. It should be noted that the observed time-weighted average values of R are probably this much in error.

Equation 41 can be written in the following dimensionless form

$$\frac{R (C - C_p) - C_p (P - R)}{K} = \ln \left(\frac{V_0/W}{V/W} \right) \tag{47}$$

It should be clear from inspection of equation 47 above and equation 26 that both equations have a limited range of validity, namely some minimum value of V/W and some maximum value of V/W. The maximum value of V/W has been previously determined from the rainfall experiments to be 8.3 ft^2. The minimum value determined from the snowfall experiments is 0.0109 ft^2. Examination of equations 21 and 22 show that if the limits of integration were reversed to lower (initial) limits of $M = M_0$ at $V = V_0$ and upper (final) limits of $M = M$ at $V = V$, the result (equation 22) would be the same. Now if we substitute into equation 47, equations 27 and 28 along with the appropriate values of C_p (in the simulated snowfall, C_p was 1,530 mg/ft^3, but in nature would probably be more nearly 105 mg/ft^3, so the following equations 48, 49, 52, and 53 apply only to the simulated snowfall runs), P-R, and $V_0/W = 0.0109$ ft^2, and changing to $\log_{10}$, one obtains

$$\frac{12.5 - i\,(c - c_P)}{K} = 1.93 + 0.975 \, \log_{10} \, (V/W) \qquad (48)$$

If one substitutes equation 29 into equation 48, the result is

$$\frac{12.5 - i\,(c - c_P)}{K} = 0.88 + 0.975 \, \log_{10} \, (i\,L\,t) \qquad (49)$$

$$\simeq 1 + \log_{10} \, (i\,L\,t)$$

Comparison of equation 49 with equation 30 shows that all the rainfall and snowfall data could be plotted on the same graph and would all be on the line given by the following equation

$$f\,(i,\,c,\,c_P,\,K) = \log_{10} \, (i\,L\,t) \qquad (50)$$

where for rainfall,

$$f\,(i,\,c,\,c_P,\,K) = 2 - \frac{(c - c_P)\,i}{K} \qquad (51)$$

and for snowfall,

$$f\,(i,\,c,\,c_P,\,K) = \frac{12.5 - i\,(c - c_P)}{K} - 1 \qquad (52)$$

One would expect that substitution of the value of $V_0/W = 0.0109 \ \text{ft}^2$ into equation 48 would give the initial value of c in the first runoff from melting snow. In other words, for $V/W = V_0/W$, equation 48 becomes

$$(c - c_P)_{\text{initial}} = 12.5/i \qquad (53)$$

Values of $(c - c_P)_{\text{initial}}$ calculated by equation 53 are 249 and 434 mg/ℓ for snowfall runs 2 and 3, respectively, versus observed values of 205 and 446 mg/ℓ. In Figure VIII-4 are plotted all the snowfall data for snowfall runs 2 and 3. The scatter in the points is caused by the fact that i varied considerably during a given run from its time weighted average value of 0.0503 and 0.0288 inches per hour for snowfall runs 2 and 3, respectively.

Using the same reasoning that led to equation 53, if one substitutes $V/W = 0.0109 \ \text{ft}^2$ into equation 29, and then substitutes the result into equation 30, one obtains for rainfall the result

