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Field and Laboratory Leaching Studies of Retorted Kentucky Oil Shale

Final Report

T.L. Robl

January 1990

Work Performed Under Contract No.: DE-FG21-84MC21144

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of Kentucky
Center for Applied Energy Research
Lexington, Kentucky

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ABSTRACT

Retorted, raw and raw and retorted mixtures of eastern oil shale from a pilot test using the Dravo Traveling Grate Retort were placed in field lysimeters and sampled weekly or biweekly over a period of 1300 days. During the period of the study the lysimeters experienced approximately two pore volume changes.

Retorting the oil shale induced significant changes in the clay minerals, with the decrystallization of kaolinite and illite being the major effects.

The leachates generated in the field lysimeters were highly acidic, with pH's varying from approximately 2.5 to 3.5. The leachates had high concentrations of dissolved elements with sulfate, Mg and Fe present at tens of thousands or thousands of ppm. Other important constituents and their approximate order of concentration included: Al, Zn, Na, Ca, K (100 to 1000 ppm); Ni and Mn (10 to 100 ppm); Cd and B (1 to 10 ppm); and Cr, Cu, Mo, Pb, As and Se (<1 ppm).

Acid generation and elemental concentrations in the leachates were highest in the first year and decreased significantly during the study (by factors of 3 to 10). However, even after 1300 days, the leachates remained very acidic with pH's in the 2.9 to 3.4 range and sulfate concentrations of 3,000 to 5,000 ppm.

Iron, Mg and sulfate were present in the highest concentrations in the leachates from the unretorted oil shale. Iron was found to be in near stoichiometric proportion with sulfate, as defined by the oxidation and hydrolysis of iron disulfide. Magnesium was solubilized by the acid attack of the brucite sheet in the chlorite. The high elemental concentrations in the raw shale leachates were, for the most part, a function of the intensity of acid generation.

The clay minerals of the retorted shale were found relatively reactive in comparison to the raw shale as indicated by much higher Al and K concentrations in their leachates compared to that of the raw shale. This was most likely due to decrystallization induced by retorting. The highest concentrations of elements present in the retorted shale leachates were sulfate, Al and Mg. Iron showed a high degree of variability in concentration which appeared to be a function of leachate residence time. Aluminum and Fe concentrations varied inversely in the retorted shale leachates suggesting a product-reactant relationship.

In general, the chemistry of the leachates was transport controlled, i.e. determined by the kinetics of solution reactions and materials transport. Calcium concentration however appeared to be controlled by mineral equilibria with respect to gypsum.

Laboratory-based leaching experiments, which included batch methods based on EPA and ASTM procedures, produced leachates with elemental concentrations much lower than the field study. Leachates from column experiments, that closely simulated field conditions, were found to have chemical compositions comparable to that from the field and also produced similar elemental release patterns.

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I. INTRODUCTION

I.1 Purpose of the Report.

The purpose of this report is to present the results of a field study on the environmental and reclamation characteristics of retorted eastern oil shale and associated materials. This study was a cooperative effort between the Center for Applied Energy Research (CAER) of the University of Kentucky and the Morgantown Energy Technology Center of the U.S. Department of Energy (METC). The project was managed by the METC Laramie Project office.

The program was divided into three project areas: the elemental release (or leaching) characteristics of eastern oil shale materials; geotechnical research into the compaction characteristics of the spent oil shale; and reclamation and vegetative response characteristics of the oil shale, associated soils and overburdens. The entire field program is referred to as the "Hope Creek Field Study". The U.S. DOE support was primarily concentrated on the leaching aspects of the effort, which is the principal focus of this report. The geotechnical work was completed early in the program and was presented in a previous report in this series and elsewhere.[1,2,3,4] Reports of the reclamation research have also been presented. [5,6,7,8]

I.2 Background and Generation of Retorted Oil Shale.

Although information relevant to processing plant emissions was available prior to this study, data was lacking on the leachate-generating characteristics of retorted eastern oil shale, the reclamation characteristics of the oil shale mined lands and geotechnical data for fill settlement and slope stability analysis.

Research conducted in 1982 by the CAER[9] for the Kentucky Natural Resources and Environmental Protection Cabinet was the first attempt to obtain critical environmental data. However that work was limited in scope and application because it was, of necessity, entirely laboratory based. Field studies were precluded due to insufficient quantities of retorted eastern oil shale. This changed in 1983 when some 1,200 tons of material became available from a large pilot plant test eastern oil shale.

Dravo Pilot Plant Test. The pilot plant was the Dravo facility located in Cleveland, Ohio. This plant consists of a circular grate retort of 88 ft^2 of area, capable of retorting up to 300 TPD of raw shale. The traveling circular grate is divided into three retorting sections. In the first section the shale is loaded onto the grate and heated with oxygen-free process gas to begin the retorting. In the second section hot process gas enriched with oxygen or air is fed to the grate which causes combustion of the residual carbon left on the shale and provides the heat for further retorting. The third section consists of a shale cool-down zone where heat is transferred to cool oxygen-free process gas which would be used, in a commercial configuration, to fire the first stage of the retort. In the pilot operation the first stage was heated by natural gas. The oil and gas are collected under the grate in a series of wind boxes. Shale oil is recovered in a condensation train consisting of a series of de-misters, coolers and electrostatic precipitators.[10]

The pilot tests were conducted during May and June of 1983. The oil shale for the tests was mined in Montgomery County, Kentucky. The sample was recovered from the Sunbury Shale, which was approximately 15 feet in thickness at the site and the upper 30 feet of the Cleveland Member of the Ohio Shale. Twelve hundred tons of 1 x 1/4-inch shale were utilized with 900 tons run under steady state conditions. The <1/4-inch material was not run due to system constraints and was stockpiled. Retorting rates of 75 and 150 TPD were used during the demonstration and 300 barrels of shale oil were produced. The test achieved Fischer Assay oil yields, scale up factors from the bench work were found to be credible, and mass and energy balances were closed. In general the tests were considered successful.[11,12]

After retorting, the oil shale was removed from the facility, transported to Kentucky, and stored outside for approximately 9 months until site preparation activities were complete enough to commence the study. The retorted oil shale material was covered during this period. The analysis of the retorted and raw oil shale is presented in Table I.

Table I. Feedstock and Spent Shale Analysis from the Dravo and PETROBRAS Pilot Plant Tests. Analyses are in Weight Percent, Mineral Carbon (C-min) as CO_2.

	C-org	H	N	S	Ash	C-min
Dravo						
Feedstock	11.4	1.38	0.82	3.35	80.5	0.53
Spent Shale	6.7	0.20	0.34	2.38	90.2	0.41
PETROBRAS						
Feedstock	13.1	1.63	0.60	2.10	79.5	<0.1
Retorted	7.9	0.48	0.45	1.42	88.5	<0.1

The PETROBRAS Pilot Plant Test. A second pilot plant test of Kentucky oil shale was conducted in 1983 by the American Syncrude Corp., in conjunction with the Kentucky Energy Cabinet and Stone and Webster Engineering Corp., for a solicitation from the Synthetic Fuels Corp. The test was conducted at PETROBRAS's PETROSIX retort pilot facility in Sao Mateus do Sul, Brazil.[13,14] Shale for the test consisted of a sample of the Cleveland Member (High Grade Zone) of the Ohio Shale, mined in Fleming County, Kentucky (Table I). The shale was crushed and screened to 1/4 x 3/4-inch in size. Approximately 20 tons of material was shipped to Brazil.

The tests were conducted in the 8-inch diameter pilot plant of the PETROSIX retort, which is capable of approximately 2.6 TPD of throughput. Nine separate runs were made in the indirectly heated (i.e. gas heated) retort, under varying conditions and approximately 8 tons of shale was processed. The test series conformed to PETROBRAS's Second Stage assessment designed to select optimum operating conditions for the retort and provide information to prepare cost estimates for a commercial plant.[15]

The amount of spent shale produced and transportation costs precluded the use of the spent shale in the field lysimeters. However, several hundred pounds of spent shale was shipped back and was used in the column leaching experiments, as described in Part III of this report, and in mineralogic comparisons discussed in Part II.4.

II. FIELD LEACHING STUDIES

II.1 Design of the Field Lysimeters

Location. The project field station is located in Montgomery County, Kentucky, on a hilltop in the Knobs region. This area contains some of the higher grade and most accessible oil shale in Kentucky.[16] Thus, the climatic conditions at the field site are very similar to those which would be present at a commercial site. The geology of the site, a detailed discussion of the genesis of the shale sample, and the construction of the lysimeters are presented in a previous report and only summarized here.[1]

Design. Eight concrete field lysimeters were designed in two clusters of four each concentric to an access chamber for leachate sample collection (Figure 1). Prior to construction, holes were excavated to a depth of 12-14 feet deep. The excavations penetrated several feet into the bedrock (Sunbury Shale) which provided an exceptionally stable foundation. The entire lysimeter base was poured in a single operation to minimize cracks. During the pour, butyl rubber seals were inserted vertically into the base, protruding about 2" above the concrete level around the perimeter of each lysimeter. This seal was designed to prevent inter-lysimeter contamination and leakage. After the base was dried and cured, the walls were formed up and poured. The inner walls (i.e. those walls common to the central access chamber) were fitted with 4-inch diameter knock-outs to allow leachate tube insertion into the access chamber.

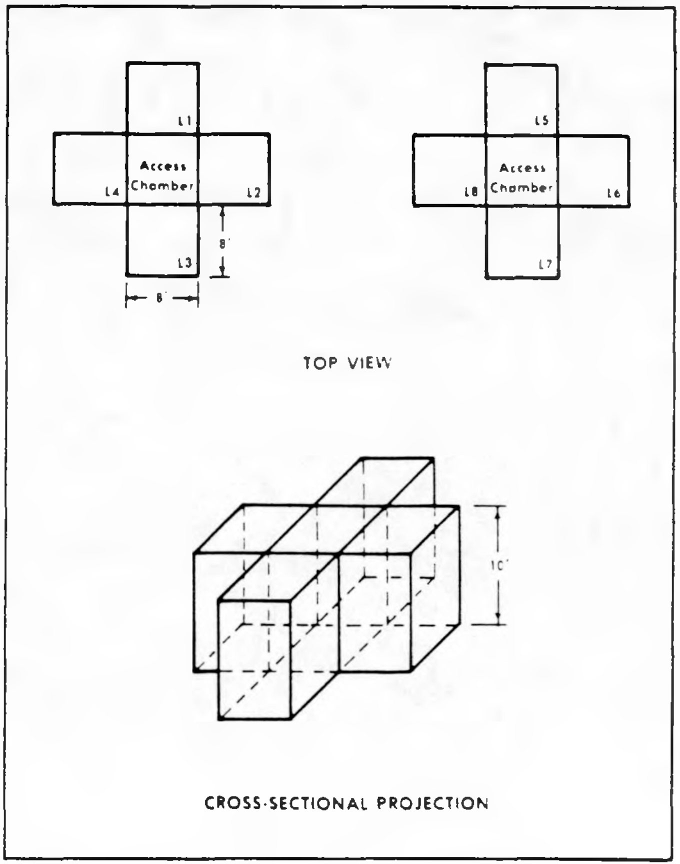

Figure 1. Lysimeter Design Schematic.

Material Fill. Four types of materials were used in the lysimeter fills; retorted oil shale, raw oil shale, raw oil shale-retorted oil shale mixtures and soil and overburden materials. The overburden material was mined from the Nancy Shale Member of the Borden Formation, which is a plastic greenish-gray shale that overlies the Sunbury Shale throughout most of Eastern Kentucky. The Nancy would be one of the major overburden materials in any commercial operation in the region. The soil was of the Gilpin soil series and was recovered from the site. This silty clay loam is also common in the region.

The spent oil shale from the pilot runs was placed in thicknesses of 10, 8, 6 and 4 feet in four of the chambers (i.e., lysimeters L2, L8, L6 and L5, respectively). A mixture of approximately 80% spent oil shale and 20% <1/4-inch raw oil shale (from crushing and screening of the pilot test feedstock shale) was placed in 6-foot thickness in two of the lysimeters (L3, L4). A 6-foot thickness of the <1/4-inch raw shale was placed in one lysimeter (L7). The final lysimeter consisted of 7 feet of soil and 3 feet of overburden material (L1).

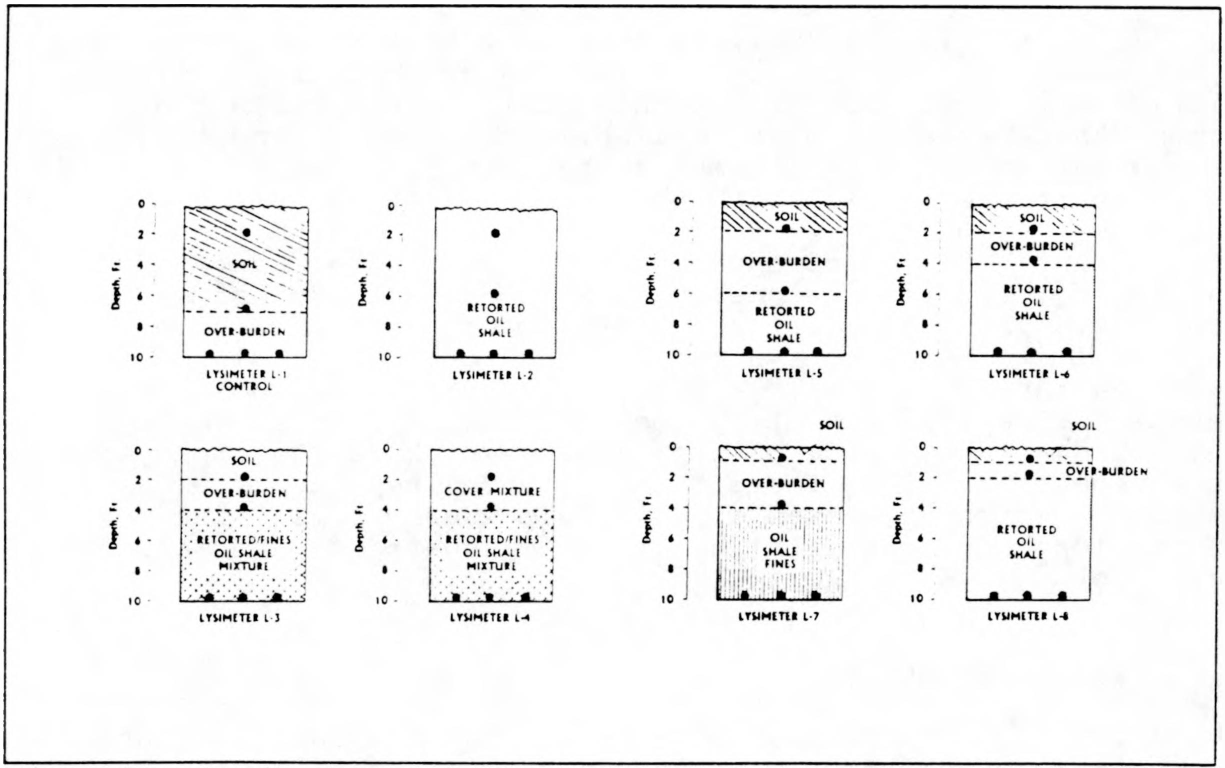

Figure 2. Lysimeter Fill Configurations. Leachate Transport Tube Locations Indicated by (●).

In filling, materials were added in approximately 1 foot layers, leveled, and compacted using a small, vibratory compactor. The 1/4 x 1-inch retorted shale proved to be somewhat difficult to compact due to its lack of fine material and high strength and durability. An average dry density of 81 lbs/ft^3 was achieved for retorted shale (Table II), with individual measurements ranging from 63 to 94 lbs/ft^3. The maximum compaction achieved in laboratory tests was 104.7 lbs/ft^3 at an optimum moisture of 11.5%. Thus, the spent shale compaction averaged 77% of optimum (range 60% to 90%). A commercial operation would be expected to achieve 90% of maximum. As expected, higher densities were achieved for the mixed spent shale-raw shale material, which averaged 107 lb/ft^3.

At the bottom of each lysimeter, at material interfaces, and at other intermediate levels, leachate transport tubes were placed on the fill materials, worked through the access hole in the access chamber wall and sealed at the wall interface. Each tube was constructed of 3-inch perforated drainage tubing and covered with a fine gauge plastic sock to keep out solids.

All of the lysimeters were covered with soil or overburden or mixes of the two (Figure 2). The lysimeter configurations allow several different assessments to be made. The use of various thicknesses of spent oil shale provides an indication of the changes in oil shale leachate chemistry with depth and time. The mixes of spent shale with the raw shale fine materials allows an assessment of the effect of co-disposal of unretorted materials with the spent shale, which is of value when considering retorting technologies which cannot process small particles. The lysimeter that contains only the raw shale provides a reference to evaluate the effect of retorting on the shale leachate composition. The configurations are not ideal as there is no replication of lysimeter chambers, nor is there an evaluation of the effect of clay layers which may be employed at the bottom of a fill. The options selected represent a compromise which the investigators felt would provide the most information congruent with the limited amounts of materials available.

II.2 Leachate Collection

Sample collection began in July of 1984 and continued until May of 1988, a period of over 1300 days. In general, the samples were collected once a week, except during periods of high precipitation when the collection frequency was increased to twice a week. The number of samples collected ranged from approximately 15 to 20 per trip. Data has been compiled on a project year basis for this report. The project years spanned the interval from September 1 to August 31, with the exception of the first year, which started on July 1 (Day 1) 1984 and the last

Table II. Compaction Data for Lysimeter Fills. Soil Mix is a Mixture of Overburden and Soil, Shale Mix is a Mixture of Unretorted and Retorted Oil Shale, Depth is in Feet and Density is as lbs/ft^3.

Lysimeter	Depth	Material	Density	Moisture (wt%)
L1	8	Overburden	101	19
L1	6	Soil	105	17
L1	4	Soil	108	16
L1	2	Soil	111	16
L2	3	Retorted	83	12
L2	1	Retorted	94	10
L3	8	Shale Mix	102	11
L3	6	Shale Mix	101	12
L3	5	Shale Mix	99	12
L3	3	Overburden	76	35
L4	8	Shale Mix	104	13
L4	6	Shale Mix	115	10
L4	6	Shale Mix	92	12
L4	5	Shale Mix	109	12
L4	4	Shale Mix	101	24
L4	3	Shale Mix	77	34
L4	1.5	Soil Mix	103	25
L5	8	Retorted	83	22
L5	6	Retorted	92	22
L5	4	Overburden	74	20
L6	8	Retorted	66	12
L6	6	Retorted	80	14
L6	3	Overburden	106	21
L6	1	Soil	119	18
L7	8	Raw Shale	128	13
L7	5	Raw Shale	111	13
L7	3	Overburden	71	29
L8	8	Retorted	81	11
L8	6	Retorted	63	11
L8	4	Retorted	83	11
L8	1	Soil	96	18

year which ended on the last of May, 1988. During the study over 3,800 samples were collected and 76,000 chemical determinations made. In addition to the collection vessels, water in the central collection chamber derived from leakage around the transport tube ports and occasional sample bottle overflow was also collected.

In general, the bottom lysimeter tubes provided samples more consistently, while shallower tubes flowed only during periods of high precipitation. All three of the bottom tubes provided samples in the lysimeters which had a more homogeneous fill and thinner cover (i.e. L1 and L8). Other material configurations showed different volume collection patterns. For example, the right and left tubes from L6 did not provide samples until half way through the study and the left tube of L8 and the center tube of L5 did not provide any samples at all (Figure 3). This is not unexpected as the chambers were small and packing, settling and wall affects were unavoidable. Only natural precipitation was used to moisturize the lysimeters and individual chambers were covered with different types of materials with differing percolation rates.

<u>Sample Volume.</u> Attempts were made to determine total volume of the samples for the individual lysimeters. Sample volume is of interest as the total amount of elements leached is a function of both concentration and volume. This effort was hampered early in the study by the lack of space for containers. Sample volume

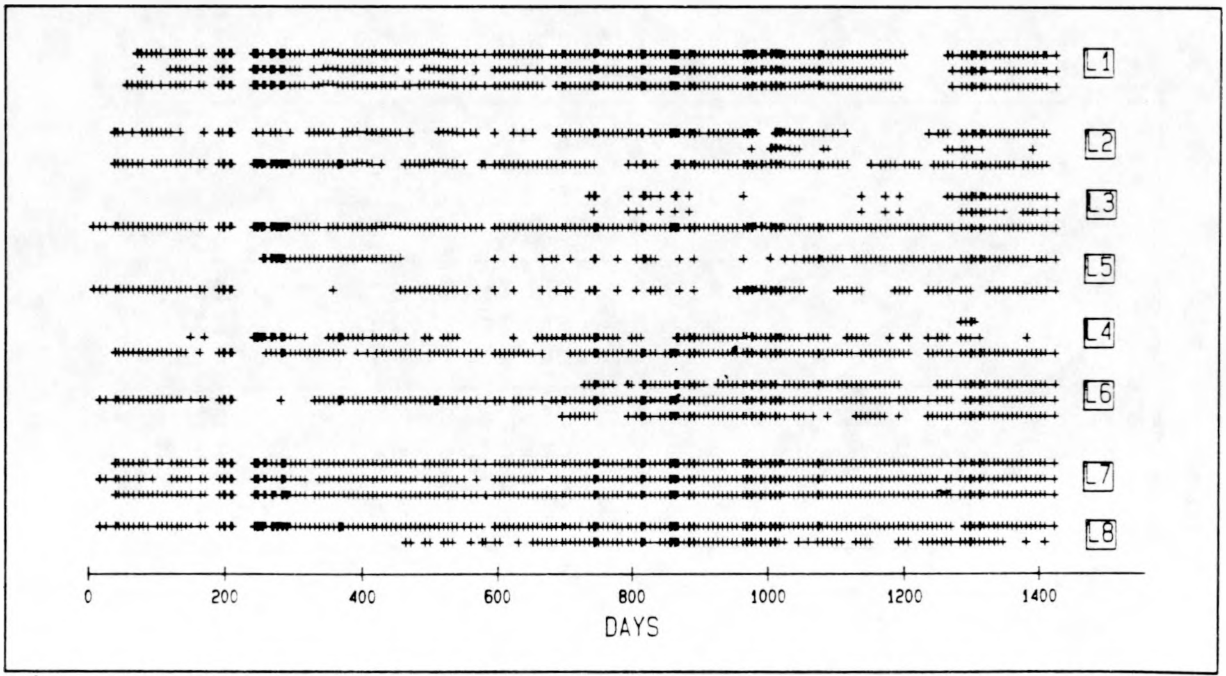

Figure 3. Sample Flow from the Bottom Transport Tubes (10' Depth) During the Study.

patterns, established during the first and second year of the study, allowed sample containers from tubes which did not flow to be replaced with smaller bottles. This in turn allowed additional sample containers to be added to tubes which consistently provided large flows. By the third year of the study reliable sample volume information was obtained.

