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# Project Summary

# Leaching and Hydraulic Properties of Retorted Oil Shale Including Effects from Codisposal of Wastewater

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**The purpose of this project was to develop methods and data on the leaching and hydraulic properties of solid residues resulting from the processing of oil shale. A column test, called the Equilibrated Soluble Mass (ESM) test, was developed as an aid to characterization of the chemical quality of the first leachate that would issue from a disposal pile of spent oil shale. Water added for cooling, compaction, and dust control will develop a chemical composition dictated by chemical reaction between the solution and solid phases. In the ESM column test, this process is simulated by moisturizing the solid to the expected field water content, followed by an equilibration period. After packing the moistened material into a column, the antecedent pore solution is displaced by injection of distilled water. Both theoretical and experimental results indicate that the first effluent from the column is displaced antecedent pore water, the chemical composition of which has been unaffected by the displacement process. The chemical characteristics of the first effluent are expected to be a reasonable index to the quality of first leachate generated from a disposal pile.**

**The ESM test was used to assess the effect on leachate quality of codisposal of process water with the solids. This was accomplished by conducting one set of tests with distilled water as the moisturizing fluid and another set of tests with process waters as the moisturizing fluid. These tests indicate an overall negative effect on leachate quality as a result of adding process water to the solids.**

**A variety of hydraulic properties were measured in addition to leachate quality. Spent shales tested included those from the Lurgi-Ruhrgas, TOSCO II, Allis Chalmers Roller Grate, Paraho Direct Mode, Chevron STB, and Hytort retorting processes. One comprehensive data set, including measurements of the vapor diffusion coefficient, was developed for the Lurgi spent shales. This was accomplished by a new technique that utilized an iodine solution and a dual source of gamma rays to measure simultaneously the iodine and water distributions. These data permit distinguishing water that has been transported by vapor diffusion from that which moves as bulk liquid flux.**

***This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

## Introduction

The total identified shale oil resources in the U.S. are estimated by the U.S. Geological Survey to be over 270 billion metric tons, with a major source in the Green River formation of Colorado, Wyoming, and Utah. Possible future commercial exploitation of this vast resource warrants careful consideration of the effects that a commercial oil shale operation might have on the other natural resources of an oil shale region. Although a great deal of attention has been focused on these effects, data gaps still exist. The report provides information pertinent to the estimation of the quantity and quality of leachate from a spent shale disposal pile. These data will contribute to the eventual assessment and alleviation of potentially undesirable impacts on the water resources that will receive this leachate.

Oil shale facilities will produce large volumes of solid wastes, and the potential for recycling these wastes is small. Therefore, establishing environmentally acceptable methods for disposing of spent shale residues is an important objective for the oil shale industry.

In addition to the solid wastes, a significant amount of liquid waste will be generated by the various retorting processes. One method being proposed for disposing of this liquid waste is to codispose it with the solid waste. Spent shale leaves the retort at elevated temperatures, and various liquid waste streams could be used to help cool it before it is transported to a disposal site. Moisture is also needed for compaction at the disposal site and for dust control. Codisposal of the liquid and solid wastes, however, may change the impact of the disposal pile on the environs compared to using higher quality water for moisturization.

The project reported in this paper addresses the components needed for the prediction of disposal pile leachate quality and quantity. The primary objectives of the research are to provide a column leaching methodology and laboratory data base that will contribute to the eventual prediction and assessment of the quantity and quality of leachates from retorted shale disposal piles. Specific objectives are to:

1. Develop a viable column leaching test for spent shales.
2. Develop and verify the theory for the column leaching test so that results can be compared and generalized.
3. Compare the chemistry of leachate from the column test with the results from batch tests using the water shake test proposed by the ASTM and EPA's RCRA acetic acid test.
4. Conduct a study of the hydraulic and physical properties of spent shales, including both its saturated and unsaturated properties.
5. Quantify the effects on leachate quality of codisposing of the wastewaters from the retort process with the solid wastes.

This report describes: 1) two column leach test procedures, 2) the mathematical theory required for interpretation of the leach test data, 3) the results of chemical analyses of column leachate and comparison of these with the results of batch tests, 4) the hydraulic and physical properties of the retorted shales, and 5) the chemical differences in leachate quality if process waters, instead of higher quality water, are used for moisturizing the retorted shales.

While the data reported here are believed valid for the particular material tested, the relationship of these data to those for materials produced by the same process under different operating conditions (e.g., at a different temperature or at commercial scale) remain largely unknown.

## Summary and Conclusions

This report summarizes the development of methods for determining the leaching and hydraulic properties of solid residues resulting from the processing of oil shale. The activities, results, and conclusions can be divided into three major categories: 1) solid leaching, 2) hydraulic properties, and 3) codisposal of solid and liquid wastes. Category 3 is actually an application of the methodology developed in Category 1.