$$(c - c_P)_{\text{initial}} = \frac{2.81\,K}{i} \qquad (54)$$

Comparing equations 53 and 54, it is observed that $(c - c_P)_{\text{initial}}$ is the same only if $K = 4.45 \ \text{mg}/(\text{ft}^2)(\text{hr})$. The calculated values of $(c - c_P)_{\text{initial}}$ for both rain and snow runs are plotted versus the corresponding observed values in Figure VIII-5. Apparently equation 54 not only applies to rainfall, but also snowfall.
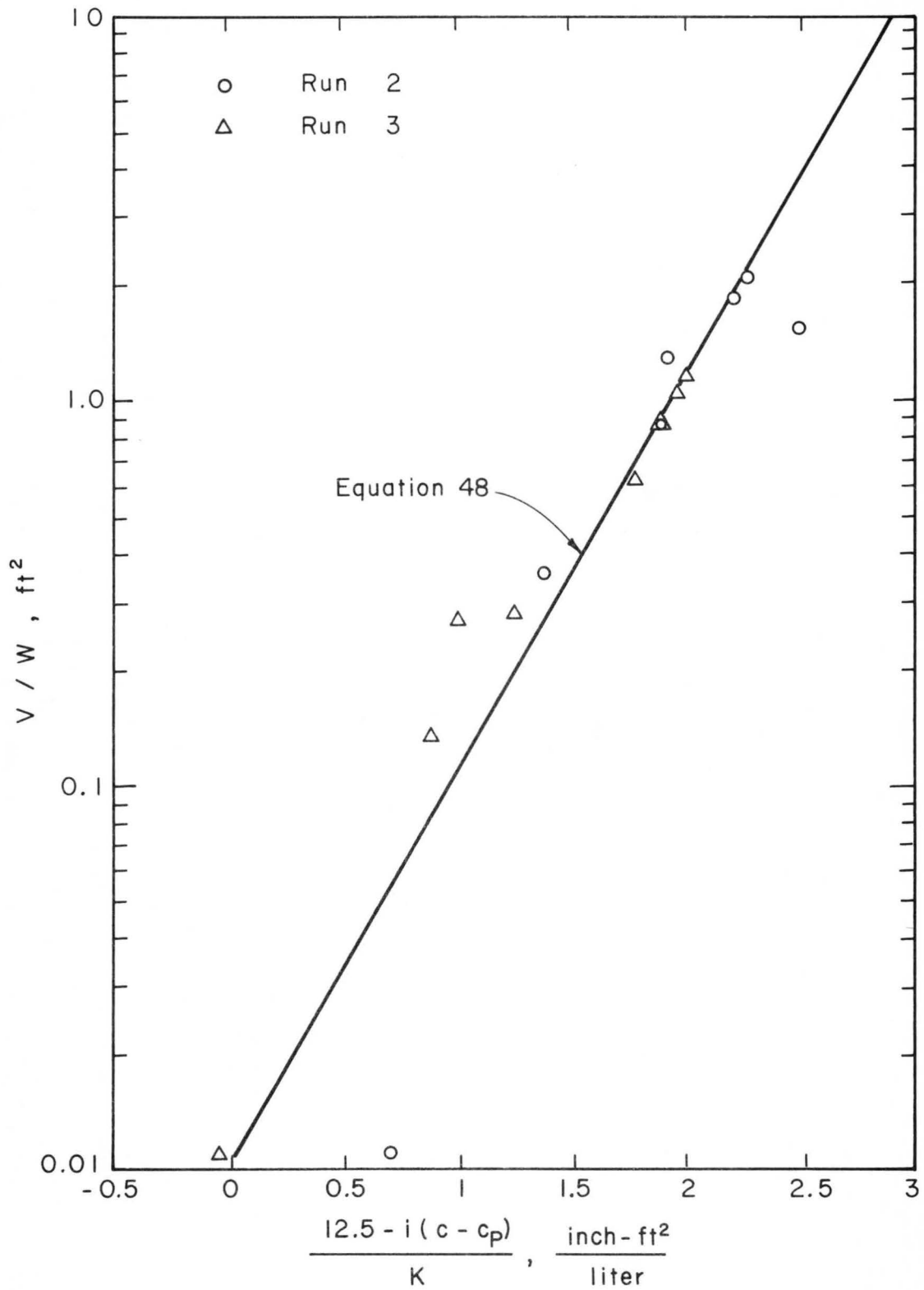
Figure VIII - 4. Comparison of Experimental Data with Prediction
Equation for Snowfall
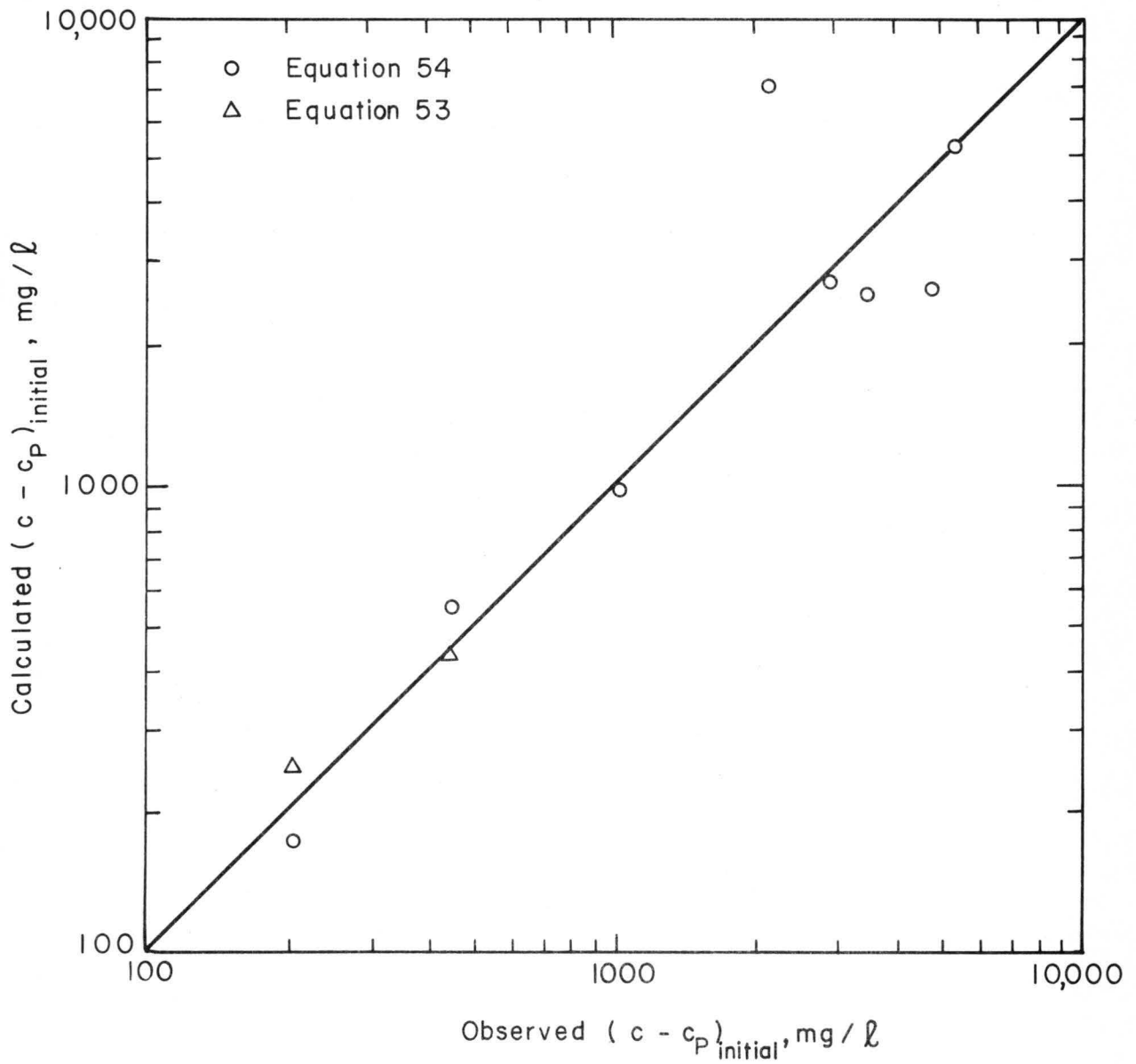
Figure VIII – 5. Observed Versus Calculated Initial Concentrations in
Runoff from Rainfall and Snowmelt