The total amount of flow through the lysimeter is of interest as it can be used to approximate the relative intensity of the leaching. Assuming dry densities of 81 lbs/ft^3 for the retorted shale, 107 lbs/ft^3 for the mixed shale and 119 lbs/ft^3 for the raw shale and a particle density of 137 lbs/ft^3 the void volumes (VV) of each lysimeter may be calculated (Table III). Comparing this with the total sample volume collected, the number of pore volume changes can be calculated. This figure ranged from a low of approximately 1 for lysimeter L2 to a high of 7 for L7, with the rest of the lysimeters having a value approximately 2, for the 1300 day study period. These calculations are only estimates for use in internal comparisons. The material densities were estimated from that measured during installation and several inches of settling were observed. Problems with inadequate sample container volume and subsequent overflow were not fully overcome until the end of the second project year. This factor would be largest from the lysimeters with higher flows. In addition, several storm events occurred during the study which resulted in the flooding of the collection chambers. One severe blizzard during the first year of the study closed the road to the site for almost two weeks. In addition, seepage between the transport tubes and the lysimeter wall knockouts was a chronic problem throughout the study, one which repeated attempts at re-caulking with several types of materials failed to cure. All these factors would tend to make the estimated pore

Table III. Lysimeter Void Space and Sample Volume. Volumes are Presented in Ft^3

Lysimeter	Volume Shale	Volume Voids	Volume Sample	Sample Vol./ Void Vol.
L1	640	147	360	2.4
L2	640	262	229	0.9
L3	384	85	249	2.9
L4	384	85	141	1.7
L5	256	105	244	2.3
L6	384	157	305	1.9
L7	384	49	356	7.2
L8	512	210	354	1.7

change values low, by factors of as much as 30 to 50%, in the authors estimation.

Ignoring L1 and L2, the amount of flow through the spent shale chambers was relatable, to some degree, to the thickness and nature of the soil and clay overburden covering the oil shale materials. The total sample volume was lowest from the L4 lysimeter (4,000 l), which had 4 feet of mixed soil and overburden, and the L5 lysimeter (6,900 l), which had a total of 6 feet of layered soil and overburden. The spent shale covered with 4 feet (L6, 8,600 l) and 2 feet (L8 10,000 l) of layered materials had proportionately more flow over the study.

Sampling Protocol. Sampling protocol varied somewhat during the study. For the first project year the five-gallon containers were returned to the laboratory and a one-liter aliquot removed for analysis. pH was measured on the filtered fraction in the laboratory. After the second project year, the samples were weighed in the field and pH was determined at that time on unfiltered samples. This provided for more accurate pH and sample volume measurement and insured that the lysimeters could be sampled during periods of severe weather when the site was not accessible by truck, a problem during the first project year.

II.3 Leachate Chemistry.

Analytic Protocol. Procedures for the analysis of the leachate samples were derived from three sources: the Standard Methods for the Examination of Water and Waste Water, 15th edition, (SMEWW) of the American Public Health and American Water Works Associations and the Water Pollution Control Federation; the test methods of the U. S. Environmental Protection Agency (EPA); and the procedures of the American Society for Testing and Materials (ASTM). Conductivity and pH were determined by meter (SMEWW); sulfate, chloride, nitrate and ammonium were determined by ion chromatography (EPA), high concentrations of sulfate were determined gravimetrically (ASTM). Arsenic (As), boron (B) calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), magnesium (Mg), nickel (Ni), lead (Pb), selenium (Se), zinc (Zn) and sodium (Na) were determined by directly coupled plasma (DCP) spectroscopy (EPA) and potassium (K) by atomic absorption spectroscopy (ASTM).

Aluminum, which was not originally slated for analysis, was added late in the third year of the study. Although many stored samples were analyzed, particularly for the L2 and L7 lysimeters, this element is missing from much of the data set for the first three years of the study. Aluminum was determined by DCP spectroscopy.

For the most part, elemental concentrations were above the limits of detection for the techniques employed. Certain elements determined by DCP spectroscopy, such as As and Pb, were present in low concentrations, often below the limits of detection. The instrument was checked frequently for its sensitivity to determine when maintenance was required. Detection limits varied during the study, depending on the instrument condition at the time and the patience of the operator. The following list gives typical values for the worst case limits determined during the study (in ppm): As (0.5), B (0.03), Cd (0.01), Cu (0.1), Cr (0.1) Fe (0.03), Ni (0.06), Mo (0.2), Mn (0.05) Pb (0.5) and Se (0.4). These values were considerably lower, by factors of 3 to 5, during times when the instrument was in peak adjustment.

Leachate Chemistry, Data Summaries. An adequate presentation of the data from the study is difficult due to the large number of analyses. To simplify, the discussion focuses on the leachates collected from the lowest transport tubes, i.e. at ten feet of depth. A partial summary of the data, compiled on a project year basis, is presented in Table IV. The 'mean' in Table IV is the average concentration of all the 10 feet transport tube samples collected for the year.

A more complete set of sample data including the ranges and standard deviations is presented in the Appendix Table 1. For those elements which were present in low concentrations, the percentage of samples which were above the limits of detection (%>dl) is presented in the right column. An exception to this is Al, where the value in this column of Table 1 of the Appendix, is the percentage of samples which were analyzed for the first three project years. Where more than half of the samples had a particular element in concentrations below the limits of detection, a mean is considered to be of no significance (ns) and is not presented. Standard deviation is presented as percentage of the mean.

The mean concentration values of Table IV, and Table 1 of the Appendix, are simple mathematical means of the analysis, as volume weighted means could not be calculated for the first two years of the study due to problems with sample container flooding. However, volume weighted elemental concentration were calculated for the final two years of the study (Table 2 of the Appendix). The mathematical and volume weighted means are essentially identical for the purposes of this discussion.

L1 Control Lysimeter. The data for the soil/overburden control lysimeter (L1) leachates (Table IV) stand in contrast to that of the shale materials. The leachates from these materials were only slightly acidic, with a mean pH of 5.60 recorded for the first year of the study, not unusual for soils in the region.[17] With very few exceptions (e.g. a few Zn and Pb values during the first year of the study), these leachates had very low elemental compositions, well below that of the oil shale

Table IV. Data Summary of Leachate Chemistry.

L1 Soil-Overburden Control

	84/85	85/86	86/87	87/88
Samples	134	136	192	86
pH	5.60	6.33	6.39	6.53
Cond	0.25	0.19	0.20	0.23
Cr	ns	ns	ns	ns
Cu	ns	ns	ns	ns
Mo	ns	ns	ns	ns
Pb	ns	ns	ns	ns
As	ns	ns	ns	ns
Se	ns	ns	ns	ns
Cd	ns	ns	ns	ns
B	0.1	ns	ns	ns
Mn	ns	ns	ns	ns
Ni	0.1	0.1	ns	ns
Fe	0.3	ns	ns	ns
Zn	1	5	0.1	ns
K	3	4	5	5
Na	15	19	16	13
Ca	8	19	24	24
Al	nd	nd	ns	nd
Mg	1	1	1	1
SO4	37	35	35	37

L7 6' Raw Shale

	84/85	85/86	86/87	87/88
Samples	153	145	193	115
pH	2.66	2.65	3.21	2.93
Cond	20.34	8.34	5.29	4.49
Cr	3.15	0.91	ns	ns
Cu	11.69	0.44	ns	0.04
Mo	2.25	0.40	ns	ns
Pb	2.08	ns	ns	ns
As	1.38	ns	ns	ns
Se	1.94	ns	ns	ns
Cd	10.2	0.6	0.2	0.1
B	1.8	1.3	1.3	1.0
Mn	140	54	22	13
Ni	155	49	16	5
Fe	5665	2434	1166	750
Zn	913	197	37	4
K	1	5	9	10
Na	16	33	28	24
Ca	398	436	443	469
Al	457	58	6	ns
Mg	1841	654	270	172
SO4	29870	9484	4698	3580

L2 10' Retorted Shale

	84/85	85/86	86/87	87/88
Samples	94	88	102	78
pH	2.96	3.02	3.50	3.37
Cond	8.77	8.55	8.22	7.49
Cr	0.33	0.46	ns	ns
Cu	0.39	0.27	0.31	ns
Mo	0.93	0.53	ns	ns
Pb	1.17	0.70	ns	ns
As	0.49	ns	ns	ns
Se	0.69	0.60	ns	ns
Cd	3.6	3.1	2.3	1.7
B	5.3	6.5	6.5	6.2
Mn	69	64	52	36
Ni	80	69	53	37
Fe	150	211	142	143
Zn	415	294	175	149
K	155	129	81	64
Na	373	371	273	219
Ca	455	394	402	430
Al	341	549	710	737
Mg	775	785	696	529
SO4	8567	9782	9312	8372

L8 8' Retorted Shale

	84/85	85/86	86/87	87/88
Samples	66	116	119	61
pH	3.13	3.14	3.42	3.22
Cond	8.98	5.90	4.84	5.26
Cr	0.31	0.23	ns	ns
Cu	0.37	0.29	0.19	0.16
Mo	0.78	ns	ns	ns
Pb	1.06	ns	ns	ns
As	0.42	ns	ns	ns
Se	0.56	ns	ns	ns
Cd	4.3	1.9	0.9	0.7
B	6.5	5.5	4.5	4.3
Mn	72	38	20	18
Ni	78	38	19	16
Fe	63	68	71	146
Zn	502	162	77	67
K	145	100	75	71
Na	451	219	118	105
Ca	448	454	439	426
Al	291	371	282	388
Mg	799	372	254	251
SO4	8412	5858	4664	5241

Table IV. Continued.

L6 6' Retorted Shale

	84/85	85/86	86/87	87/88
Samples	48	86	168	99
pH	2.92	2.97	3.39	3.22
Cond	6.49	5.17	4.13	4.09
Cr	ns	ns	ns	ns
Cu	0.07	0.10	0.15	ns
Mo	0.59	ns	ns	ns
Pb	1.02	ns	ns	ns
As	0.42	ns	ns	ns
Se	0.74	ns	ns	ns
Cd	0.9	0.5	0.4	0.4
B	5.1	3.6	2.8	2.5
Mn	44	30	17	15
Ni	39	23	14	10
Fe	531	315	135	173
Zn	146	83	54	46
K	113	96	81	69
Na	209	145	92	76
Ca	448	440	414	411
Al	nd	nd	148	174
Mg	432	289	210	181
SO4	5704	4363	3491	3475

L5 4' Retorted Shale

	84/85	85/86	86/87	87/88
Samples	71	127	108	53
pH	2.91	2.95	3.38	3.10
Cond	6.65	5.79	4.04	4.47
Cr	0.38	0.34	ns	ns
Cu	0.17	0.13	0.10	0.13
Mo	1.07	0.72	ns	ns
Pb	1.35	0.96	ns	ns
As	0.59	ns	ns	ns
Se	0.82	ns	ns	ns
Cd	1.6	1.0	0.5	0.4
B	5.2	5.0	3.1	3.0
Mn	51	36	13	13
Ni	52	35	13	11
Fe	389	379	73	110
Zn	214	132	60	52
K	90	86	75	74
Na	243	194	96	92
Ca	449	428	422	423
Al	nd	318	183	251
Mg	470	346	172	177
SO4	5623	4999	3532	3931

L3 6' Mixed Shale

	84/85	85/86	86/87	87/88
Samples	65	75	81	84
pH	2.97	2.98	3.49	3.24
Cond	10.00	7.16	5.49	5.51
Cr	0.62	0.50	ns	ns
Cu	0.05	0.12	ns	0.11
Mo	1.91	0.46	ns	ns
Pb	1.92	ns	ns	ns
As	0.64	ns	ns	ns
Se	1.06	ns	ns	ns
Cd	3.5	1.1	0.6	0.6
B	5.0	4.5	4.0	3.6
Mn	102	61	39	34
Ni	100	51	31	27
Fe	803	459	233	217
Zn	459	188	120	115
K	70	59	51	48
Na	315	249	167	154
Ca	436	388	418	432
Al	155	134	152	235
Mg	1104	664	426	396
SO4	10408	6864	4918	5005

L4 6' Mixed Shale

	84/85	85/86	86/87	87/88
Samples	56	39	59	66
pH	2.89	2.93	3.22	3.12
Cond	6.63	5.10	4.65	4.97
Cr	0.59	0.22	ns	ns
Cu	0.06	0.03	ns	0.04
Mo	0.67	0.25	ns	ns
Pb	0.83	ns	ns	ns
As	ns	ns	ns	ns
Se	0.63	ns	ns	ns
Cd	0.7	0.2	0.2	0.2
B	4.1	2.9	2.6	2.5
Mn	44	29	29	29
Ni	33	13	17	16
Fe	899	498	194	283
Zn	121	64	66	71
K	72	68	71	69
Na	144	122	112	114
Ca	437	391	415	435
Al	17	22	69	87
Mg	436	282	327	334
SO4	5828	4041	3873	4140

material by a level of 1 to 2 orders of magnitude. By the third year of the study almost all the elements analyzed, except for K, Na, Ca, Mg and sulfate, were below the limits of detection.

TOC. During the first two years of the study the leachates were analyzed for total organic carbon (TOC). Values were low in the leachates from the spent shale, averaging approximately 4 to 5 ppm the first year (Table V). Values in the leachates from the soil control lysimeter (L1) were generally higher. The highest values were from the raw shale (L7), probably from the oxidation of bitumen. At the end of the second year the analysis was discontinued and the release of organic compounds from the spent shale was not considered to be a major problem.

Table V. Total Organic Carbon, Averages and Ranges.

Material	Lysimeter	Year	Mean (ppm)	Range (ppm)
Soil	L1	84/85	9.4	3.2 - 39.8
		85/86	4.3	3.3 - 5.2
Retorted Shale	L2	84/85	4.0	2.2 - 17.2
		85/86	2.8	0.8 - 10.7
	L8	84/85	4.5	2.8 - 13.8
		85/86	2.4	0.8 - 9.8
	L6	84/85	5.3	3.8 - 17.7
		85/86	2.8	0.7 - 13.0
	L5	84/85	4.8	1.8 - 19.3
		85/86	3.9	0.7 - 19.3
Mixed Shale	L3	84/85	6.4	5.2 - 21.1
		85/86	3.1	4.3 - 36.1
	L4	84/85	5.5	2.0 - 17.6
		85/86	2.9	0.8 - 11.1
Raw Shale	L7	84/85	55.0	5.0 - 266.
		85/86	13.0	4.1 - 47.6

pH. The pH of the shale leachates generally increased during the first three years of the study (Figure 4), with mean values having the greatest change between years 2 and 3. The mean pH of the leachates from the raw shale was generally the lowest for any given period. During the first year mean pH for the raw shale ranged from ~2.5 to ~2.7, while that for the retorted shale collected from similar depths was in the 2.9 to 3.1 range. Leachate pH values for the mixed materials were generally close to the values of the retorted shale, but slightly lower (e.g., ~2.8 to ~3.0 during the first year). The pH values in the leachates declined during the fourth year of the study, most likely due to lower precipitation during the interval, which would have resulted in relatively longer residence times for the leachates.

Elemental Concentration Ranges and Averages. Although the elements varied widely in concentration in the leachates, they can be ranked into concentration ranges. Those elements which were general present in the shale leachates in concentrations of 1 ppm or less included Cr, Cu, Mo, Pb, As and Se; those which were present in concentrations of 1 to 10 ppm included Cd and B; from 10 to 100 ppm K, Mn, Ni, and Fe; from 100 to 1,000 Zn, Na, Ca, Al and Mg; and >1,000 ppm sulfate and Mg. Some elements including, Fe and Mg, spanned several ranges depending upon the material. By the third year of the study the elements in the less than 1 ppm group fell below the limits of detection in most leachates.

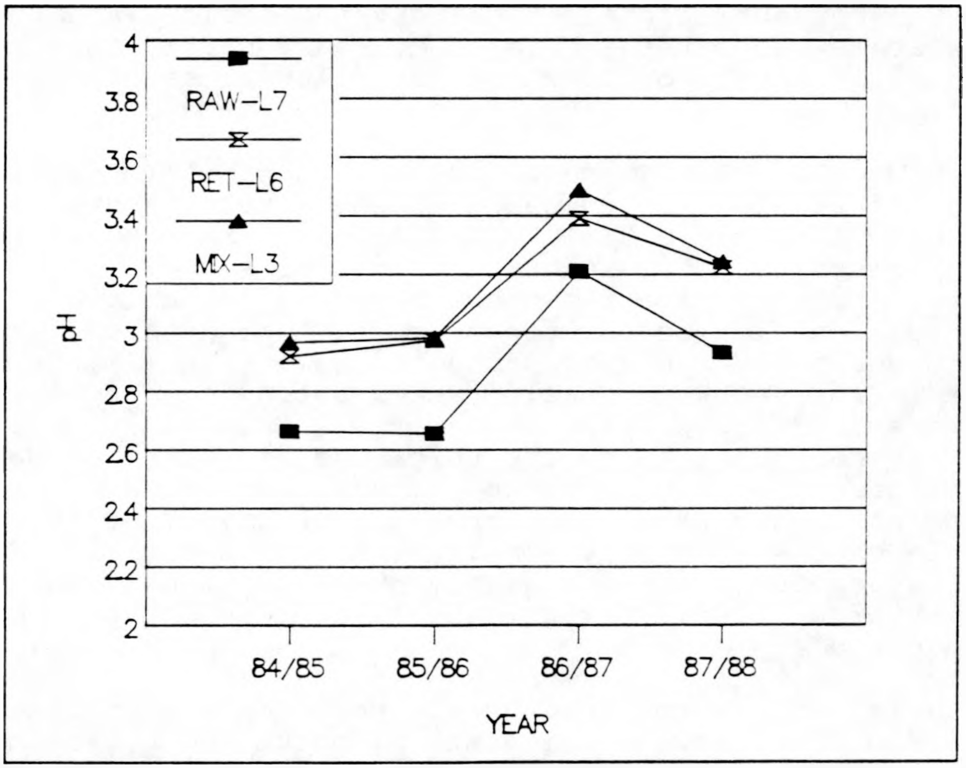

Figure 4. Change in Mean Sample pH for Leachates from Retorted (L6), Raw (L7) and Mixed Shale (L3).

The highest concentrations for most elements (i.e. Fe, Cr, Cu, Mo, Pb, As, Se, Cd, Mn, Fe, Zn, Al, Mg and sulfate) were found in the leachates from the raw shale during the first year of the study. Sulfate concentrations of 66,000 ppm and Fe and Mg values of 12,500 and 3,640 ppm, respectively were measured, along with Zn, Al, Ni, Mn, Cu and Cd concentrations of 7,750, 1,200, 380, 550, 120 and 35 ppm, respectively. Relative to the retorted shale leachates, the mean concentrations of the raw shale were 5 to 10 times greater (Table IV). The mean concentration values from the mixed material leachates fell intermediate between the retorted and raw shale materials.

Concentration Changes. With a few exceptions, the mean elemental concentrations in the leachates declined during the study. In contrast to pH, the greatest change was generally between year 1 and 2. The leachates from the unretorted or raw shale (Lysimeter L7) demonstrated the largest change. For example, mean sulfate concentrations in the leachates for the L7 samples decreased from 30,000 ppm to 9,500 ppm the second year, to 4,700 ppm the third year and 3,580 ppm the fourth year (Figure 5). The decline in mean elemental concentrations in the leachates from the retorted oil shales was not as great. Mean sulfate declined in the L6 lysimeter from 5,700 ppm the first year to 3,470 ppm the fourth year. This pattern was similar for many other elements as well, with mean concentrations for the fourth year declining to 20 to 40% of their first year levels in the retorted shale leachates and 2 to 10% of there first year levels in the raw shale leachates (Figure 6). Thus, by the end of the study, many elements, including Zn, Ni, Mn and Cd, had higher concentrations in the retorted shale leachates than in the raw shale leachates. This is at least partly attributable to the higher intensity of leaching (i.e. larger sample volume/pore volume, Table II) in the raw shale lysimeter.

The L2, L8, L6 and L5 lysimeters had thicknesses of 10, 8, 6 and 4 feet of retorted shale, respectively, and pore to sample volume ratios of 0.9, 1.7, 1.9 and 2.3, respectively. The comparison of these leachates provided some insight into the effects of leachate residence times on composition. As expected, the elemental concentrations in the L2 leachates were higher throughout the study compared to the others (Figure 7). Those of the L8 lysimeter generally ranked second in concentration. However, a simple proportionality is not found. For example, the L8 lysimeter had twice the thickness of shale and half of the computed pore volume change compared to L5. However, the mean elemental concentrations for the fourth year of the study in the L8 leachates were only about 25% higher than L5, and the ranges of values for the year largely overlap. Thus, a simple breakthrough curve for the elemental concentration changes is not indicated.

