

**SOLID/RETORT WATER INTERACTIONS:
THE FATE OF ORGANICS AND INORGANICS**

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ABSTRACT

Codisposal of solid wastes and low-quality aqueous effluents from oil shale operations is among the disposal methods being considered for these wastes. A preliminary experimental evaluation of this practice focused on the validation of analytical techniques for studying the chemistry that occurs when these wastes are mixed. Three shale types were contacted with a single retort water to evaluate the effects of shale type and surface area on the behavior of organics when in contact with solid shales and the mobilization of inorganics within solid shales. Distilled water leachates from these shales were used as the base-line case. The inorganic compositions of distilled water and retort water leachates were compared. The pH and conductivities of these leachates suggest that the ultimate compositions of leachates from codisposal are dependent on both the shale type and the leaching medium. The concentrations of the trace elements suggest that they are mobilized by the retort water leaching medium. This mobilization probably is due to complexation by organic ligands or by increased solubility caused by the ionic strength of the leaching medium. The organic compositions of these leachates are dependent on the shale type. Because of the nature of the analytical methods, only about 5 wt% of the solvent extractable material was analyzed. However, previous work suggests that the material being analyzed contains the majority of the mutagenic compounds.

INTRODUCTION

During oil shale retorting, by-products are formed, including spent shale and retort water. The solid waste form has been the subject of extensive study (1-5), primarily as a function of the two independent variables, the starting materials and the retorting process (6-8). The waste retort waters also have been extensively characterized (9-11), but are not well understood in the context of those variables important in the formation and behavior of these aqueous effluents.

Oil shale developers have long recognized the advantages of disposing of low-quality retort water by codisposing the water with spent shale. This method has several advantages: (a) aiding in the cooling of spent shale, (b) moistening spent shale piles for long-term stability, and (c) minimizing the need for extensive cleanup of retort water before disposal. The purpose of our experiment was to validate analytical methods for characterization of the aqueous composition of leachates after contacting spent shale with waste retort water so a preliminary evaluation of the codisposal strategy could be made. This experimental approach, in conjunction with future experiments, could be used to examine the environmental implications of codisposal practices.

Quantitative and qualitative characterization of both inorganic and organic constituents is necessary to understand the chemical principles governing the behavior of these species while spent shale and waste retort water are in contact. Procedures for the preparation and analysis of retort water for inorganic constituents have been well established (12). The initial concern was to

develop an organic fractionation procedure that would be manageable and reproducible and could be used as a standard operating procedure for the preparation of samples for organic analysis. The results of some preliminary experiments in this area are described.

EXPERIMENTAL SECTION

1. Sample Descriptions. Three shales were used in these experiments; the legend for their mineralogy is as follows: strong = S, moderate = M, weak = W, very weak = VW, trace = T, and none detected = O. The first shale (denoted LW-156) was prepared from samples from the Logan Wash site and heated to 1200 K in a flowing air atmosphere for 6 h. The minerals present in this sample include α -quartz (W), akermanite-gehlenite (M-S), periclase (W-M), wollastonite (M), and merwinite (M). The second shale (denoted LANL) was prepared from Anvil Points shale combusted in the Los Alamos biological test retort in a flowing air atmosphere at approximately 875 K. The mineralogy of this sample is α -quartz (S), dolomite (M), calcite (M), analcime (M), albite (M), orthoclase (T), illite (W), and periclase (T). The third shale is a Lurgi-type processed shale using tract C-a raw material (denoted Lurgi-type shale). The minerals present in this shale include α -quartz (S), dolomite (W-M), calcite (M), analcime (VW), albite (M), orthoclase (VW), illite (VW), anhydrite (M), and periclase (VW).

The retort water sample used in this study was obtained from the Occidental Oil Shale, Inc., retort 6 operations. This water was chosen because of our extensive experience in its characterization.

