

EPA, ASTM, AND COLUMN LEACHING OF PROCESSED
OIL SHALE--A COMPARATIVE STUDY

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ABSTRACT

Four laboratory leaching methods (the Environmental Protection Agency [EPA] extraction procedure, ASTM method D3987, and two column tests) were used to extract leachates from four low-void retorted oil shales to 1) compare the leaching procedures based on the chemical characterization of leachates derived from each leaching method and 2) establish the toxicity of each leachate relative to published EPA water quality criteria.

The EPA extraction procedure extracted the greatest concentration of trace elements of the methods tested. None of the concentrations of the seven metals (arsenic, barium, cadmium, chromium, lead, selenium, and silver) selected from those listed in the Resource Conservation and Recovery Act (RCRA) exceeded the RCRA limits defining a hazardous waste. On that basis, the low-void retorted oil shales would not be classified as hazardous.

INTRODUCTION

One area of environmental concern in the development of the oil shale industry is potential contamination of ground and surface waters by

organic and inorganic species leached from retorted oil shale. Whether the waste is disposed of on the surface or remains in an underground chamber after in situ retorting, the interaction between percolating water and retorted oil shale is a potential threat to water quality. A standard laboratory leaching procedure that characterizes retorted oil shale would be beneficial to solid waste management planning.

Numerous leaching experiments have been applied to retorted oil shales [1, 2, 3], but results of such studies cannot be directly compared because of varying test parameters (e.g., solid-to-liquid ratios, leaching media, agitation methods, and contact times). In only a few studies have the leaching procedures been similar enough to allow data comparison and interpretation. For these reasons, two batch and two column laboratory leaching methods were applied to four low-void retorted oil shales to provide comparative data that may be useful in the eventual formulation of a standard laboratory leaching procedure for processed oil shale.

The research objectives were to 1) compare the batch and column leaching procedures based on the chemical characteristics of oil shale leachates derived from each leaching method, and 2) establish the toxicity of each leachate relative to published EPA water quality criteria. Each leachate was analyzed for elements that are known to occur in

retorted oil shale but whose mobilities are questionable (beryllium, cobalt, lithium, molybdenum, nickel, and vanadium) [4], and elements for which Environmental Protection Agency [5,6] water quality criteria exist (antimony, arsenic, barium, boron, cadmium, chromium, copper, iron, lead, manganese, selenium, silver, and zinc).

EXPERIMENTAL

Oil Shale Samples

Retorted oil shale samples were obtained from the Engineering Office of Western Research Institute (WRI). The processed shales were produced in the WRI low-void retort (LVR) using Green River Formation oil shales from the Anvil Points mine, Colorado. The shales were indirectly heated to maximum average shale bed temperatures ranging from 450° to 580°C. A vertical retort was used with hot nitrogen gas. A continuous vertical pressure was maintained on the oil shale to simulate conditions in a commercial in situ retort [7]. Average retorting times were approximately eight days. The four oil shales used in this study are designated by their retort run number (LVR 24, 27, 28, and 29). Following the retorting process, the oil shales were crushed and riffled to obtain representative samples. All samples passed through a 0.95-mm standard sieve.

Oil Shale Analysis

Fischer assay values for the oil shales used in this study were determined using procedure ASTM D3904-80. These shales, which have Fischer assay values in the 20-40 gal/ton range, are generally representative of the oil shale likely to be mined commercially. Elemental analysis of the LVR oil shales was performed via sodium peroxide-sodium hydroxide fusions [8] dissolved in 20% HCl solution. The shales were analyzed by inductively

coupled plasma (ICP) emission spectroscopy for the 19 elements of interest (antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, lithium, manganese, molybdenum, nickel, selenium, silver, vanadium, and zinc). To reduce the impact of sample variability, 10 representative samples of each oil shale were fused and analyzed.

Methods of Leaching

Four methods were used to generate leachates from each processed oil shale sample. Two standard batch leaching procedures were used: ASTM D3987 [9] and EPA/RCRA extraction procedure (EP) [10]. The EP procedure was designed by EPA to simulate the leaching a waste will undergo if disposed of in an improperly designed sanitary landfill [11]. It requires a leaching medium of 0.1 N acetic acid solution simulating the formation of organic acids during anaerobic degradation at a disposal site. In contrast, ASTM method D3987 uses deionized-distilled water as the leaching medium. Two column methods were also used. Column method 1 (C1) is a column test designed to replicate the extraction medium, solid-to-liquid ratio, and contact time of ASTM method D3987. Column method 2 (C2) is a leaching method previously used at WRI [12]. The same extraction medium is used in both column methods, but column method 1 has a lower solid-to-liquid ratio, shorter contact time, and faster flow rate.