From equation 47, it is clear that, for snowfall, $C - C_P = 0$ when

$$\frac{V_*}{W} = \frac{V_0}{W} \exp \frac{C_P (P - R)}{K} \tag{55}$$

Ordinarily C_P is very small for natural snow so that $V_*/W \simeq V_0/W$. However, this was not the case with the simulated snowfall runs.

For snowfall, the average volume-weighted concentration in the snowmelt runoff is (assuming that P and R are both constants and that $V/W \leq V_*/W$)

$$\bar{C}_V = C_P (\frac{P}{R}) + \frac{K}{R} (1 + \ln \frac{V_0}{W} - \ln \frac{V}{W}) \tag{56}$$

which is the same as equation 25 when P=R. If one substitutes equation 55 into equation 56, one obtains

$$\bar{C}_{V_*} - C_P = K/R \tag{57}$$

which is the same as the analogous equation determined for rainfall when $V_* = V_0$. Using equation 56, and $V_0/W = 0.0109$ ft^2, the calculated value of $\bar{c}_V - c_P$ for snowfall run 2 was 175 mg/ℓ versus an observed value of 152 mg/ℓ. For snowfall run 3, the calculated value of $\bar{c}_V - c_P$ using equation 56 was 170 mg/ℓ versus an observed value of 217 mg/ℓ. It should be noted that there is bound to be some error in the observed value of $\bar{c}_V - c_P$. At any rate, equation 56 appears to be accurate within about $\pm$ 20% for the snowfall data. The above values of $\bar{c}_V - c_P$ are also plotted in Figure VIII-3 for comparison.

Comparisons of Rainfall and Snowfall Relationships and Experimental Results

In both the snowfall and rainfall tests, it was necessary to take into consideration C_P because in both cases, the value of C_P was significantly large (42.8 mg/ℓ for rainfall and 54 mg/ℓ for snowfall). However, in nature, the value of C_P is insignificant (< 3.7 mg/ℓ for snowfall for example) and therefore it can be assumed to be 0. As a consequence the rainfall equations simplify to the following:

$$\frac{CR}{K} \simeq \ln (\frac{V_0/W}{V/W}) \tag{23 and 26}$$

$$\bar{C}_{V_0} \simeq K/R \tag{58}$$

$$, \quad \bar{C}_V \simeq \frac{K}{R} [1 + \ln (\frac{V_0/W}{V/W})] \tag{25}$$

In addition, snowfall equations 39 and 47, 57, and 56 reduce to equations 23 and 26, 58 and 25 respectively when $C_P = 0$. $M_0 = 0$ for both rain and snow. $V_0/W = 8.3$ ft^2 for both rain and snow. In addition, the initial or maximum value of C occurs when $V/W = 0.0109$ ft^2. The range of validity of equations 23 and 26, 58, and 25 is $0.0109 \leq V/W \leq 8.3$ ft^2.