Exceptions to the general trends in elemental concentrations are found for several elements. Sodium and K were much higher in concentration, by more than an order of magnitude, in the leachates from the spent shale compared to the raw shale. Concentrations as high as 238 ppm K and 832 ppm Na were measured in the retorted shale leachates during the first year of the study, compared to maxima of 5 ppm K and 38 ppm Na in the raw

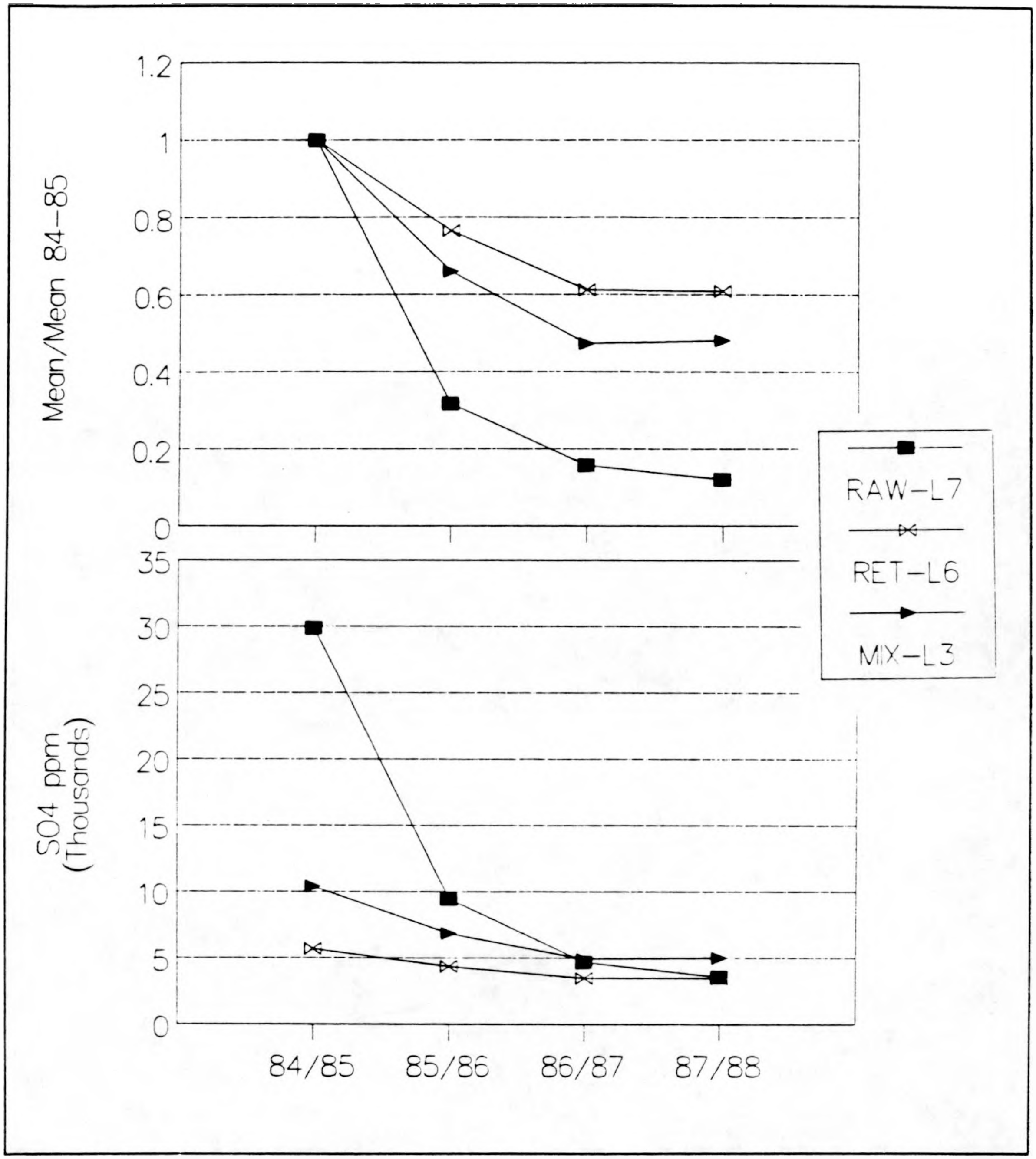

***Figure* 5**. *Change in Mean Sample Sulfate Concentration (Bottom) and Relative Concentration (Top) for Shale Leachates.*

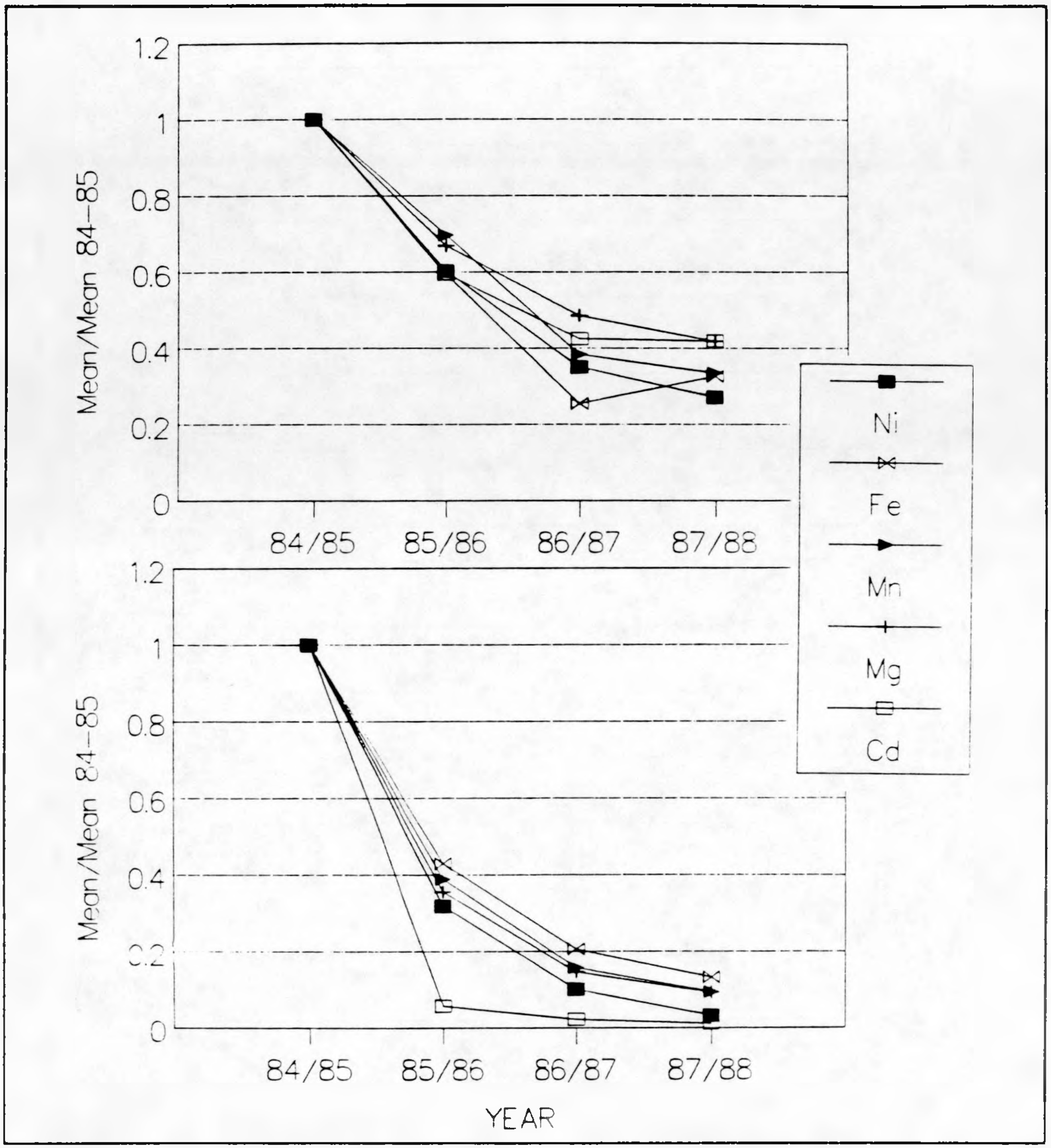

Figure 6. Comparison of Changes in Relative Mean Sample Concentration for Ni, Fe, Mn, Mg and Cd in Leachates from Retorted (L6 Upper) and Raw (L7 Lower) Shale.

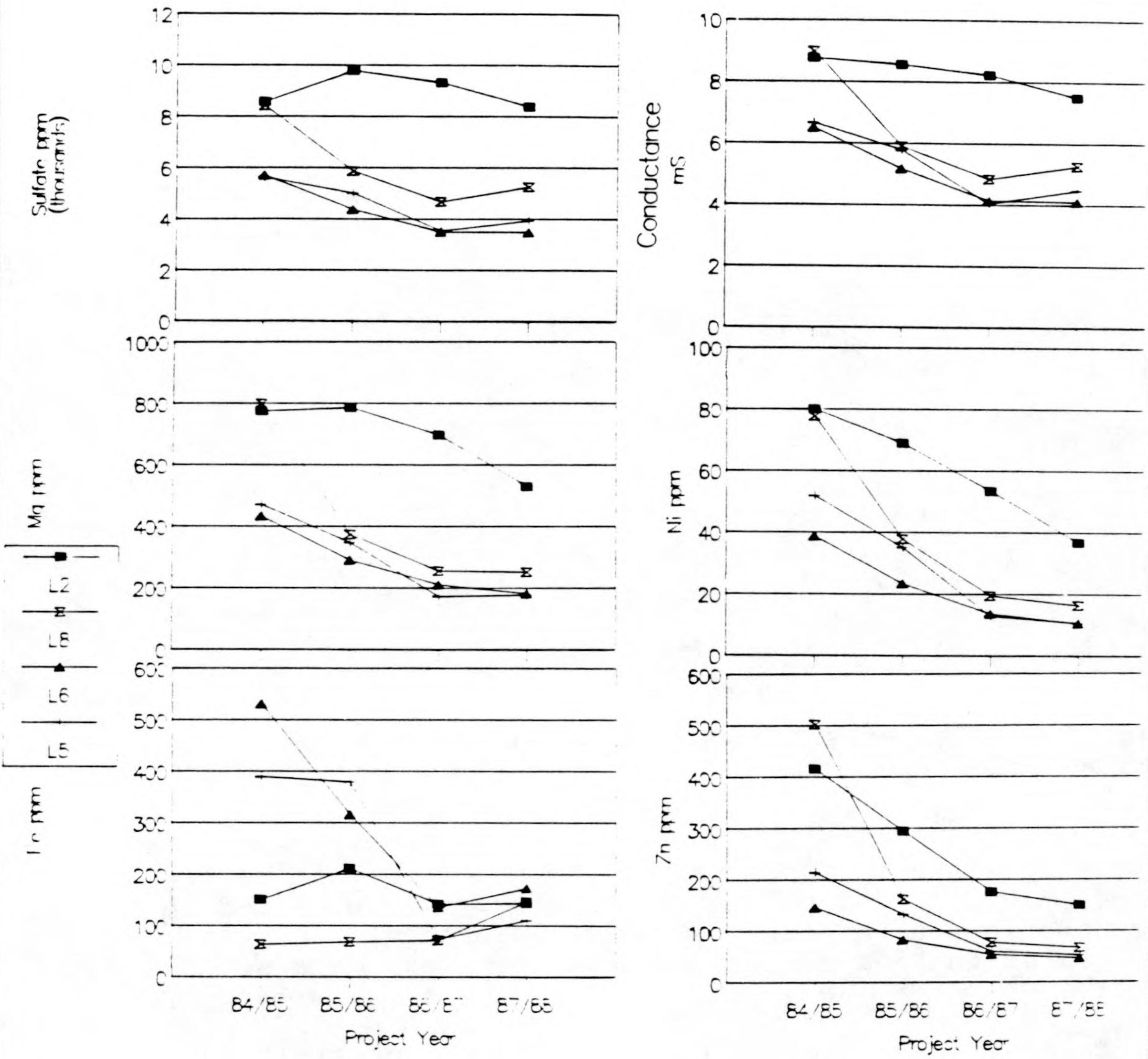

Figure 7. Comparison of Changes in Mean Concentrations for Leachates from the Four Lysimeters Filled with Retorted Shale.

shale leachates. Sodium and K both declined in concentration in the retorted shale leachates, but K increased in concentration in the raw shale leachates.

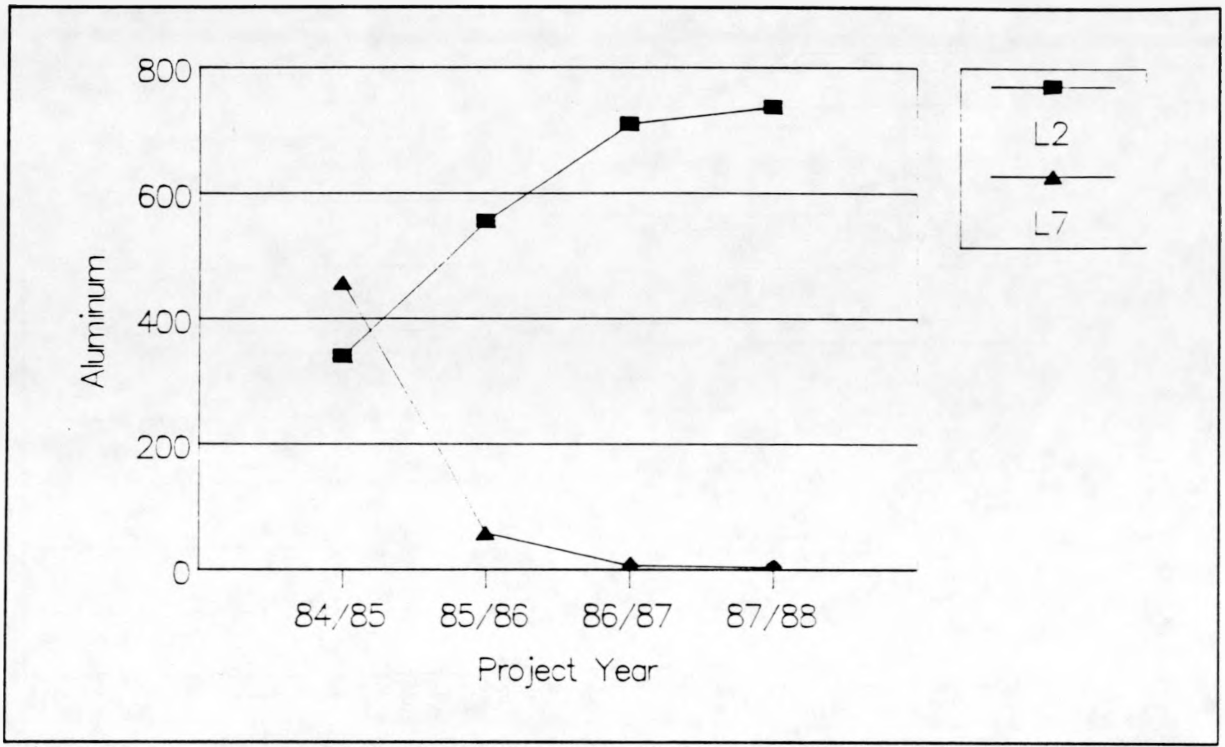

Figure 8. Comparison of Mean Aluminum Concentration in Raw (L7) and Retorted Leachates (L2).

Aluminum, initially higher in the raw shale leachates, rapidly declined in concentration to below the limits of detection by the fourth year. Conversely Al increased in concentration in the retorted shale leachates. This is illustrated in Figure 8 for the most complete data set (L2 and L7).

Calcium was found to remain relatively constant in concentration throughout the study in all the leachates and had approximately the same average concentration (~430 ppm), with the exception of the L1 lysimeter. Calcium also had the lowest standard deviation of any of the elements (Appendix Table 1).

Changes in Elemental Proportions. The relative cationic compositions of the raw and spent shale leachates were also found to differ considerably. The principal cation in the raw shale leachate was Fe. Mg and Al also were important constituents during the first year, but by the end of the study, Al had greatly decreased in concentration (Figure 9). In the retorted shale leachate Mg was the predominant cation for the first year along with significant Al, K and Na. By the end of the study, Al had increased in concentration and was the principal cation.

Elemental Release Patterns. Plots of elemental concentration versus time for leachates show contrasting patterns of elemental release (Figures 10 to 13). Elemental concentrations in the raw shale leachates were the highest generally within the first 140 to 170 days of the study, i.e., between mid-November and mid-December of 1984 and rapidly declined to very low levels by the end of the study. Also, many of the elements exhibited very similar trends, for example, the concentration trends for Mg, Fe, Zn, Ni and Cd are almost identical (Figures 10, 11).

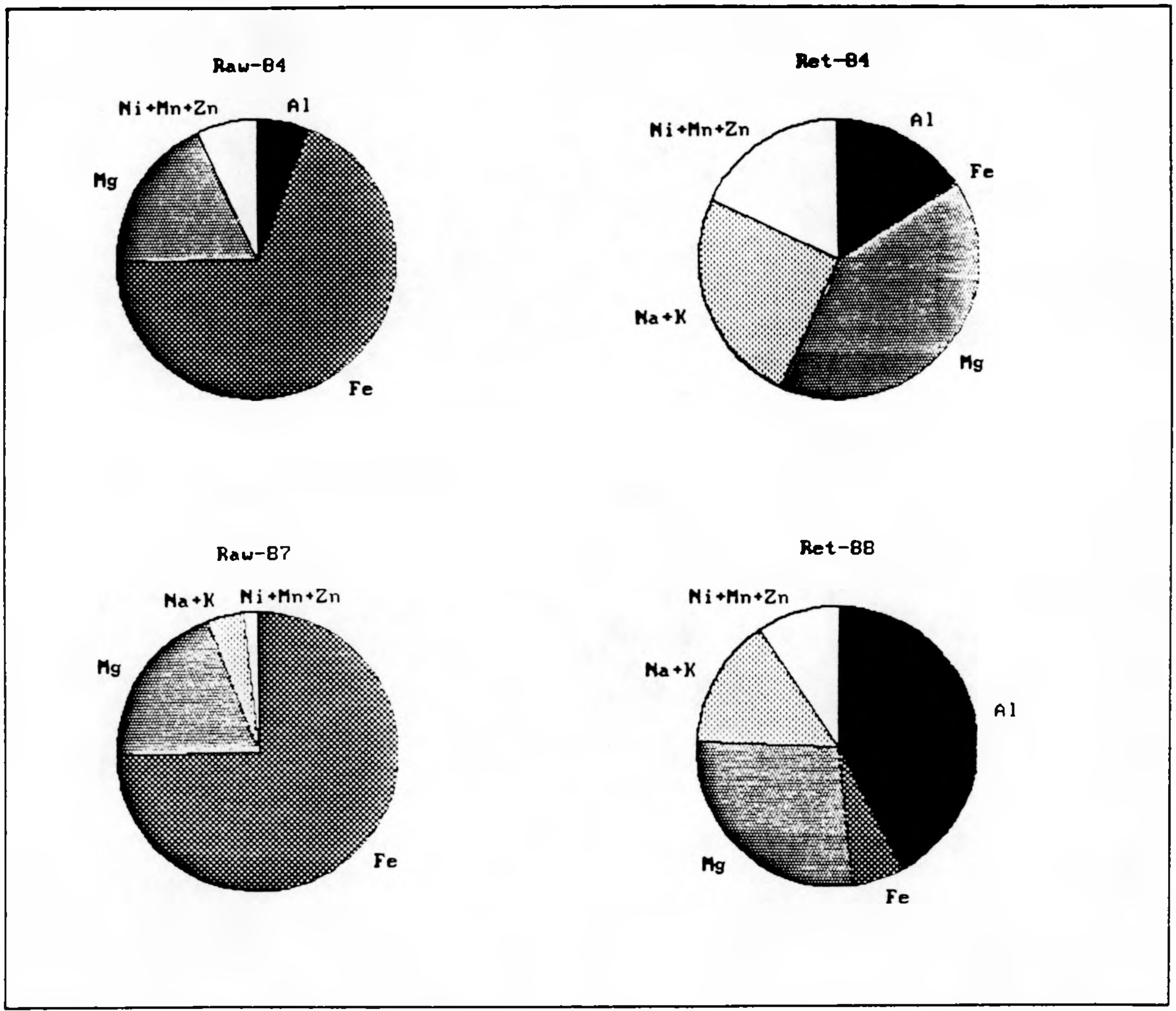

Figure 9. Comparison of Major Cationic Composition Changes for L7 and L6 Leachates Collected During the Winter of Project Year 84/85 and 87/88.

Elemental concentrations in the retorted shale leachates generally reached the highest values somewhat later, i.e., late November of 1984 to late March of 1985 (days 170 to 270) compared to the raw shale and had flatter slopes. Also in contrast, the elemental release pattern for the retorted shale leachates had more scatter and did not show similar trends for many elements (Figures 12, 13). For example, Fe in the retorted shale leachates showed periodic maxima reaching peak concentrations during the early fall of the year, i.e. September and October. Iron also showed the highest degree of variability, its concentrations having highest standard deviations of the elements determined.