High-density polyethylene, wide-mouth bottles were used as extraction vessels in the batch tests. Precision borosilicate glass columns with chemically inert Teflon™ components were used in both column methods. Influent and effluent solutions passed through 0.45-µm filters and leachates were collected as single fractions. Extraction temperatures ranged between 20-25°C. Experimental parameters for the four leaching methods are given in Table 1.

Table 1. Experimental Parameters of Leaching Tests

| Parameter | ASTM | EP | Column-1 | Column-2 |
|-----------------------|---|---|---|---|
| Leaching medium | Deionized- distilled H ₂ O | 0.1 N acetic acid solution | Helium-purged deionized- distilled H ₂ O | Helium-purged deionized- distilled H ₂ O |
| Solid-to-liquid ratio | 1:4 | 1:20 | 1:4 | 1:30 |
| Agitation method | Reciprocating shaker, 70 strokes per min. | End-over-end rotating extractor, 30 RPM | None | None |
| Contact time (hrs) | 48 | 24 | 48 | 24 |
| Flow rate | -- | -- | 0.14 ml/min (upward) | 1.0 ml/min (upward) |

Methods of Leachate Analysis

Environmental Protection Agency analytical methods [13] were used to determine leachate pH, conductivity, and alkalinity within 24 hours of leachate generation. Leachate concentrations of antimony, barium, beryllium, boron, chromium, cobalt, copper, iron, lithium, manganese, molybdenum, nickel, silver, vanadium, and zinc were determined by ICP. Flame atomic absorption was used to determine arsenic and cadmium levels and furnace atomic absorption was used to analyze the leachates for their concentrations of lead and selenium.

Quality Assurance

All leaching methods were performed in duplicate on one shale sample (LVR 27). In addition, ASTM and EP batch tests were performed in duplicate for each shale. Results and conclusions are based on averages of the duplicate values for

those leachates. To check instrument precision, one sample in five was split and analyzed blindly.

RESULTS AND DISCUSSION

Leachate Characteristics

The pH, conductivity, and alkalinity differ markedly between those oil shale leachates extracted with distilled water and those extracted by acetic acid solution. pH values of the leachates generated by ASTM, C1, and C2 methods were all similar (approximately 11), whereas EP extracts had lower pH values ranging from 7 to 9 (Table 2). A linear relationship was found to exist between conductivity and alkalinity for the ASTM and column leachates (Figure 1), indicating a single major ionic species contributing to both. These leachates required very small amounts of sulfuric acid to reach the 4.5 endpoint of the alkalinity test (Table 3), indica-

Table 2. Leachate pH Values

| SHALE | LEACHING METHOD | pH* |
|--------|--------------------|------|
| LVR 24 | C1 | 11.4 |
| | C2 | 11.1 |
| | ASTM | 11.4 |
| | EP | 8.7 |
| LVR 27 | C1 | 11.5 |
| | C2 | 11.8 |
| | ASTM | 12.1 |
| | EP | 8.7 |
| LVR 28 | C1 | 11.0 |
| | C2 | 11.3 |
| | ASTM | 11.4 |
| | EP | 9.1 |
| LVR 29 | C1 | 11.3 |
| | C2 | 11.2 |
| | ASTM | 11.3 |
| | EP | 7.2 |

* at 25°

Table 3. Millimoles of Acid Required to Reach Alkalinity Test Endpoints, pH 8.2 and 4.5

| SHALE | LEACHING METHOD | 0.0245 N H ₂ SO ₄ | |
|--------|--------------------|---|-------------------------|
| | | MILLIMOLES to pH 8.2 | MILLIMOLES to pH 4.5 |
| LVR 24 | C1 | 0.212 | 0.017 |
| | C2 | 0.047 | 0.01 |
| | ASTM | 0.134 | 0.015 |
| | EP | 0.001 | 0.661 |
| LVR 27 | C1 | 0.284 | 0.012 |
| | C2 | 0.12 | 0.01 |
| | ASTM | 0.380 | 0.01 |
| | EP | 0.0 | 0.525 |
| LVR 28 | C1 | 0.316 | 0.017 |
| | C2 | 0.167 | 0.01 |
| | ASTM | 0.469 | 0.023 |
| | EP | 0.0 | 0.542 |
| LVR 29 | C1 | 0.234 | 0.01 |
| | C2 | 0.11 | 0.01 |
| | ASTM | 0.319 | 0.01 |
| | EP | 0.0 | 0.567 |

ting that bicarbonate and carbonate were of minor ionic importance in the leachate solutions [14]. The high pH values of the ASTM, C1, and C2 leachates further suggest that the hydroxyl ion was the major source of alkalinity and conductivity. The EP leachates did not show a linear relationship between conductivity and alkalinity (Figure 1). These leachates required little or no addition of sulfuric acid to reach the 8.2 endpoint of the alkalinity test because of the initial acidity of the

extraction media (Table 2). However, relatively large amounts of acid were required to reach the 4.5 endpoint. This suggests that the acetate ions present in the leachates reacted with the sulfuric acid ($\text{HAC} + \text{AC}^- + \text{H}^+$; $-\log K_a$ (25°C) 4.7) [15], adding to the total alkalinity.