At this point, it would appear worthwhile to compute numerical results for a hypothetical rain and snowstorm. These results are listed in Table VIII-2.

For the maximum leach rain or snow storm, the mass of salt leached per unit horizontal surface area, m/A, is

$$m/A = \left(\frac{1}{L}\right)\left(\frac{V_0}{W}\right)\frac{K}{R} \tag{59}$$

where m = mass of salt leached, mg and A = horizontal surface area, ft^2. Because A = LW, the mass of salt leached per unit width is

$$m/W = \left(\frac{V_0}{W}\right)\frac{K}{R} = 8.3 \, K/R \tag{60}$$

For $V/W \geq V_0/W$,

$$\frac{m/W}{V/W} = m/V = 8.3 \, K/R^2 \, L \, t \tag{61}$$

is the average volume-weighted concentration in the runoff. For most practical applications where L is quite large, equation 61 probably applies for essentially all values of R and t. For example, for t = 1 hour, L = 10,000 feet, R (rain) = 0.01 ft/hr, R (snow) = 0.001 ft/hr, K (rain) = 10,000 mg/(ft^2)(hr), K (snow) = 10 mg/(ft^2)(hr), then m/V (rain) = 8.3 × 10^4 mg/ft^3 and m/V (snow) = 8.3 × 10^3 mg/ft^3. The concentrations in mg/ℓ are 2,930 (rain) and 293 (snow). Using the same figures, the mass of salt leached per unit width is 8,300 grams/foot (rain) and 83 grams/foot (snow).

For tests 2 and 3 given in Appendix B, equation 46 gives the following values for K: For test 2, K = 3.12 mg/(ft^2)(hr). For test 3, K = 5.65 mg/(ft^2)(hr). For both tests 2 and 3, the cumulative volume is given in inches. Because the tests were conducted on an area 80 feet long,

$$\frac{V}{W} = 6.67 \text{ (cumulative volume in inches)}.$$

In Figure VIII-4, the quantity

$$\frac{12.5 - i \, (c-c_P)}{K}$$

becomes $4.01 - 0.0161 \, (c-c_P)$ for test 2 and

$2.22 - 0.0051 \, (c-c_P)$ for test 3, respectively. It should be noted that all of the dissolved solids values in mg/ℓ for tests 1, 2, and 3 are $c-c_P$ values.

TABLE VIII-2. HYPOTHETICAL RAIN AND SNOW STORM.

	Assumed	
	rain	snow
V/W, ft^2	8.3	8.3
ε, dimensionless	0.345	0.345
$\Delta\omega/\omega_s$, dimensionless	0.638	0.638
L, feet	226	226
C_p, mg/ft^3	0	0
P, ft/hr	0.0123*	0.0235
R, ft/hr	0.0123	0.00240
V_0/W, ft^2	8.3	8.3

	Calculated	
	rain	snow
K, $mg/(ft^2)(hr)$	12,300	11.2
K calculated by	equation 24	equation 46
$\overline{C}_{V_0}$, mg/ft^3 (equation 58)	1,230,000	4,670
initial value of C at $V/W = 0.0109$ ft^2, mg/ft^3 (equation 23 and 26)	8,180,000	31,100
mass of salt leached per unit horizontal surface area = $(1/L)(V/W)\,\overline{C}_{V_0}$, mg/ft^2	45,100	171
$\overline{c}_{V_0}$, mg/ℓ (equation 27)	43,500	165
initial value of c, mg/ℓ	289,000	1,100

* Based on a 1 year frequency, 3 hour rain at Grand Junction, Colorado.

SECTION IX

ACKNOWLEDGEMENTS

One of the authors of this report (Dr. Ward) is Professor of Civil Engineering at Colorado State University. Mr. Reinecke was a graduate research assistant in the Environmental Engineering Program of the Department of Civil Engineering at Colorado State University during the course of this project.

The first draft of the final report was sent to the following people for review:

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> Environmental Protection Agency

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SECTION X

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2. A Procedure for Evaluating Environmental Impact by L. B. Leopold, F. E. Clarke, B. B. Hanshaw and J. R. Balsley, U. S. Geological Survey Circular 645, Washington, D. C. 20242, 1971.

