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BEHAVIOR OF MERCURY, LEAD, CESIUM, AND URANYL IONS ON FOUR SRS SOILS (U)

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TO: D.L. FISH, 773-A

FROM J.P. BIBLER, 773-A, and D.B. MARSON

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1.0 SUMMARY

Samples of four SRS soils were tested for sorption behavior with Hg^{2+}, Pb^{2+}, UO_2^{2+}, and Cs^+ ions. The purpose of the study was to determine the selectivity of the different soils for these ions alone and in the presence of the competing cations, H^+ and Ca^{2+}. Distribution constants, Kd's, for the test ions in various solutions have been determined for the four soils. In general, sorption by all of the soils appeared to be more complex than a simple ion exchange or adsorption process. In particular, the presence of organic matter in soil increased the capacity of the soil due to its chelating ability. Similar soils did not react similarly toward each metal cation. The "soft" metal ions, Hg^{2+} and Pb^{2+}, were sorbed by silica sand in the absence of clay, whereas the "hard" Cs^+ and UO_2^{2+} ions were not. Competition with H^+ and Ca^{2+} in reacting solutions reduced the ability of each soil to sorb the test metal ions. Sorption reactions were not easily reversible, however, indicating that the use of Kd values for modeling desorption is too simplistic an approach. Zeta potential, pH, and particle size also dictate the sorption behavior of soils.

2.0 INTRODUCTION

To date, the method of managing contaminated soils at the Savannah River Site (SRS) remains loading in a B-25 and transfer of the soils to the burial ground. The volume of contaminated and suspect soil that must be dealt with in this way on an annual basis is large and generates large costs, estimated at $51/ft^3. Several new technologies, such as soil washing, leaching, and electrolytic migration, are being considered to minimize costs and the amount of soil that must be dug up and moved. Scouting experiments designed to test the feasibility of some of those new technologies have shown that the composition of the soil, soil swelling, and the nature of the ion impurities of concern are very interdependent relative to sorption and desorption parameters. This study represents an initial attempt to quantify the behavior of four common contaminant ions, Hg^{2+}, Pb^{2+}, $UO_2{}^{2+}$, and Cs^+, with soils from four different site locations relative to the selectivity of those soils for the metal ions and the ability of the soils to desorb them.

3.0 EXPERIMENTAL

Four soil samples were obtained from larger samples that had already been collected on site for other studies. Two of these, TF1 and TF2, were soils taken from two different locations in the SRS burial ground. A third, the TNX soil, was collected at a seep line near the old TNX basin. The fourth, ETF, was collected near the F/H Effluent Treatment Facility. Soil samples were air-dried before weighing. TF1, TF2, and TNX soils were processed on sieves and the 40-60 mesh and 80-100 mesh fractions were collected for use in this study. Kaolinite was separated from sand in these samples by making a slurry of the soil and making several decantations of the finer kaolinite particles. The heavier sand particles remained behind in the slurry vessel. The ETF soil was not sieved because it had a residual activity of 4000 dpm β/γ at one inch and would have contaminated the sieves. All work with the ETF soil was done in a radioactive hood. Although every effort was made to try to generate ETF samples that appeared as physically similar to each other as possible, more variablility is to be expected in these relative to the other soil samples that were sieved.

Samples of each soil were sent for characterization by X-ray diffraction.

3.1 Bulk Density Determination

The bulk density, ρ_B, is defined as the mass of dry material per unit volume of wetted material. Air-dried soil samples of 40-60 mesh TF1, TF2, and TNX soils and unsieved ETF soil were weighed and placed in a 10 mL graduate cylinder. The solutions used for determining distribution constants (Section 3.2) were added to the cylinder such that the soil was thoroughly wetted and an excess of about 5 mL of solution remained above the soil sample. The soil was then allowed to stand in the solution for 24 hours, after which time the volume of the soil sample was measured.

3.2 Distribution Constant, Kd, Determination of Sorption

Weighed samples of air-dried soil were shaken for 48 hours with a measured amount of solution. Solutions used were:

- Pb^{2+} - 125 ppm, 100 ppm, 75 ppm, 50 ppm as $Pb(NO_3)_2$

  Pb^{2+} and H^+ - 100 ppm Pb^{2+} at pH 1,2,3,4

Pb^{2+} in 2M Ca^{2+} - 125 ppm Pb^{2+}, 100 ppm Pb^{2+}, 75 ppm Pb^{2+}, 50 ppm Pb^{2+} all in 2M $Ca(NO_3)$

Pb^{2+} in 1M Ca^{2+} - 125 ppm Pb^{2+}, 100 ppm Pb^{2+}, 75 ppm Pb^{2+}, 50 ppm Pb^{2+} all in 1M $Ca(NO_3)_2$

- **Hg^{2+}** - 1ppm, 2ppm, 3ppm, 5ppm as $Hg(NO_3)_2$

  Hg^{2+} and H^+ - 5 ppm Hg^{2+} at pH 1,2,3,4

  Hg^{2+} in 2M Ca^{2+} - 1 ppm Hg^{2+}, 2 ppm Hg^{2+}, 3 ppm Hg^{2+}, 5 ppm Hg^{2+} all in 2M $Ca(NO_3)_2$

  Hg^{2+} in 1M Ca^{2+} - 1 ppm Hg^{2+}, 2 ppm Hg^{2+}, 3 ppm Hg^{2+}, 5 ppm Hg^{2+} all in 1M $Ca(NO_3)_2$

- **Cs^+** - 1M, 0.1M, 0.05M, 0.01M $CsNO_3$ (non-radioactive) and 2.80 E-3 μCi/mL Cs-137 as $Cs(NO_3)_2$

- **UO_2^{2+}** - 2,245 ppm U as $UO_2(NO_3)_2$

The soil was then separated from the equilibrium solution by filtration and the filtrate was sent for analysis to determine equilibrium concentrations of ions of interest. These were compared with concentrations of the same ions in the feed solutions. Kd values, which have units of mL/g, were calculated from the following relationship.

$$Kd = [(Co-C)/C][V/m] \qquad (1)$$

where Co = initial concentration of the ion
C = equilibrium concentration of the ion
V = mL of solution used
m = grams of dry soil

Distribution constants for silica sand were determined in the same manner using Cs^+, UO_2^{2+}, Hg^{2+}, and Pb^{2+} solutions.

3.3 Desorption Studies

Weighed samples of air-dried soils were soaked for 48 hours in measured volumes of solutions containing known concentrations of Hg^{2+}, Pb^{2+}, Cs^+, and UO_2^{2+} ions. The soils were separated from the liquor by filtraton. The precipitate was washed with 10 ml of deionized water and the wash was mixed in with the equilibrium liquor. This mixture was analyzed for the remaining concentration of the ion of interest and a correction was made for the additional volume of water added. The amount of ion sorbed by the soil was determined by difference between the concentrations in the original solution before contacting the soil and the volumecorrected equilibrium solution. The milligrams of ion of interest per gram of soil was calculated.

The air-dried, contaminated soil was then divided into smaller, weighed samples which were shaken vigorously for 48 hours with measured volumes of 0.1M HNO_3 or 1M $Ca(NO_3)_2$. At the end of that time, the soil was again separated from the liquid by filtration and the filtrate was analyzed for the concentration of the ion of interest in order to quantify the amount of ion desorbed in the process.

3.4 Determination of Organic Content of TNX Soil

The physical appearance of the TNX soil, which was black and contained leaves and other organic matter that made it amorphous, was different from the other three soils. The TF1, TF2, and ETF soils were reddish brown, granular materials. A weighed sample of 40-60 mesh TNX soil was heated 2 hours at 90°C in a crucible in an oven to drive off any interstitial water. After weighing to constant weight, the soil was transferred to a smaller, weighed crucible and then heated to 150°C to drive off bound water. The sample was brought to constant weight and heated again to 600°C for 16 hours to burn away organic matter. The difference between the weights of the sample heated to 150°C and heated to 600°C was used to determine the per cent organic matter associated with the TNX soil.