2. Experimental Design. To obtain the liquid constituent for investigation, contact between spent shale and retort water was achieved by shaking the solid in the liquid at a 1/5 weight/volume ratio for 48 h at ambient temperature. The two phases were separated by centrifugation and Millipore filtration. Liquid/solid contact was carried out on two sizes of the same solid, -3/8 in. and -100 mesh, which gave a surface area ratio of 1/200 (except for the Lurgi-type

shale experiment). The two sizes were contacted with both distilled water and retort water, using four shaking containers. To establish a base-line control, a shaking container with only retort water was subjected to the same preparation procedure. This procedure was not meant to simulate any disposal scenario, but was designed to validate analytical methods and to give some insight into retention properties as a function of shale type. The adsorption capacities of all shales were greatly exceeded by these experimental conditions, but some gross effects were recognized. A second experiment was performed to observe the effect of releaching with distilled water. The solids from the first experiment were recovered, dried in a nitrogen atmosphere, reweighed, and subjected to the same liquid/solid contacting conditions, sample preparation, and analysis, as previously described.

The resulting liquids were used for pH, conductivity, total organic carbon, elemental, and, after using the fractionation described below, organic analysis. Elemental concentrations of soluble inorganics were obtained with a Beckman Spectraspan IIIB direct-current argon plasma emission spectrometer. Simulated distillation analysis was accomplished using a Hewlett Packard 5711A gas chromatograph (GC) with capillary column SE-54, 0.025-mm ID X 30 m, for organic base/neutral analysis and a Carbowax 20M capillary column, 0.025-mm ID X 30 m, for organic acid analysis.

3. Organic Fractionation Methods Development. Fully recognizing the potential limitations and drawbacks of liquid/liquid extraction procedures, we nevertheless investigated these procedures. A number of organic solvents (toluene, methylene bromide, cyclohexane, chloroform, ethyl acetate) were investigated using various extractant/water ratios and pH conditions. Extraction of the organics was incomplete as shown by carbon analysis (analysis for carbon was carried out on a direct-injection module instrument--Oceanographic International Corporation Model 0524B-HR).

The fractionation procedure that satisfied the operating criteria proved to be a liquid/liquid separation using methylene dichloride and pH adjustments with concentrated hydrochloric acid and a 50% solution of sodium hydroxide (Fig. 1).

The mass of each fraction was determined by drying to constant weight at ambient temperature for all precipitates and final dry fractions. Gravimetric data showed incomplete solubility in methylene dichloride and salt formation during the titration with sodium hydroxide and hydrochloric acid during the pH adjustments. An emulsion was observed at the interface. Although it is possible to separate the base fraction from the neutral fraction, GC analysis showed that this separation was not complete and showed losses of sample. Therefore, we separated the sample into final base/neutral and acid fractions, which were dried in a nitrogen atmosphere, reconstituted using tetrahydrofuran, and analyzed using the procedures and conditions described above.

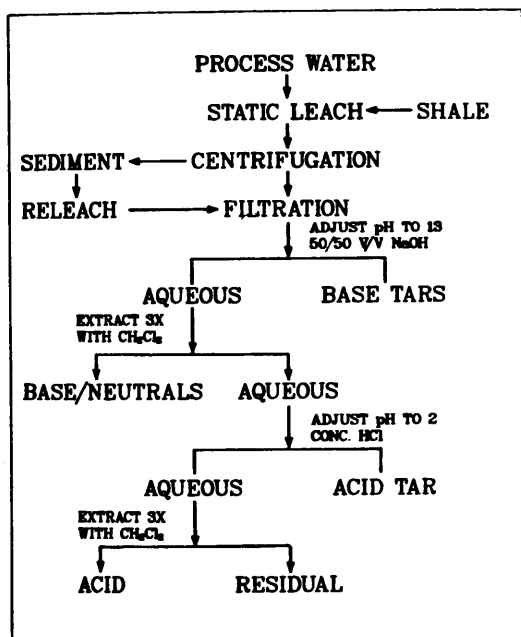


Fig. 1. The organic fractionation procedure.

4. Chromatography and Data Reduction. The chromatographic techniques were a modification of ASTM Method D-3710, in that the calibration of the retention time/boiling point relationship was accomplished by injection of a series of normal hydrocarbons. For the base/neutral fraction, hydrocarbons from nonane to eicosane were used. The boiling point was found to be related to the retention time of the normal hydrocarbons by the formula $BP(^{\circ}C) = 61.81 * T_r(\text{min})^{.448}$. A standard mixture of compounds (Hewlett Packard capillary

performance evaluation standard, part number 18740-60900) was run before each day's chromatographic runs. The concentration was determined by the area of the pentadecane peak in this standard and was used to mass calibrate the samples determined that day. The run conditions for the base/neutral constituents were $4^{\circ}C/\text{min}$, 40 to $250^{\circ}C$, and a $4.0\text{-}\mu\text{L}$ sample load.