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SECTION XI

SYMBOLS AND ABBREVIATIONS

Symbols

English Letters

a, a' = constant for a given type of precipitation, mg/ℓ

A = horizontal surface area, ft^2

b = constant for a given type of precipitation, $\dfrac{mg/\ell}{me/\ell}$

b' = constant for a given type of precipitation, $\dfrac{mg/\ell}{\mu\ mho/cm\ at\ 25^oC}$

c = inorganic dissolved solids concentration, mg/ℓ

C = inorganic dissolved solids concentration, mg/ft^3

$\underline{D}$ = depth of water in overland flow across a solid surface, ft

$\overline{D}$ = mean or average value of D, ft

e = 2.718 = base of natural system of logarithms, dimensionless

E = evaporation intensity, ft/hr

g = acceleration of gravity, $\dfrac{32.2\ ft}{sec^2}$

i = runoff intensity, in./hr

I = defined term

j = index, dimensionless

k = permeability, cm^2

K = constant mass transfer coefficient for a given storm event, $mg/(ft^2)(hr)$

K_1 = constant of proportionality = 2.56×10^{-22}

K_2 = constant = 3,720 for snowfall on TOSCO oil shale retorting residue

K_3 = constant for a given type of precipitation, g/cm^3 (K_3 = 10.34 g/cm^3 for rainfall and K_3 = 1.8 g/cm^3 for snowfall on TOSCO oil shale retorting residue).

K_4 = constant = 7.24×10^{-8} for snowfall on TOSCO oil shale retorting residue

L = total length of overland flow, ft

m = mass of salt leached, mg

M = rate of mass transfer from the solid surface to the overlying water, $mg/(ft^2)(hr)$

M_g = geometric mean of the particle size distribution, cm (M_g = 0.007 cm for TOSCO oil shale retorting residue)

n = power = 6.78 for snowfall on TOSCO oil shale retorting residue (this definition does not hold for Section VIII).

N = upper limit of summation, dimensionless

P = rainfall intensity or rate at which snow melts to water, ft/hr

Q = water flow rate, ft^3/hr

R = runoff intensity, ft/hr

s = slope of the spent oil shale residue surface, dimensionless (s is in % in equation 7 of Section IV and in all equations in Section VI only)

S = seepage (infiltration) intensity, ft/hr

t = time, hr

T = tortuosity, dimensionless (T = 2 for saturated unconsolidated porous media)

v = cumulative volume of snowmelt runoff, inches

V = volume, ft^3

W = width, perpendicular to overland flow direction, ft

$x \cos \theta$ = horizontal distance downstream from the beginning of overland flow, ft

Δx = increment of x, ft

$\Delta x \cos\theta$ = horizontal distance between vertical sections i and i + 1, ft (section i + 1 is downstream from section i)

X = defined term, mg/ft^3

X_s = defined term, mg/ft^3

Y = defined term, dimensionless

Greek Letters

α_j = constant for snowfall run j, mg/ℓ

β_j = constant for snowfall run j

ε = porosity, dimensionless

θ = angle between horizontal and solid surface, deg

κ = constant, dimensionless (κ = 2.36 for unconsolidated porous media)

ν = water kinematic viscosity, ft^2/sec

ρ = soil bulk density, g/cm^3

ρ_s = soil solids density, g/cm^3 (ρ_s = 2.46 g/cm^3 for the TOSCO oil shale retorting residue)

σ_g = geometric standard deviation of the particle size distribution dimensionless (σ_g = 3.27 for the TOSCO oil shale retorting residue)

Σ = summation, dimensionless

ϕ = particle shape factor, dimensionless (ϕ = 0.097 for the TOSCO oil shale retorting residue)

ω = soil moisture content, cm^3/g

ω_s = saturation soil moisture content, cm^3/g

$\Delta\omega$ = $\omega_s - \omega$, cm^3/g

Conventional Symbols

/ = per

% = percent

= Number

→ = Approaches

∞ = Infinity

$\cong$ = approximately equal to
$\equiv$ = equal by definition
$\propto$ = is proportional to

Abbreviations

cfm	= cubic feet/minute
cm	= centimeter
cos	= cosine
$^{\circ}C$	= deg. centigrade
deg	= degrees
exp ( )	= $e^{(\ )}$
f( )	= function of ( )
ft	= feet
g	= gram
hr	= hour
in.	= inch
ℓ	= liter
ℓn	= natural logarithm = ℓn_e
$\log_{10}$	= common logarithm = $\log_{10}$
me	= milliequivalent = 10^{-3} equivalents
mg	= milligram = 10^{-3} grams
psi	= pounds per square inch
sec	= second
TDS	= total dissolved solids, mg/ℓ
TOSCO	= The Oil Shale Corporation
US	= United States
μ mho	= micromho = 10^{-6} mhos = 10^{-6} ohms^{-1}

SECTION XII

APPENDICES

APPENDIX A

ARTIFICIAL SNOW GENERATION

Artificial snow can be generated by contacting high pressure water with high pressure air in an expansion nozzle. The nozzle is designed to atomize the water into tiny droplets and eject them at high velocity. A sufficiently low air temperature will freeze these droplets to form snow.

The particle size and wetness of the snow depend upon careful adjustment of the air and water pressure at the input to the nozzle. In the case where only a limited flow rate of air is available at a given pressure, the size of the nozzle tip can be changed to accommodate the size of air compressor. A large size nozzle tip produces more snow, but requires a larger flow rate of air and a larger compressor.