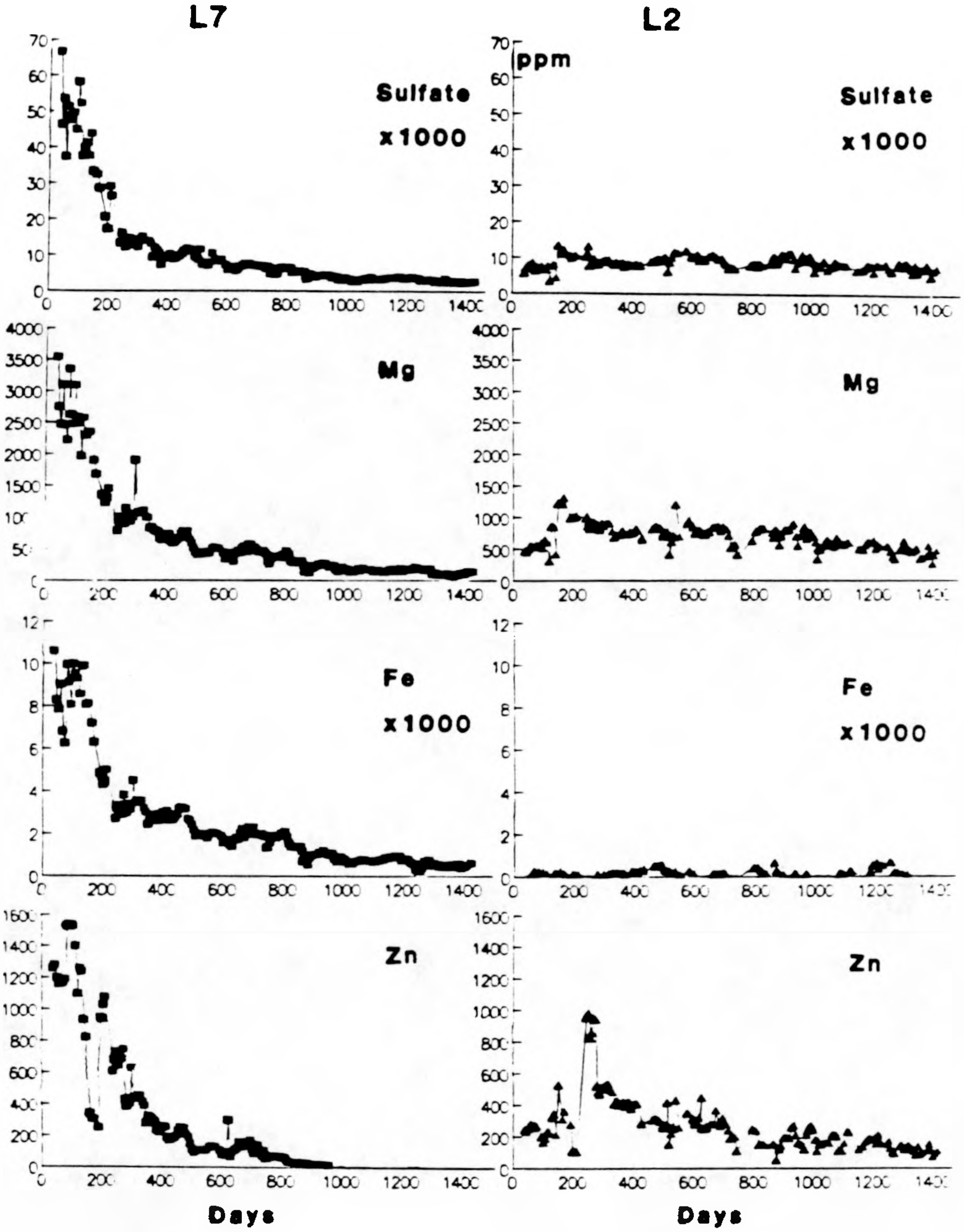

Figure 10. *Comparison of Sulfate, Mg, Fe and Zn Concentration (in ppm) Between Raw (L7) and Retorted (L2) Leachates.*

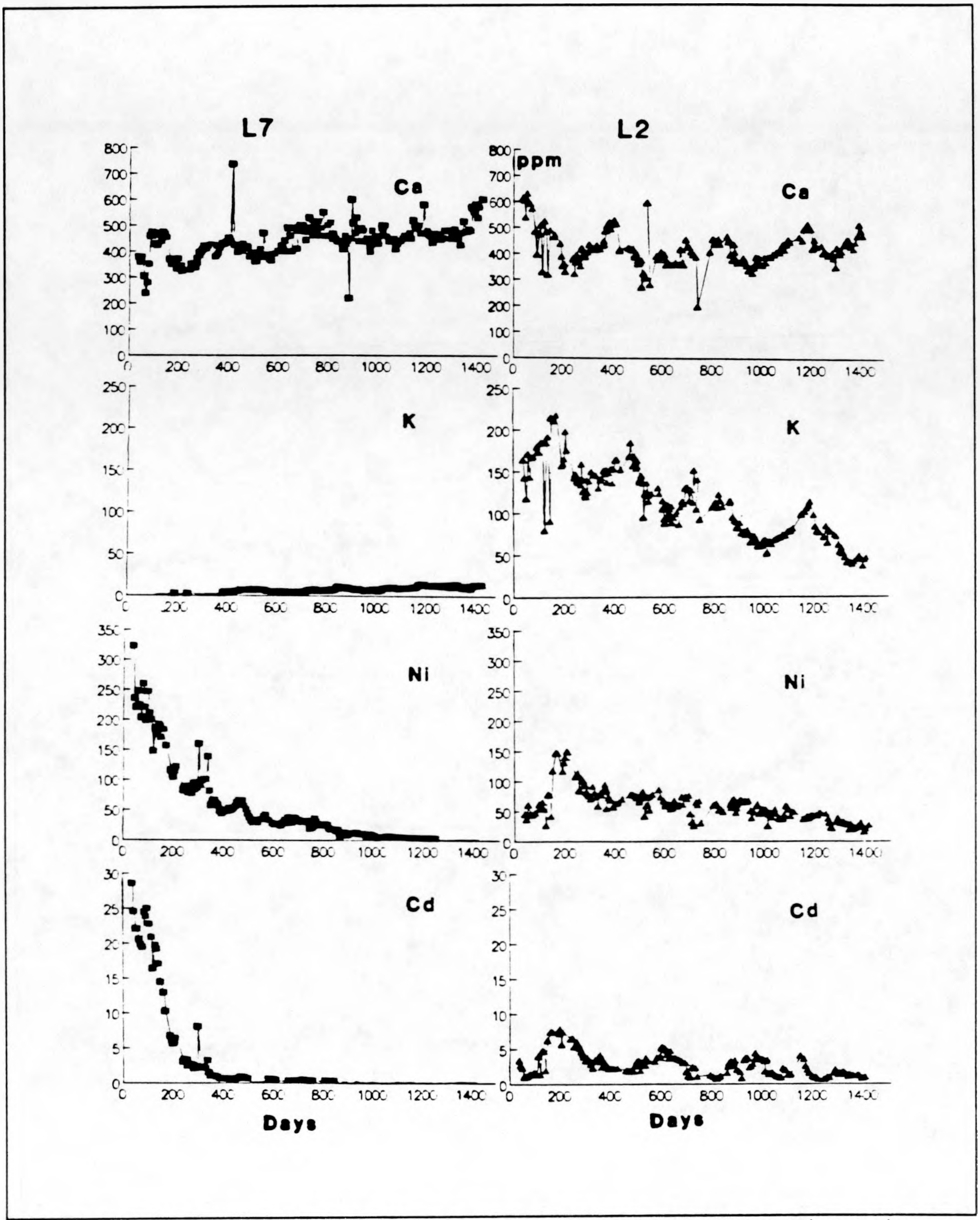

Figure 11. Comparison of Ca, K, Ni and Cd Concentration (in ppm) Between Raw (L7) and Retorted (L2) Shale Leachates.

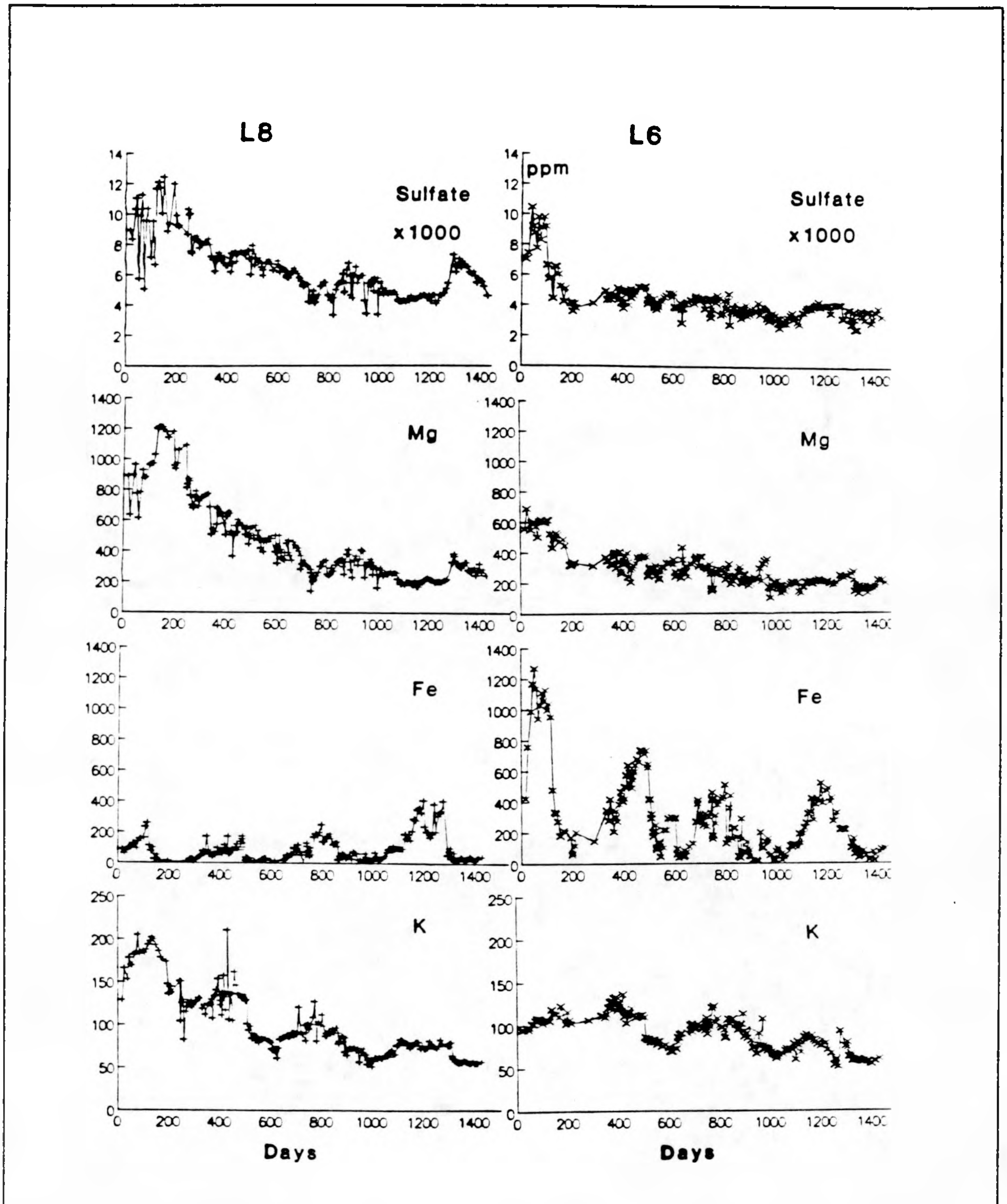

Figure 12. Comparison of Sulfate, Mg, Fe, and K Concentrations (in ppm) Between Retorted Shale Leachates from L8 and L6.

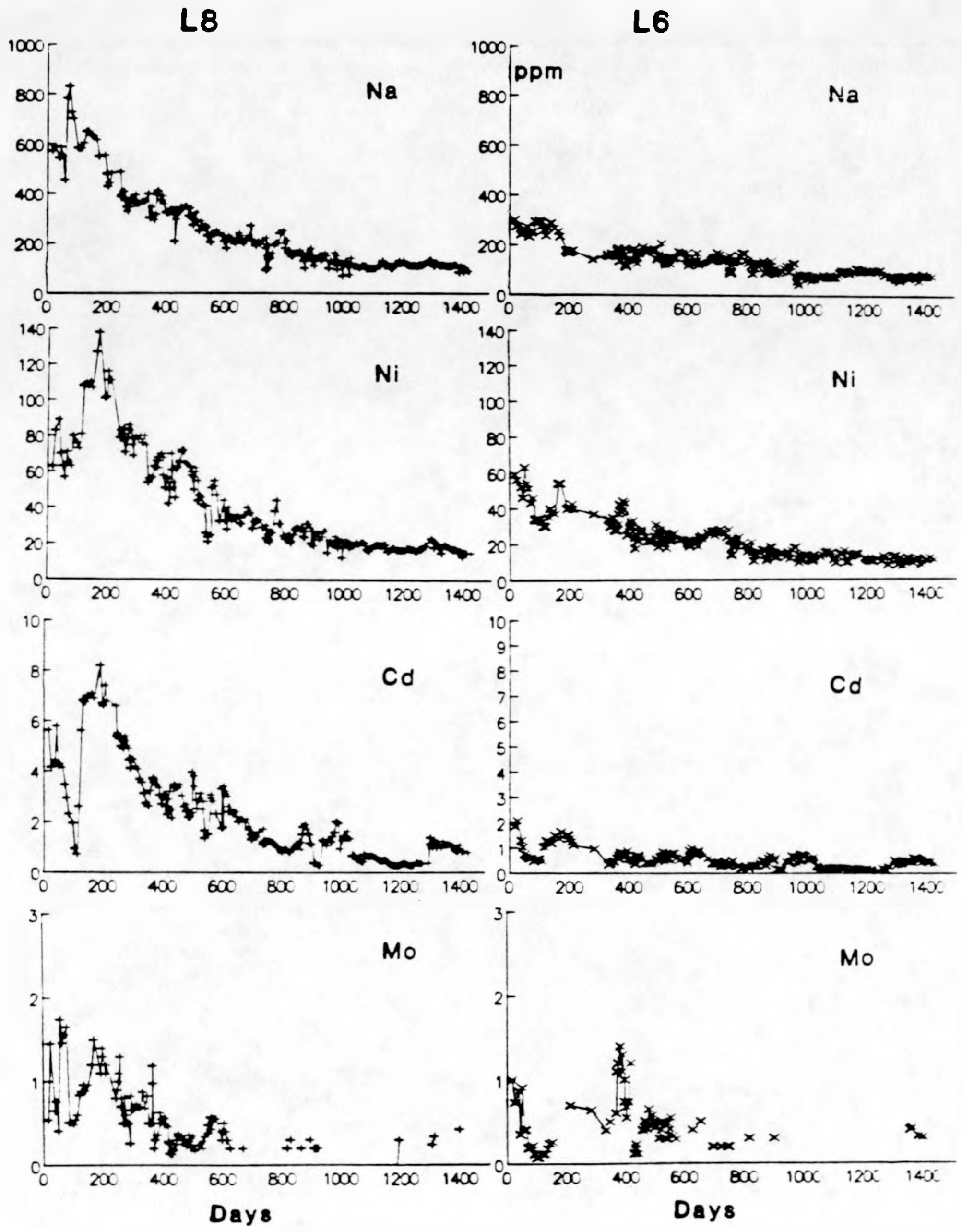

Figure 13. Comparison of Na, Ni, Cd and Mo Concentrations (in ppm) Between Retorted Shale Leachates L8 and L6.

II.4 Factors Controlling Leachate Chemistry

Feedstock Composition In addition to organic matter, the shales used in the study consist of silicates (principally clays and quartz) and sulfides (primarily pyrite, FeS_2). The small amount of carbonates in this shale (Table I) are present in the form of calcite ($CaCO_3$). Dolomite ($CaMg(CO_3)_2$) is restricted to stratigraphic intervals below the oil shale horizon. The clays present include illite, a potassium deficient 2:1 mica (i.e. two silica tetrahedral layers and one aluminum tetrahedral layer); chlorite (2:1 clay inter-layered with a brucite ($Mg(OH)_2$) sheet; and kaolinite, a 1:1 clay. X-ray diffraction studies indicated the silicate fraction of the shale to consist of approximately 20% quartz, 60% illite, 11% chlorite, and 9% kaolinite.[18] Various treatments with heat and potassium and magnesium saturation and glycerated were performed on the shales, using published procedures.[19,20] These tests indicated that mixed-layer clays were, at most, a small component (i.e. <4%).

Pyrite Oxidation. The low pH and high concentrations of dissolved ions present in the shale leachates result from the oxidation and hydrolysis of iron sulfides. The important reactions in the oxidation of iron disulfide are expressed in the following equations:[21]

1. $FeS_{2(s)} + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$

2. $Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2H_2O$

3. $Fe^{3+} + 3H_2O = Fe(OH)_{3(s)} + 3H^+$

Under the conditions of this study, the above reactions can be considered irreversible.

Raw Shale Leaching Chemistry. The chemistry of the raw shale leachates can be largely explained by the above reactions. The oxidation of iron sulfides in the shale results in the formation of ferrous iron, sulfate and 2 hydronium ions, with Fe^{2+} and SO_4^{2-} generated in molar proportion of 1:2. When these molar proportions are compared from the raw shale leachates they are found to be reasonably close, with mean values of 0.7:2, 0.9:2, 0.9:2 and 0.7:2 calculated on an individual sample basis for the four project years, respectively. When the stoichiometry of equation 1 is used to calculate an iron concentration from sulfate and compared to measured iron, the agreement is very good (Figure 14), with the exception of some of the very high sulfate concentrations measured early in the study. That iron is present in a proportion of less than 1:2 to sulfate can easily be explained by the oxidation of Fe^{2+} to Fe^{3+} and precipitation of ferric hydroxide (eqs. 2 and 3). The samples from the L7 lysimeter were frequently turbid and had a brownish-yellow filtrate, indicating the presence of ferric iron.

Magnesium is present in the shale primarily in the brucite ($Mg(OH)_2$) interlayer of the chlorite clay. The high concentration of Mg^{2+} in the leachates is due to acid attack on the brucite:

4. $Mg(OH)_{2(s)} + 2H^{+} = Mg^{2+} + 2H_2O$

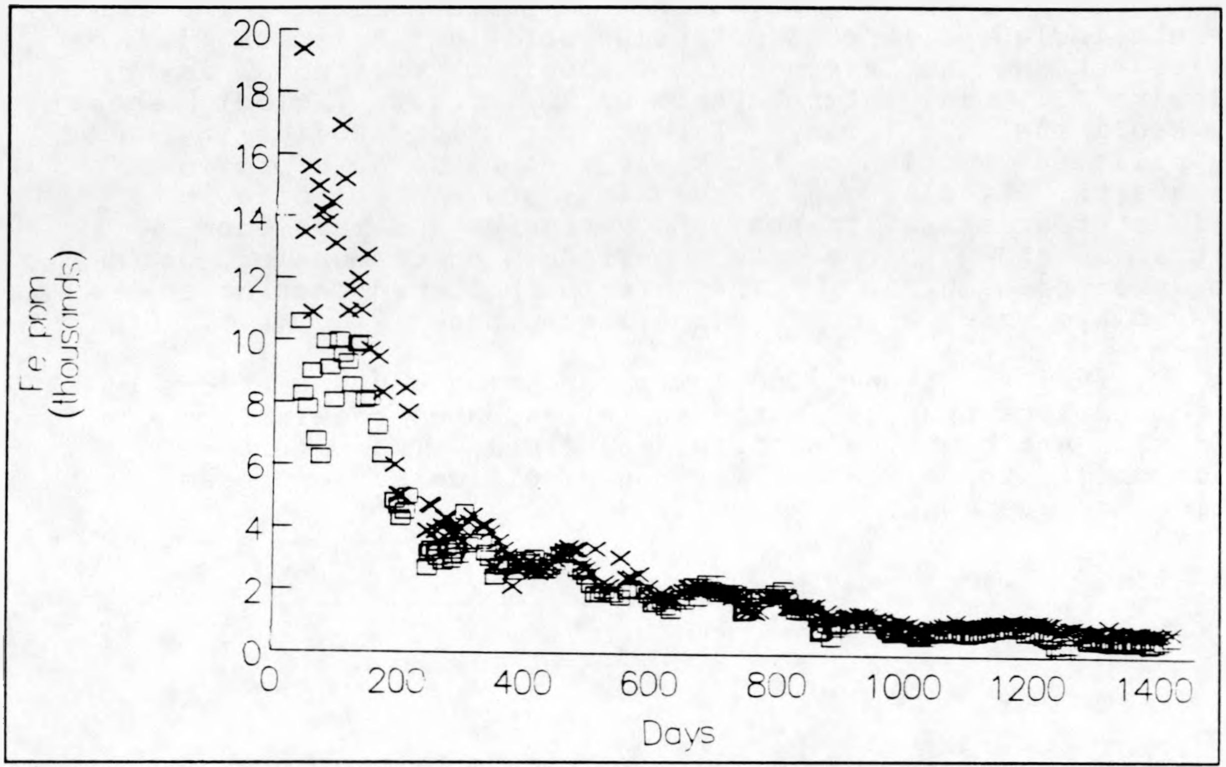

***Figure 14**. Plot of Measured Fe (X) with Fe Calculated as 1/2 Sulfate Concentration (Box) for Raw Shale Leachates.*

The chemistry of the raw shale leachates is definable by simple reactions, dominated by the hydrolysis and oxidation of pyrite resulting in the generation of acid. The concentration of trace metals such as Mn, Ni, Zn and Cr is a function of the degree of acid generation. Strong correlations were found between sulfate and iron and most of the other elements measured (Table VI). Early in the study the intensity of acid generation was very high, sufficient to attack the octahedral layers of the clays and dissolve high concentrations of Al^{3+} and solubilize elements (e.g., Cr) which are generally considered insoluble under most conditions. Considering that some of the sulfate levels measured in these leachates during the first year were equivalent to ~1.5 to ~1.0 N solutions of sulfuric acid, this is not entirely surprising. The low concentration of K in the leachates, however, (Figure 11) attests to the unreactive nature of the unretorted shale matrix with respect to chemical attack on the clay components.