The acid fractions were analyzed differently from the normal procedure. A volatile acid standard containing 0.1 milliequivalent of the following acids was prepared: acetic, propionic, i-butyric, n-butyric, i-valeric, n-valeric, i-caproic, n-caproic, and n-heptanoic acids were added volumetrically to distilled, deionized water. The mixture was placed in a crimp-top vial and stored in the refrigerator. The measured retention times and areas under the peaks from the standard acid solution were used to calibrate the chromatographic determinations made on each day. The mass response factor for n-heptanoic acid was used to estimate the amount of n-octanoic, n-nonanoic, n-decanoic, and n-undecanoic acids in the samples.

The simulated distillation curves were generated from digitized area slices of the individual chromatograms for both the base/neutral and acid fractions. The areas were determined by manual digitization using a Hewlett Packard 9111A graphics tablet connected to a Hewlett Packard 85 computer. Retention times were determined from the original chromatograms and used with the appropriate relational formula to give equivalent boiling points for the beginning and end of each area slice. The areas were converted to micrograms using the appropriate response factor from the standards. The running sum of micrograms in each area slice was plotted versus the average of the boiling points for the area, giving the simulated distillation curve for that fraction.

RESULTS AND DISCUSSION

1. Inorganics. Tables 1A, B, and C show the inorganic analysis data. For comparison, the analysis of the original retort water for each experiment also is given in the tables. Noticeable differences between the base-line data and both of the experimental (size) conditions (columns A and

TABLE 1A. INORGANIC RESULTS FOR HIGH-TEMPERATURE LW-156 SHALE (ppm)

Element	Retort Water	-3/8-in. shale		-100-mesh shale	
		DW ^a	RW ^b	DW	RW
pH	8.8	11.0	9.1	10.6	9.3
Cond. (mS)	10.2	4.2	12.0	4.5	11.6
B	15.9	1.1	17.0	0.92	16.7
Ca	3.1	221	9.	254	11.9
Cu	0.29	0.04	0.17	0.07	2.8
K	185	99.8	498	106	630
Li	0.92	2.47	4.14	2.54	5.46
Mg	7.67	0.88	241	0.86	349
Mo	0.20	0.88	1.77	0.78	2.28
V	0.01	0.41	3.18	0.51	3.16

TABLE 1B. INORGANIC RESULTS FOR LOS ALAMOS-RETORTED ANVIL POINTS SHALE (ppm)

Element	Retort Water	-3/8-in. shale		-100-mesh shale	
		DW	RW	DW	RW
pH	8.8	12.3	11.5	12.2	11.6
Cond. (mS)	18.0	8.9	12.2	8.9	12.6
B	12.7	0.11	11.6	0.13	4.35
Ca	4.2	492	11.2	460	82.1
Cu	0.02	0.01	0.20	0.01	0.26
K	106	182	297	171	317
Li	1.98	3.00	6.95	2.91	5.24
Mg	6.0	0.08	0.05	<0.01	0.15
Mo	0.31	0.8	1.97	0.72	1.72
V	0.04	0.08	1.91	0.09	0.43

TABLE 1C. INORGANIC RESULTS FOR LURGI-TYPE SHALE PROCESSED FROM TRACT C-a RAW MATERIAL (ppm)

Element	Retort Water	+6- to 40-mesh shale		-100-mesh shale	
		DW	RW	DW	RW
pH	8.9	11.8	10.3	11.5	10.9
Cond. (mS)	11.6	3.5	11.7	3.6	12.4
B	16.6	0.08	2.4	0.05	7.4
Ca	4.4	838	10.6	792	775
Cu	0.12	<0.01	0.20	<0.01	0.24
K	95	57	284	89	263
Li	1.84	2.51	5.91	2.92	8.3
Mg	4.0	0.13	6.8	0.19	3.0
Mo	0.32	0.79	2.5	1.35	3.74
V	0.06	0.07	0.11	0.08	0.49

^aDistilled water 48-h leach.

^bRetort water 48-h leach.