An optimum water and air pressure for a standard nozzle is 100 psi. Fluctuation in air temperature, atmospheric pressure, and humidity necessitate slight adjustment of the air pressure.

Snow could be generated at the CSU snowfall-runoff facility at a temperature of $-2^{\circ}C$. Optimum snow generation occurred at $-5^{\circ}C$ or less. A 250 cfm compressor was used for the air supply and water was available at 100 psi. The size of the compressor made it necessary to use a 3/8 inch nozzle tip, the smallest available. At a single setting, the tripod supported nozzle would place snow on an area 60 feet long and 10-14 feet wide. The nozzle was moved periodically during snow application to equalize the snow depth.

List of equipment used:

    1 Blizzard king expansion nozzle with supporting tripod
    Nozzle tips of sizes 3/8, 5/8, and 3/4 in.
    200 feet of pressure hose
    Diaphram waterflow regulator with pressure gauge
    250 cfm Worthington compressor

APPENDIX B

EXPERIMENTAL DATA

The experimental data for all snowmelt events are summarized below:

In place density of top 3 inches of residue: ρ = 1/2 g/cm^3

Overall in place density of residue: ρ = 1.36 g/cm^3

Saturation moisture content: ω_s = 0.431 cm^3/g

Porosity: ε = 0.518

Permeability: $k = 4 \times 10^{-10}$ cm^2

In the following tables, the total me/ℓ = me/ℓ anions —me/ℓ cations. Also the total mg/ℓ = mg/ℓ HCO$_3^-$ + mg/ℓ SO$_4^=$ + mg/ℓ Na$^+$ + mg/ℓ Ca^{++} + mg/ℓ Mg^{++} + mg/ℓ K$^+$.

For the CSU snowfall-runoff facility, L = 80 ft, W = 12 ft, A = LW = 960 ft^2, s = 0.0075, and $\overline{D} \cong (10^{-3})(100\ i)^{1/3}$. In general, V/W = vL/12. For the CSU snowfall-runoff facility V/W = 6.67v.

Test: 1

Maximum depth of residue Saturation: 4 in.

Artificial Snowfall
  plus Natural Snowfall

Snow Contacted Surface for 3 Weeks
  before runoff began

Estimated applied Water: 1 inch

Snow Depth: 3" Artificial, 3" Natural

$\Delta\omega = 0$ cm³/g

f   < 0.01 inches/hour

Sample	Time (PM)	Date	Air Temp. °C	Residue Temp.°C 5" below surface	Residue Temp.°C 15" below surface	i, (in/hr)	v, (in.)	Comments
1 - 1	1:55	3-10-71	10	0.2	0.6	< 0.01		First to run
1 - 2	2:25	3-10-71	9	0	0.6	< 0.01		
1 - 3	2:58	3-10-71	8	0	0.5	< 0.01	~ 0.02	Last to run
1 - 4	3:05	3-11-71	15	1.0	1.0			Taken from residue bed

Sample	Conductance µmhos/cm at 25 °C	pH at 25°C	Dissolved Solids (me/ℓ / mg/ℓ) (Corrected for applied water)						
			HCO₃⁻	SO₄⁼	Na⁺	Ca⁺⁺	Mg⁺⁺	K⁺	Total
1 - 1	280	8.04	0.58 / 35.4	2.24 / 108	0.70 / 16.1	1.14 / 22.8	0.59 / 13.0	0.04 / 1.5	0.35 / 196
1 - 2	257	8.03	0.49 / 29.9	1.90 / 91.3	0.60 / 13.8	1.04 / 20.8	0.59 / 13.0	0.02 / 0.9	0.14 / 170
1 - 3	266	7.89	0.23 / 14.0	1.86 / 89.4	0.68 / 15.6	0.98 / 19.6	0.55 / 12.2	0.02 / 0.9	-0.14 / 152
1 - 4	97	8.15	1.24 / 75.6	0.64 / 30.8	0.08 / 1.84	1.00 / 20.0	0.67 / 14.8	0.0005 / 0.2	0.12 / 143

TEST: 2

Artificial Snowfall

Avg. Snow Depth: 6 in.