Effects of Retorting on the Shale Leachate Chemistry. The chemistry of the retorted shale leachates is more complex than the raw shale and is reflective of changes which take place in the shale upon retorting. Two materials have been examined mineralogically; the spent shale from the Dravo Traveling Grate Technology, used in the field study, and that from a pilot plant test of the PETROBRAS PETROSIX Technology. The spent shale from the Dravo process has been exposed to a higher temperature than that of the Petrosix. Comparison of X-ray diffraction scans for feedstocks and spent shale from the two tests illustrate the nature of mineralogic changes induced by retorting.

The major change observed for the spent shale from the PETROSIX technology was the loss of the kaolinite peak (Figure 15). Kaolinite undergoes dehydroxylation, beginning at ~450°C, which destroys its crystallinity. Although some attenuation of the illite peaks is clearly evident, much of the crystallinity of the illite appeared to be maintained and chlorite appeared to be largely unaffected. Kaolinite is also absent in the Dravo spent shale. Changes in the illite component of the Dravo material were much larger than that of the PETROSIX. The sharp 10 angstrom illite 001 peak was almost completely lost and the 5 angstrom 002 peak was absent, indicating that the crystallinity of illite was destroyed. Quartz and chlorite did not appear to be strongly affected. The iron sulfides were also affected by retorting. Estimates from X-ray diffraction scans indicated that about half of the pyrite (FeS_2) was converted to pyrrhotite ($Fe_{1-x}S$). About 2/3 of the original minerals in the shale were largely decrystallized in the Dravo spent shale and no neoformed minerals were found. Thus, much of the inorganic matrix of the shale must exist in something of a glassy or at least a microcrystalline state.

Retorted Shale Leaching Chemistry. The chemistry of the leachates from the spent shale strongly contrasts with that of the raw shale. In general, the correlations of elemental concentrations in the retorted shale leachates are weak (Table VI). The mineralogic changes induced upon retorting provide explanation for some of the major differences in leachate chemistry. For example, the disruption of illite must be a major factor in the significantly higher concentrations of K in the retorted shale leachates, as K largely resides in the illite interlayer in the shale. The disruption of the octahedral layers in the illite and particularly the dehydroxylation of kaolinite, results in minerals which are much more susceptible to acid attack and Al dissolution.

Table VI. Correlation Matrix for Elemental Compositions of L7 and L2 Leachates.

L2 Retorted Shale					L7 Raw Shale				
	Sulfate	Fe	Mg	Al		Sulfate	Fe	Mg	Al
Cr	.41	-.02	.16	.39	Cr	.56	.55	.56	.37
Mo	-.08	-.13	.33	-.22	Mo	.91	.83	.88	.87
As	.31	-.38	.33	.32	As	.74	.56	.71	.71
Cd	.49	-.28	.61	-.02	Cd	.96	.89	.90	.93
Pb	.03	-.15	.27	-.21	Pb	.79	.85	.81	.66
Se	.14	-.17	.26	-.15	Se	.89	.85	.74	.62
Ni	.50	.15	.83	-.40	Ni	.95	.95	.98	.93
Fe	.02		.19	-.49	Fe	.93		.97	.90
Mn	.50	.23	.79	-.37	Mn	.94	.92	.96	.89
Cu	-.22	-.17	-.15	-.09	Cu	.71	.48	.61	.69
Zn	.22	-.02	.49	-.47	Zn	.91	.89	.93	.88
B	.39	-.36	.22	.11	B	.57	.61	.52	.08
Mg	.69	-.19		.22	Mg	.96	.97		.93
Ca	-.31	.22	-.02	-.31	Ca	-.33	-.31	-.31	-.41
Na	.47	.34	.84	-.46	Na	-.48	-.39	-.46	-.41
Al	.35	-.46	-.07		Al	.96	.90	.93	
K	.06	.38	.56	-.72	K	-.69	-.73	-.76	.57
Sulfate		-.02	.69	.35	Sulfate		.93	.96	.96
As vs Se		.76			As vs Se		.76		
Ni vs Mn		.93			Ni vs Mn		.97		
Na vs K		.81			Na vs K		.27		

As in the case of the raw shale, the high concentrations of sulfate and low pH's of the leachates must be due to the oxidation of the iron sulfides. The concentration of iron was low compared to that of sulfate. For example, mean Fe to sulfate molar ratios for the L2 leachates were 0.06:2, 0.08:2, 0.05:2 and 0.06:2, respectively, for the four successive years of the study, far below the values of almost 1:2 in the raw shale leachates.

Magnesium and Al were the most abundant elements in the retorted shale leachates. These two elements displayed inverse elemental release patterns, with Mg decreasing in concentration and Al increasing in concentration (Figure 16). The sum of their concentrations is present in approximately stoichiometric proportion of 1:2 with sulfate (Figure 17).

Aluminum and Fe displayed a product-reactant relationship, which is illustrated in Figure 18, a plot of their concentrations in the L2 leachates over time. Low concentrations of Al clearly correspond to high values of Fe and low values of sulfate. Reactions of Fe^{2+} with the spent shale (e.g. 5 and 6 below) must

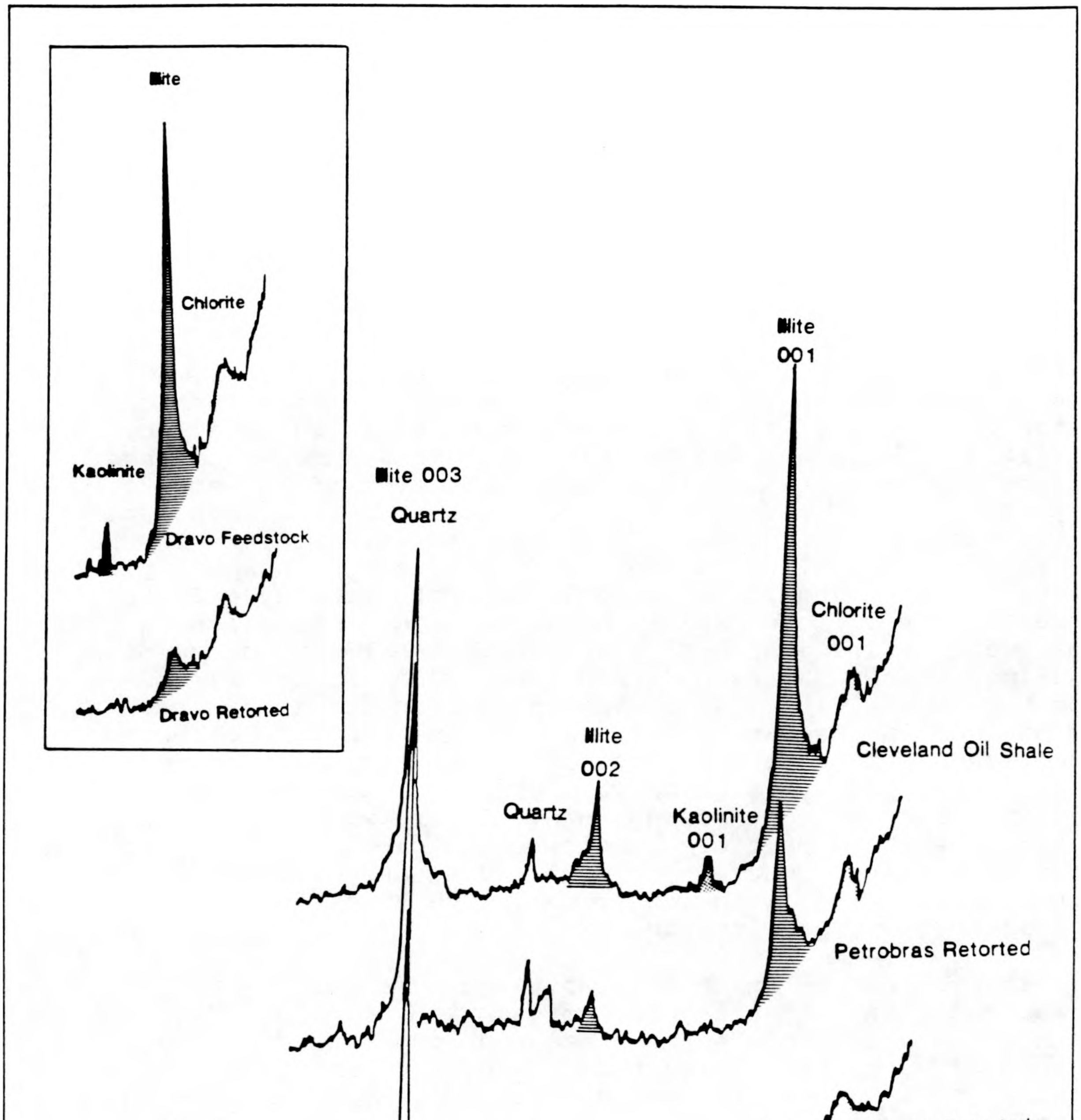

Figure 15. X-ray diffraction Patterns of Silt (>.2 micron) and Clay (<.2 micron, Insert) Size Fractions of Unretorted and Retorted Oil Shale. (Mg-Saturated, Glycerated Samples).

occur, in addition to simple acid dissolution reactions (eq. 7). The hydrolysis of Al^{3+} can also contribute to acidity via reactions such as 8 below.

5. $3Fe^{2+} + Al_2O_{3(s)} + 5H_2O + 1/2O_2 = 3Fe(OH)_{3(s)} + 2Al^{3+} + H^+$

6. $2Fe^{2+} + 3Mg(OH)_{2(s)} + 2H^+ + 1/2O_2 = 2Fe(OH)_{3(s)} + 3Mg^{2+}$

7. $6H^+ + 2Al_2O_{3(s)} = Al^{3+} + 3H_2O$

8. $Al^{3+} + H_2O = AlOH^{2+} + H^+$

Some additional insight in the product-reactant relationship of Al and Fe can be gained from examining the short term changes in the chemistry of the leachates. October of 1986 was dry at the field site and by the end of the month sample volume had declined to very low levels. During the week of November 4 to 11 (days 856 to 863) severe storms resulted in over 6 inches of precipitation, effectively "flushing" the lysimeters. In the November 10 sample, collected immediately after the precipitation event, Fe was found to increase in concentration by a factor of three (Figure 19) and rapidly declined in concentration in subsequent collections. Al steadily increased in the samples, doubling in concentration during the period October 13 to December 3. Sulfate also increased in concentration, reaching its maximum in the same sample as Al. The samples collected immediately after the precipitation event represent the rapid displacement of waters which were present at levels above field capacity, i.e. already moving down. Later, water which was wetting the shale particles, below field capacity, was displaced. These waters are higher in sulfate and Al and effectively represent solutions with longer residence times than the initial flow after the precipitation.

This effect is further illustrated by comparing the variation of Fe with the volume of sample collected (Figure 20). The highest values of Fe are present during and immediately after periods of very low sample volume, when the lysimeters are barely flowing (this is also reflected in the volume weighted means of Fe and Al, for the retorted shale leachates of project year 87/88 (Appendix Table 2)). Lysimeter samples represent water present in excess of field capacity. These sample waters have shorter residence time than that which is still present in the lysimeter wetting the shale particles. Thus, the variation in Fe concentration appears to be a function of residence time, with longer residence time correlating to lower Fe and higher Al concentration.

Oxygen also has a role in the relationship of Fe and Al. The relative proportion of Fe to Al can be related to the thickness of soils and overburden materials covering the spent shale. The ratio of mean Al to Fe for the last four years of the

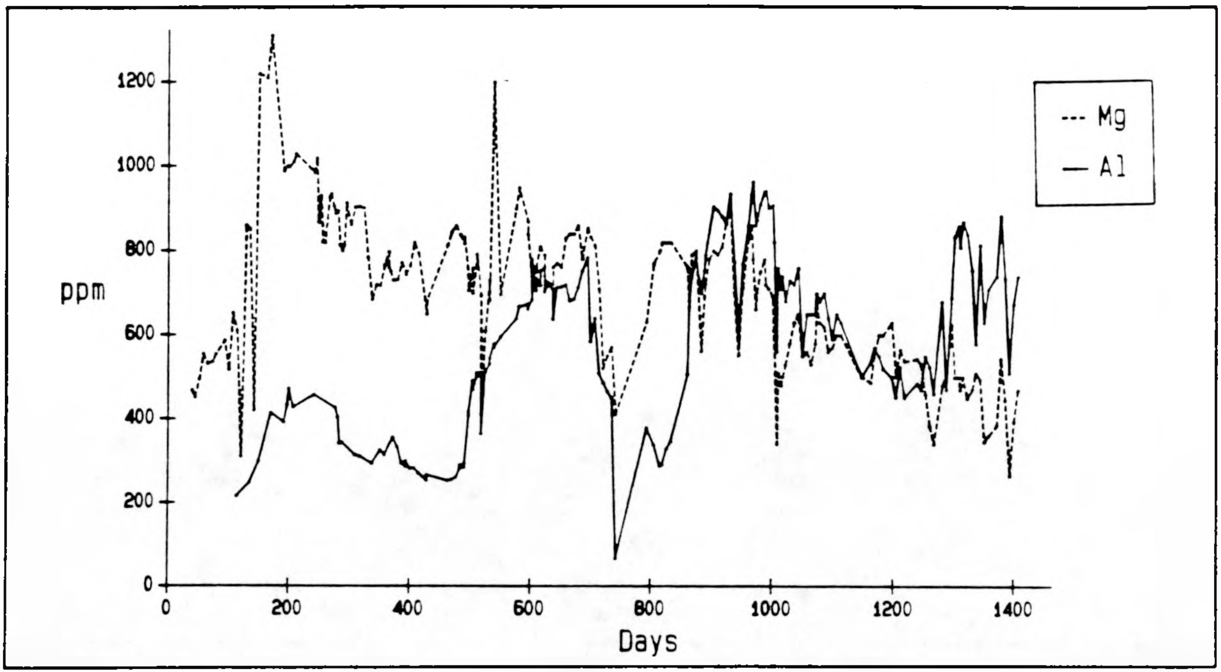

Figure 16. Plot of Mg and Al Concentrations for Leachates Collected from the L2 Lysimeter (Left Side Transport Tube).

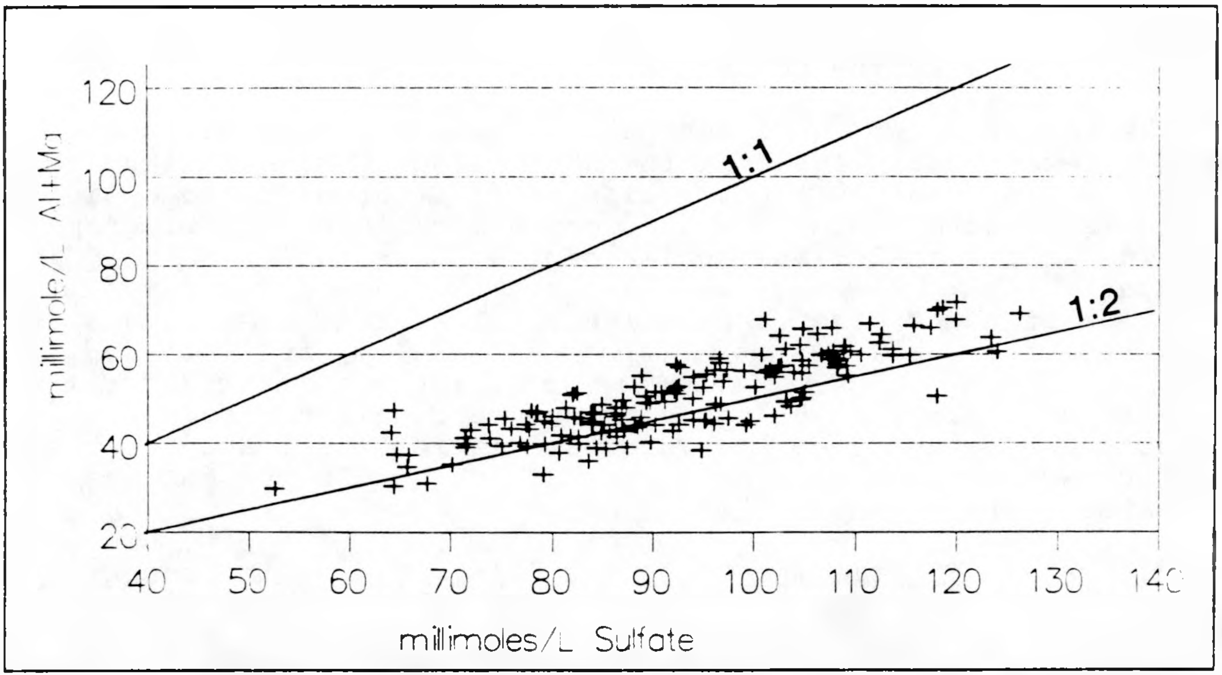

Figure 17. Concentration of Mg plus Fe versus Sulfate for L2 Leachates.

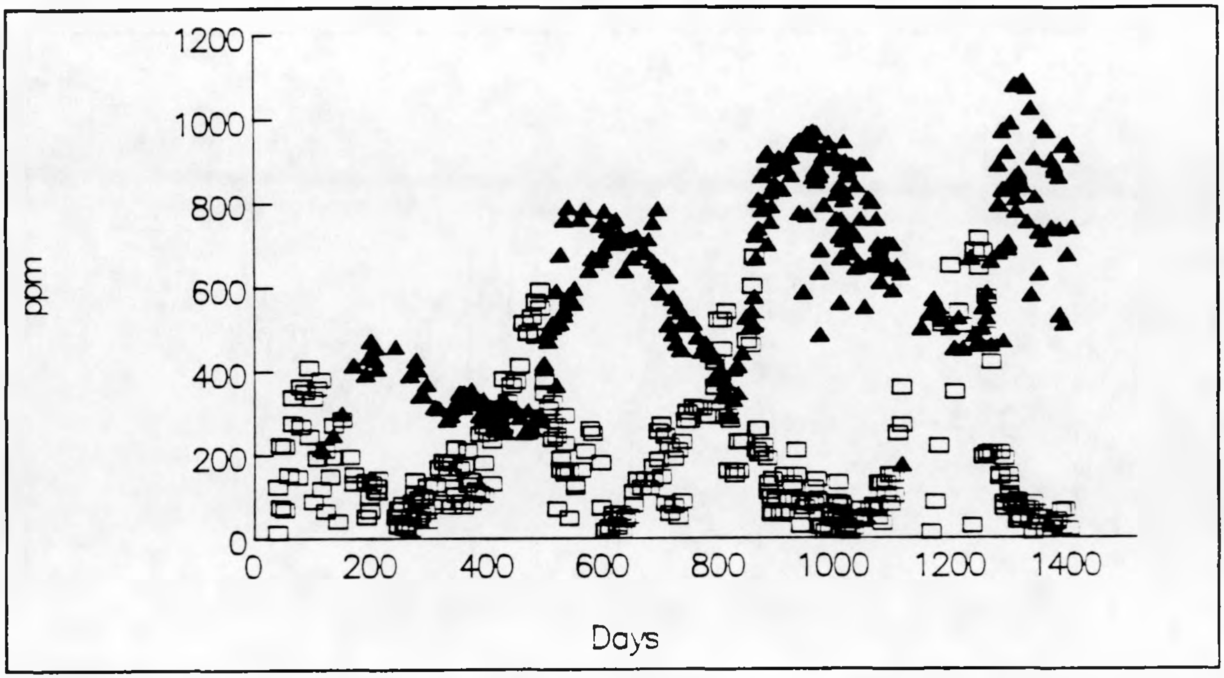

Figure 18. *Fe (square)* and Al (triangle) Concentration in L2 Leachates.

study averaged 2.3, 2.4, 2.7 and 5 for the L5, L6, L8 and L2 lysimeters, respectively (6, 4, 2, and 0 feet of cover). The thicker cover would restrict aeration, retarding the oxidation of Fe^{2+} and the generation of hydronium ion, and possibly the reaction of Fe with the shale matrix.

The chemistry of the leachate-spent shale interactions is more complex than expressed in the above reactions. Aluminum is not entirely present as the trivalent ion; a large degree of ion pairing is expected. The U.S.G.S. geochemical computer program WATEQ was used to calculate ionic species distribution in the leachates.[22] Using the mean values for the L2 leachates for the final year of the project, approximately 18% of Al was calculated to be present as Al^{3+}, 42% as the pair ion $AlSO_4^{1+}$, and 40% as $Al(SO_4)_2^{1-}$. $AlOH^{2+}$, $Al(OH)_2^{1+}$, $Al(OH)_4^{1-}$ combined were calculated to comprise less than 0.1% of the aluminum bearing ions, suggesting that acid generation from Al hydrolysis is insignificant for the conditions of this study. More than 80% of the Fe present was calculated to be as the paired ion $FeSO_4^{1+}$.

<u>Mineral Equilibria and Calcium Concentration.</u> In general, the chemistry of the spent shale leachates did not show any strong evidence of a mineral equilibria control. The variations in elemental concentrations were too large to be provided by solution-precipitation reactions. During the time of observation, the chemistry of the leachates appear to be a

ions are moved into and out of the system.

One exception was the behavior of Ca. It was found in very similar concentrations in all of the shale leachates, regardless of shale type or thickness, and did not change in concentration to any large degree with respect to time. This pattern suggests that its concentration was controlled by a mechanism of equilibrium or near equilibrium with a solid phase. The high concentration of sulfate suggests the most likely phase is gypsum ($CaSO_4 \cdot 2H_2O$) or anhydride ($CaSO_4$). Using the free energy values of Garrels and Christ, an equilibrium solubility product was calculated for these minerals[23]

$$^{a}[Ca^{2+}]^{c}[Ca^{2+}]^{a}[SO_4^{2-}]^{c}[SO4^{2-}] = 10^{-4.4}\ \text{anhydride},\ 10^{-4.6}\ \text{gypsum}$$

where $^{a}[X]$ denotes the activity coefficient and $^{c}[X]$ the concentration of species X. Again using WATEQ and the mean concentrations from the L2 leachates for the fourth year of the study (Appendix Table 1) an ion activity product of $10^{-4.58}$ was calculated for Ca^{2+} and SO_4^{2-}, corrected for ion pairing. This value is essentially identical to the equilibrium solubility product, indicating that solution-precipitation reactions with gypsum were likely responsible for the narrow range of variability and concentration found for Ca in the leachates.