B) occur for each shale type, indicating that leachate quality is altered by the composition of the leaching medium. The pH values are higher, in all cases, for the leachates compared to the retort water, suggesting that alkali metals and alkaline earth elements are being dissolved. The pH values for the retort water leachates are less than those of the distilled water leachates, with the LW-156 shale leachates having the lowest values. This is consistent with the high-temperature preparation of this shale (5-7). The conductivity of the leachate solutions indicates bulk movement of solutes from the solids to the leachates for LW-156 and Lurgi-type shales, although it appears that solutes were lost from the aqueous phase during the LANL leaching experiment. Note that the inorganic composition of this water appears to be different from the water used in the other two experiments. The difference between calcium concentrations in the distilled water and retort water leach (in the LANL shale experiment) suggests that precipitation reactions are occurring, as a result of carbonate concentrations or the organic composition of these waters. It is not obvious that calcium concentrations can account for the large conductivity differences. Elevated values for conductivity, copper, vanadium, and molybdenum for the LW-156 and Lurgi-type shales indicate a movement of inorganic constituents from the solid phase into the liquid phase. These movements probably are caused by chemical changes, such as organic complexation of copper and the effects of dissolved solids on the solubilities of some elements. Previous work has indicated that the ionic strength of the leaching medium plays a major role in the mobilization of trace elements from spent shales (13). Although the data are not presented here, copper, molybdenum, vanadium, and lithium show markedly decreased values for re-leaching experiment solutions, compared with both the original distilled water leachate and the retort water leachate.

2. Organics. Organic analyses were carried out on the fractionated, soluble base/neutral, and acidic portions of solvent extractable material from the leachates. Table 2 summarizes the materials recovered from various parts of the fractionation procedures, as well as the amounts of

materials that were actually analyzed by the experimental procedures. Examination of Table 2 indicates that approximately 70 to 85% of the solvent extractable material was insoluble as a result of the basic or acidic extraction. Thus, approximately 25% of the total extractable material was available for analysis. In addition, the GC technique is capable of analyzing only the volatile constituents, so the total amount of extractable material analyzed is approximately 5%. Previous work has indicated that the bulk of the mutagenic activity in shale oils and retort waters resides in the soluble base/neutral fraction; thus, even though we are studying only a small fraction of the sample, it is the most important material from the standpoint of biological activity (14). It also should be noted that fractionation followed by GC typically analyzes only 3 to 8% of organic-laden waters of this type.

Further examination of Table 2 provides insights into these experiments. The trends for the total dissolved solids (TDS) are similar to the trends in the conductivities presented in Table 1, indicating qualitative agreement between the instrumental and gravimetric results. In addition, the weight percent of solvent extractable material increases from retort water to the large surface area shale leachate for the LW-156 shale, but the opposite trend occurs for the Lurgi-type shale. The data are not available for the LANL shale. This suggests that salts, and perhaps organometallics, are being extracted into the organic fractions. Examination of the data for the three retort waters indicates differences among the individual fractions (base tar, acid tar, soluble base/neutral, and soluble acidic), but the total amount of basic material and acidic material is relatively constant for the three retort water extractions. The total base material and acidic material probably are better indicators of trends in the leachate data than are any of the individual fractions. The following paragraphs discuss the details of the base/neutral and acidic fractions that were both soluble in the original extraction and volatile enough to be analyzed by the GC technique.

a. Base/Neutrals. The simulated distillation curves for the organic base/neutral fractions are

TABLE 2. SUMMARY OF EXTRACTION DATA

Sample ^a	TDS (g/100 mL)	Extract (wt% TDS)	Base Tar ^b	Acid Tar ^b	B/N ^b	Acid ^b	ΣB^b	ΣA^b	Wt% B/N Vol.	Wt% A Vol.	Wt% Ext. Anal.
LW-156 A	1.189	44.7	39.3	32.3	14.0	14.4	53.3	46.7	44.5	0.35	6.28
B	1.502	45.5	50.6	24.8	10.5	14.2	61.1	39.0	42.1	0.28	4.46
C	1.617	53.9	62.3	22.6	7.1	8.0	69.4	30.6	38.6	0.37	2.77
LANL A	*	*	47.9	31.9	5.5	14.8	53.4	46.7	42.6	0.03	2.35
B	1.558	33.9	69.2	1.7	10.1	19.0	79.3	20.7	51.8	0.04	5.24
C	1.605	32.1	44.0	30.7	9.0	16.3	53.0	47.0	55.3	0.05	4.99
Lurgi A	1.253	36.1	40.3	41.6	10.1	8.1	50.4	49.7	80.2	0.07	8.11
B	1.291	35.5	50.6	29.2	7.1	13.1	57.7	42.3	62.1	0.11	4.42
C	1.751	25.4	38.2	38.3	8.4	15.1	46.6	53.4	60.4	0.04	5.09

^a A is retort water; B is -3/8 mesh (6-40 mesh for Lurgi); and C is -100 mesh.