### *Solid Leaching*

The difficulty in establishing an initially saturated condition without causing some leaching led to a test in which the leachant (distilled water) was injected at a constant rate into the bottom of an initially dry column of solid. The salient feature of this test is incorporation of easily dissolved chemicals into the advancing wetting front upon contact by the leachant. An approximate mathematical model for this test was developed, applicable to conservative species instantaneously dissolved at the wetting front. For this reason, the test was called the Instantaneously Soluble Mass (ISM) test.

Several data sets collected from the ISM test are presented in this report. While it was determined that the test was reproducible and amenable to a reasonably simple mathematical analysis (for conservative species), important shortcomings remained. First, the injection of leachant into an initially dry medium did not simulate the expected field conditions in which the materia would be disposed of in a moist condition. Also, the results of the test were highly sensitive to the length of the column, an undesirable feature because it was not possible to construct the columns long enough to approach the depth of a field pile.

These shortcomings were eliminated by another type of column test, called the Equilibrated Soluble Mass (ESM) test developed by researchers under the project. In this procedure, the solid was moistened by distilled water (process water in the case of codisposal tests) until the water content was that expected to be a reasonable value for disposal under commercial operations. The moisturizing process was carried out by sprinkling the solid, spread on a plastic sheet, with frequent mixing and respreading. The moisturized material was then placed in a closed container and allowed to approach chemical equilibrium. The material, thus prepared, was packed into the leach column, and constant-rate injection into the bottom was started.

Both theoretical and experimental ev idence was developed that indicate that the pore solution existing in the column antecedent to injection is dis placed ahead of the invading solution This is the salient feature of this test Because of the displacement process the first effluent from the column is the antecedent pore solution and exhibit the chemical composition thereof. Be cause the chemical composition re sulted from equilibration of the wate with the solid at a liquid-to-solid rati approximately that expected durin field disposal operations, the quality o the first effluent should be a reasonabl index to the quality of the pore solutic in the field. Furthermore, the firs leachate generated in the field will b the antecedent pore solution, regard less of whether the leachate result from drainage or from net infiltratior Net infiltration will displace the an tecedent pore solution in the field, jus as does the injected water in the colum test.

A degree of mixing exists betwee the injected water and the displaced ar tecedent water due to hydrodynami dispersion. When this mixing zon reaches the outflow end of the colum the chemical composition of the efflu ent is no longer that of the anteceder pore solution. The subsequent brea through curve is affected by such expe imental parameters as column length, injection rate, particle size, and initial moisture content.

Examples of the chemical composition of the first effluent from ESM column tests are summarized in Table 1. Such data are expected to be reasonable indices to the quality of the first leachate that would occur from these materials. The two experiments on Lurgi ULG and on TOSCO II indicate the reproducibility of the test. Additional data relating to the assertion that the antecedent pore solution is displaced and to reproducibility are contained in the report.

Batch leaching tests, details of which are presented in the report, were also performed. The salient features of the batch tests, both RCRA and ASTM, are the violent agitation and the very large liquid-to-solid ratios that are utilized. Neither feature is remotely similar to field conditions. Nevertheless, batch tests can be used to assess the maximum quantity of extractable chemicals in a given quantity of raw or retorted shale. However, concentrations of most chemical components of leachate from disposal piles greatly exceed the concentrations observed in the batch tests, because the liquid-to-solid ratios that will exist in the waste piles will be much smaller than in the batch tests.

## Hydraulic Properties

The permeability at saturation, the moisture characteristic, and the permeability as a function of water content were measured on materials by recognized methods. These data are presented in the report. During the project, it became apparent that water transport at very low water contents would be an important consideration in the question of leachate generation. Extensive measurements of the hydraulic properties were made for one Lurgi retorted shale provided by the Rio Blanco Oil Shale Company.

A method was developed for measuring the hydraulic diffusivity down to practically zero water content. In this method, a horizontal column of the spent shale is injected at a very low rate with a syringe pump. The water content distribution is measured as a function of time and position in the column using gamma attenuation. These data permit the direct calculation of the hydraulic diffusivity.

As expected, the data indicated a range of water contents on the dry end of the water-content scale in which flow was dominated by vapor transport. The measurements were repeated using an iodine solution for injection and a dual source of gamma rays which permitted the simultaneous measurement of the concentration distribution of iodine and the water content distribution. It was observed that iodine-free water indeed moved ahead of water containing iodine. The iodine-free water moved by vapor diffusion. Further, it was observed that the plane separating the iodine-free water from the other liquid, while moving progressively farther into the medium, always occurred at a constant, characteristic water content. This characteristic water content was interpreted as being the value below which bulk, Darcian-type flow of liquid water could not occur. It is likely that liquid water at or below this characteristic value existed in adsorbed films not capable of bulk flow.