4.0 RESULTS

4.1 General Soil Characterization

As noted earlier, the TF1, TF2, and ETF soil samples were reddish brown, granular soils that contained no measurable organic component. The TNX soil was black, less crystalline, and contained organic debris. X-ray diffraction patterns for the 40-60 mesh TF1, TF2, and TNX samples revealed kaolinite and silicon oxide (sand), in different ratios for each soil. A small fraction of organic matter would not generate a crystalline pattern and could not be recognized in the spectra found in Appendix 1. The X-ray analysis of the ETF soil showed trace amounts of illite, kaolinite, and rutile clays in greater than 99% silicon oxide.

The results of separation by slurrying gives a better picture of the ratios of sand to kaolinite in the TF1, TF2, and TNX samples. These are shown graphically in Figure 1 for 40-60 mesh and 80-100 mesh for those soils. Because of its residual radioactivity, apparently due to naturally occurring thorium and uranium, corresponding data was not generated for the ETF soil.

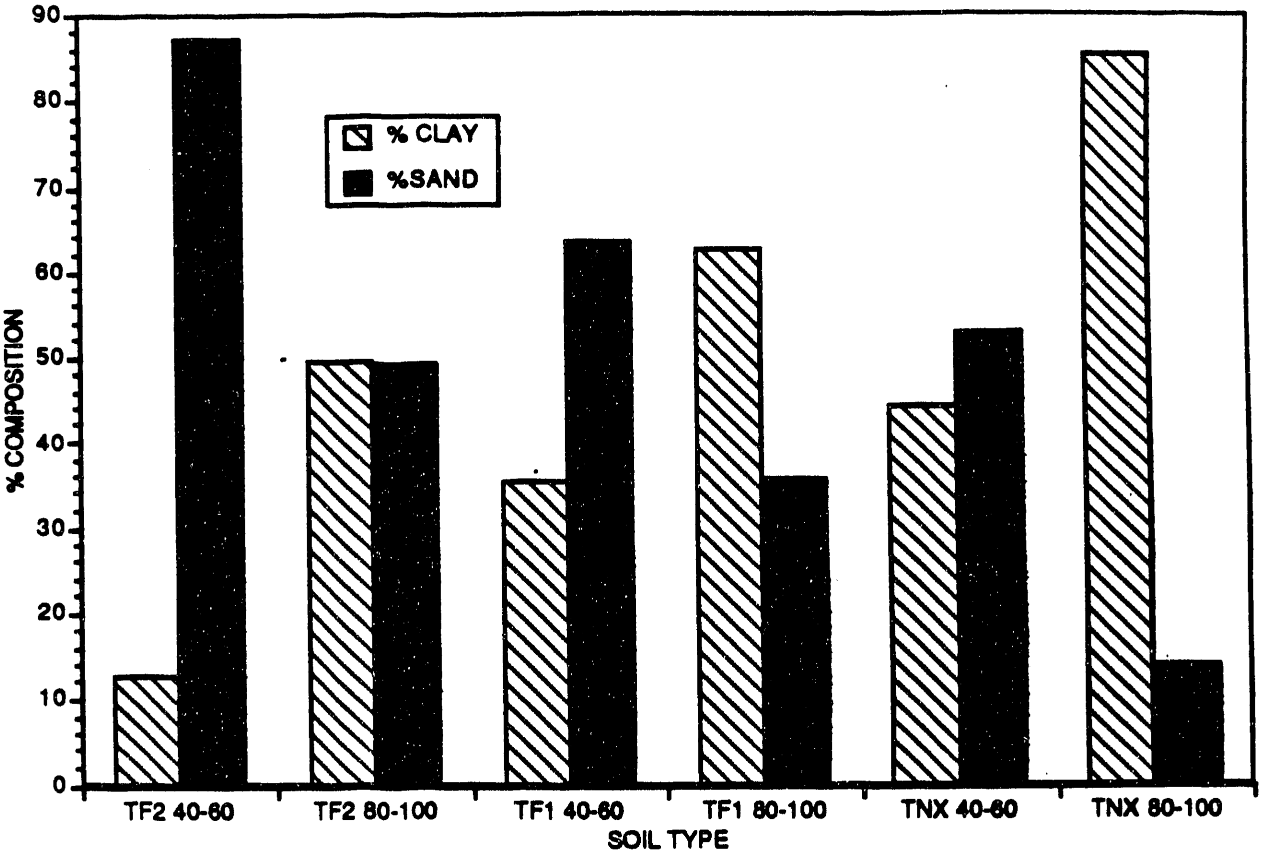

Figure 1. **Sand and Kaolinite Percentages in Three SRS Soils of Mesh Sizes 40-60 and 80-100**

Data for the determination of percent organic matter in the TNX soil are presented in Table 1.

Table 1. Percent Water and Organic Matter in TNX Soil (40-60 mesh)

	Soil weights, g		
Conditions	Before	After	weight % material
2 hours at 90°C	5.00	4.94	1.2% interstitial water
2 hours at 150°C	4.93	4.85	1.6% bound water
16 hours at 600°C	4.85	4.49	7.2% organic matter

4.2 Bulk Densities of Soils in Several Solutions

Bulk densities of the soils in most of the solutions used for Kd determinations are recorded in Tables 2 and 3. The purpose in using two tables for this data is to separate sieved (more uniformly sized, Table 3) soil data from unsieved soil (ETF) data, Table 2.

Table 2. Bulk Densities of ETF Soil

Sample	Medium	pH	g. Dry Soil	mL Wet Soil	ρ_B,g/mL
	Deionized water	4.45	0.99	0.90	1.10
2	Nitric acid	3.02	1.00	0.90	1.11
3	NaOH	10.01	1.07	0.80	1.34
4	KOH	10.00	1.03	0.80	1.29
5	1M $CsNO_3$	6.60	1.04	0.80	1.30
6	0.01M UO_2^{2+}	3.00	1.03	1.00	1.03
7	10 pm Hg^{2+}	2.27	1.05	0.90	1.17
8	2M $Ca(NO_3)_2$	5.40	1.00	0.90	1.11

Table 3. Bulk Densities of Three SRS Soils - 40-60 mesh

Soil	Medium	pH	g Dry Soil	mL Wet Soil	Bulk Density
TF1 1	Deionized Water	6.33	1.03	1.10	0.94
TF1 2	Nitric Acid	1.22	1.01	1.10	0.92
TF1 3	Nitric Acid	3.02	1.02	1.20	0.85
TF1 4	Nitric Acid	5.05	1.01	1.20	0.84
TF1 5	NaOH	8.30	1.01	1.15	0.88
TF1 6	NaOH	10.01	1.03	1.00	1.03
TF1 7	KOH	10.00	1.00	1.10	0.91
TF1 8	10 ppm Hg(NO3)2	2.27	1.03	1.80	0.57
TF1 9	1M CsNO3	6.60	1.01	1.00	1.01
TF1 10	0.01M UO2 2+	3.00	1.00	1.10	0.91
TF1 11	2M Ca(NO3)2	5.40	1.01	1.20	0.84
TF1 12	20 ppm Pb2+	5.63	1.01	1.00	1.01
TF2 1	Deionized Water	6.33	1.02	1.01	1.01
TF2 2	Nitric Acid	1.22	1.01	0.85	1.19
TF2 3	Nitric Acid	3.02	1.00	1.00	1.00
TF2 4	Nitric Acid	5.05	1.02	1.01	1.01
TF2 5	NaOH	8.30	1.02	0.90	1.13
TF2 6	NaOH	10.01	1.01	0.85	1.19
TF2 7	KOH	10.00	1.00	1.00	1.00
TF2 8	10 ppm Hg(NO3)2	2.27	1.03	1.20	0.86
TF2 9	1M CsNO3	6.60	1.00	1.10	0.91
TF2 10	0.01M UO2 2+	3.00	1.01	0.90	1.12
TF2 11	2M Ca(NO3)2	5.40	1.03	1.00	1.03
TF2 12	20 ppm Pb2+	5.63	1.00	0.80	1.25
TNX 1	Deionized Water	6.19	1.02	1.70	0.60
TNX 2	Nitric Acid	1.22	1.01	1.80	0.56
TNX 3	Nitric Acid	3.02	1.01	1.80	0.56
TNX 4	Nitric Acid	5.05	1.02	1.90	0.54
TNX 5	NaOH	8.30	1.02	1.85	0.55
TNX 6	NaOH	10.01	1.00	1.80	0.56
TNX 7	KOH	10.00	1.03	1.70	0.61
TNX 8	10 ppm Hg(NO3)2	2.27	1.03	0.90	1.14
TNX 9	1M CsNO3	6.60	1.00	1.50	0.67
TNX 10	0.01M UO2 2+	3.00	1.00	1.80	0.56
TNX 11	2M Ca(NO3)2	5.40	1.01	1.70	0.59
TNX 12	20 ppm Pb2+	5.63	1.00	1.40	0.72