^b Percentage of solvent extractable material.

shown in Figs. 2-4. Table 2 shows the amount of TDS (constant weight at ambient temperature), the quantities of base tar, acid tar, base neutral, acid, and percent volatile material in both the acid and base/neutral fractions. These data show a marked difference between the base-line control values and the three experimental conditions. For the base/neutral fractions, it is apparent that the different shales have a profound effect on the volatile portion of the water. In the case of the high-temperature LW-156 shale, particle size has a small but noticeable effect on the volatile base/neutral compounds, probably because of the porous nature of the high-temperature shale. The overall effect of treating the water with shale is to decrease the amount of higher boiling compounds present in the resulting water. The larger surface area shale appears to remove base/neutral compounds over the entire boiling point range. This conclusion is supported by examination of the individual chromatograms.

For the Los Alamos-retorted Anvil Points shale (Fig. 3), it is apparent that volatile compounds are being added to the retort water during the leaching process. Leachate from larger surface area shale contains more organic compounds as the boiling point increases, suggesting that the lower retorting temperature has left more material to be leached by the water, or that the larger surface area shale has promoted more reactions of the organic material to produce a greater amount of volatile constituents in the shale leachate compared to the original retort water.

The water used for the leaching experiments with the LW-156 and LANL shales was from the same storage container, and the extracts of the water used in these two experiments are very similar. The water used for the Lurgi-type shale was nominally from the same retort operations but was stored in a different container under different conditions. This difference in storage and handling is reflected in the increased amount of volatile compounds seen in Fig. 4. The data indicate that the Lurgi shale gives the greatest difference in base/neutral volatiles, which may indicate that either the Lurgi shale more strongly adsorbs or precipitates the compounds or that the adsorption phenomena or precipitation reactions are strongly influenced by the quantity of the more volatile base/neutral compounds present in the starting water.

The quantity of volatile material in the base/neutral fraction is a function of the shale used in the leaching experiment. For both the LW-156 and LANL shale, only about 40% of the base/neutral fraction was volatile (eluted at an effective boiling point of less than 325°C). This result is not surprising, given that the compounds in the base/neutral fraction may be rather large molecules with a polar group capable of forming a neutral salt with sufficient methylene chloride solubility to be extracted. These organic salts would have quite high boiling points and would not be eluted from the capillary column. A second type of compound possibly present in the base/neutral fraction is neutral metal-containing complexes.

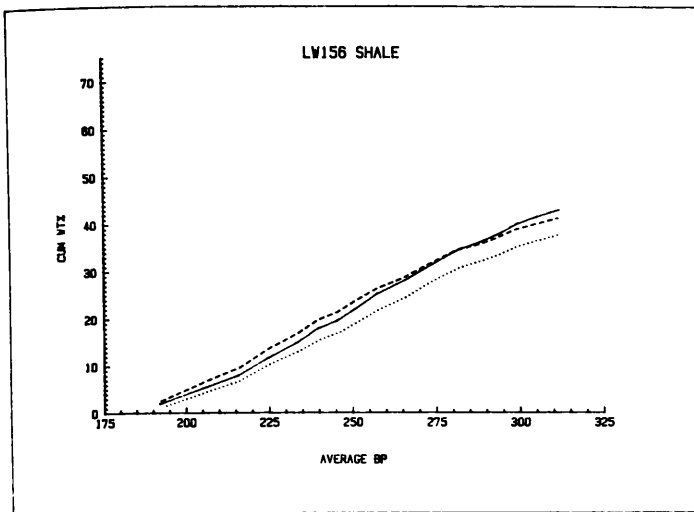


Fig. 2. The simulated distillation curves for the organic base/neutral fractions from the LW-156 shale leachate. The figure legend is as follows: the solid line denotes retort water, the dashed line the -3/8-in. shale leachate, and the dotted line the -100-mesh shale leachate.

