Title
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Publication Date
1977-02-01
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February 1977
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FACTORs THAT INFLUENCE THE LEACHING OF ORGANIC MATERIAL FROM IN SITU SPENT SHALE

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Abstract

A series of batch and continuous flow experiments were run in order to assess the potential for contamination of groundwater by organic material leached from in situ spent shale. The specific objectives of these experiments were to 1) estimate the concentration of organic material present in leachate derived from various types of in situ spent shale, and 2) identify variables that affect the concentration of organic material in leachate. Concentrations of total organic carbon (TOC) as high as 50 milligrams per liter were detected during experimentation. Factors that significantly influenced the concentration of organic material present in leachate included 1) retorting conditions associated with spent shale, 2) spent shale particle size, 3) water temperature, and 4) leaching time.

INTRODUCTION

Rich deposits of oil shale often exist as impermeable strata situated between two groundwater aquifers. The preliminary preparation of in situ retorts (i.e., fracturing, etc.) and subsequent in situ retorting destroy the impermeability of oil shale strata, thus creating a potential for groundwater to migrate through an exhausted in situ retort. Groundwater, migrating through an exhausted in situ retort, may be degraded in quality as a consequence of leaching processes acting on spent shale. (1,2) Groundwater resources in some areas of potential in situ oil shale development are often used for a variety of beneficial uses, including domestic water supply. The contamination of groundwater resources by organic material leached from spent shale may preclude one or more of these beneficial uses. The purposes of this paper are to assess the potential for groundwater contamination by organic material leached from in situ spent shale and to identify factors that affect the release of organic material during the leaching process.

LABORATORY EXPERIMENTS

Two types of experiments were run in order to assess the leaching of organic material from spent shale. These experiments included 1) "batch" experiments in which a series of beakers were each filled with 50 grams of spent shale and 50 milliliters of distilled water, and 2) "continuous flow" experiments in which a series of small-scale columns were each filled with 50 grams of spent shale and connected to a pump that continuously recirculated 50 milliliters of distilled water through the packed column at various flow rates.

The batch experiments examined three different types of spent shale produced by Lawrence Livermore Laboratory's 125-kilogram simulated in situ retort. The retorting conditions associated with each of these three types of spent shale are described in Table 1. The following variables were examined in the batch experiments:

- Particle size range of spent shale:
  - 0.14 to 0.28 cm (.055 to .110 inches)
  - 0.28 to 0.64 cm (.110 to .250 inches)
- Water temperature

After various leaching times up to 10 days, samples of leachate were filtered through a fiberglass filter and analyzed for TOC (total organic carbon), an indicator of the total dissolved organic material present in the leachate. In addition to TOC, the leachate was analyzed for specific conductance, an indicator of the TDS (total dissolved solids) present in the leachate. The rationale for measuring specific conductance is that high concentrations of TDS can influence the solubility of certain organic compounds in water. Certain inorganic materials initially leached from the spent shale increase the TDS, thus potentially affecting the solubility of organic material.

The "continuous flow" experiments examined the same set of variables as the "batch" experiments with the following exceptions: 1) the spent shale produced in an Air+N2 atmosphere was not examined, 2) only the smaller particle size was examined, and 3) only the lower water temperature was examined. Two flow rates were employed during the "continuous flow" experiments; one milliliter per minute and three milliliters per minute. In the "continuous flow" experiments, the leachate was filtered and analyzed for the same parameters (i.e., TOC and specific conductance).
RESULTS AND DISCUSSION

Batch Experiments Conducted at a Water Temperature of 20°C. The results of the batch experiments conducted at a water temperature of 20°C are presented in Figure 1. As revealed by Figure 1, leachate from the Type 3 spent shale contained the greatest concentration of organic carbon, whereas leachate from the Type 1 spent shale contained the least. The Type 1 spent shale was produced during a combustion run at a high retorting temperature in the presence of oxygen (without recycle gas) at a low retorting rate, thus enabling the combustion of most of the residual organic material on the spent shale after oil extraction.

Type 2 spent shale was produced during an inert gas run at a low retorting temperature in the absence of oxygen and thus no combustion of residual organic material occurred. Although the Type 3 spent shale was produced during a combustion run in the presence of oxygen at a high retorting temperature, its leachate contained the most organic carbon. This is likely due to the use of recycle gas as part of the input gas. Recycle gas contains various volatile organic compounds and thus it is hypothesized that certain volatile organic compounds associated with the recycle gas adsorbed onto the Type 3 spent shale as input gas was supplied behind the flame front in the retort. It is interesting to note that leachate from the Type 3 spent shale contained a greater concentration of organic carbon than leachate derived from the Type 2 spent shale. This is likely due to two factors; 1) the aforementioned adsorption of volatile organics present in the recycle gas onto the Type 3 spent shale, and 2) the greater efficiency of oil extraction achieved during the inert gas run (the yield of shale oil during the inert gas run was reported to be about 99% of the Fischer Assay), suggesting that there was less residual organic material remaining on the Type 2 spent shale after oil extraction.