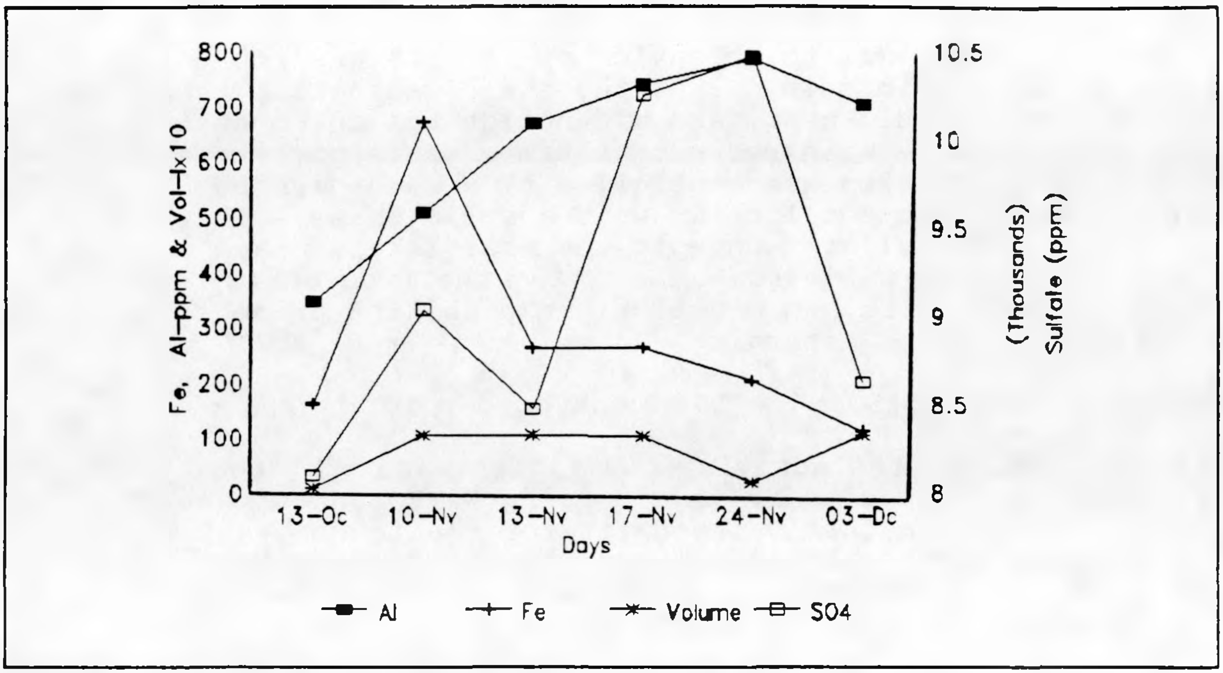

Figure 19. Plot of Al, Fe, Sample Volume and Sulfate for Leachates from L2 Lysimeter (Left Transport Tube).

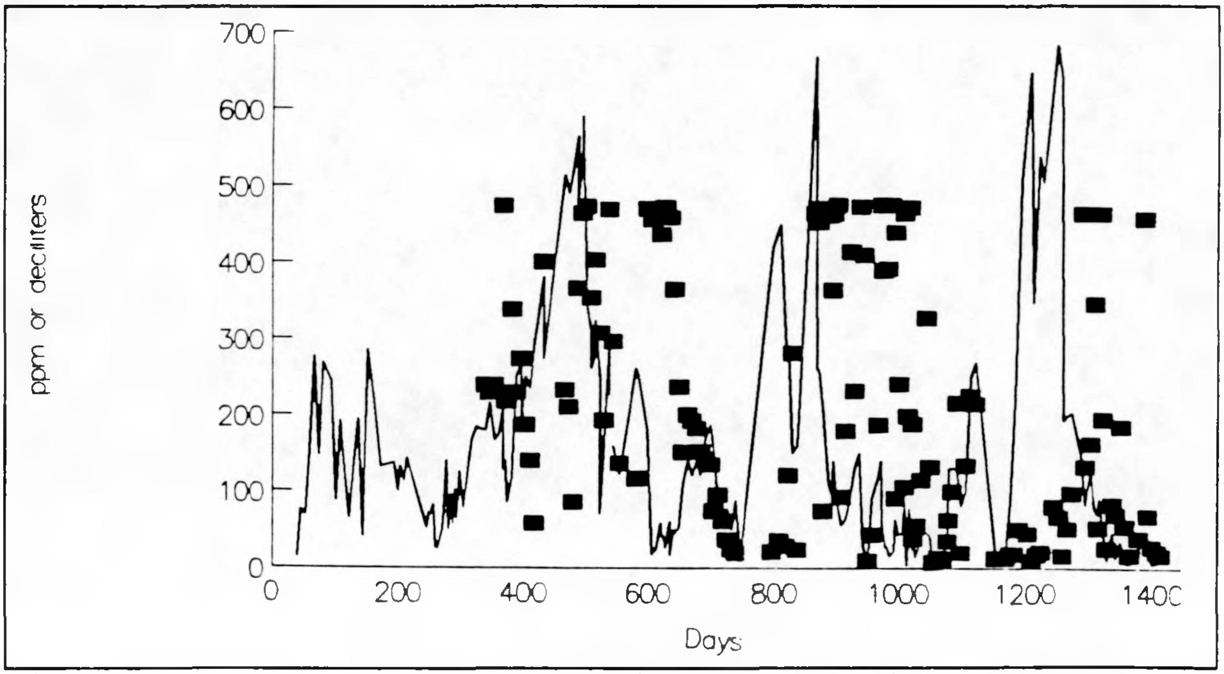

Figure 20. Plot of Fe Concentration (lines) with Sample Volume (squares) for Leachates from L2 Lysimeter (Left Transport Tube).

III. LABORATORY LEACHING STUDIES

III.1 Introduction

Having effective laboratory methods to assess leaching characteristics of the oil shale is of great value. Field studies, such as the one discussed here, are very expensive and labor intensive. In addition, credible field studies require a large amount of materials, which are rarely available. Also, research and development efforts are producing new retort designs with the potential for better efficiencies and higher yields. Technologies such as fluidized bed retorting, combined with secondary heat and gas recovery processes such as gasification and combustion, will result in different chemical and physical properties for the spent shale. Technologies that only exist at the PDU- or bench-scale cannot provide sufficient materials for anything beyond laboratory scale leaching tests. Since the ability to produce a more innocuous spent shale is a critical consideration in commercial development, early assessment of the environmental characteristics of waste materials is important.

Two approaches were used to study the leaching characteristics of Kentucky oil shale in the laboratory: batch tests, such as those proposed by the American Society for Testing and Materials (ASTM) and the Environmental Protection Agency (EPA),[24,25] and column tests.

Table VII. Parameters Used in Batch Extraction Tests.

Test	Duration (Hrs.)	Solid/ Liquid	Medium
EP	24	1:16	Water, adjusted with acetic acid to maintain pH <5.0
ASTM A	48	1:4	Water
ASTM B	48	1:4	1M solution of sodium acetate pH adjusted to 4.5 with acetic acid
Maximum Release	24	1:4	Water, a portion of the shale was exposed to 3 fresh aliquots of water
Maximum Concentration	24	Varied	Water aliquots of water exposed to 3 fresh portions of shale in ratios of 1:10, 1:7.5, and 1:5.

III.2 Batch Tests.

The batch tests were carried out using shaker tables to provide agitation. Test conditions are outlined in Table VII.

Batch Test Results. All of the elemental concentrations from leachates generated in batch tests were much lower, in some cases by orders of magnitude, than that found for the field-generated leachates (Table XIII). The concentrations generated from the batch tests were generally a full order of magnitude less than those from the field, even when the highest lab values are compared with field means. Similar results from batch leach tests have been obtained on earlier studies of Kentucky oil shale materials.[26,27] Most of the leachates generated by batch tests would be in compliance with RCRA limits.[28] Sullivan, Yelton and Reddy, using the more recent Toxicity Characteristic Leaching Procedure (TCLP) of the U.S. EPA on raw and retorted New Albany and Chattanooga Shales also found the elemental concentrations in the leachates below the limits specified by RCRA.[29]

Table VIII. Comparison of Highest Elemental Concentrations For Laboratory Batch Tests and Mean Composition of Leachates from Field Lysimeter L2 For First Year of Study. Values in ppm.

	ASTM A	ASTM B	EP	C*	L2	L2/MLAB+
Cu	0.26	0.39	0.04	0.15	0.39	3
Cr	<	<	<	0.03	0.33	11
Mo	<	<	<	0.05	0.93	19
As	<	0.20	<	0.04	0.49	2
Cd	0.61	0.49	0.11	0.65	3.64	6
Pb	<	<	<	<	1.17	--
Se	<	0.29	<	0.10	0.69	7
Mn	3.05	4.67	0.72	4.52	69.	15
Ni	5.92	6.62	1.16	5.50	80.	12
Fe	1.06	0.48	0.12	0.03	150.	141
Mg	37.3	58.9	9.54	17.0	774.	13
Na	35.7	nd	8.61	10.7	373.	10

*Maximum Concentration Test
+Maximum Field Concentration/Maximum Lab Concentration
nd Not Determined
< Below Detection Limit

There are two important reasons that the batch tests of Kentucky oil shale materials were low compared to the field results. First, the solid-to-liquid ratios in the batch tests were much lower than the field (e.g., 1:4 versus about 5:1). Second, the batch tests were of comparatively short duration and grossly understate the amount of ions which can be extracted. Kentucky oil shales are composed of silicates and sulfides. The reaction of these materials, particularly the hydrolysis and oxidation of the sulfides, are slow.

III.3 Column Studies

An alternate approach to the batch leaching tests is the use of packed columns. A review of the literature found a large variety of approaches and configurations used. There is not currently a standard approach, although ASTM did consider establishing one.[30] Also, results have not been reported on a uniform basis. Because of this, some researchers have concluded that column tests are of limited applicability and batch tests provide almost the same information with better reproducibilty.[31]

Some laboratory column studies have been successful in generating leachates similar to field data, although this work utilized fluidized bed combustion materials and retorted western oil shale.[32,33,34] These materials had high carbonate content, which may have been partially or fully calcined, were comparatively reactive, and produced alkaline leachates. Contrary to these results, previous column leaching tests of Kentucky oil shale materials generally did not agree with the field data, although the delayed release of some elements has been noted.[35,36]

Materials and Procedures. The approach taken for this study was to establish a set of columns which closely simulated the field conditions. Materials, packing densities and watering regimes similar to the conditions of the field site were used in the tests.

Materials used in the columns included the spent shale from the Dravo test, as used in the field study, and the spent shale from the PETROSIX technology. Fractions of both spent shales were combusted at 800 °C in an oxidizing furnace to simulate the

Table IX. Compositions of Oil Shale Materials Used in Column Tests.

Material	C	H	N	S	Ash	Moi.
Dravo						
Retorted	6.36	0.32	0.27	2.48	88.3	1.4
Combusted	4.32	0.09	0.16	1.18	94.6	0.6
Petrobras						
Retorted	7.85	0.48	0.45	1.42	88.5	0.8
Combusted	6.14	0.22	0.29	1.15	92.6	0.5

effect of additional carbon recovery. Carbon reductions of 22% and 32%, and sulfur reductions of 19% and 52% were achieved for the PETROSIX and Dravo spent shales, respectively (Table IX).

Unprocessed shale feedstocks included a <1/4-inch and 1/4 x 3/4-inch Cleveland shale used in the test. Material from a core was substituted for the Dravo feedstock material, which could not be obtained. The core was drilled in Montgomery County, Kentucky, near the Dravo sample site, and sections of the Cleveland and Sunbury shales were crushed and mixed in the same proportion as the Dravo feedstock. Soil and overburden materials from the field site were also included in the tests.

The materials were loaded in 40 x 600 mm chromatography tubes containing a fritted disc at the bottom above the delivery tube. The columns were packed to the densities measured during the filling operations of the field units. Two types of column conditions were employed, an open continuous flow regime (similar to the field lysimeters) and a closed saturation configuration which allowed some estimate of what the leachate composition would be in the saturated zone of a spent shale embankment.

Table X. Comparison of Leachate Composition from Column (C1) and Field Lysimeter (L2) Containing Dravo Retorted Shale.

Field Lysimeter L2			Lab Column C1		MeanL2/
	Mean	Range	Mean	Range	Mean C1
Conductance (ms)	8.8	[4.1-15.]	6.2	[3.9-12.]	1.4
pH	3.0	[2.5-3.6]	3.4	[2.9-3.6]	0.9
Cr	0.33	[< -0.66]	0.34	[< -0.78]	1.0
Cu	0.39	[< -1.79]	1.85	[0.50-6.90]	0.2
As	0.49	[< -1.00]	*	[< -8.80]	*
Se	0.69	[< -1.40]	*	[< -1.10]	*
Mo	0.93	[0.32-3.08]	*	[< -0.90]	*
Pb	1.17	[< -2.60]	*	[< -1.40]	*
Cd	3.64	[0.20-8.00]	4.79	[0.20-16.2]	0.8
B	5.35	[2.60-6.93]	5.65	[3.00-10.3]	0.9
Mn	69	[30-142]	49	[9-185]	1.4
Ni	80	[27-150]	54	[9-200]	1.5
Fe	150	[14-409]	20	[1- 77]	7.5
K	155	[75-238]	120	[48-470]	1.3
Na	373	[140-579]	205	[58-560]	1.8
Ca	454	[170-634]	443	[410-490]	1.0
Mg	774	[307-1310]	473	[110-1570]	1.6
Sulfate	8570	[3370-13410]	4345	[416-12940]	2.0

< Below detection limit
*Means were not calculated for elements where greater than 50% of samples were below limits of detection.

Table XI. Comparison of Average Concentrations of Dravo Retorted Shale Leachate for Open Flow and Saturated Column Conditions with Combusted Dravo Shale (Open Flow Column). Elemental Values as ppm.

	Retorted		Combusted	Retorted/+ Combusted
	Open Column	Saturated Column	Open Column	
pH	3.4	4.3	4.7	0.7
Cond(ms)	6.2	5.2	4.6	1.3
Cr	0.3	--*	--	
Cu	1.8	--	0.6	3
Cd	4.8	0.7	0.2	24
B	5.6	5.5	4.4	1
Fe	20	363	0.7	29
Mn	48	40	4.8	10
Ni	53	27	4.7	11
Na	205	163	206	1
Zn	220	75	12	18
Ca	443	474	426	1
Mg	473	316	211	2
Sulfate	4345	4706	3351	1

*More than 50% of samples below detection limits.
+Value from Open Flow Column

The saturated columns were kept with a 2-inch water layer on top of the material and sampled every two weeks by opening a tubing clamp in the lowermost part of the delivery stem. After collecting a sample of 30-40 cc, the same amount of water was added to the upper water layer and the column re-sealed.

In the open flow columns, a water regime which reflects the precipitation pattern at the Hope Creek site was used. Zero to three inches of water added weekly, to simulate the amount and pattern of precipitation as measured in the field site, up to a total of 42-inches. Whenever at least 30 cc of leachate was collected in the polyethylene bottle connected to the delivery tube, the sample was removed and analyzed.

<u>Column Results, Comparison with Field Data.</u> The columns were operated for 340 days, close to an annual cycle. Thus, the data from the columns is reasonably comparable to the first year of data from the field lysimeters. The agreement between the field data and the laboratory data is excellent (Table X). The elemental concentration of the leachates from the open flow

column with the Dravo retorted shale and the mean concentration of the leachates from the L2 lysimeter were almost all within a factor of two and the range of determined values overlapped in most cases. One exception is that of iron, which was much lower in the leachates from the open flow column. This might be explained by precipitation of $Fe(OH)_3$ in the open column due to oxidation. The oxidation conditions in the field lysimeters are expected to be more variable due their size and are subject to less aeration. Thus, in the lysimeters, more dissolved iron would remain in its soluble reduced form (Fe^{+2}). This is supported by the concentration of iron in the closed column leachates (Table XI), which were considerably higher than the lysimeters or the open column.

Significant quantities of residual carbon were left on Kentucky oil shales during pyrolysis. Since several retorting technologies would recover an increment of this carbon via gasification or combustion, the impact of additional carbon recovery on leachate chemistry is of interest. Combusting the Dravo retorted shale greatly lowered its leaching potential. The pH levels of the leachates from the combusted material were higher, 4.7 versus 3.4 (Table XI and Table XII), and the concentration of most elements, including Ni, Cd, Pb, As, Mn and Zn were greatly reduced, in some cases by an order of magnitude.

In addition to providing a closer approximation of the leachate chemistry of the materials, the column data also mimicked the field lysimeter data in terms of elemental release patterns. Some examples are presented in Figures 21 and 22. The feedstock sample from the PETROBRAS test was used in the comparison with the raw shale, as the core material used to simulate the Dravo feedstock provided leachates with very low elemental concentrations and relatively high pH's. The reason for this is not completely understood. It is probably due to an aging affect in the pilot plant materials, which has been noted in previous research.[37] This points out the necessity of closely matching materials in this type of test.

The timing and relative concentrations were not exactly comparable between the lab and field data, the elemental maxima from the columns were slightly higher and occurred somewhat earlier for many of the elements. The elemental release patterns, however, were very similar. For example, in the Ni and Mn from the spent shale leachates were very similar to one another in both the field and laboratory leachates. Iron in the column leachates showed a high degree of variability similar to

Table XII. Comparison of Mean Leachate Chemistry from Column Test of Petrobras Combusted and Retorted Shales.

	Retorted	Combusted	Retorted /Combusted
pH	3.1	4.6	0.7
Cond. (ms)	2.53	2.89	0.9
As	--	--	--
Cr	--	--	--
Pb	--	--	--
B	1.2	4.6	0.3
Cd	5.1	1.3	4
Cu	7.7	0.3	26
Mn	7.8	4.6	2
Fe	18	2.6	7
Ni	25	8	3
Mg	39	91	0.4
K	156	414	0.4
Na	87	138	0.6
Ca	42	41	1
Zn	230	138	1.8
Sulfate	1845	2025	0.9

that of the field leachates. Calcium had approximately the same concentration and low degree of variability in the lab column leachates as that from the field, suggesting that its concentration was controlled by the solution and precipitation of gypsum.

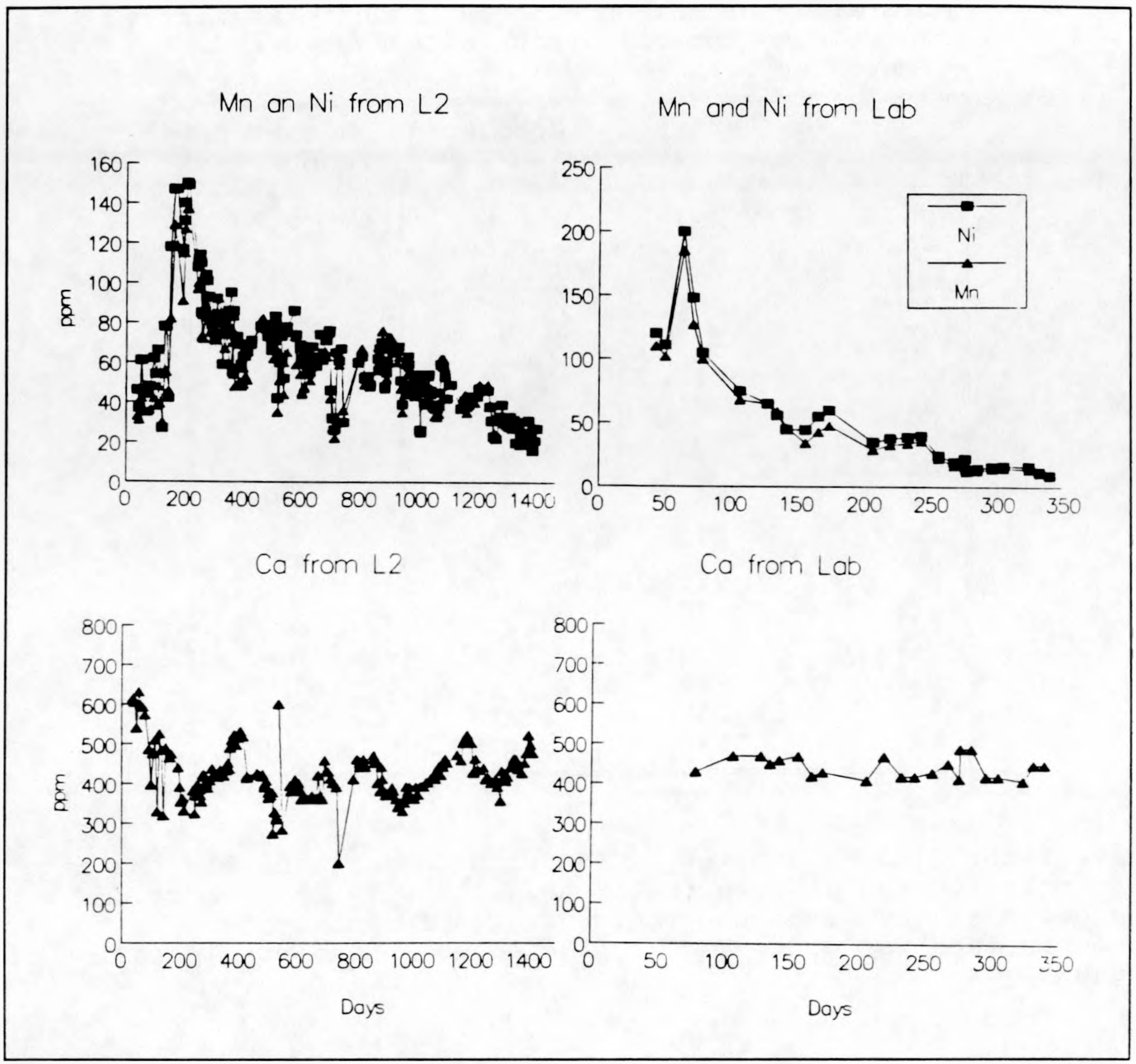

Figure 21. Comparison of Elemental Release Patterns Between Field Lysimeter and Laboratory Columns.