4.3 DISTRIBUTION CONSTANTS-Kd

4.3.1 Soil Kd's for Hg^{2+}

The Kd values derived for sorption of mercuric ion on two mesh sizes of TF1, TF2, and TNX soils and on ETF soil are presented in Tables 4-7. The notation for all duplicate samples in following tables is: The first sample in a set of duplicates will have the number 1,2,3,...n associated with its name. The duplicate sample will have the number designation 11, 21, 31,...n1 associated with it. Duplicate samples differ slightly in the number of grams of soil used, but experienced the same initial solution in the experiments.

Table 4. Kd Values for 1-6 mg/L Mercuric Ion With TF1 Soil - 40-60 and 80-100 Mesh

Sample	Hg i,mg/L	Hg eq,mg/L	g Soil	Kd, mL/g
40-60 Mesh				
TF1-1	1.0800	0.0229	0.2029	3.41E+03
TF1-11	1.0800	0.0103	0.2038	7.64E+03
TF1-2	2.3292	0.8600	0.2003	1.28E+02
TF1-21	2.3292	0.8333	0.2092	1.29E+02
TF1-3	3.2919	2.2167	0.2173	3.35E+01
TF1-31	3.2919	1.8500	0.2119	5.52E+01
TF1-4	6.6000	4.0645	0.2005	4.67E+01
TF1-41	6.6000	3.1290	0.2220	7.50E+01
80-100 Mesh				
TF1-5	1.0516	0.0112	0.2243	6.21E+03
TF1-51	1.0516	0.0112	0.2159	6.45E+03
TF1-6	2.3179	0.3944	0.2030	3.60E+02
TF1-61	2.3179	0.3766	0.2020	3.83E+02
TF1-7	3.0380	1.4873	0.2092	7.48E+01
TF1-71	3.0380	1.5190	0.2269	6.61E+01
TF1-8	5.8228	4.2722	0.2045	2.66E+01
TF1-81	5.8228	4.0190	0.2048	3.29E+01

---

i = Initial concentration
eq = Equilibrium concentration

Table 5. Kd Values for 1-6 mg/L Mercuric Ion With TF2 Soil - 40-60 and 80-100 Mesh

Sample	Hg i,mg/L	Hg eq,mg/L	g Soil	Kd, mL/g
40-60 Mesh				
TF2-1	1.0800	0.0994	0.2140	6.91E+02
TF2-11	1.0800	0.0697	0.2141	1.02E+03
TF2-2	2.3292	0.0413	0.2134	3.89E+03
TF2-21	2.3292	0.9355	0.2155	1.04E+02
TF2-3	3.2919	2.1613	0.2064	3.80E+01
TF2-31	3.2919	2.0000	0.2161	4.48E+01
TF2-4	6.6000	3.5161	0.2235	5.89E+01
TF2-41	6.6000	4.4194	0.2195	3.37E+01
80-100 Mesh				
TF2F-5	1.0516	0.0392	0.2025	1.91E+03
TF2F-51	1.0516	0.0278	0.2287	2.42E+03
TF2F-6	2.3179	0.6899	0.2247	1.58E+02
TF2F-61	2.3179	0.5380	0.2137	2.32E+02
TF2F-7	3.0380	1.6772	0.2129	5.72E+01
TF2F-71	3.0380	1.1709	0.2100	1.14E+02
TF2F-8	5.8228	3.9873	0.2256	3.06E+01
TF2F-81	5.8228	3.6709	0.2135	4.12E+01

---

i = Initial concentration
eq = Equilibrium concentration

Table 6. Kd Values for 1-6 mg/L Mercuric Ion With TNX Soil - 40-60 and 80-100 Mesh

Sample	Hg i,mg/L	Hg eq,mg/L	g Soil	Kd, mL/g
40-60 Mesh				
TNX-1	1.0800	0.0103	0.2028	7.68E+03
TNX-11	1.0800	0.0103	0.2099	7.42E+03
TNX-2	2.3292	0.0103	0.2027	1.67E+04
TNX-21	2.3292	0.0103	0.2027	1.67E+04
TNX-3	3.2919	0.0103	0.2024	2.36E+04
TNX-31	3.2919	0.0103	0.2144	2.23E+04
TNX-4	6.6000	0.1349	0.2086	3.45E+03
TNX-41	6.6000	0.0960	0.2013	5.05E+03
80-100 Mesh				
TNX-5	1.0516	0.0119	0.2028	6.46E+03
TNX-51	1.0516	0.0119	0.2136	6.14E+03
TNX-6	2.3179	0.0119	0.2156	1.35E+04
TNX-61	2.3179	0.0119	0.2231	1.30E+04
TNX-7	3.0380	0.0119	0.2023	1.89E+04
TNX-71	3.0380	0.0119	0.2155	1.77E+04
TNX-8	5.8228	0.0758	0.2057	5.53E+03
TNX-81	5.8228	0.0671	0.2028	6.34E+03

---

i = Initial concentration
eq = Equilibrium concentration

Table 7. Kd Values for 1-5 mg/L Mercuric Ion With ETF Soil

Sample	pH	g Soil	Hg i,mg/L	Hg eq,mg/L	Kd, mL/g
ETF-5	3.030	0.1977	5.0311	2.3099	8.94E+01
ETF-3	3.580	0.2040	3.5093	1.8129	6.88E+01
ETF-2	3.760	0.1978	2.1273	0.5731	2.06E+02
ETF-1	4.120	0.2028	1.0621	0.0468	1.60E+03

---

i = Initial concentration
eq = Equilibrium concentration

4.3.2 Mercury, Hg^{2+}, Kd's When 1M or 2M Ca^{2+} is Present

Solutions were tested in which mercuric nitrate and calcium nitrate were both present. Calcium ion was either 1M or 2M in concentration and was added to determine whether its presence would inhibit sorption of mercuric ion. The Kd values for these systems are in Tables 8-11.