In the material on which these measurements were made, the critical water content was about 7% (by volume). This means, for example, that water contents up to about 7% in this material can be regarded as being nondrainable. Other materials are expected to have different values. Detection of the critical water content permitted separation of

***Table 1.*** *First Effluent Concentrations for ESM Tests*

| Run No. | Lurgi ULG 33 | Lurgi ULG 34 | TOSCO II 29 | TOSCO II 35 | Allis Chalmers 4 | Lurgi RB-II 3 | Paraho II 7 | Chevron 9 |
|---|---|---|---|---|---|---|---|---|
| EC(dS/m)[a] | 15.81 | 14.91 | 38.90 | 36.50 | 8.50 | 24.6 | 43.7 | 10.8 |
| F[b] | 17.8 | 13.0 | 29.2 | 24.9 | – | – | – | 8.2 |
| Cl | 355 | 341 | – | 218 | 298 | 145 | 240 | 234 |
| $SO_4$ | 9,650 | 9,840 | 23,300 | 28,510 | 6,820 | 6,480 | 35,300 | 2,400 |
| Na | 3,830 | 3,680 | – | 9,910 | 194 | 3,190 | 11,400 | 738 |
| Ca | 519 | 466 | 397 | 368 | 644 | 683 | 583 | 1,150 |
| Mg | 0.619 | 0.478 | 483 | 695 | 1,380 | 0.03 | 2,100 | 0.13 |
| Mo | 5.53 | 7.24 | 56.4 | 26.3 | 1.41 | 1.41 | 10.10 | 5.3 |
| K | | | | 109 | 340 | 629 | 1,440 | 130 |
| Fe | | | | | 32.20 | 0.02 | 0.14 | 0.07 |
| Mn | | | | | 31.90 | 0.01 | 0.05 | 0.03 |
| Sr | | | | | 4.10 | 31.90 | 5.3 | 32.9 |
| B | | | | | 5.64 | 2.25 | 1.92 | 1.96 |

[a]*Electric conductance in deci-siemens per meter.*
[b]*All concentrations in milligrams per liter.*

the diffusivity data into regions of vapor-dominated and liquid-dominated contributions. The method permits measurement of vapor diffusion coefficients.

### Codisposal

The ESM column test was used to assess the effect of codisposing process water with the solid. This was accomplished by utilizing distilled water as the moisturizing fluid in one set of tests and process water as the moisturizing fluid in an otherwise identical set of tests.

Table 2 summarizes the results of these codisposal trials. It is evident that moisturizing these materials with these waters tended to result in greater TDS concentration in the first effluent as compared to the tests in which the material was moisturized with distilled water. Even in the tests with distilled water moisturization, the TDS concentrations were quite large; therefore, the additional increment due to the process water may not be too significant.

The total organic carbon (TOC) concentration in the first effluent from materials moisturized with process water is markedly greater than from materials moisturized with distilled water. The data indicate significant adsorption of organic carbon by the solid, but adsorption is not sufficient to reduce the TOC in the first effluent to that observed in tests with distilled water moisturization.

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*The complete report, entitled "Leaching and Hydraulic Properties of Retorted Oil Shale Including Effects from Codisposal of Wastewater," (Order No. PB 87-120 507/AS; Cost: $18.95, subject to change) will be available only from:*
*National Technical Information Service*
*5285 Port Royal Road*
*Springfield, VA 22161*
*Telephone: 703-487-4650*
*The EPA Project Officer can be contacted at:*
*Air and Energy Engineering Research Laboratory*
*U.S. Environmental Protection Agency*
*Research Triangle Park, NC 27711*

***Table 2.*** *Summary of Results of Codisposal Tests*

| | Run No. | Moisturizing Fluid | Total Dissolved Solids, mg/l | | | Total Organic Carbon, ppm | | |
|---|---|---|---|---|---|---|---|---|
| | | | Moisturizing Fluid | First Effluent | Last Effluent | Moisturizing Fluid | First Effluent | Last Effluent |
| Lurgi RB-II | 1 | Unstripped Retort Water | 48,900 | 32,700 | 3,900 | 5,470 | 4,380 | 36 |
| | 2 | Stripped Retort Water | 8,430 | 18,200 | 4,020 | 3,700 | 2,660 | 54 |
| | 3 | Distilled Water | - | 13,200 | 38,200 | - | <5 | <5 |
| Paraho-II | 5 | Retort Water | 14,250 | 59,700 | 5,020 | 2,960 | 1,950 | 56 |
| | 6 | Gas Condensate | 79,200 | 65,900 | 5,150 | 4,140 | 1,820 | 118 |
| | 7 | Distilled Water | - | 52,900 | 4,770 | - | 531 | 12 |
| Chevron | 8 | Process Water | 3,790 | 9,300 | 2,690 | 660 | 565 | 20 |
| | 9 | Distilled Water | - | 5,680 | 3,900 | - | 380 | 18 |

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