Fig. 3. The simulated distillation curves for the organic base/neutral fractions from the LANL shale leachate (see Fig. 2 caption for figure legend).

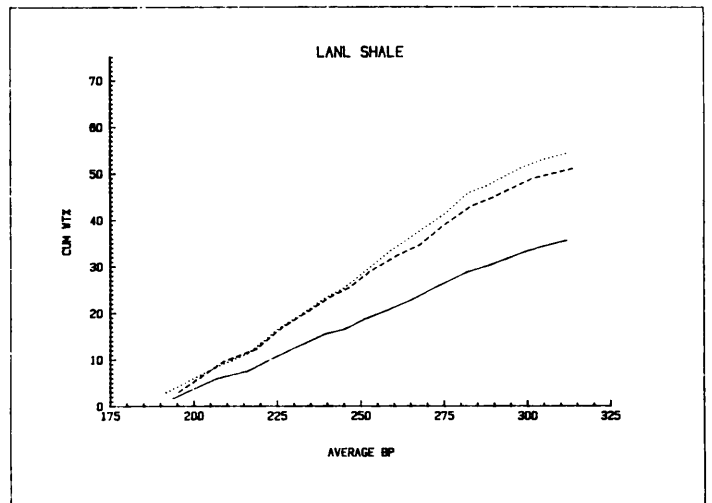
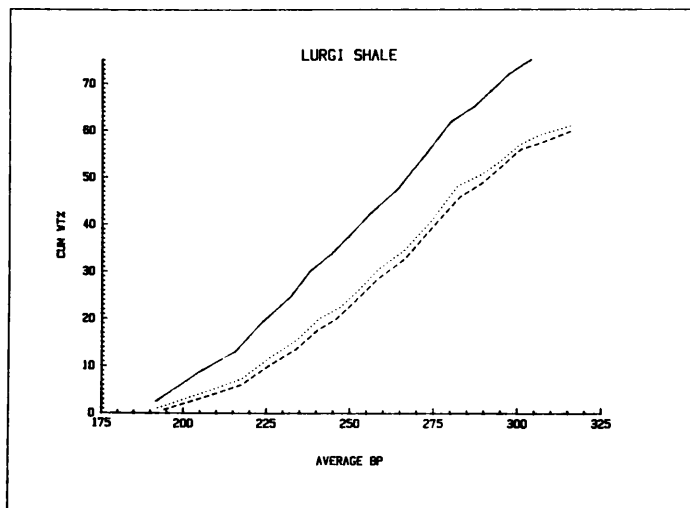


Fig. 4. The simulated distillation curves for the organic base/neutral fractions from the Lurgi-type shale leachate (see Fig. 2 caption for figure legend).



These compounds have been reported in retort waters and also are nonvolatile. For base/neutral compounds that are volatile, GC mass spectrometry analysis showed a variety of compounds to be present. A complete description of these compounds is beyond the scope of this paper and will be presented in the future.

b. Acids. The acid fractions all show extremely low amounts of volatile components. The micrograms of material eluted for each area slice in the chromatogram are very low. (The data are given in tabular form in Table 3; they are not given for each boiling range, but only for the total

methanol showed that a large amount of the non-volatile components in the acid fraction consisted of acids, including long-chain fatty acids, aromatic acids, and probably other hydrocarbon-oxyacids. A variety of low molecular weight amides were present, suggesting the presence of a nonvolatile homologous series of amides also contributing to the nonvolatile portion of the acid fraction. It also is possible that the acid fraction contained salts, either organic hydrochlorides or acid metal salts. The high boiling point of such compounds precludes their elution from the untreated acid fraction.