Table 8. Kd Values for Mercuric Ion in the Presence of 1M and 2M Calcium Ion-40-60 Mesh TF1 Soil

SAMPLE	Hg i,mg/L	Hg eq,mg/L	g Soil	Kd, mL/g
1M $Ca(NO_3)_2$				
TF1-HG-1M Ca-1	1.0191	0.3759	0.2016	1.27E+02
TF1-HG-1M Ca-11	1.0191	0.3652	0.2026	1.33E+02
TF1-HG-1M Ca-2	1.9745	1.2910	0.2082	3.81E+01
TF1-HG-1M Ca-21	1.9745	1.2060	0.2022	4.73E+01
TF1-HG-1M Ca-3	3.0255	2.1280	0.2144	2.95E+01
TF1-HG-1M Ca-31	3.0255	2.2340	0.2170	2.45E+01
TF1-HG-1M Ca-4	5.7325	5.3900	0.2110	4.52E+00
TF1-HG-1M Ca-41	5.7325	4.1460	0.2258	2.54E+01
2M $Ca(NO_3)_2$				
TF1-HG-2M Ca-1	1.0191	0.4459	0.2277	8.47E+01
TF1-HG-2M Ca-11	1.0191	0.5796	0.2140	5.32E+01
TF1-HG-2M Ca-2	2.1338	1.4268	0.2081	3.57E+01
TF1-HG-2M Ca-21	2.1338	1.4522	0.2063	3.41E+01
TF1-HG-2M Ca-3	3.3758	2.4841	0.2044	2.63E+01
TF1-HG-2M Ca-31	3.3758	2.4841	0.2003	2.69E+01
TF1-HG-2M Ca-4	5.1911	4.7771	0.2040	6.37E+00
TF1-HG-2M Ca-41	5.1911	4.7134	0.2027	7.50E+00

---

i = Initial Hg concentration
eq = Equilibrium Hg concentration

Table 9. Kd Values for Mercuric Ion in the Presence of 1M and 2M Calcium Ion- 40-60 Mesh TF2 Soil

SAMPLE	Hg i,mg/L	Hg eq,mg/L	g Soil	Kd, mL/g
1M Ca(NO3)2				
TF2-HG-1M Ca-1	1.0191	0.3987	0.2157	1.08E+02
TF2-HG-1M Ca-11	1.0191	0.4051	0.2077	1.09E+02
TF2-HG-1M Ca-2	1.9745	1.4062	0.2254	2.69E+01
TF2-HG-1M Ca-21	1.9745	1.4399	0.2182	2.55E+01
TF2-HG-1M Ca-3	3.0255	2.3266	0.2108	2.14E+01
TF2-HG-1M Ca-31	3.0255	2.4684	0.2199	1.54E+01
TF2-HG-1M Ca-4	5.7325	5.0633	0.2076	9.55E+00
TF2-HG-1M Ca-41	5.7325	5.1582	0.2004	8.33E+00
2M Ca(NO3)2				
TF2-HG-2M Ca-1	1.0191	0.7389	0.2107	2.70E+01
TF2-HG-2M Ca-11	1.0191	0.7516	0.2068	2.58E+01
TF2-HG-2M Ca-2	2.1338	1.6879	0.2227	1.78E+01
TF2-HG-2M Ca-21	2.1338	1.7516	0.2106	1.55E+01
TF2-HG-2M Ca-3	3.3758	2.7704	0.2137	1.53E+01
TF2-HG-2M Ca-31	3.3758	2.3885	0.2011	3.08E+01
TF2-HG-2M Ca-4	5.1911	4.6178	0.2139	8.71E+00
TF2-HG-2M Ca-41	5.1911	4.7452	0.2046	6.89E+00

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i = Initial Hg concentration
eq = Equilibrium Hg concentration

Table 10. Kd Values for Mercuric Ion in the Presence of 1M and 2M Calcium Ion-40-60 Mesh TNX Soil

SAMPLE	Hg i,mg/L	Hg eq,mg/L	g Soil	Kd, mL/g
1M Ca(NO3)2				
TNX-HG-1M Ca-1	1.0191	0.0100	0.2033	7.45E+03
TNX-HG-1M Ca-11	1.0191	0.0100	0.2008	7.54E+03
TNX-HG-1M Ca-2	1.9745	0.0100	0.2117	1.39E+04
TNX-HG-1M Ca-21	1.9745	0.0100	0.2179	1.35E+04
TNX-HG-1M Ca-3	3.0255	0.0681	0.2114	3.08E+03
TNX-HG-1M Ca-31	3.0255	0.0780	0.1998	2.84E+03
TNX-HG-1M Ca-4	5.7325	0.4043	0.2024	9.77E+02
TNX-HG-1M Ca-41	5.7325	0.4184	0.2034	9.37E+02
2M Ca(NO3)2				
TNX-HG-2M Ca-1	1.0191	0.0107	0.2030	6.96E+03
TNX-HG-2M-Ca-11	1.0191	0.0107	0.2103	6.72E+03
TNX-HG-2M-Ca-2	2.1338	0.0160	0.2039	9.74E+03
TNX-HG-2M-Ca-21	2.1338	0.0102	0.2066	1.51E+04
TNX-HG-2M Ca-3	3.3758	0.1401	0.2113	1.64E+03
TNX-HG-2M Ca-31	3.3758	0.1783	0.2121	1.27E+03
TNX-HG-2M Ca-4	5.1911	0.7134	0.2087	4.51E+02
TNX-HG-2M Ca-41	5.1911	0.8662	0.2088	3.59E+02

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i = Initial Hg concentration
eq = Equilibrium Hg concentration

Table 11. Kd Values for Mercuric Ion With ETF Soil in the Presence of 1M and 2M Calcium Ion

SAMPLE	Hg i,mg/L	Hg eq,mg/L	g Soil	Kd, mL/g
1M Ca(NO3)2				
ETF-HG-1M Ca-1	3.8562	4.2466	0.2243	-6.15E+00
ETF-HG-1M Ca-11	3.8562	4.4863	0.2165	-9.73E+00
ETF-HG-1M Ca-2	4.2810	4.6667	0.2174	-5.70E+00
ETF-HG-1M Ca-21	4.2810	5.1852	0.2170	-1.21E+01
ETF-HG-1M Ca-3	1.0327	0.1747	0.2123	3.47E+02
ETF-HG-1M Ca-31	1.0327	0.1918	0.2161	3.04E+02
ETF-HG-1M Ca-4	0.9150	0.3259	0.2075	1.31E+02
ETF-HG-1M Ca-41	0.9150	0.2333	0.2023	2.17E+02
2M Ca(NO3)2				
ETF-HG-2M Ca-1	1.7974	1.4247	0.2012	1.95E+01
ETF-HG-2M-Ca-11	1.7974	1.3288	0.2061	2.57E+01
ETF-HG-2M-Ca-2	2.1569	1.4658	0.2025	3.49E+01
ETF-HG-2M-Ca-21	2.1569	1.3973	0.2065	3.95E+01
ETF-HG-2M Ca-3	1.0621	2.3151	0.2109	-3.85E+01
ETF-HG-2M Ca-31	1.0621	0.8296	0.2041	2.06E+01
ETF-HG-2M Ca-4	2.7451	2.5856	0.2109	4.39E+00
ETF-HG-2M Ca-41	2.7451	2.3116	0.2033	1.38E+01

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i = Initial Hg concentration
eq = Equilibrium Hg concentration

4.3.3 Mercury, Hg^{2+}, Kd's With Added H^+ Present

Solutions containing about 5 mg/L Hg^{2+} and varying amounts of acid were contacted with the four soils to determine the effect of hydrogen ion on the ability of the soils to sorb mercuric ion. The Kd's resulting from these tests are found in Tables 12-15.