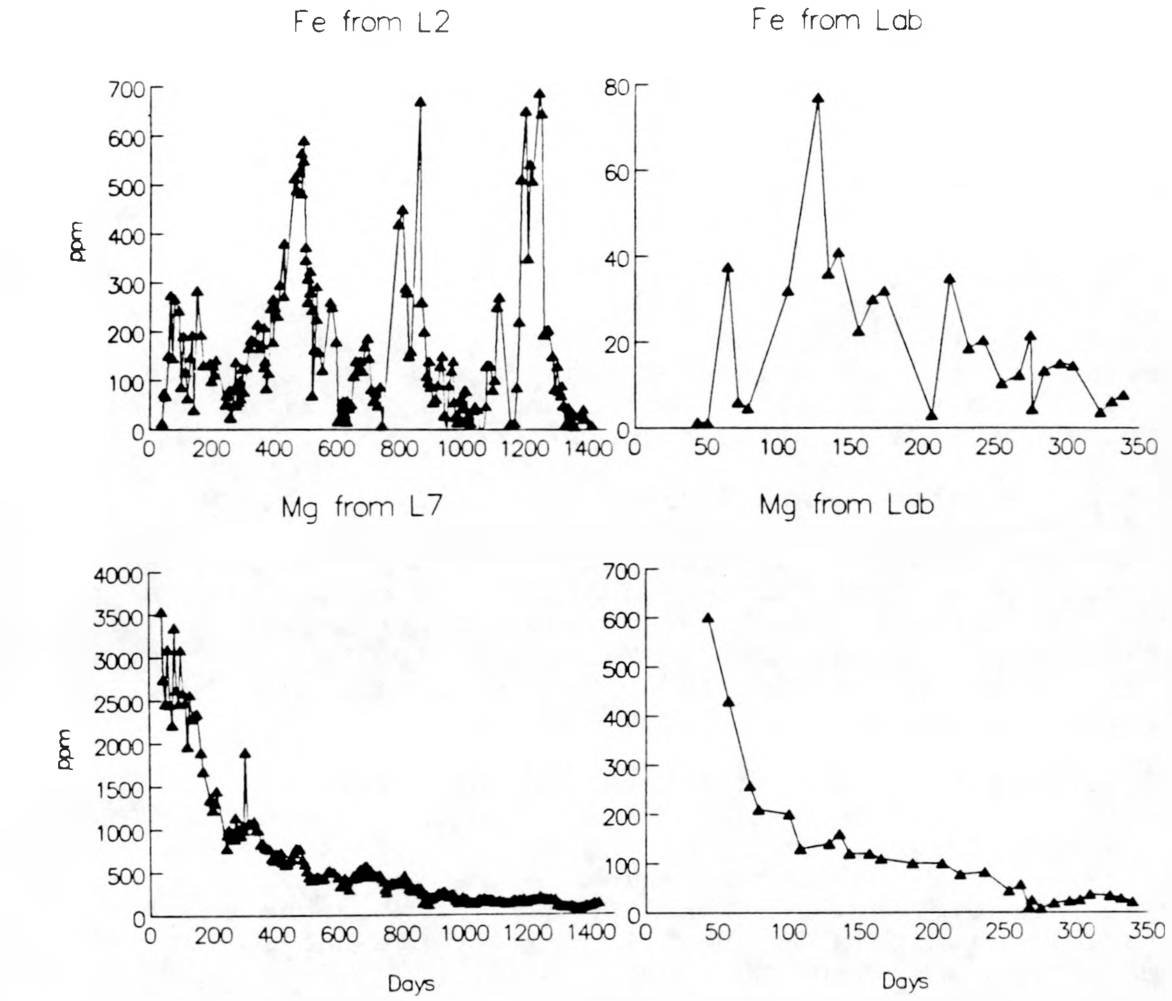

Figure 22. Comparison of Elemental Release Pattern Between Field Lysimeter and Laboratory Column. Mg from Lab Column is For Petrobras <1/4-inch Raw Shale.

IV. PROJECT SUMMARY

IV.1 The Field Leaching Studies.

The retorted, raw and mixed raw shale were placed in field lysimeters and compacted to densities which were close to optimum. The lysimeters were sampled weekly or biweekly over a period of 1300 days. Measurements of sample volume indicated that two void volumes of precipitation percolated through the lysimeters over the period of the study.

In addition to kerogen, the oil shales consisted of iron sulfides and silicates including quartz (~20%), and the clay minerals; illite (~60%), chlorite (~11%) and kaolinite (~9%). Retorting the oil shale induced significant changes in the clay minerals, with the dehydroxylation and decrystallization of kaolinite and illite as the major effects.

The leachates generated in the field lysimeters were highly acidic with pH's varying from approximately 2.5 to 3.5 during the study. The leachates had high concentrations of dissolved elements with sulfate, Mg and Fe present at concentrations of tens of thousands or thousands of ppm. Other important constituents included: Al, Zn, Na, Ca, K (100 to 1000 ppm in concentration); Ni and Mn (10 to 100 ppm); Cd and B (1 to 10 ppm); and Cr, Cu, Mo, Pb, As and Se (<1ppm).

The intensity of acid generation and elemental concentrations in the leachates were highest in the first year and decreased significantly during the period of the study. Many elements declined in concentration in the leachates by factors of 3 to 10. However, even after 1300 days, the leachates remained very acidic with pH's in the 2.9 to 3.4 range and sulfate concentrations of 3,000 to 5,000 ppm.

The acidity of the leachates was caused by the oxidation and hydrolysis of iron sulfides and the resultant generation of sulfuric acid and the oxidation of Fe^{2+} to Fe^{3+} and the further generation of hydronium ion.

In the raw shale leachates iron, magnesium, and sulfate were present in the highest concentrations. Fe was found to be in near stoichiometric proportion with sulfate, indicating that the magnesium was solubilized by the acid attack of the brucite sheet in the chlorite. The high correlation of the concentrations of most of the transition elements measured in the leachates to that of sulfate and iron indicated that the mobilization of most of these elements was for the most part a function of the intensity of acid generation.

The clay minerals of the retorted shale were reactive relative to the raw shale, providing leachates with higher Al and K concentrations. This was most likely due to changes induced by retorting. The highest concentrations of elements present in the retorted shale leachates were sulfate, Al and Mg. Iron showed a high degree of variability in concentration, which appeared to be a function of leachate residence time. Al and Fe concentrations also varied inversely suggesting a product-reactant relationship.

In general, the variability of the concentration of the dissolved ions and their response to short term changes induced by precipitation suggests that the overall chemistry of the leachates to be transport controlled, i.e. determined by the kinetics of solution reactions and materials transport. Little evidence was found for mineral equilibrium control. The one exception was calcium which had a relatively constant concentration in all of the shale leachates, suggesting a solution-precipitation equilibria control with respect to the mineral gypsum.

IV.2 Laboratory Leaching Studies

Laboratory based leaching experiments on Kentucky oil shale included batch methods and column experiments. The batch methods were based on proposed EPA and ASTM methods and produced leachates with elemental concentrations much lower than that from the field study. Column experiments were designed which utilized packing densities, watering regimes and times (i.e. 1 year versus 24 hours for the batch tests) which closely simulated the field conditions. Leachates from the column tests were in good agreement with the levels of concentration determined for the field case. In addition, elemental release patterns very similar to the field case were observed with the column experiments.

IV.3 Discussion

The field study indicated that all the oil shale materials investigated capable of generating significant quantities of acid and producing leachates with high transition element concentrations. Thus, acid mine drainage appears to be a potential problem for oil shale disposal.

Two mitigation strategies are apparent. One is to manage the problem. That is, to design the disposal area in a manner to minimize percolation into the disposal pile and intercept and channel what does occur to a treatment pond. This approach may be feasible under a scenario where the retorted shale is returned to the mine. The oil shale comprise the upper portions of the shale unit and if not excessively damaged in the mining process, the base of an oil shale mine would be impermeable and would serve as an aquiclude to further retard percolation. This could serve as a transport surface to collect leachate waters and channel them to a pond for treatment. The by-product recovery of certain elements such as Zn from the leachate treatment may even offset some of the treatment costs. The treatment of the drainage would present a case of perpetual care and would require essentially a zero discharge basis for mine design.

A second, and in the authors opinion, more desirable approach would be to remove the sources of acidity in the processing of the oil shale. This would require the development of a retort which would remove sulfur and oxidize the Fe to the ferric state. This concept has been integrated into the design of KENTORT II, a retort for eastern oil shale, currently under development at the CAER.[38]

V. ACKNOWLEDGEMENTS.

This project spanned five years and had some complex logistics which required the help and cooperation of many individuals and organizations. The help and support of Frank Forbes and Lou Colaianni of Dravo Engineering, Inc. were critical in the early stages of project development as was the support of Barry Soloman, George Llyod and John Gannon of Southern Pacific Petroleum. The help of David Meyers, on whose farm the field station is located, and Frank Walker of Walker Construction was also critical. The efforts of Moshe Shirav of the Geological Survey of Israel, who designed and developed the laboratory column study, is gratefully acknowledged. Richard Barnhisel of the UK department of Agronomy was also a major contributor to the project and was responsible for much field work and the mineralogic characterization of the materials. Robert Meade and David Allen of the UK Highway Transportation Research were responsible for the laboratory compaction studies and determination of the lysimeter fill compactions.

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APPENDIX

Table 1. Data Summary for the lowest (10-feet) lysimeter Transport Tubes. Data is as the mean of all samples collected during each of the four project years. The standard deviation is presented as a percentage of the mean. The mean was not calculated for elements (ns) where more than 50% of the samples fell below the limits of detection for the analytical technique employed. The percentage of samples above the limits of detection (%>dl) is presented in the right hand column with the exception of Al. The value presented for Al in this column, for the first three years of the study, is the percentage of samples which were determined.

Appendix Table 1.1 Leachate Data Summary.

L1-84/85 #Samples 134 Soil Materials

	Mean	Std	Max- Min	%>dl
pH	5.60	23	8.34- 2.4	
Cond	0.25	78	1.94-0.09	
Cr	ns	ns	0.05- <dl	9
Cu	ns	ns	0.20- <dl	38
Mo	ns	ns	0.44- <dl	4
Pb	ns	ns	1.00- <dl	19
As	ns	ns	0.40- <dl	6
Se	ns	ns	0.50- <dl	8
Cd	ns	ns	0.0- <dl	20
B	0.1	87	0.3- <dl	57
Mn	ns	ns	0.1- <dl	43
Ni	0.1	49	0.2- <dl	62
Fe	0.3	182	4- <dl	78
Zn	1	235	13- 0.1	
K	3	85	16- 1.0	
Na	15	15	24-11.0	
Ca	8	89	31- 1.1	
Al	nd	nd		
Mg	1	60	4- 0.4	
SO4	37	47	95-10.0	

L1-85/86 #Samples 136

	Mean	Std	Max- Min	%>dl
pH	6.33	13	8.05-4.22	
Cond	0.19	42	0.44-0.09	
Cr	ns	ns	0.20- <dl	21
Cu	ns	ns	0.10- <dl	38
Mo	ns	ns	0.30- <dl	5
Pb	ns	ns	0.50- <dl	6
As	ns	ns	0.30- <dl	1
Se	ns	ns	0.80- <dl	11
Cd	ns	ns	1.4- <dl	10
B	ns	ns	0.2- <dl	45
Mn	ns	ns	0.1- <dl	30
Ni	0.1	54	0.2- <dl	58
Fe	ns	ns	1- <dl	38
Zn	5	541	256- 0.0	
K	4	73	14- 1.3	
Na	19	47	73-10.9	
Ca	19	85	78- 2.1	
Al	nd	nd		
Mg	1	122	17- 0.4	
SO4	35	28	58-14.0	

L1-86/87 #Samples 192

	Mean	Std	Max- Min	%>dl
pH	6.39	7	7.2- 5.14	
Cond	0.20	35	0.38- 0.1	
Cr	ns	ns	0.20- <dl	3
Cu	ns	ns	0.02- <dl	8
Mo	ns	ns	0.40- <dl	5
Pb	ns	ns	0.60- <dl	4
As	ns	ns	0.70- <dl	2
Se	ns	ns	0.80- <dl	9
Cd	ns	ns	0.04- <dl	17
B	ns	ns	0.3- <dl	42
Mn	ns	ns	0.1- <dl	6
Ni	ns	ns	0.2- <dl	19
Fe	ns	ns	1- <dl	3
Zn	0.1	52	1- <dl	91
K	5	49	12- 1.3	
Na	16	34	51-11.8	
Ca	24	67	97- 2.6	
Al	ns	ns	2- <dl	8
Mg	1	45	4- 0.4	
SO4	35	10	50-27.0	

L1-87/88 #Samples 86

	Mean	Std	Max- Min	%>dl
pH	6.53	6	7.33-5.37	
Cond	0.23	36	0.66-0.11	
Cr	ns	ns	<dl- <dl	0
Cu	ns	ns	0.02- <dl	1
Mo	ns	ns	0.27- <dl	3
Pb	ns	ns	<dl- <dl	0
As	ns	ns	0.40- <dl	1
Se	ns	ns	0.50- <dl	6
Cd	ns	ns	0.02- <dl	8
B	ns	ns	0.7- <dl	31
Mn	ns	ns	<dl- <dl	0
Ni	ns	ns	0.1- <dl	3
Fe	ns	ns	0.1- <dl	1
Zn	ns	ns	0.1- <dl	28
K	5	33	10- 2.3	
Na	13	10	17-10.5	
Ca	24	44	49- 4.2	
Al	nd	nd	nd- nd	
Mg	1	32	3- 0.5	
SO4	37	22	78-12.0	

Appendix **Table 1.2** Continued.

L2-84/85	#Samples 94	Retorted Shale 10'			**L2-85/86**	#Samples 88		
	Mean	Std	Max- Min	%>dl	Mean	Std	Max- Min	%>dl
pH	2.96	5	3.59-2.47		3.02	8	3.81-2.63	
Cond	8.77	22	15-4.09		8.55	14	9.88-2.77	
Cr	0.33	34	0.66- <dl	98	0.46	45	0.90- <dl	73
Cu	0.39	69	1.79- <dl	91	0.27	61	0.70- <dl	99
Mo	0.93	49	3.08- <dl	93	0.53	51	1.40- <dl	72
Pb	1.17	58	2.60- <dl	83	0.70	61	2.60- <dl	69
As	0.49	52	1.00- <dl	65	ns	ns	1.20- <dl	45
Se	0.69	48	1.40- <dl	72	0.60	41	1.40- <dl	67
Cd	3.6	56	8.0- 0.2		3.1	35	5.7- 1.0	
B	5.3	14	6.9- 2.6		6.5	12	7.9- 2.3	
Mn	69	40	142- 30		64	25	98- 22	
Ni	80	37	150- 27		69	22	111- 26	
Fe	150	61	409- 14		211	68	591- 6	
Zn	415	58	983- 97		294	18	450- 110	
K	155	18	238- 75		129	18	185- 86	
Na	373	19	579- 140		371	14	595- 219	
Ca	455	17	634- 170		394	14	599- 200	
Al	341	63	472- 2	44	549	30	788- 258	98
Mg	775	25	1310- 307		785	15	1200- 410	
SO4	8567	20	13409-3372		9782	12	12189-6185	

L2-86/87	#Samples 102				**L2-87/88**	#Samples 78		
	Mean	Std	Max- Min	%>dl	Mean	Std	Max- Min	%>dl
pH	3.50	7	4.34-2.91		3.37	7	3.91-2.81	
Cond	8.22	12	9.72-5.36		7.49	12	9.17-5.18	
Cr	ns	ns	0.30- <dl	9	ns	ns	0.31- <dl	1
Cu	0.31	320	9.60- <dl	91	ns	ns	4.30- 0.1	
Mo	ns	ns	0.30- <dl	6	ns	ns	0.78- <dl	9
Pb	ns	ns	0.70- <dl	4	ns	ns	0.32- <dl	1
As	ns	ns	0.00- <dl	0	ns	ns	0.20- <dl	1
Se	ns	ns	0.70- <dl	8	ns	ns	0.62- <dl	14
Cd	2.3	46	4.4- 0.4		1.7	46	3.9- 0.7	
B	6.5	15	8.3- 3.9		6.2	16	8.2- 3.8	
Mn	52	24	82- 18		36	28	66- 16	
Ni	53	21	72- 21		37	26	62- 16	
Fe	142	105	670- 1		143	134	715- 2	
Zn	175	26	290- 54		149	22	247- 73	
K	81	26	129- 21		64	33	168- 37	
Na	273	20	410- 160		219	21	346- 115	
Ca	402	10	540- 320		430	10	634- 350	
Al	710	27	967- 174	98	737	27	1090- 451	
Mg	696	18	930- 340		529	18	696- 265	
SO4	9312	14	11864-6317		8372	15	11226-5057	

Appendix Table 1.3 Continued.

L8-84/85 #Samples 66 Retorted Shale 8'

	Mean	Std	Max- Min	%<dl
pH	3.13	6	3.53-2.68	
Cond	8.98	17	13.1-6.74	
Cr	0.31	45	0.68- 0.2	
Cu	0.37	68	1.14- 0.1	
Mo	0.78	48	1.74- 0.1	
Pb	1.06	44	2.00- <dl	77
As	0.42	40	0.74- <dl	56
Se	0.56	40	1.08- <dl	77
Cd	4.3	38	8.2- 0.7	
B	6.5	20	9.3- 2.7	
Mn	72	30	137- 36	
Ni	78	25	138- 42	
Fe	63	85	260- 7	
Zn	502	34	877- 188	
K	145	20	205- 83	
Na	451	29	832- 295	
Ca	448	22	897- 335	
Al	291	43	458- 24	61
Mg	799	24	1210- 504	
SO4	8412	20	12428-5060	

L8-85/86 #Samples 116

	Mean	Std	Max- Min	%>dl
pH	3.14	7	3.72-2.36	
Cond	5.90	12	7.37-4.55	
Cr	0.23	59	0.99- <dl	66
Cu	0.29	66	0.90- .04	95
Mo	ns	ns	0.57- <dl	49
Pb	ns	ns	2.20- <dl	43
As	ns	ns	1.20- <dl	38
Se	ns	ns	1.10- <dl	41
Cd	1.9	42	4.0- 0.6	
B	5.5	21	8.8- 3.6	
Mn	38	42	79- 18	
Ni	38	36	72- 19	
Fe	68	77	200- 5	
Zn	162	42	460- 47	
K	100	25	210- 55	
Na	219	28	348- 70	
Ca	454	11	554- 220	
Al	371	13	502- 272	20
Mg	372	31	604- 125	
SO4	5858	18	7893-3309	

L8-86/87 #Samples 119

	Mean	Std	Max- Min	%>dl
pH	3.42	7	3.98-2.73	
Cond	4.84	12	6.07-3.35	
Cr	ns	ns	0.30- <dl	40
Cu	0.19	79	0.70- .01	
Mo	ns	ns	0.40- <dl	10
Pb	ns	ns	0.80- <dl	4
As	ns	ns	0.50- <dl	3
Se	ns	ns	0.80- <dl	10
Cd	0.9	50	2.0- 0.1	
B	4.5	23	7.9- 2.2	
Mn	20	29	35- 9	
Ni	19	28	31- 8	
Fe	71	77	250- 3	
Zn	77	27	130- 29	
K	75	17	111- 51	
Na	118	29	280- 39	
Ca	439	12	880- 360	
Al	282	19	410- 200	34
Mg	254	31	630- 110	
SO4	4664	19	6724-2881	

L8-87/88 #Samples 61

	Mean	Std	Max- Min	%>dl
pH	3.22	7	3.67- 2.7	
Cond	5.26	10	6.27-4.01	
Cr	ns	ns	<dl- <dl	0
Cu	0.16	133	1.22- .02	
Mo	ns	ns	0.42- <dl	10
Pb	ns	ns	0.40- <dl	3
As	ns	ns	<dl- <dl	0
Se	ns	ns	0.63- <dl	15
Cd	0.7	51	1.4- 0.2	
B	4.3	16	5.7- 2.6	
Mn	18	17	23- 10	
Ni	16	18	23- 9	
Fe	146	92	520- 7	
Zn	67	17	92- 39	
K	71	18	97- 55	
Na	105	16	135- 65	
Ca	426	9	520- 370	
Al	388	42	635- 168	
Mg	251	23	385- 160	
SO4	5241	17	7284-3745	

Appendix Table 1.4 Continued.