Trace Metal Extractability

Metals in the mineral phases of oil shale may be 1) insoluble in the leaching medium, 2) solubilized and in solution, 3) solubilized and then

precipitated out of solution as a hydroxide or oxide, or 4) solubilized and absorbed onto the surface of an insoluble species and precipitated. The extractability of a metal from oil shale depends largely upon its mineralogical residence in the shale, the effects of processing on those mineral phases, the concentration of the metal present in the shale, and the pH of the leaching medium.

Several metals (arsenic, beryllium, cadmium, chromium, cobalt, copper, nickel, selenium, and silver) were present in low concentrations in the shales used in this study. As a result, their leachate concentrations were also very low or below instrumental detection limits (Table 4). These metals would also most likely be precipitated from the alkaline leachates as hydroxides or carbonates (Table 5).

In Figures 2-12, the leaching methods' effectiveness in extracting trace metals can be

quantitatively compared. Data on arsenic, beryllium, cadmium, cobalt, copper, lead, selenium, and silver are not included because the concentrations of these trace metals were below instrumental detection limits in all leachates (Table 6).

In two cases the shales contained a significant amount of a trace metal but the leachates did not. The LVR shales contained an average of 400µg of lead per gram of shale, but the lead concentrations in the leachates were below detection limit. Low levels of lead in the leachates would be expected because of the low solubility product constants for lead hydroxide and lead carbonate (Table 5). The processed shales also contained significant amounts of iron (approximately 17,000µg/g); however, only very low concentrations were detected in the EP leachates (Figure 9). The solubility product constants for iron hydroxides and iron carbonate

Table 4. Elemental Concentrations in the Processed Oil Shales and Oil Shale Leachates (µg/g)

| Element | LVR 24 | LVR 27 | LVR 28 | LVR 29 |
|---------|----------------------------|----------------------------|----------------------------|----------------------------|
| | Shale / Leachate | Shale / Leachate | Shale / Leachate | Shale / Leachate |
| Ag | $\bar{x} < 50 / *$ | $\bar{x} = 158 / *$ | $\bar{x} < 50 / *$ | $\bar{x} < 50 / *$ |
| As | $\bar{x} < 50 / *$ | $\bar{x} = 195 / *$ | $\bar{x} < 50 / *$ | $\bar{x} < 50 / *$ |
| Be | $\bar{x} < 50 / *$ | $\bar{x} < 50 / *$ | $\bar{x} < 50 / *$ | $\bar{x} < 50 / *$ |
| Cd | $\bar{x} < 50 / *$ | $\bar{x} < 50 / *$ | $\bar{x} < 50 / *$ | $\bar{x} < 50 / *$ |
| Co | $\bar{x} < 50 / *$ | $\bar{x} = 112 / *$ | $\bar{x} < 50 / *$ | $\bar{x} < 50 / *$ |
| Cr | $\bar{x} < 50 / 0.06-1.36$ | $\bar{x} = 99 / 0.98$ (EP) | $\bar{x} < 50 / 1.24$ (EP) | $\bar{x} < 50 / 1.21$ (EP) |
| Cu | $\bar{x} = 91 / *$ | $\bar{x} = 60 / *$ | $\bar{x} = 60 / *$ | $\bar{x} = 58 / *$ |
| Ni | $\bar{x} < 50 / 2.27$ (EP) | $\bar{x} = 54 / 1.46$ (EP) | $\bar{x} < 50 / 2.18$ (EP) | $\bar{x} < 50 / 2.29$ (EP) |
| Se | $\bar{x} = 313 / *$ | $\bar{x} < 50 / *$ | $\bar{x} = 421 / *$ | $\bar{x} < 50 / *$ |

* Concentration below instrumental detection limit (Table 6) in ASTM, EP, C1, and C2 leachates.