Table 12. Hg Kd Values for 5 mg/L Mercuric Ion and Different pH With TF1 Soil - 40-60 Mesh

Sample	Hg i,mg/L	[H] i	Hg eq,mg/L	[H] eq	g Soil	Hg Kd
TF1-PH1	5.20	7.08E-02	4.35	6.76E-02	0.2205	1.33E+01
TF1-PH11	5.20	7.08E-02	5.00	6.76E-02	0.2061	2.91E+00
TF1-PH2	5.86	1.05E-02	4.09	9.77E-03	0.2100	3.10E+01
TF1-PH21	5.86	1.05E-02	4.28	9.77E-03	0.2077	2.66E+01
TF1-PH3	5.53	3.39E-03	4.02	2.63E-03	0.2106	2.68E+01
TF1-PH31	5.53	3.39E-03	4.44	2.45E-03	0.2118	1.73E+01
TF1-PH4	5.59	3.24E-03	3.99	2.29E-03	0.2100	2.87E+01
TF1-PH41	5.59	3.24E-03	4.15	2.40E-03	0.2043	2.55E+01

i = initial
eq = equilibrium

Table 13. Hg Kd Values for 5 mg/L Mercuric Ion and Different pH With TF2 Soil - 40-60 Mesh

Sample	Hg i,mg/L	[H] i	Hg eq,mg/L	[H] eq	g Soil	Hg Kd
TF1-PH1	5.20	7.08E-02	4.35	6.76E-02	0.2205	1.33E+01
TF1-PH11	5.20	7.08E-02	5.00	6.76E-02	0.2061	2.91E+00
TF1-PH2	5.86	1.05E-02	4.09	9.77E-03	0.2100	3.10E+01
TF1-PH21	5.86	1.05E-02	4.28	9.77E-03	0.2077	2.66E+01
TF1-PH3	5.53	3.39E-03	4.02	2.63E-03	0.2106	2.68E+01
TF1-PH31	5.53	3.39E-03	4.44	2.45E-03	0.2118	1.73E+01
TF1-PH4	5.59	3.24E-03	3.99	2.29E-03	0.2100	2.87E+01
TF1-PH41	5.59	3.24E-03	4.15	2.40E-03	0.2043	2.55E+01

i = initial
eq = equilibrium

Table 14. Hg Kd Values for 5 mg/L Mercuric Ion and Different pH With TNX Soil - 40-60 Mesh

Sample	Hg i,ppm	[H] i	Hg eq,ppm	[H] eq	g Soil	Hg Kd
TNX-PH1	5.20	7.08E-02	1.17	6.92E-02	0.2040	2.53E+02
TNX-PH11	5.20	7.08E-02	1.33	6.61E-02	0.2138	2.04E+02
TNX-PH2	5.86	1.05E-02	1.17	8.91E-03	0.2077	2.89E+02
TNX-PH21	5.86	1.05E-02	1.60	9.12E-03	0.2000	2.00E+02
TNX-PH3	5.53	3.39E-03	0.60	2.45E-03	0.2003	6.16E+02
TNX-PH31	5.53	3.39E-03	0.47	2.63E-03	0.2123	7.54E+02
TNX-PH4	5.59	3.24E-03	0.76	2.45E-03	0.2014	4.76E+02
TNX-PH41	5.59	3.24E-03	0.54	2.45E-03	0.2013	6.97E+02

---

i = initial
eq = equilibrium

Table 15. Hg Kd Values for 5 mg/L Mercuric Ion and Different pH With ETF Soil

Sample	Hg i,mg/L	[H] i	Hg eq,mg/L	[H] eq	g Soil	Hg Kd
ETF-HgH-1	4.941	7.24E-02	3.856	6.08E-02	0.2654	1.59E+01
ETF-HgH-11	4.941	7.24E-02	4.379	6.07E-02	0.2324	8.28E+00
ETF-HgH-2	4.941	7.59E-03	4.381	6.21E-03	0.2351	8.16E+00
ETF-HgH-21	4.941	7.59E-03	4.673	6.43E-03	0.2439	3.53E+00
ETF-HgH-3	4.762	8.32E-04	2.843	4.24E-04	0.2213	4.58E+01
ETF-HgH-31	4.762	8.32E-04	1.895	5.63E-04	0.2464	9.21E+01
ETF-HgH-4	5.06	3.63E-03	3.758	1.45E-03	0.2663	1.95E+01
ETF-HgH-41	5.06	3.63E-03	4.248	1.45E-03	0.2470	1.16E+01

---

i = initial
eq = equilibrium

4.3.4 Soil Kd's for Lead, Pb^{2+}

The Kd values derived for sorption of lead ion on 40-60 mesh samples of TF1, TF2, and TNX soils and on ETF soil are presented in Tables 16-19.

Table 16. Kd Values for 50-125 mg/L Lead Ion With TF1 Soil - 40-60 Mesh

Sample	Pb i,mg/L	Pb eq, mg/I	g Soil	Kd, mL/g
TF1-P1	47.428	<0.020	0.5145	≥6.91E+04
TF1-P11	47.428	<0.020	0.5138	≥6.92E+04
TF1-P2	71.654	<0.020	0.5127	≥1.05E+05
TF1-P21	71.654	<0.020	0.4997	≥1.08E+05
TF1-P3	97.935	<0.020	0.5089	≥1.44E+05
TF1-P31	97.935	<0.020	0.5025	≥1.46E+05
TF1-P4	121.400	0.241	0.5051	1.49E+04
TF1-P41	121.400	0.466	0.5000	7.79E+03

i = initial
eq = equilibrium

Table 17. Kd Values for 50-125 mg/L Lead Ion With TF2 Soil - 40-60 Mesh

Sample	Pb i, mg/L	Pb eq,mg/L	g Soil	Kd, mL/g
TF2-P1	47.428	2.772	0.5010	4.82E+02
TF2-P11	47.428	1.459	0.5110	9.25E+02
TF2-P2	71.654	10.982	0.5089	1.63E+02
TF2-P21	71.654	13.372	0.5026	1.30E+02
TF2-P3	97.935	24.212	0.5100	8.96E+01
TF2-P31	97.935	17.797	0.5135	1.32E+02
TF2-P4	121.400	37.444	0.5143	6.54E+01
TF2-P41	121.400	38.651	0.5125	6.27E+01

i = initial
eq = equilibrium

Table 18. Kd Values for 50-125 mg/L Lead Ion With TNX Soil - 40-60 Mesh

Sample	Pb i,mg/L	Pb eq,mg/L	g Soil	Kd, mL/g
TNX-P1	47.428	<0.02	0.5010	>7.03E+03
TNX-P11	47.428	<0.02	0.5110	>6.95E+03
TNX-P2	71.654	0.037	0.5089	5.71E+04
TNX-P21	71.654	0.028	0.5026	7.63E+04
TNX-P3	97.935	<0.02	0.5100	>1.42E+05
TNX-P31	97.935	<0.02	0.5135	>1.46E+05
TNX-P4	121.400	0.025	0.5143	1.42E+05
TNX-P41	121.400	<0.02	0.5125	>1.77E+05

---

i = initial
eq = equilibrium

Table 19. Kd Values for 5-50 mg/L Lead Ion With ETF Soil

Sample	Pb i, mg/L	Pb eq,mg./L	g Soil	Kd, mL/g
ETF-1	35.370	0.203	0.1020	2.42E+06
ETF-11	35.370	0.823	0.1066	5.61E+05
ETF-2	12.276	<0.02	0.1077	≥8.11E+06
ETF-21	12.276	<0.02	0.1014	≥8.61E+06
ETF-3	6.916	<0.02	0.1056	≥4.65E+06
ETF-31	6.916	0.027	0.1067	3.41E+06
ETF-4	3.150	<0.02	0.1031	≥2.16E+06
ETF-41	3.150	<0.02	0.1028	≥2.17E+06

---

i = Initial Pb concentration
eq = Equilibrium Pb Concentration

4.3.5 Lead, Pb^{2+}, Kd's When 1M or 2M Ca^{2+} is Present

The Kd values observed for sorption of lead ion from solutions of lead nitrate in the presence of 1M or 2M calcium nitrate are presented in Tables 20-23.

