WATER POLLUTION POTENTIAL OF SNOWFALL ON SPENT OIL SHALE RESIDUES

By

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Introduction

Because of space limitations, this paper omits a great deal of information pertinent to this subject. Therefore, the reader is referred to references 1 and 2.

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 paper.

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

The residue used for the snowfall experimentation described in this paper 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 snowmelt 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.

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.

Experimental Procedure

All experiments were conducted on the snowfall-runoff facility at the Engineering Research Center on the foothills campus of Colorado State University. Modification of this facility for these experiments is described below. (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. (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 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.

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Ionic Composition of Snowmelt Runoff

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 a 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 3.

Analytical instruments used included: Orion model 801 digital pH meter, Orion specific ion electrodes, Model 290 Perkins Elmer Atomic Absorption Unit, Beckman Na^+-K^+ Flame Photometer, and Sargent Welch recording titrator.

As mentioned above, 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 snowmelt 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. The initial ionic composition of runoff from rainfall and snowfall is quite different, but this initial difference tends to disappear as the cumulative volume of runoff increases.

Snowmelt Runoff, Percolation, and Evaporation

As shown in Table 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 the bed. When analyzed this water gave a dissolved solids concentration of $\sim$20,000 mg/ℓ.

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).

TABLE 1. WATER BALANCE DATA

Snowmelt event	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

Discussion of Results

The first water to appear as runoff from precipitation on the oil shale residue surface carries the highest contentration 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.

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 by 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 conbination 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.

An Overland Flow Water Quality Model

The following quantities are shown in the definition sketch (Figure 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:

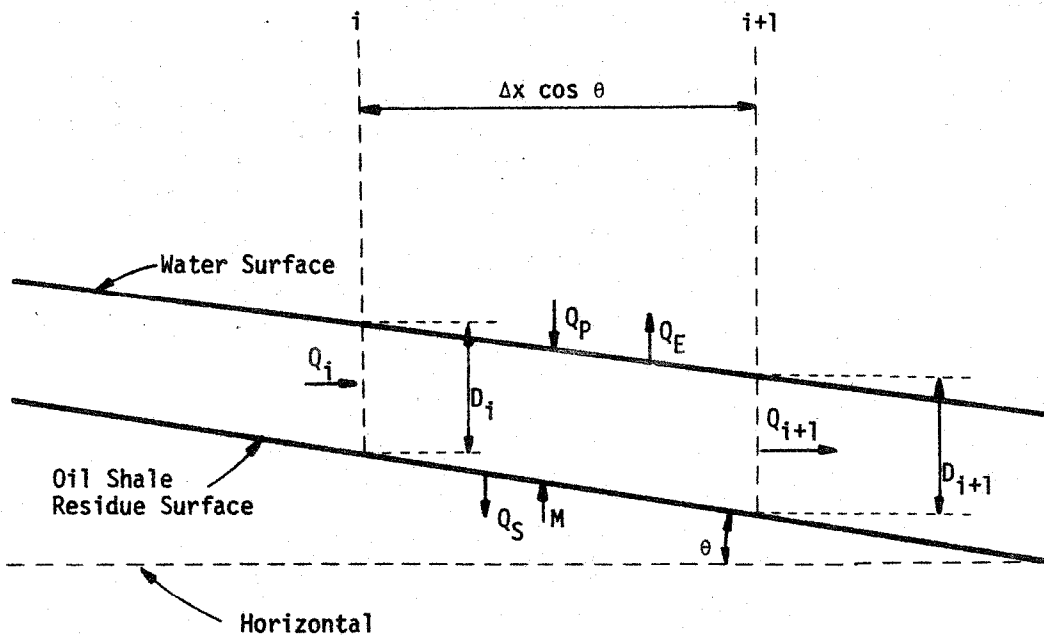$$Q_i + Q_P = Q_S + Q_{i+1} + Q_E \tag{1}$$

Figure 1. Definition sketch for overland flow water quality model.