(EP): detected in EP leachates only

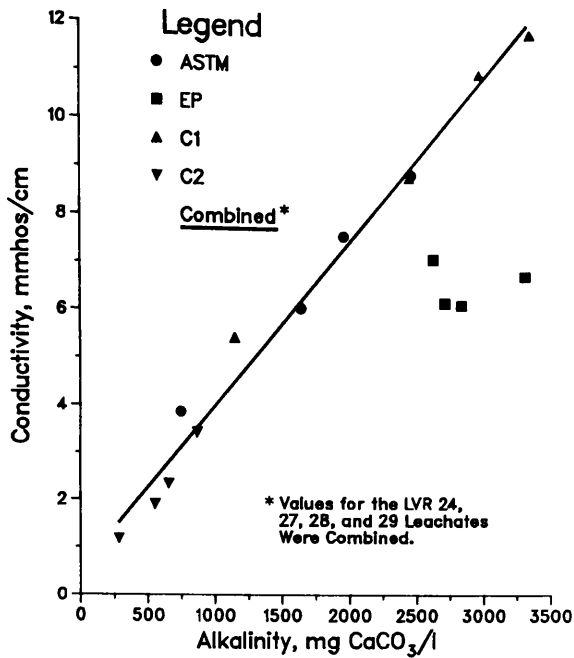


Figure 1. Alkalinity Vs. Conductivity in the Oil Shale Leachates (Data Points for the EP Samples Not Used in Generating the Regression Line)