Table 20. Kd Values for Lead Ion in the Presence of 1M and 2M Calcium Ion
40-60 Mesh TF1 Soil

SAMPLE	Pb i, mg/L	Pb eq,mg/L	g Soil	Kd,mg/L
1M Ca(NO3)2				
TF1-5	42.600	14.100	0.5093	5.96E+01
TFI-51	42.600	20.300	0.5070	3.26E+01
TF1-6	66.800	31.400	0.5159	3.28E+01
TF1-61	66.800	31.100	0.5124	3.36E+01
TF1-7	86.288	48.041	0.5042	2.37E+01
TF1-71	86.288	54.417	0.5127	1.71E+01
TF1-8	153.810	114.330	0.5139	1.01E+01
TF1-81	153.810	105.240	0.5098	1.36E+01
2M Ca(NO3)2				
TF1CA-1	35.488	12.269	0.5061	5.61E+01
TF1CA-11	35.488	14.944	0.4999	4.13E+01
TF1CA-2	55.976	26.229	0.5197	3.27E+01
TF1CA-21	55.976	30.426	0.5101	2.47E+01
TF1CA-3	77.028	43.999	0.5037	2.24E+01
TF1CA-31	77.028	45.530	0.5002	2.07E+01
TF1CA-4	96.556	60.878	0.5121	1.72E+01
TF1CA-41	96.556	56.138	0.5256	2.05E+01

i = initial
eq = equilibrium

Table 21. Kd Values for Lead Ion in the Presence of 1M and 2M Calcium Ion - 40-60 Mesh TF2 Soil

SAMPLE	Pb i, mg/L	Pb eq,mg/L	g Soil	Kd,mg/L
1M Ca(NO3)2				
TF2-5	42.60	31.34	0.5136	1.05E+01
TF2-51	42.60	33.64	0.5133	7.79E+00
TF2-6	66.80	53.26	0.5059	7.54E+00
TF2-61	66.80	51.30	0.5070	8.94E+00
TF2-7	86.29	76.88	0.5023	3.66E+00
TF2-71	86.29	71.80	0.5148	5.88E+00
TF2-8	153.81	135.09	0.5099	4.08E+00
TF2-81	153.81	133.40	0.5450	4.21E+00
2M Ca(NO3)2				
TF2CA-1	35.49	31.48	0.5110	3.74E+00
TF2CA-11	35.49	31.88	0.5086	3.34E+00
TF2CA-2	55.98	50.99	0.5415	2.71E+00
TF2CA-21	55.98	62.26	0.5030	1.00E+00
TF2CA-3	77.03	74.75	0.5084	9.00E-01
TF2CA-31	77.03	75.96	0.5270	4.02E-01
TF2CA-4	96.56	105.02	0.5067	1.00E+00
TF2CA-41	96.56	97.68	0.5013	1.00E+00

i = initial
eq = equilibrium

Table 22. Kd Values for Lead Ion in the Presence of 1M and 2M Calcium Ion - 40-60 Mesh TNX Soil

SAMPLE	Pb i, mg/L	Pb eq, mg/L	g Soil	Kd, mg/L
1M Ca(NO3)2				
TNX-5	42.60	30.25	0.5038	1.22E+01
TNX-51	42.60	29.00	0.5046	1.39E+01
TNX-6	66.80	46.74	0.4960	1.30E+01
TNX-61	66.80	46.74	0.5135	1.25E+01
TNX-7	86.29	64.65	0.5198	9.66E+00
TNX-71	86.29	63.39	0.5138	1.05E+01
TNX-8	153.81	114.83	0.5074	1.00E+01
TNX-81	153.81	115.22	0.5106	9.84E+00
2M Ca(NO3)2				
TNX2CA-1	35.488	31.989	0.5175	3.17E-03
TNX2CA-11	35.488	31.981	0.5041	3.26E-03
TNX2CA-2	55.976	50.885	0.4914	3.05E-03
TNX2CA-21	55.976	50.492	0.4960	3.28E-03
TNX2CA-3	77.028	69.138	0.5018	3.41E-03
TNX2CA-31	77.028	68.905	0.5100	3.47E-03
TNX2CA-4	96.556	98.819	0.5183	-6.63E-04
TNX2CA-41	96.556	95.264	0.5025	4.05E-04

i = initial
eq = equilibrium

Table 23. Kd Values for Lead Ion in the Presence of 1M and 2M Calcium Ion - ETF Soil

SAMPLE	Pb i, mg/L	Pb eq,mg/L	g Soil	Kd,mg/L
1M Ca(NO3)2				
ETF-5	42.60	20.36	0.5040	3.25E+01
ETF-51	42.60	18.77	0.5057	3.77E+01
ETF-6	66.80	29.92	0.5082	3.64E+01
ETF-61	66.80	34.23	0.4953	2.88E+01
ETF-7	86.29	52.28	0.5038	1.94E+01
ETF-71	86.29	52.67	0.5066	1.89E+01
ETF-8	153.81	120.14	0.5080	8.28E+00
ETF-81	153.81	118.33	0.5077	8.86E+00
2M Ca(NO3)2				
ETF2CA-1	41.96	24.14	0.5069	2.19E+01
ETF2CA-11	41.96	27.86	0.5014	1.51E+01
ETF2CA-2	57.95	38.50	0.5070	1.49E+01
ETF2CA-21	57.95	45.29	0.5094	8.23E+00
ETF2CA-3	89.61	56.58	0.5084	1.72E+01
ETF2CA-31	89.61	65.62	0.4997	1.10E+01
ETF2CA-4	144.99	116.30	0.5067	7.30E+00
ETF2CA-41	144.99	123.48	0.5056	5.17E+00

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i = initial
eq = equilibrium

4.3.6 Lead, Pb^{2+}, Kd's With Added H^+ Present

Solutions containing about 100 mg/L Pb^{2+} and varying amounts of acid were contacted with the four soils to determine the effect of hydrogen ion on the ability of the soils to sorb lead ion. The Kd's resulting from these tests are found in Tables 24-27.

Table 24. Pb Kd Values for 100 mg/L Lead Ion and Different pH With TF1 Soil - 40-60 Mesh

Sample	Pb i, mg/L	[H] i	Pb eq, mg/L	[H] eq	g Soil	Pb Kd
TF1PH-1	97.21	3.50E-01	94.21	4.79E-01	0.5163	9.27E-01
TF1PH-11	97.21	3.50E-01	94.80	5.25E-01	0.5335	7.17E-01
TF1PH-2	105.06	3.09E-02	99.01	8.32E-02	0.5123	1.79E+00
TF1PH-21	105.06	3.09E-02	98.39	5.75E-02	0.5163	1.97E+00
TF1PH-3	108.67	1.66E-03	65.38	1.35E-04	0.5139	1.93E+01
TF1PH-31	108.67	2.43E-03	62.50	2.04E-04	0.5009	2.21E+01
TF1PH-4	104.70	2.45E-05	<0.02	5.75E-07	0.5098	≥1.54E+05
TF1PH-41	104.70	2.45E-05	<0.02	4.07E-07	0.5316	≥1.48E+05

i = initial
eq = equilibrium

Table 25. Pb Kd Values for 100 mg/L Lead Ion at Different pH Values With TF2 Soil - 40-60 Mesh

Sample	Pb i, mg/L	[H] i	Pb eq, mg/L	[H] eq	g Soil	Pb Kd
TF2PH-1	97.21	3.50E-01	93.67	5.50E-01	0.5163	4.43E+01
TF2PH-11	97.21	3.50E-01	93.98	6.03E-01	0.5335	4.42E+01
TF2PH-2	105.06	3.09E-02	100.40	8.13E-02	0.5123	5.08E+02
TF2PH-21	105.06	3.09E-02	100.38	2.88E-02	0.5163	5.08E+02
TF2PH-3	108.67	1.66E-03	93.34	8.51E-04	0.5139	1.05E+04
TF2PH-31	108.67	1.66E-03	93.52	8.32E-04	0.5009	1.05E+04
TF2PH-4	104.70	2.45E-05	36.04	4.27E-06	0.5098	1.78E+06
TF2PH-41	104.70	2.45E-05	32.74	3.02E-06	0.5316	1.96E+06

i = initial
eq = equilibrium

Table 26. Pb Kd Values for 100 mg/L Lead Ion at Different pH Values With TNX Soil - 40-60 Mesh