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 or the rate at which snow melts to water in ft/hour, then

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

If S is the intensity of the 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

$$R = P - S - E \qquad (6)$$

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

$$Q_X = R \, W \, x \cos \theta \qquad (7)$$

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

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

$$C_{i+1} = \frac{C_i \, \{(S + E) \, \Delta x + Rx\} + P \, \Delta x \, (C_p - C_i) + M \, \Delta x}{S \, \Delta x + Rx} \qquad (8)$$

If Δx is chosen small enough, then $S \, \Delta x \ll Rx$, and equation 8 becomes

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

Using equation 9, it can be shown that

$$C = \frac{P}{R} \, C_p + \frac{M}{R} \qquad (10)$$

For snowfall, P is the rate at which the snow melts to water. Clearly $P \geq R$, so that the ratio $P/R \geq 1$.

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

$$V = R \, W \, L \, t \qquad (11)$$

where t is the time in hours, and L is the total length of overland flow in feet.

One of the assumptions involved in the derivation of equation 10 is that M is constant (at a given time for a given slope) along the length L. Experimental data from simulated rainfall experiments[1] show that this is true. M would not be expected to change with width. Therefore, it seems reasonable to assume that

$$\frac{dM}{d(V/W)} = \frac{- K}{(V/W)} \qquad (12)$$

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. Integrating equation 12 between the lower (initial) limits of $M = M$ at $V = V$ and upper (final) limits of $M = M_o$ at $V = V_o$, one obtains

$$M = M_o + K \ln(V_o/W) - K \ln (V/W) \tag{13}$$

Assuming that $M_o = 0$, then equation 13 can be substituted into equation 10 to give

$$(C - \frac{P}{R}C_p) \, R = K \ln(V_o/W) - K \ln(V/W) \tag{14}$$

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 14 can be rewritten as follows:

$$C \, R - P \, C_p = R(C - C_p) + C_p(R - P) \tag{15}$$

In order to use equation 14 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 14 can be rewritten as follows:

$$R(C - C_p) = \{C_p(P - R) + K \ln(V_o/W)\} - K \ln(V/W) \tag{16}$$

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

$$\frac{V}{W} = L \sum_{j=1}^{j=N} R_j \, \Delta t_j \tag{17}$$

where

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

K is given by the following empirical equation for snowmelt on a horizontal surface of oil shale retorting residue:

$$\log_{10} K = \frac{0.256}{\varepsilon} + 0.4777 \, (\frac{\Delta \omega}{\omega_s}) \tag{18}$$

where ε = porosity, dimensionless; $\Delta \omega = \omega_s - \omega$; $\omega_s = \varepsilon/\rho$ = saturation moisture content, cm^3/g; ω = moisture content, cm^3/g; ρ = bulk density of the residue, g/cm^3. 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. 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 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 16 can be written in the following dimensionless form

$$\frac{R(C - C_p) - C_p(P - R)}{K} = \ln \left(\frac{V_o/W}{V/W} \right) \tag{19}$$

It should be clear from inspection of equation 19 above that it has 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 was determined from rainfall experiments to be 8.3 ft^2. The minimum value was determined from snowfall experiments to be 0.0109 ft^2.

In the simulated snowfall, C_p was 1,530 mg/ft^3, but in nature would probably be more nearly 105 mg/ft^3. Substituting equation 11 into equation 19 along with the appropriate value of V_o/W, one obtains

$$\frac{R(C - C_p) - C_p(P -R)}{K} = \ln(\frac{8.3}{RLt}) \tag{20}$$

Therefore, if ε, ω_s, and $\Delta\omega$ are known, K can be calculated by equation 18. Knowing K, R, C_p, P, L, and t, C can be calculated by equation 20. For all the snowmelt events, ρ = 1.2 g/cm^3 and ω_s = 0.432 cm^3/g, so equation 18 simplifies to

$$\log_{10}K = 0.494 + 1.107 \Delta\omega \tag{21}$$

Clearly $0 \leq \Delta\omega \leq \omega_s$, so that $3.12 \leq K \leq 9.35$ mg/(ft^2)(hr). Using the maximum value of K, and C_p = 105 mg/ft^3, equation 20 simplifies to

$$C - C_p = \frac{19.82 + 105(P - R) - 9.35 \ln(RLt)}{R} \tag{22}$$

Using the average values of P - R and R observed during the snowmelt runs, equation 22 further reduces to

$$C - C_p = 6,697 - 2,833 \ln(0.0033 \ Lt) \tag{23}$$

The difference $C - C_p$ reduces to zero when the product Lt is 3,212 feet-hours.

REFERENCES

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