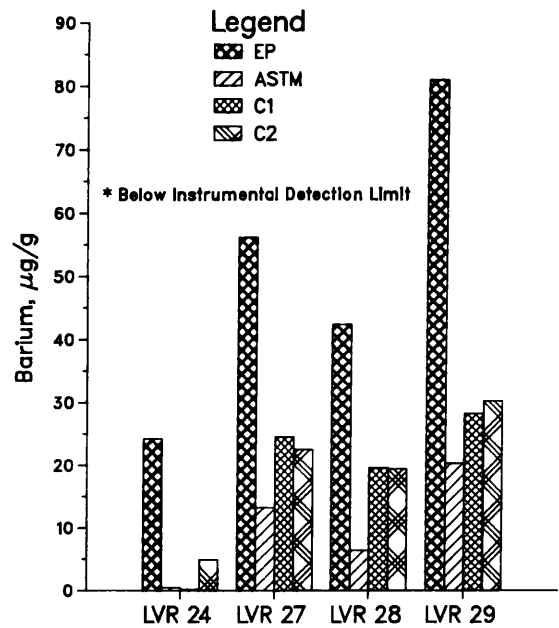


Figure 2. Comparison of Leaching Methods for Barium

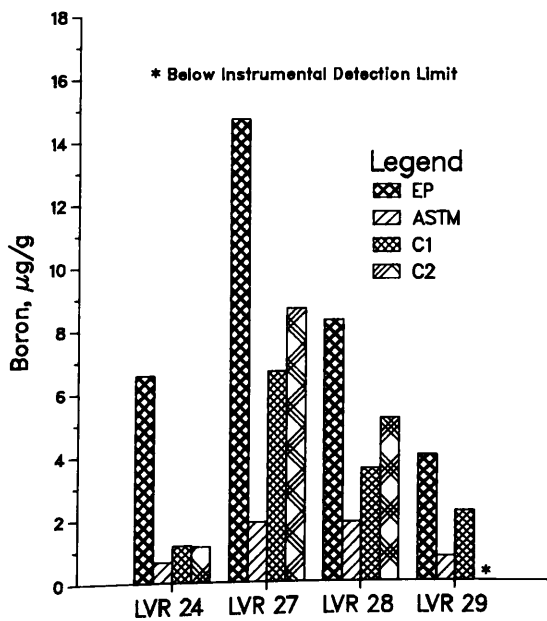


Figure 3. Comparison of Leaching Methods for Boron

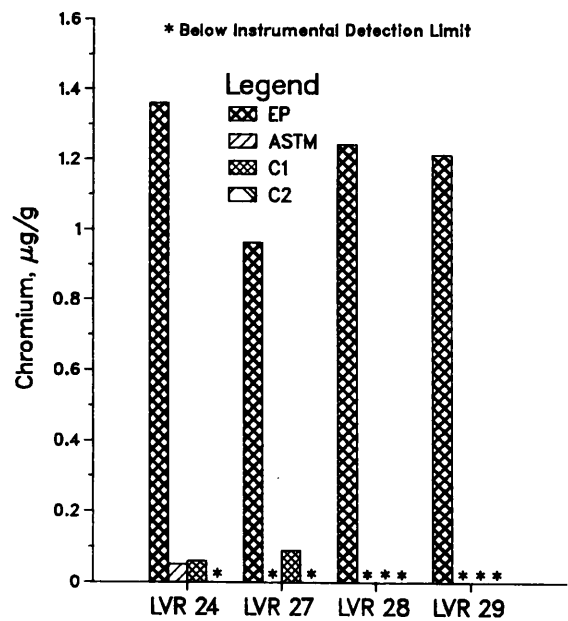


Figure 4. Comparison of Leaching Methods for Chromium

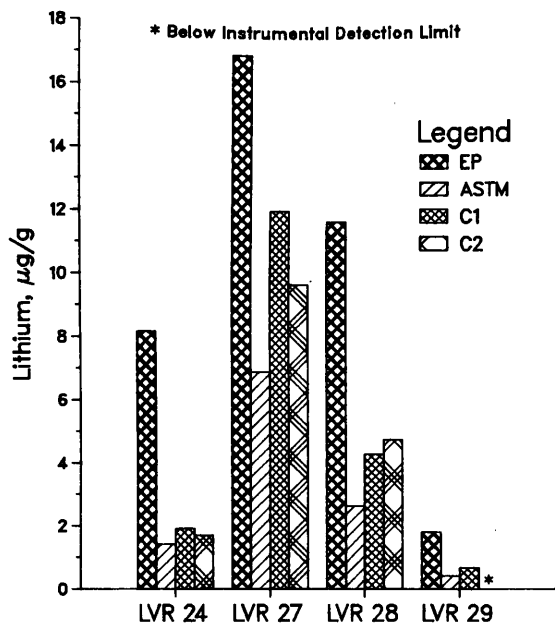


Figure 5. Comparison of Leaching Methods for Lithium

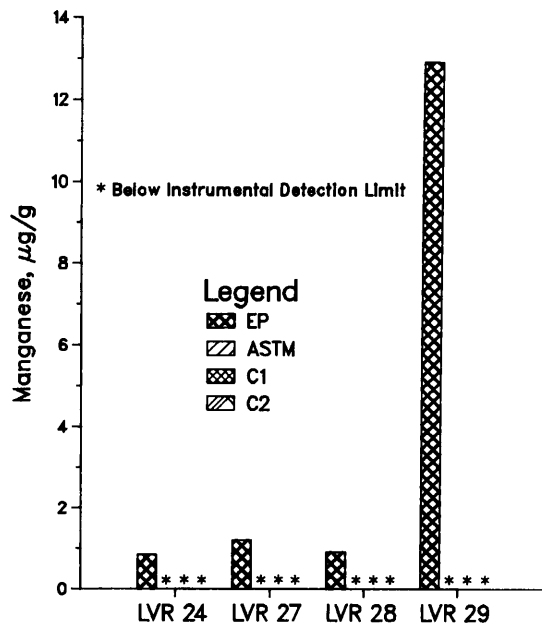


Figure 6. Comparison of Leaching Methods for Manganese

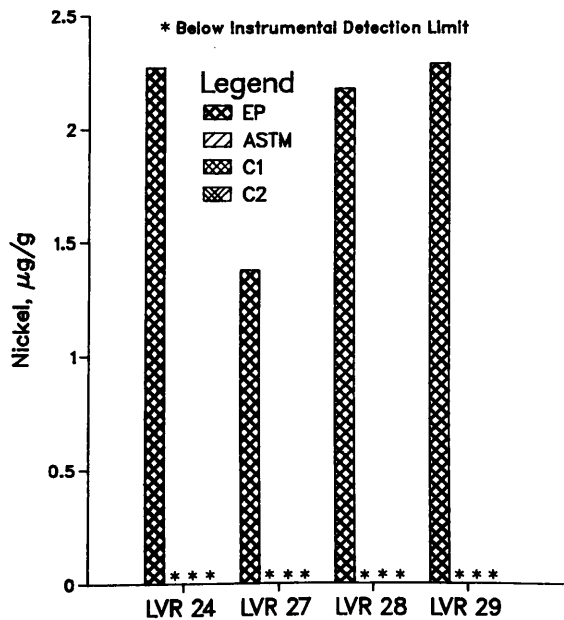


Figure 7. Comparison of Leaching Methods for Nickel