Sample	Pb i, mg/L	[H] i	Pb eq, mg/L	[H] eq	g Soil	Pb Kd
TNXPH-1	97.21	3.50E-01	102.89	5.75E-01	0.5090	-2.37E+00
TNXPH-11	97.21	3.50E-01	101.87	5.23E-01	0.5184	-1.96E+00
TNXPH-2	105.06	3.09E-02	102.54	4.16E-02	0.5013	1.19E+01
TNXPH-21	105.06	3.09E-02	102.82	4.68E-02	0.5042	1.06E+01
TNXPH-3	108.67	1.66E-03	42.67	2.40E-04	0.5108	1.40E+04
TNXPH-31	108.67	1.66E-03	36.17	1.91E-04	0.5232	1.81E+04
TNXPH-4	104.70	2.45E-05	0.11	1.58E-06	0.5106	5.67E+08
TNXPH-41	104.70	2.45E-05	0.15	1.86E-07	0.5301	4.27E+08

i = initial
eq = equilibrium

Table 27. Pb Kd Values for 100 mg/L Lead Ion and Different pH With ETF Soil

Sample	Pb i, mg/L	[H] i	Pb eq, mg/L	g Soil	Pb Kd
ETFPH-1	99.07	1.00E-01	96.29	0.0920	4.71E+00
ETFPH-11	99.07	1.00E-01	95.93	0.1066	4.60E+00
ETFPH-2	99.53	7.94E-03	99.59	0.1043	-7.65E-02
ETFPH-21	99.53	7.94E-03	99.81	0.0922	-4.48E-01
ETFPH-3	101.10	1.00E-03	96.57	0.1015	6.93E+00
ETFPH-31	101.10	1.35E-03	97.39	0.0137	4.17E+01
ETFPH-4	102.19	1.35E-03	94.83	0.0953	1.22E+01
ETFPH-41	102.19	1.35E-03	94.00	0.1016	1.29E+01

i = initial
eq = equilibrium

4.3.7 Soil Kd's for Cesium Ion, Cs^+

Four different concentrations of cesium nitrate solution were contacted with 0.01 gram of each of the soils, 40-60 mesh fraction except for the ETF soil which was not sieved. These solutions, 1M, 0.1M, 0.05M, and 0.01M $CsNO_3$, were contacted with the soils for three days on the shaker. Results of the Kd determinations appear in Table 28.

Table 28. Kd Values for 1M, 0.1M, 0.05M, and 0.01M Cesium Ion with Each Soil

Sample	Cs i,mg/L	Cs,eq,mg/L	g Soil	Cs Kd,mL/g
TF1 Soil 40-60 mesh				
TF1-Cs1M	120808	120573	0.1003	2.91E-01
TF1-Cs0.1M	9756	10807	0.1008	-1.45E+01
TF1-Cs0.05M	5946	5271	0.1009	1.90E+01
TF1-Cs0.01M	1235	998	0.1045	3.41E+01
TF2 Soil 40-60 mesh				
TF2-Cs1M	120808	87498	0.1009	5.66E+01
TF2-Cs0.1M	9756	10833	0.1040	-1.43E+01
TF2-Cs0.05M	5946	4932	0.1003	3.07E+01
TF2-Cs0.01M	1235	985	0.1029	3.70E+01
TNX Soil 40-60 mesh				
TNX-Cs1M	120808	125499	0.1000	-5.61E+00
TNX-Cs0.1M	9756	12744	0.1004	-3.50E+01
TNX-Cs0.05M	5946	5431	0.1047	1.36E+01
TNX-Cs0.01M	1235	1069	0.1019	2.29E+01
ETF Soil				
ETF1-Cs1M	120808	123089	0.1098	-2.53E+00
ETF2-Cs1M	120808	121266	0.1096	-5.17E-01
ETF1-Cs0.1M	9756	11942	0.1090	-2.52E+01
ETF2-Cs0.1M	9756	11827	0.1059	-2.48E+01
ETF1-Cs0.05M	5946	5634	0.1006	8.26E+00
ETF2-Cs0.05M	5946	5778	0.1098	3.97E+00
ETF1-Cs0.01M	1235	1191	0.1055	5.25E+00
ETF2-Cs0.01M	1235	1176	0.1062	7.09E+00

i = initial
eq = equilibrium

4.3.8 Uranyl Ion, UO_2^{2+}, Kd's for Each Soil

The Kd values observed for sorption of uranyl ion from a 0.01 M uranyl nitrate solution at pH 3 on 40-60 mesh samples of TF1, TF2, and TNX soils and the unsieved ETF soil are found in Table 29.

Table 29. Kd Values for Uranyl Ion With Each Soil
(pH = 3)

Sample	U i,mg/L	U,eq,mg/L	g Soil	U Kd,mL/g
TF1 Soil	2245	2168	0.1005	5.30E+00
TF2 Soil	2245	2211	0.1004	2.30E+00
TNX Soil	2245	2108	0.1002	9.73E+00
ETF Soil	2245	2151	0.1027	6.38E+00

i = initial
eq = equilibrium

4.3.9 Silica Sand Kd's

The results of contacting silica sand with solutions of UO_2^{2+}, Hg^{2+}, Pb^{2+}, and Cs^+ are found in Table 30.

Table 30. Kd Values for four Ions, UO_2^{2+}, Hg^{2+}, Pb^{2+}, and Cs^+ With Silica Sand

Contacting Solution	g Sand	Metal i, mg/L*	Metal eq, mg/L*	Kd, mL/g
$CsNO_3$	0.2033	8.08E-3 µCi/mL	8.50E-3 µCi/mL	-7.17E+00
$UO_2(NO_3)_2$	0.2017	2173	2226	-1.77E+00
$Hg(NO_3)_2$	0.2010	5.69	4.94	1.13E+01
$Pb(NO_3)_2$	0.2037	2.19	1.50	3.44E+01

---

* Units except for Cs data which was analyzed by γ-counting
i = initial metal concentration
eq = equilibrium metal concentration

4.4 Soil Capacities and Isotherms

Isotherms for mercury and lead were plotted for most of the soils.