L6-84/85	#Samples 48	Retorted Shale 6'			**L6-85/86**	#Samples 86		
	Mean	Std	Max- Min	%>dl	Mean	Std	Max- Min	%>dl
pH	2.92	8	3.9-2.57		2.97	8	3.51-2.48	
Cond	6.49	19	10.1-3.89		5.17	10	6.29-4.05	
Cr	ns	ns	4.22-0.03		ns	ns	0.50- <dl	48
Cu	0.07	56	0.18- <dl	90	0.10	70	0.40- <dl	83
Mo	0.59	65	1.40- <dl	77	ns	ns	0.65- <dl	44
Pb	1.02	67	2.70- <dl	81	ns	ns	1.70- <dl	24
As	0.42	66	1.20- <dl	63	ns	ns	0.89- <dl	19
Se	0.74	51	1.70- <dl	77	ns	ns	1.50- <dl	31
Cd	0.9	48	2.1- 0.3		0.5	36	1.0- 0.2	
B	5.1	29	8.2- 2.8		3.6	24	6.5- 2.0	
Mn	44	31	70- 21		30	20	52- 19	
Ni	39	25	63- 18		23	15	31- 14	
Fe	531	65	1270- 58		315	59	736- 38	
Zn	146	36	251- 55		83	23	160- 40	
K	113	10	136- 95		96	14	122- 69	
Na	209	27	300- 113		145	15	208- 89	
Ca	448	9	524- 357		440	13	840- 362	
Al	nd	nd	nd- nd		nd	nd	nd- nd	
Mg	432	28	690- 241		289	18	430- 145	
SO4	5704	33	10448-3591		4363	17	9479-2872	

L6-86/87	#Samples 168				**L6-87/88**	#Samples 99		
	Mean	Std	Max- Min	%>dl	Mean	Std	Max- Min	%>dl
pH	3.39	8	3.98-2.68		3.22	8	3.67-2.67	
Cond	4.13	17	7.54- 2.2		4.09	20	5.21-1.66	
Cr	ns	ns	0.30- <dl	11	ns	ns	<dl- <dl	0
Cu	0.15	85	0.60- <dl	95	ns	ns	0.97-0.01	
Mo	ns	ns	0.40- <dl	5	ns	ns	0.42- <dl	9
Pb	ns	ns	0.50- <dl	4	ns	ns	<dl- <dl	0
As	ns	ns	0.50- <dl	5	ns	ns	0.40- <dl	3
Se	ns	ns	1.10- <dl	16	ns	ns	0.60- <dl	4
Cd	0.4	50	0.8- 0.1		0.4	71	1.3- 0.1	
B	2.8	27	4.4- 0.9		2.5	33	4.0- 0.6	
Mn	17	33	32- 5		15	36	24- 3	
Ni	14	27	23- 4		10	30	19- 2	
Fe	135	90	510- 1		173	101	549- 2	
Zn	54	24	87- 19		46	27	75- 11	
K	81	19	127- 47		69	20	96- 28	
Na	92	28	170- 34		76	30	116- 20	
Ca	414	11	540- 250		411	15	505- 160	
Al	148	33	320- 63	37	174	53	380- 32	
Mg	210	28	390- 77		181	27	335- 45	
SO4	3491	20	5518-1625		3475	21	4732-1041	

Appendix Table 1.5 Continued.

L5-84/85 #Samples 71 Retorted Shale 4'

	Mean	Std	Max- Min	%>dl
pH	2.91	6	3.34-2.53	
Cond	6.65	27	15.3-4.63	
Cr	0.38	155	2.90-0.04	
Cu	0.17	73	0.57- <dl	96
Mo	1.07	85	3.58- <dl	85
Pb	1.35	49	2.69- <dl	82
As	0.59	48	1.99- <dl	65
Se	0.82	37	1.50- <dl	79
Cd	1.6	51	3.4- <dl	99
B	5.2	32	9.2- 2.9	
Mn	51	37	102- 26	
Ni	52	36	101- 27	
Fe	389	120	1650- 12	
Zn	214	36	373- 93	
K	90	11	117- 66	
Na	243	25	419- 159	
Ca	449	8	530- 367	
Al	nd	nd	nd nd	
Mg	470	40	891- 265	
SO4	5623	40	12129-3433	

L5-85/86 #Samples 127

	Mean	Std	Max- Min	%>dl
pH	2.95	9	3.82-2.45	
Cond	5.79	25	10.5-3.28	
Cr	0.34	153	2.90- <dl	76
Cu	0.13	89	0.65- <dl	85
Mo	0.72	120	3.58- <dl	62
Pb	0.96	68	2.69- <dl	53
As	ns	ns	1.99- <dl	38
Se	ns	ns	1.37- <dl	43
Cd	1.0	61	3.4- <dl	98
B	5.0	34	9.2- 1.4	
Mn	36	55	102- 6	
Ni	35	56	101- 6	
Fe	379	111	1650- 4	
Zn	132	53	373- 27	
K	86	16	117- 42	
Na	194	34	419- 40	
Ca	428	10	530- 283	
Al	318	31	430- 115	6
Mg	346	53	891- 95	
SO4	4999	37	12129-2743	

L5-86/87 #Samples 108

	Mean	Std	Max- Min	%>dl
pH	3.38	8	4.11-2.61	
Cond	4.04	16	5.6- 2.8	
Cr	ns	ns	0.10- <dl	11
Cu	0.10	71	0.40- <dl	90
Mo	ns	ns	0.50- <dl	15
Pb	ns	ns	0.50- <dl	3
As	ns	ns	0.40- <dl	4
Se	ns	ns	0.80- <dl	9
Cd	0.5	48	1.1- 0.1	
B	3.1	33	6.0- 1.3	
Mn	13	48	30- 4	
Ni	13	36	27- 6	
Fe	73	123	440- 0	
Zn	60	30	130- 30	
K	75	21	115- 48	
Na	96	37	200- 51	
Ca	422	8	500- 320	
Al	183	15	250- 88	42
Mg	172	36	340- 85	
SO4	3532	20	6847-2300	

L5-87/88 #Samples 53

	Mean	Std	Max- Min	%>dl
pH	3.10	9	3.58- 2.6	
Cond	4.47	11	5.52-3.28	
Cr	ns	ns	<dl- <dl	0
Cu	0.13	97	0.65- <dl	98
Mo	ns	ns	0.30- <dl	2
Pb	ns	ns	0.50- <dl	11
As	ns	ns	0.30- <dl	2
Se	ns	ns	0.60- <dl	17
Cd	0.4	54	0.9- 0.1	
B	3.0	25	4.5- 1.4	
Mn	13	29	18- 6	
Ni	11	20	14- 6	
Fe	110	85	338- 4	
Zn	52	20	69- 27	
K	74	19	100- 42	
Na	92	25	140- 35	
Ca	423	17	535- 25	
Al	251	40	430- 76	
Mg	177	24	260- 80	
SO4	3931	13	4946-2630	

Appendix Table 1.6 Continued.

L3-84/85 #Samples 65 Mixed Shale 6'

	Mean	Std	Max- Min	%>dl
pH	2.97	7	3.74-2.55	
Cond	10.00	18	15.4-6.54	
Cr	0.62	109	3.14- 0.1	
Cu	0.05	69	0.21- <dl	77
Mo	1.91	117	8.83- <dl	98
Pb	1.92	66	5.68- <dl	86
As	0.64	44	1.40- <dl	72
Se	1.06	41	2.29- <dl	82
Cd	3.5	37	5.8- 1.2	
B	5.0	27	7.6- 2.9	
Mn	102	22	178- 56	
Ni	100	20	134- 57	
Fe	803	99	2710- 34	
Zn	459	36	849- 105	
K	70	12	98- 51	
Na	315	13	467- 218	
Ca	436	17	929- 349	
Al	155	38	247- 60	52
Mg	1104	16	1550- 656	
SO4	10408	27	18567-6629	

L3-85/86 #Samples 75

	Mean	Std	Max- Min	%>dl
pH	2.98	8	3.72-2.55	
Cond	7.16	16	9.65-3.82	
Cr	0.50	57	1.21- <dl	64
Cu	0.12	125	0.61- <dl	53
Mo	0.46	62	1.10- <dl	57
Pb	ns	ns	3.50- <dl	44
As	ns	ns	1.50- <dl	25
Se	ns	ns	1.20- <dl	37
Cd	1.1	42	2.2- 0.2	
B	4.5	19	6.1- 2.4	
Mn	61	37	112- 15	
Ni	51	32	86- 12	
Fe	459	88	1840- 45	
Zn	188	31	433- 50	
K	59	13	79- 48	
Na	249	22	527- 84	
Ca	388	20	806- 247	
Al	134	47	344- 50	97
Mg	664	32	1630- 150	
SO4	6864	21	9777-3539	

L3-86/87 #Samples 81

	Mean	Std	Max- Min	%>dl
pH	3.49	7	4.28-2.83	
Cond	5.49	16	8.55-3.5	
Cr	ns	ns	<dl- <dl	0
Cu	ns	ns	0.75- <dl	47
Mo	ns	ns	0.40- <dl	11
Pb	ns	ns	0.60- <dl	2
As	ns	ns	0.30- <dl	1
Se	ns	ns	0.30- <dl	6
Cd	0.6	49	1.6- 0.2	
B	4.0	24	6.8- 1.9	
Mn	39	27	69- 15	
Ni	31	23	53- 13	
Fe	233	87	860- 1	
Zn	120	26	210- 59	
K	51	12	74- 36	
Na	167	25	400- 90	
Ca	418	9	510- 200	
Al	152	50	540- 51	86
Mg	426	24	700- 190	
SO4	4918	18	6959-2802	

L3-87/88 #Samples 84

	Mean	Std	Max- Min	%>dl
pH	3.24	6	3.73-2.77	
Cond	5.51	16	6.72-2.95	
Cr	ns	ns	<dl- <dl	0
Cu	0.11	100	0.47- <dl	79
Mo	ns	ns	0.36- <dl	6
Pb	ns	ns	0.40- <dl	1
As	ns	ns	0.40- <dl	5
Se	ns	ns	0.64- <dl	13
Cd	0.6	42	1.1- 0.2	
B	3.6	25	5.4- 1.6	
Mn	34	27	52- 12	
Ni	27	24	37- 10	
Fe	217	104	737- 16	
Zn	115	23	174- 42	
K	48	11	65- 39	
Na	154	21	220- 46	
Ca	432	11	525- 335	
Al	235	39	380- 72	
Mg	396	23	560- 165	
SO4	5005	18	6107-2407	

Appendix Table 1.7 Continued.

L4-84/85 #Samples 56 Mixed Material 6'

	Mean	Std	Max- Min	%>dl
pH	2.89	8	3.63-2.27	
Cond	6.63	22	10.2-4.58	
Cr	0.59	130	3.14-0.01	
Cu	0.06	152	0.62- <dl	80
Mo	0.67	58	2.25- <dl	70
Pb	0.83	40	1.50- <dl	80
As	ns	ns	0.81- <dl	34
Se	0.63	45	1.56- <dl	68
Cd	0.7	134	5.9- 0.1	
B	4.1	37	7.0- 1.5	
Mn	44	26	82- 21	
Ni	33	47	90- 17	
Fe	899	65	2060- 118	
Zn	121	56	359- 32	
K	72	15	90- 32	
Na	144	22	241- 72	
Ca	437	8	504- 354	
Al	17	111	95- 4	54
Mg	436	30	839- 181	
SO4	5828	42	11502-2051	

L4-85/86 #Samples 39

	Mean	Std	Max- Min	%>dl
pH	2.93	9	4.13-2.58	
Cond	5.10	23	9.42-2.89	
Cr	0.22	50	0.50- <dl	69
Cu	0.03	101	0.10- <dl	59
Mo	0.25	59	0.74- <dl	56
Pb	ns	ns	1.70- <dl	36
As	ns	ns	1.20- <dl	28
Se	ns	ns	1.50- <dl	41
Cd	0.2	42	0.3- 0.1	
B	2.9	26	4.5- 1.6	
Mn	29	46	68- 6	
Ni	13	33	21- 4	
Fe	498	70	1230- 4	
Zn	64	103	374- 21	
K	68	22	96- 44	
Na	122	31	210- 61	
Ca	391	10	440- 287	
Al	22	72	46- 4	31
Mg	282	30	440- 97	
SO4	4041	20	5638-1860	

L4-86/87 #Samples 59

	Mean	Std	Max- Min	%>dl
pH	3.22	10	4.0-5 2.5	
Cond	4.65	16	6.55-1.96	
Cr	ns	ns	<dl- <dl	0
Cu	ns	ns	0.03- <dl	32
Mo	ns	ns	0.50- <dl	10
Pb	ns	ns	0.40- <dl	2
As	ns	ns	<dl- <dl	0
Se	ns	ns	0.50- <dl	8
Cd	0.2	61	0.5- 0.1	
B	2.6	33	4.8- 1.3	
Mn	29	39	57- 8	
Ni	17	30	28- 5	
Fe	194	75	940- 1	
Zn	66	29	103- 19	
K	71	18	97- 37	
Na	112	30	190- 54	
Ca	415	13	600- 170	
Al	69	42	130- 29	59
Mg	327	26	490- 130	
SO4	3873	17	5605-2531	

L4-87/88 #Samples 66

	Mean	Std	Max- Min	%>dl
pH	3.12	6	3.72-2.68	
Cond	4.97	20	6.99-2.96	
Cr	ns	ns	<dl- <dl	0
Cu	0.04	120	0.33- <dl	70
Mo	ns	ns	<dl- <dl	0
Pb	ns	ns	<dl- <dl	0
As	ns	ns	<dl- <dl	0
Se	ns	ns	0.50- <dl	5
Cd	0.2	48	0.4- 0.1	
B	2.5	32	3.9- 1.2	
Mn	29	43	57- 7	
Ni	16	30	27- 4	
Fe	283	81	804- 4	
Zn	71	30	105- 19	
K	69	22	98- 42	
Na	114	31	170- 35	
Ca	435	11	680- 330	
Al	87	55	150- 14	
Mg	334	34	532- 75	
SO4	4140	23	6275-2160	

Appendix Table 1.8 Continued.

L7-84/85 #Samples 153 Raw Shale 6'

	Mean	Std	Max- Min	%>dl
pH	2.66	7	3.28- 2.1	
Cond	20.34	38	38.5-8.22	
Cr	3.15	166	36.00- <dl	99
Cu	11.69	199	123.00- 0.0	
Mo	2.25	63	6.24- <dl	71
Pb	2.08	63	4.98- <dl	61
As	1.38	81	7.15- <dl	64
Se	1.94	59	4.35- <dl	69
Cd	10.2	87	35.3- 0.6	
B	1.8	82	8.4- <dl	97
Mn	140	48	550- 44	
Ni	155	44	384- 45	
Fe	5665	42	12500-2380	
Zn	913	46	1750- 191	
K	1	88	5- 0	
Na	16	45	36- 1	
Ca	398	14	736- 239	
Al	457	62	1200- 63	43
Mg	1841	41	3640- 622	
SO4	29870	54	66794-7329	

L7-85/86 #Samples 145

	Mean	Std	Max- Min	%>dl
pH	2.65	9	3.88-2.16	
Cond	8.34	20	12.24-4.69	
Cr	0.91	106	3.60- <dl	60
Cu	0.44	123	2.38- <dl	82
Mo	0.40	41	0.74- <dl	56
Pb	ns	ns	1.40- <dl	43
As	ns	ns	0.70- <dl	29
Se	ns	ns	1.60- <dl	44
Cd	0.6	71	2.1- 0.1	
B	1.3	30	2.4- 0.3	
Mn	54	38	116- 26	
Ni	49	42	109- 20	
Fe	2434	30	4900-1340	
Zn	197	49	445- 56	
K	5	43	11- 0	
Na	33	29	88- 19	
Ca	436	11	740- 360	
Al	58	89	251- 3	
Mg	654	37	1400- 262	
SO4	9484	30	17509-4617	

L7-86/87 #Samples 193

	Mean	Std	Max- Min	%>dl
pH	3.21	14	5.43-2.09	
Cond	5.29	18	7.85-3.55	
Cr	ns	ns	0.90- <dl	30
Cu	ns	ns	1.00- <dl	48
Mo	ns	ns	0.44- <dl	7
Pb	ns	ns	0.50- <dl	3
As	ns	ns	0.70- <dl	8
Se	ns	ns	0.70- <dl	10
Cd	0.2	53	0.8- 0.04	
B	1.3	30	2.3- 0.6	
Mn	22	40	49- 9	
Ni	16	53	39- 4	
Fe	1166	30	2100- 540	
Zn	37	95	230- 3	
K	9	29	14- 1	
Na	28	32	70- 16	
Ca	443	9	600- 220	
Al	6	122	36- 0.3	80
Mg	270	39	750- 120	
SO4	4698	25	7551-2667	

L7-87/88 #Samples 115

	Mean	Std	Max- Min	%>dl
pH	2.93	12	3.95-2.21	
Cond	4.49	15	6.08-3.25	
Cr	ns	ns	<dl- <dl	0
Cu	0.04	96	0.22- <dl	69
Mo	ns	ns	0.44- <dl	8
Pb	ns	ns	0.42- <dl	5
As	ns	ns	0.72- <dl	4
Se	ns	ns	0.80- <dl	18
Cd	0.1	46	0.3-0.03	
B	1.0	43	2.0- 0.1	
Mn	13	34	24- 6	
Ni	5	66	11- 1	
Fe	750	34	1520- 221	
Zn	4	83	12- 1	
K	10	28	16- 3	
Na	24	26	65- 17	
Ca	469	8	600- 415	
Al	ns	ns	15- <dl	41
Mg	172	36	341- 70	
SO4	3580	21	5300-2407	

Table 2. Comparison of the mathematical and volume weighted means for the bottom (10-foot depth) transport tubes for the last two project years. The mathematical means are calculated as,

$$X_m = \frac{\Sigma X_i}{n}$$

the volume weighted means are calculated as,

$$X_v = \frac{\Sigma\{X_i V_i\}}{\Sigma V_i}$$

where n = the number of samples; X_i = the elemental concentration in ppm of the sample; and V_i = the volume of the individual sample.

Appendix Table 2.1 Comparison of Mathematical and Volume Weighted Elemental Concentration Means.

Lysimeter L1			Overburden & Soil	
	Means 86/87		Means 87/88	
	Simple	Volume Weighted	Simple	Volume Weighted
pH	6.39	6.39	6.53	6.52
B				
Cd				
Ni				
Fe				
Mn				
Zn				
Mg	1	1	1	1
Ca	24	25	24	27
Na	16	16	13	13
Al				
K	5	5	5	5
Sulfate	35	35	37	37

Lysimeter L2			Retorted Shale 10'	
	Means 86/87		Means 87/88	
	Simple	Volume Weighted	Simple	Volume Weighted
pH	3.50	3.57	3.37	3.45
Cd	2.3	2.7	1.7	1.9
Ni	53	56	37	38
Fe	142	143	143	139
Mn	52	55	36	37
Zn	175	174	149	154
Mg	696	719	529	542
Ca	402	396	430	421
Na	273	280	219	225
Al	710	743	728	791
K	81	80	64	62
Sulfate	9312	9728	8372	8903

Appendix Table 2.2 Continued

Lysimeter L8			Retorted Shale 8'	
	Means 86/87		Means 87/88	
	Simple	Volume Weighted	Simple	Volume Weighted
pH	6.39	6.39	6.53	6.52
B				
pH	3.42	3.47	3.22	3.33
Cd	0.89	0.99	0.66	0.84
B	4	5	4	4
Ni	19	22	16	17
Fe	71	80	146	113
Mn	20	22	18	19
Zn	77	85	67	72
Mg	254	277	251	278
Ca	439	433	426	429
Na	118	127	105	110
Al			388	470
K	75	75	71	66
Sulfate	4664	4967	5241	5730

Lysimeter L6			Retorted Shale 6'	
	Means 86/87		Means 87/88	
	Simple	Volume Weighted	Simple	Volume Weighted
pH	3.39	3.50	3.22	3.36
Cd	0.37	0.38	0.37	0.35
B	3	3	2	2
Ni	14	13	10	9
Fe	135	136	173	123
Mn	17	16	15	13
Zn	54	52	46	41
Mg	210	204	181	170
Ca	414	406	411	397
Na	92	90	76	69
Al			174	186
K	81	82	69	65
Sulfate	3491	3493	3475	3214

Appendix Table 2.3 Continued

Lysimeter L5			Retorted Shale 4'	
	Means 86/87		Means 87/88	
	Simple	Volume Weighted	Simple	Volume Weighted
pH	3.38	3.42	3.10	3.29
Cd	0.52	0.52	0.38	0.49
B	3	3	3	2
Ni	13	12	11	10
Fe	73	70	110	57
Mn	13	12	13	10
Zn	60	56	52	46
Mg	172	166	177	159
Ca	422	430	423	413
Na	96	94	92	77
Al			251	296
K	75	77	74	67
Sulfate	3532	3506	3931	3778

Lysimeter L3			Mixed Shale 6'	
	Means 86/87		Means 87/88	
	Simple	Volume Weighted	Simple	Volume Weighted
pH	3.49	3.53	3.24	3.33
Cd	0.62	0.67		
B	4	4	4	4
Ni	31	32	27	27
Fe	233	212	217	234
Mn	39	39	34	34
Zn	120	121	115	119
Mg	426	422	396	402
Ca	418	419	432	431
Na	167	168	154	162
Al	152	143	235	250
K	51	50	48	48
Sulfate	4918	4901	5005	5119

Appendix Table 2.4 Continued.

Lysimeter L4			Mixed Shale 4'	
	Means 86/87		Means 87/88	
	Simple	Volume Weighted	Simple	Volume Weighted
pH	3.22	3.30	3.12	3.19
Cd	0.21	0.23	0.19	0.21
B	3	3	2	2
Ni	17	18	16	15
Fe	194	222	283	237
Mn	29	30	29	25
Mg	327	339	334	299
Ca	415	417	435	438
Na	112	107	114	103
Al			87	103
K	71	74	69	65
Sulfate	3873	3998	4140	3907

Lysimeter L7			Raw Shale 6'	
	Means		Means	
	Simple	Volume Weighted	Simple	Volume Weighted
pH	3.21	3.31	2.93	3.10
Cd	0.23	0.21	0.11	0.12
B	1	1	1	1
Ni	16	14	5	3
Fe	1167	1089	750	728
Mn	22	20	13	11
Zn	38	31	4	2
Mg	271	245	172	145
Ca	443	441	469	474
Na	28	27	24	21
Al				
K	9	9	10	10
Sulfate	4702	4404	3580	3261