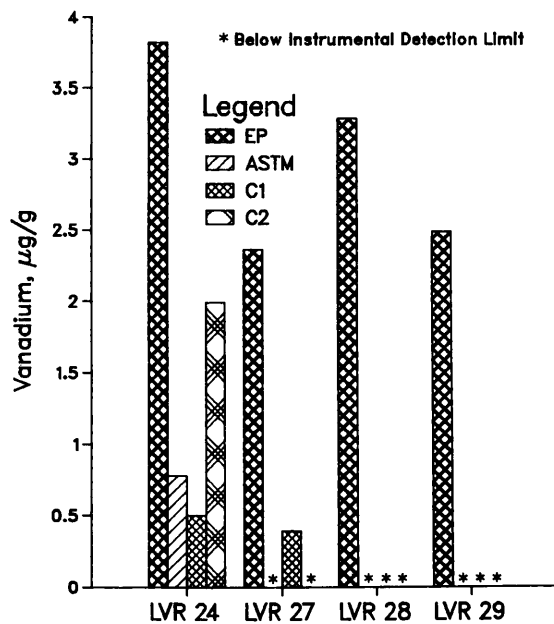


Figure 8. Comparison of Leaching Methods for Vanadium

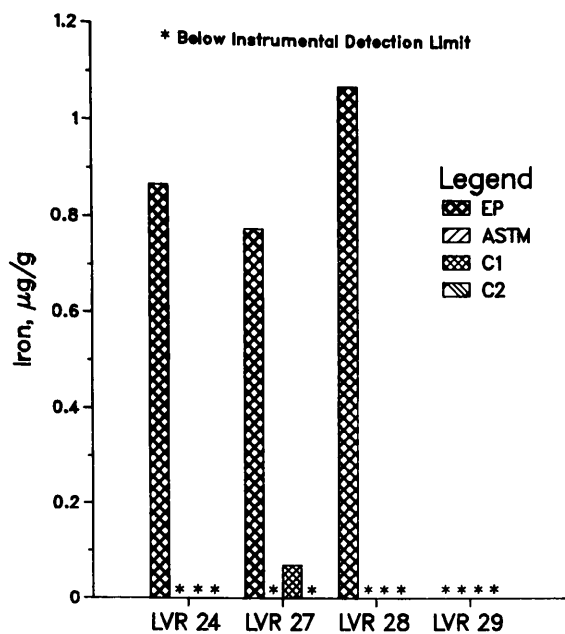


Figure 9. Comparison of Leaching Methods for Iron

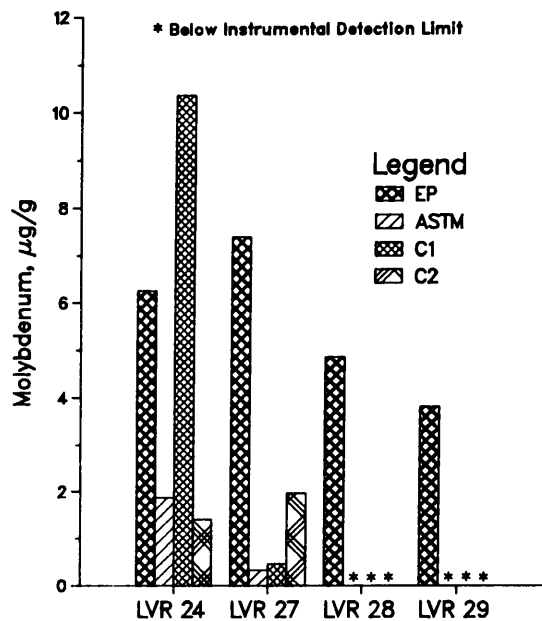


Figure 10. Comparison of Leaching Methods for Molybdenum

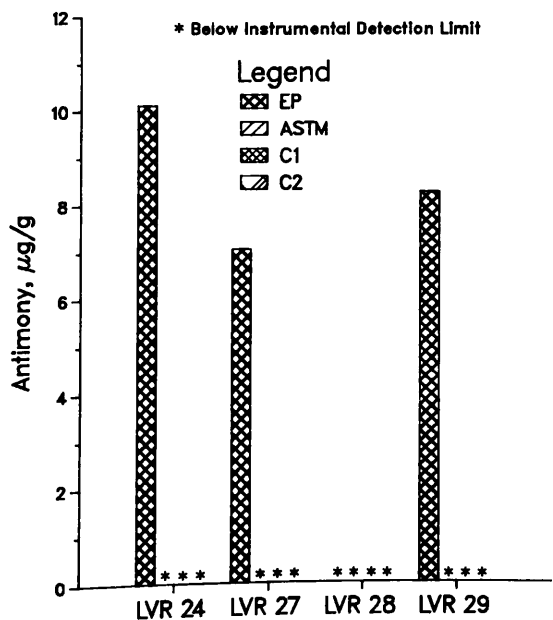


Figure 11. Comparison of Leaching Methods for Antimony

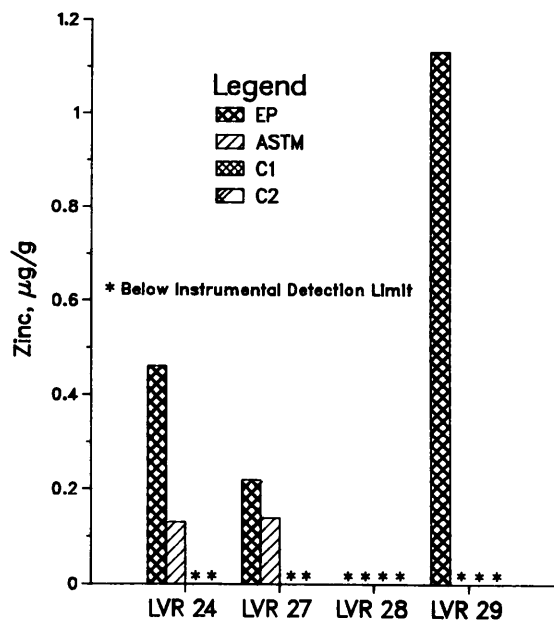


Figure 12. Comparison of Leaching Methods for Zinc

Table 5. Hydroxide and Carbonate Solubility

Product Constants, K_{sp} [16,17]