Snow Water Content: 1/3

$\Delta\omega$ = 0 cm^3/g

i   = 0.0536 inches/hour

Max. depth of residue saturation: 4 inches

Total Cumulative Volume of runoff: 0.317 inches

% Applied Water appearing as runoff: 15.8%

i(time weighted average) = 0.0503 inches/hour

Sample	Time (PM)	Date	Air Temp. °C	Residue Temp. °C 5" below surface	Residue Temp. °C 15" below surface	i, (in./hr)	v, (in.)	Comments
2 - 1	1:20	3-20-71	16	0.7	1.8	0.034	0	First to run
2 - 2	2:20	3-20-71	15	0.7	1.8	0.0637	0.054	
2 - 3	3:20	3-20-71	15	0.7	1.6	0.0795	0.129	
2 - 4	4:20	3-20-71	15	0.7	1.6	0.053	0.196	
2 - 5	5:20	3-20-71	14	0.7	1.6	0.021	0.232	Quit running at 6:05 PM
2 - 6	1:45	3-21-71	11.5	0.9	1.5	0.048	0.278	Running since 12:30 PM
2 - 7	2:45	3-21-71	10.7	1.0	1.4	0.013	0.314	Quit running at 3:30 PM

Sample	Conductance mhos/cm at 25°C	pH at 25°C	Dissolved Solids (me/ℓ / mg/ℓ) (Corrected for Applied Water)						
			HCO$_3^-$	SO$_4^=$	Na$^+$	Ca^{++}	Mg^{++}	K$^+$	Total
2 - 1	243	8.00	1.22 / 74.5	1.62 / 77.9	0.28 / 6.45	1.40 / 28.1	0.77 / 17.0	0.04 / 1.5	0.35 / 205
2 - 2	190	8.07	0.90 / 54.9	1.36 / 65.4	0.27 / 6.20	1.10 / 22.0	0.63 / 13.9	0.02 / 0.9	0.24 / 163
2 - 3	162	8.06	0.71 / 43.3	1.14 / 54.8	0.08 / 1.84	1.14 / 22.8	0.37 / 8.2	0.01 / 0.4	0.25 / 131
2 - 4	168	8.05	0.67 / 41.5	1.14 / 54.8	0.07 / 1.61	1.22 / 24.4	0.29 / 6.4	0.004 / 0.2	0.22 / 129
2 - 5	165	7.99	0.29 / 17.7	1.04 / 50.0	0.08 / 1.84	0.98 / 19.6	0.19 / 4.2	0.004 / 0.2	0.07 / 94
2 - 6	123	8.36	0.69 / 42.1	0.86 / 41.3	0.05 / 1.15	1.12 / 22.4	0.22 / 4.9	0.01 / 0.4	0.15 / 112
2 - 7	126	8.93	0.60 / 36.6	0.82 / 39.4	0.03 / 0.69	1.10 / 22.0	0.13 / 2.9	<.001 / <0.1	0.15 / 108

TEST: 3

Artificial Snowfall

Avg. Snow Depth: 7 inches

Snow Water Content: 1/4

$\Delta\omega$ = 0.233 cm³/g

i = 0.0318 inches/hour

Residue bed fully saturated on lower end.

Volume of Water percolated through bed:
44 gal. (0.073 inches)

Total Cumulative Volume of runoff: 0.178 inches

% Applied Water appearing as funoff: 10.2%
i(time weighted average) = 0.0288 inches/hr

Sample	Time (PM)	Day	Air Temp. °C	Residue Temp. °C 5" below surface	Residue Temp. °C 15" below surface	i, in./hr	v, (in.)	Comments
3 - 1	12:30	4-2-71	15	1.6	3.9	0.0112	0	First to run
3 - 2	1:30	4-2-71	15	1.5	3.7	0.0238	0.020	
3 - 3	2:30	4-2-71	15	1.4	3.5	0.0127	0.041	Last to run
3 - 4	12:45	4-6-71	14	3.2	2.4	0.0251	0.043	First to run
3 - 5	1:45	4-6-71	15	3.8	2.6	0.0476	0.094	
3 - 6	2:45	4-6-71	15.7	4.7	2.7	0.0340	0.133	
3 - 7	3:45	4-6-71	16	5.8	2.9	0.0191	0.159	
3 - 8	4:45	4-6-71	15	6.3	3.2	0.0087	0.173	Last to run

Sample	Conductance µmhos/cm at 25°C	pH at 25°C	Dissolved Solids (me/l / mg/l) (Corrected for Applied Water)						
			HCO₃⁻	SO₄⁼	Na⁺	Ca⁺⁺	Mg⁺⁺	K⁺	Total
3 - 1	572	7.58	1.45 / 88.5	4.98 / 239	0.48 / 11.0	4.18 / 83.8	1.01 / 22.3	0.05 / 1.8	0.71 / 446
3 - 2	389	7.83	0.89 / 54.2	2.76 / 133	0.28 / 6.45	2.64 / 53.0	0.57 / 12.6	0.04 / 1.6	0.12 / 261
3 - 3	340	7.74	0.87 / 53.0	2.52 / 121	0.27 / 6.21	2.34 / 47.0	0.46 / 10.2	0.03 / 1.1	0.29 / 239
3 - 4	221	8.07	1.50 / 91.5	1.02 / 49.0	0.22 / 5.06	1.46 / 29.2	0.51 / 11.3	0.03 / 1.0	0.30 / 187
3 - 5	86	7.97	0.69 / 42.1	0.42 / 20.2	0.04 / 0.92	0.82 / 16.4	0.25 / 5.5	0.01 / 0.4	0.01 / 85
3 - 6	58	8.21	0.50 / 30.5	0.36 / 17.3	0.01 / 0.23	0.64 / 12.8	0.16 / 3.5	<0.1	0.04 / 64
3 - 7	67	8.95	0.34 / 20.8	0.34 / 16.3	0.01 / 0.23	0.56 / 11.2	0.04 / 0.9	≤0.1	0.06 / 49
3 - 8	60	7.89	0.22 / 13.4	0.38 / 18.2	0.04 / 0.92	0.46 / 9.2	0.06 / 1.3	<0.1	0.03 / 43