The size of spent shale particles significantly affects the amount of organic material leached, as revealed by Figure 1. In accordance with theory, leachate from the smaller particle size range of spent shale contained a greater concentration of organic carbon for all three types of spent shale investigated. This is due to the fact that, for the smaller particle size range, there is a greater surface area per given weight available for leaching.

The amount of organic material leached from all three types of spent shale at a water temperature of 20°C generally appeared to increase as a function of leaching time, as revealed by Figures 1a, 1b, and 1c. However, close scrutiny of these graphs indicates that there were occasional decreases in organic carbon concentration over certain ranges of leaching time. This is particularly apparent for the Type 2 spent shale (see Figure 1b) in which the organic carbon concentration increases up to day 2, decreases slightly from day 2 to day 7, and then significantly increases from day 7 to a maximum value (over time period investigated) on day 10. Possible explanations for these occasional decreases in organic carbon concentration over time include 1) the occurrence of precipitation reactions between various soluble organic components of the leachate, 2) decreased solubility of various soluble organic components of the leachate as a consequence of inorganic material leached from spent shale (the leaching of inorganic material, as indicated by the conductivity measurements in Figure 1, was quite significant and possibly decreased the solubility of certain organic components present in the leachate).
It is interesting to note that the greatest rate of leaching for all three types of spent shale occurred during the first day. Thereafter, the rate of leaching decreased significantly until "pseudo" equilibrium conditions were approached by the tenth day of leaching.

Batch Experiments Conducted at a Water Temperature of 80°C. The results of the batch experiments conducted at a water temperature of 80°C are presented in Figure 2.

From Figure 2, it can be seen that leachate derived from Type 2 and Type 3 spent shale at a water temperature of 80°C contained considerably greater concentrations of organic carbon than leachate derived from the Type 1 spent shale. This is similar to observations made during the batch experiments conducted at a water temperature of 20°C in which the leachate from the Type 1 spent shale contained considerably less organic carbon.

A comparison of Figures 1 and 2 suggests that water temperature enhances the leaching of organic material from Type 1 and Type 2 spent shale. In contrast, water temperature appears to inhibit the leaching of organic material from Type 3 spent shale. A possible explanation for this phenomenon is that the organic components in leachate from Type 3 spent shale may be less soluble at higher water temperatures while the organic components in leachate from Type 1 and Type 2 spent shale may be more soluble at higher water temperatures.

The amount of organic material leached from the small particle size range at a water temperature of 80°C was greater than that from the large particle size range for all three types of spent shale investigated. These results correspond to the results of the batch experiments conducted at a water temperature of 20°C.

For both Type 1 and Type 2 spent shale, the concentration of organic carbon generally increased as a function of leaching time except for slight decreases occurring over certain ranges of leaching time. In contrast, the concentration of organic carbon in leachate from the Type 3 spent shale increased to a maximum level after one-half day of leaching and thereafter tended to decrease with time. This may be due to precipitation reactions involving various organic components as a consequence of inorganic materials leached from the spent shale. For all three types of spent shale, the rate of leaching was greatest during the first day and thereafter decreased although "pseudo" equilibrium conditions were not approached by the tenth day of leaching as was the case in the batch experiments conducted at a water temperature of 20°C.

Continuous Flow Experiments. The results of the continuous flow experiments are presented in Figure 3.

Figures 3a and 3b reveal that the two flow rates investigated (one milliliter per minute and three milliliters per minute) did not significantly differ with respect to the amount of organic material leached from Type 1 and Type 2 spent shale (Type 3 spent shale was not examined in the continuous flow experiments). It is possible that a somewhat greater flow rate (i.e., 10 milliliters per minute or greater) may have resulted in a significantly greater amount of organic material being leached from the spent shale.

Since the water temperature employed in the continuous flow experiments was 20°C, the graphs in
REFERENCES

(1) Parker, H.W., "Simulated Groundwater Leaching of In Situ Retorted or Burned Oil Shale," 1976. (Quarterly Progress Report for Grant #G0254011, funded by ERDA for Texas Tech University.)

(2) Ward, J.C., "Water Pollution Potential of Spent Oil Shale Residues," 1971. (EPA Publication.)

(3) Sherwood, Pigford, and Wilke, Mass Transfer

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.