| <u>Compound</u> | <u>K_{sp}</u> |
|---------------------------------|----------------------------|
| AgOH | 2×10^{-8} |
| Ag ₂ CO ₃ | 8.2×10^{-12} |
| Be(OH) ₂ | 1×10^{-18} |
| Cd(OH) ₂ | 1.2×10^{-14} |
| CdCO ₃ | 2.5×10^{-14} |
| Co(OH) ₂ | 2×10^{-16} |
| Co(OH) ₃ | 2.5×10^{-43} |
| CoCO ₃ | 1.0×10^{-12} |
| Cr(OH) ₃ | 6.7×10^{-31} |
| Cu(OH) ₂ | 5.6×10^{-20} |
| CuCO ₃ | 1.37×10^{-10} |
| Fe(OH) ₂ | 7.9×10^{-15} |
| Fe(OH) ₃ | 1.1×10^{-36} |
| FeCO ₃ | 2.11×10^{-11} |
| Ni(OH) ₂ | 1.6×10^{-14} |
| NiCO ₃ | 1.36×10^{-7} |
| Pb(OH) ₂ | 2.8×10^{-16} |
| PbCO ₃ | 1.5×10^{-13} |

(Table 5) indicate there would be limited iron solubility at the leachate pH values.

The effect of pH on solubility is further illustrated by the concentrations of manganese in the leachates. In oil shale of the Green River

Table 6. Instrumental Detection Limits

ICP Metal Detection Limits

| | |
|----|----------|
| Ag | 0.02 ppm |
| B | 0.02 ppm |
| Ba | 0.02 ppm |
| Be | 0.02 ppm |
| Co | 0.02 ppm |
| Cr | 0.02 ppm |
| Cu | 0.02 ppm |
| Fe | 0.02 ppm |
| Li | 0.02 ppm |
| Mn | 0.01 ppm |
| Mo | 0.02 ppm |
| Ni | 0.02 ppm |
| Sb | 0.2 ppm |
| V | 0.02 ppm |
| Zn | 0.02 ppm |

AA Metal Detection Limits

| | |
|----|-----------|
| As | 0.01 ppm |
| Cd | 0.003 ppm |
| Pb | 0.01 ppm |
| Se | 0.01 ppm |

Formation, manganese has been associated with carbonate phases (ferroan dolomite, siderite, and magnesium-siderite) [18]. The major carbonate constituents of oil shale begin to decompose in the range of 570-650°C [19]. The maximum average bed temperatures were at or below 580°C when the shales used in this study were retorted. Thus, it is assumed that little carbonate decomposition occurred during retorting and manganese in the retorted shales remained associated with the carbonate

phases. Manganese carbonate dissolves at a pH less than 8.5 [20]. As a result, manganese was leachable only in the acidic EP media (Figure 6).

The dependence of manganese solubility on pH is further emphasized by the difference between the manganese concentration in the LVR 29 leachate (pH ~7) compared with the concentrations in the other leachates (pH ~9). While the LVR 29 shale contained slightly less manganese than the other three shales, the LVR 29 leachate contained more than 10 times as much manganese as the EP leachates of the other oil shales. The very low concentrations of manganese in the LVR 24, 27, and 28 EP leachates (approximately 1µg/g) could be attributed to their pH values being near the borderline of Mn^{+2} solubility. Once Mn^{+2} is released into the aqueous solution it may be hydrolyzed to manganese hydroxide, which precipitates out of solution at a pH of about eight [21]. In addition, the lower pH of the LVR 29 leachate would reduce Mn^{+2} adsorption and subsequent coprecipitation that might occur. Hydrogen ions can modify or compete for active sites on a sorbing material and reduce metal binding [22]. The sorption of Mn^{+2} on precipitated manganese oxide has been shown to decrease with pH because of changes in the sorption sites [23].

Comparison of Leaching Methods

The EP extraction procedure was the most powerful based on the number of micrograms of antimony, barium, boron, chromium, iron, lithium, manganese, molybdenum, nickel, vanadium, and zinc extracted per gram of shale by each of the leaching procedures studied (Figures 2-12). In an earlier study, the EP procedure was also the more powerful leaching method, compared with the ASTM method, when the more aggressive end-over-end rotating extractors were used for agitation in both tests [24]. Based

on the results of the earlier study and of this study, the general capability of the EP procedure to extract greater concentrations of trace metals than the other methods studied can be attributed to the acidic leaching medium rather than the method of agitation.