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MISCELLANEOUS SAMPLES

Sample	Conduct- ance μmho/cm at 25°C	Comments
1	347	Runoff occurring after natural snowfall
2	79	Applied water sample
3	71	Applied snow sample
4	10,730	First percolated water to appear in barrel
5	9,630	Composite percolated sample

Sample	pH at 25°C	Dissolved Solids (me/ℓ / mg/ℓ)							
		HCO_3^-	$SO_4^=$	Cl^-	Na^+	Ca^{++}	Mg^{++}	K^+	Total
1	8.06	1.02 / 62.2	1.96 / 94.7	---- / ----	0.84 / 19.3	1.38 / 27.7	0.68 / 15.3	0.02 / 0.7	0.08 / 219
2	7.98	0.62 / 37.8	0.06 / 3.0	---- / ----	0.01 / 2.6	0.36 / 7.2	0.15 / 3.3	0.02 / 0.8	0.14 / 55
3	7.64	0.59 / 36.0	0.06 / 3.0	---- / ----	0.01 / 2.6	0.40 / 8.0	0.15 / 3.3	0.02 / 0.8	0.07 / 54
4*	7.90	5.95 / 363	300 / 14,400	2.6 / 92	148 / 3,400	34 / 1,360	125 / 1,525	0.6 / 23	0.6 / 21,160
5*	7.79	5.87 / 358	248 / 11,900	2.1 / 73	132 / 3,040	28 / 1,120	96.6 / 1,175	0.6 / 23	0.9 / 17,690

* Concentrations corrected for applied water.

Samples of natural snow taken from Pingree Park, Roosevelt National Forest

Altitude at which samples were taken: 9130 ft.

Date samples were taken: 2-27-71

Snow surface temperature: -10°C

Sample	Conductance μmho/cm at 25°C	pH at 25°C	Dissolved Solids (me/ℓ mg/ℓ)						
			HCO_3^-	$SO_4^=$	Na^+	Ca^{++}	Mg^{++}	K^+	Total
1	26.4	7.20	0.19 / 11.6	0.04 / 2	Tr	0.184 / 3.7	0.020 / 0.25	0.004 / 0.2	0.02 / 17.8
2	9.2	6.70	0.06 / 3.7	0.02 / 1	Tr	0.060 / 1.2	0.006 / 0.07	0.002 / 0.1	0.01 / 6.1
3	5.1	6.10	0.03 / 1.8	0.02 / 1	Tr	0.040 / 0.8	0.002 / 0.02	0.002 / 0.1	<0.01 / 3.7
4	16.0	6.03	0.05 / 3.0	0.08 / 4	Tr	0.050 / 1.0	0.032 / 0.40	0.035 / 1.4	0.01 / 9.8

Notes:

Sample 1: Taken from snow drift of 65 inches depth

Sample 2: Taken from snow drift of 16 1/2 inches depth

Sample 3: Taken from snow drift of 13 1/4 inches depth

Sample 4: Taken from forest snow of 10 inches depth

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16. Abstract Concentration and composition of total dissolved solids were determined in both surface runoff water and in water which had percolated through a bed of the residue. An empirical equation was developed to predict the concentration of the runoff water as a function of independent parameters. A tendency for saturation of the residue to occur during a period of snowmelt was revealed. The effects of this saturation on the residue were also considered.

An overland flow water quality model was developed and successfully applied to runoff resulting from rainfall and snowfall on oil shale retorting residue. The surface water runoff from snowfall on oil shale residue has less water pollution potential than the runoff from rainfall.

It was shown that the concentration of dissolved solids in the runoff was a function of the cumulative volume of runoff per unit width, the porosity of the oil shale retorting residue, the soil moisture content, and the snowmelt rate, and the fraction of the snowmelt water that appears as runoff.

17a. Descriptors
*Salinity, *Oil Shale, *Colorado River, *Colorado, *Snowmelt, *Overland Flow, Snowfall, Soil Temperature, Rainfall Intensity, Environmental Engineering

17b. Identifiers
*Water Quality Hydrology, *Snowmelt water quality, *Snowfall Simulators, TOSCO II Process, Piceance Basin, Parachute Creek.

17c. COWRR Field & Group 05E

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