It should be pointed out that the complete analysis of the volatile portions of both the acid and base/neutral fractions of GC or GC mass spectrometry techniques would result in the analysis and identification of only about 5 wt% of the total amount of material removed from the waters. We have not addressed the base or acid tar fractions nor have we addressed the nonvolatile portions of the base/neutral and acid fractions. The intractability of these samples to GC analysis clearly indicates the need for different analytical techniques. However, as mentioned above, the majority of the biological activity resides in the soluble base/neutral fraction, which was analyzed more completely than other fractions. Although some trends may be seen in the data, the evaluation of the effects of codisposal on the organic portion of low-quality water remains an open question. We believe that compound class or type analysis will prove most useful in the evaluation of the organic portions of the retort water. There are several areas that must be addressed before the question of the fate of organics may be clarified. The existing techniques of analysis (liquid/liquid extraction followed by GC analysis) are not adequate for

amount of material eluted.) The volatile components of the acid fraction are principally normal and branched-chain carboxylic acids, with phenols and some amide compounds also present. The concentrations of the normal carboxylic acids in parts per million of the acid fraction are shown in Table 4. The concentrations of acetic and propionic acid probably are low, since these materials would be lost to an undetermined degree in the drying step of the acid fraction preparation. The carboxylic acids dominate this fraction, accounting for at least 90% of the volatile, underivatized components. Derivatization of the fraction with BF_3 and

TABLE 3. GC RECOVERY OF ACID FRACTIONS

Name	Micrograms Injected	Micrograms Eluted
LW-156 3/8	619	1.71
LW-156 100	447	1.68
Raw water	455	1.58
LANL 3/8	643	0.24
LANL 100	536	0.25
Raw water	946	0.24
Lurgi 6/40	275	0.29
Lurgi 100	307	0.28
Raw water	167	0.11

TABLE 4. CONCENTRATIONS OF NORMAL CARBOXYLIC ACIDS IN ACID FRACTIONS (ppm)

Acid	LW-156 3/8	LW-156 100	LW-156 RW	LANL 3/8	LANL 100	LANL RW	Lurgi 6/40	Lurgi 100	Lurgi RW
Acetic	0	112.5	84.8	0	0	50.6	67.3	93.3	138.1
Propionic	10.4	0	0	27.5	20.4	61.7	0	0	0
Butyric	71.7	74.8	0	72.2	56.4	35.5	5.1	6.1	8.9
Pentanoic	200.7	189.3	84.7	68.5	56.7	42.2	42.5	44.9	65.5
Hexanoic	261.8	330	181	113.9	101.9	49	0	27.8	0
Heptanoic	329.8	458.7	335.5	56.1	50	20	88.6	92.9	9.9
Octanoic	211.9	340	340	62.4	49.9	21.2	130.5	124.6	63.3
Nonanoic	127.1	185.9	254.6	39.9	33.3	15.9	71	60.8	48.3
Decanoic	22.4	58.8	116.2	16.4	14.4	7.9	31.6	22.6	21
Undecanoic	70.1	87.7	138.5	0	0	0	0	0	0

a complete definition of the problem. The disposition of metals within the extracts has not yet been addressed and may prove to be a crucial question for metal mobilization routes. The composition of the nonvolatile portions of the extracts, including the tars, must be studied before the total effects of treatment of the waste with shale may be addressed. These topics are under study at this laboratory and will be subjects of future reports.

CONCLUSIONS

These experiments indicated that we can begin to characterize the liquid constituents of retort waters that have been in contact with spent shale. The fractionation procedure developed is both manageable and reproducible. It analyzes only a portion of the total solvent extractable material from the leachates and original retort water, but previous work indicates that most of the mutagenic compounds are in the fractions most amenable to analysis. This information can be used to aid in the evaluation of procedures for the codisposal of retort waters and spent shale. The experiments show that the shale type and the size of the spent oil shale in contact with the retort water are important influencing variables on the amounts of both inorganic and organic constituents found in the resulting liquid phases. The organic analysis data also revealed different behavior patterns for acidic and base/neutral moities found in the resulting liquids after liquid/solid contact. More retention of base/neutral organics was observed as the particle size decreased for two of the three shales studied, with concomitant rise in active surface area. However, acidic organics increased in the leachates contacted with the larger surface area shales in these studies. This increase may be due to solubility of carboxylic acids originally trapped in the interior of the larger shale particles, or it may be due to microbial degradation or catalyst-enhanced reactions of higher molecular weight acidic compounds to lower molecular compounds that are more amenable to GC analysis. These results are the subject of further study.

The releaching experiment indicated that the subsequent mobility of retained base/neutral

fractions appears to be low. This may prove to be very significant, since previous investigation has shown that much of the mutagenic and carcinogenic activity in retort waters resides in this fraction (14).

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