No comparisons of the ASTM, C1, and C2 methods could be made because many concentrations in their leachates were below instrumental detection limits.

Hazard Evaluation

Trace metal concentrations generated by the EP extraction procedure generally exceeded maximum limits and recommended maximum limits of EPA water quality criteria for domestic drinking water, irrigation water, and livestock drinking water [5, 6]. However, none of the concentrations of the seven metals (arsenic, barium, cadmium, chromium, lead, selenium, and silver) selected from those listed in the Resource Conservation and Recovery Act (RCRA) [11] exceeded the RCRA limits that define a hazardous waste. On that basis, the low-void retorted oil shales would not be classified as hazardous.

CONCLUSIONS

The EPA extraction procedure was the most aggressive of those tested in this study. This is attributable to the presence of acetic acid in the extraction media because mineral and elemental solubility are dependent upon solution pH. Based on the trace metal concentrations generated by the EPA method, the LVR shales would not be classified as hazardous.

REFERENCES CITED

1. Bethea, R.B., D.R. Barber, H.W. Parker, and N. Guven. Soc. Petroleum Engineers J., 1983, 23, 809-18.

2. Stollenwerk, K.G. and D.D. Runnells. "Leachability of Arsenic, Selenium, Molybdenum, Boron, and Fluoride from Retorted Oil Shale," Second Annual Pacific Chem. Eng. Congress Proceedings, vol. II, Denver, CO, 1977.
3. Esmaili, E. Ph.D. Dissertation, University of Colorado, Boulder, CO, 1983.
4. National Research Council, Board on Mineral and Energy Resources, Committee on Accessory Elements. "Redistribution of Accessory Elements in Mining and Mineral Processing," National Academy of Sciences: Washington, D.C., 1979.
5. United States Environmental Protection Agency. "Quality Criteria for Water," Washington, D.C., 1976.
6. National Academy of Sciences, National Academy of Engineering. "Water Quality Criteria, 1972," Washington, D.C., 1972.
7. Fahy, L.J. Western Research Institute, Laramie, WY, May, 1985, Report prepared for USDOE under contract no. DE-FC21-83FE60177, in press.
8. Corbett, J.A., W.C. Goodbeer and N.C. Watson. Australas. Inst. Min. Metall., Proc., 1974, no. 250, 51-54.
9. American Society for Testing and Materials, Annual Book of ASTM Standards, 1983, 11.04, proc D3987-81.
10. EPA, "Rules and Regulations," Federal Register, May 19, 1980, 45, 33128.
11. "Test Methods for Evaluating Solid Wastes: Physical and Chemical Methods, 2nd Ed.," Envir. Prot. Agency, 1982, Pub. SW-846.
12. McGowan, L.J. Western Research Institute, Laramie, WY, May 1985, Report prepared for USDOE under contract no. DE-FC21-83FE60177, in press.
13. EPA, "Methods for Chemical Analysis of Water and Waste," 1974, EPA-625/6-74-003a.
14. American Society for Testing and Materials. "Manual on Water, 3rd Edition," ASTM Special Technical Publication 442, 1969.
15. Snoeyink, V.L. and D. Jenkins. In "Water Chemistry," John Wiley and Sons: New York, 1980; Chapter 4.
16. Nebergall, W.H., F. Schmidt, and H. Holtzclaw, Jr. In "General Chemistry," 5th ed.; D.C. Heath and Company: Lexington, Massachusetts, 1976; Appendix E.
17. Sposito, G. and S.V. Mattigod. Geochem: A computer program for the calculation of chemical equilibria in soil solutions and other natural water systems. The Kearney Foundation of Soil Science, University of California, Riverside, CA, 1980.
18. Desborough, G.A., J.K. Pitman, and C. Huffman, Jr. Chem. Geol., 1976, 17, 13-26.
19. Jukkola, E.E. Ind. and Eng. Chem., 1953, 45, 2711-2714.

20. Wedepohl, K.H. In "Handbook of Geochemistry,"
Wedepohl, K.H., Ed., Springer-Verlag: Berlin,
1978, II/3, 25-D-1 through 25-D-26.
21. Baes, C.F. and R.E. Mesmer. "The Hydrolysis of
Cations," 1st ed.; John Wiley and Sons: New
York, 1976.
22. Rubin, A.J. "Aqueous-Environmental Chemistry of
Metals," 1st ed.; Ann Arbor Science Publishers:
Ann Arbor, Michigan, 1974.
23. Morgan, J.J. and W. Stumm. J. Colloid Sci.,
1964, 19, 347-359.
24. Donovan, R. and S. Sorini. Western Research
Institute, Laramie, WY, Nov. 1985, Report
prepared for USDOE under contract no. DE-FC21-
83FE60177, in press.