4.4.1 TF1 Soil Isotherms

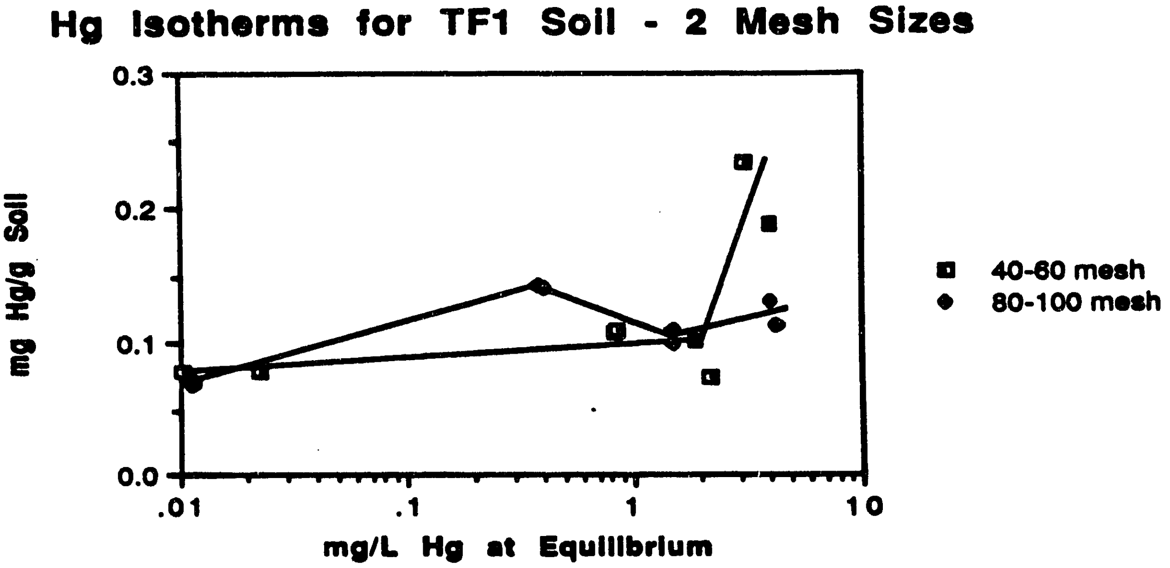

Figure 2. Hg^{2+} **on TF1 Soils**

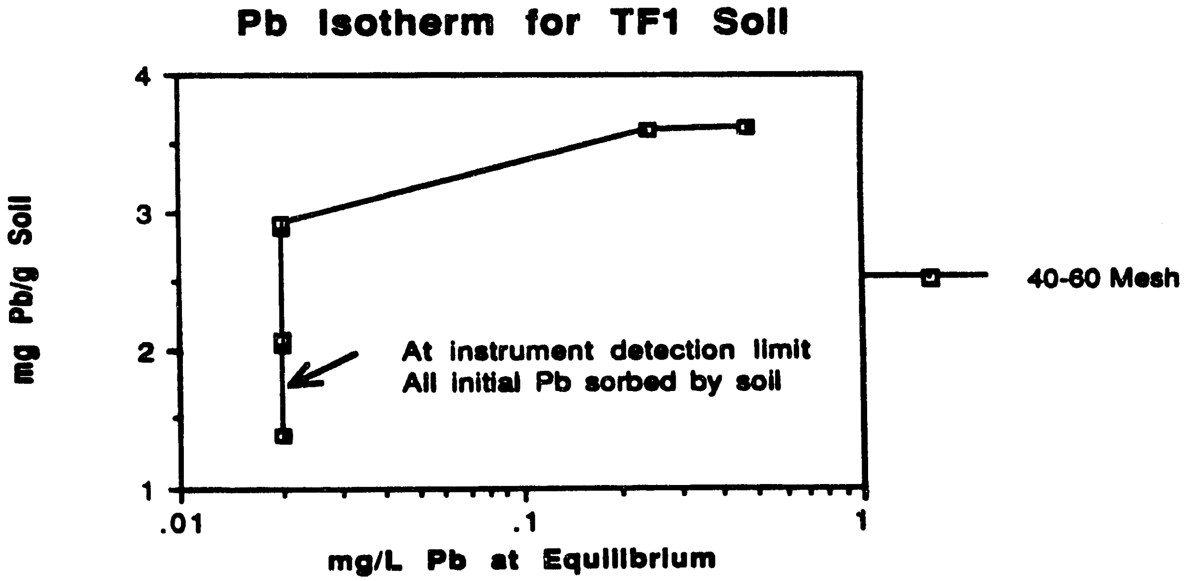

Figure 3. Pb^{2+} **on TF1 Soils**

4.4.2 TF2 Soil Isotherms

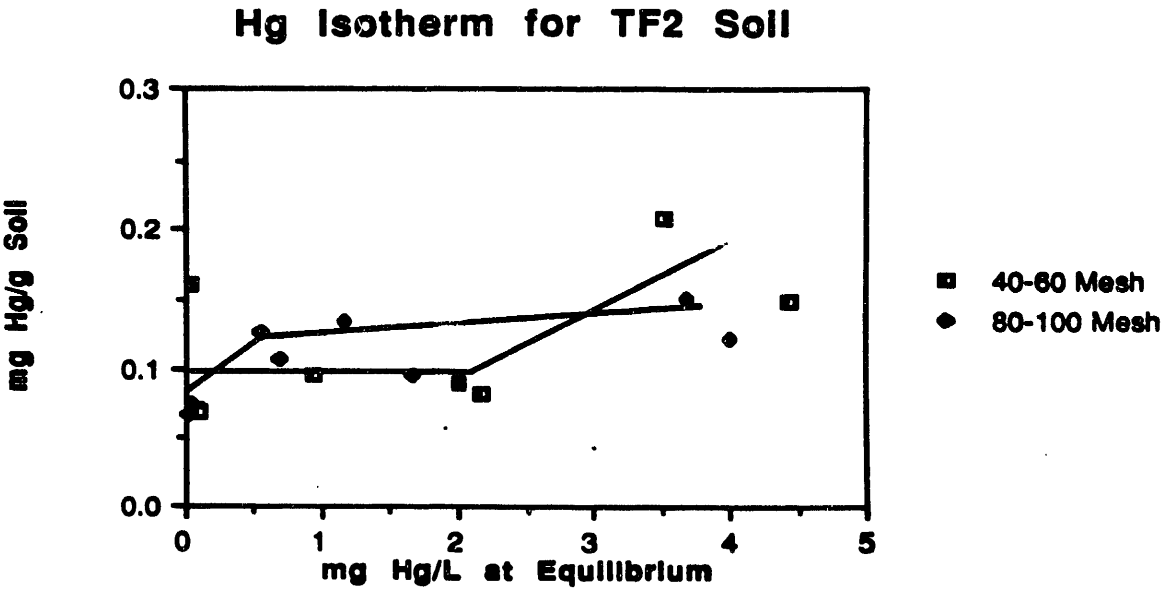

Figure 4. Hg^{2+} on TF2 Soils

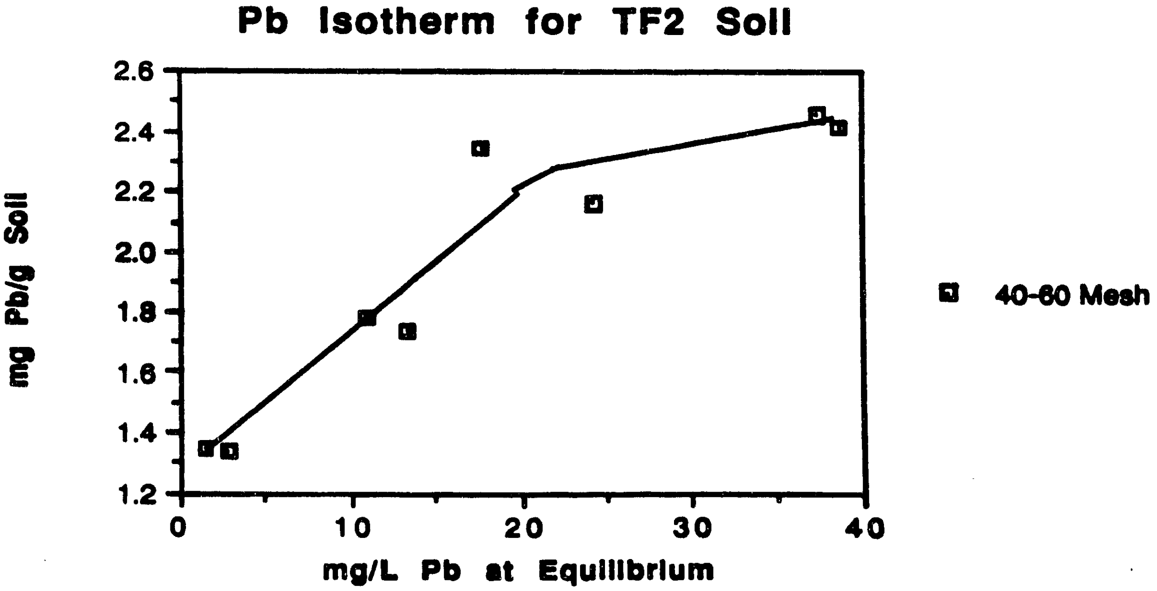

Figure 5. Pb^{2+} on TF2 Soil

4.4.3 TNX Soil Isotherms

Only the mercury isotherms for TNX soils have significance. Lead ion was sorbed so well by this soil that equilibrium concentrations were below the detection limit of the ICPES instrument for nearly every sample (Table 22).

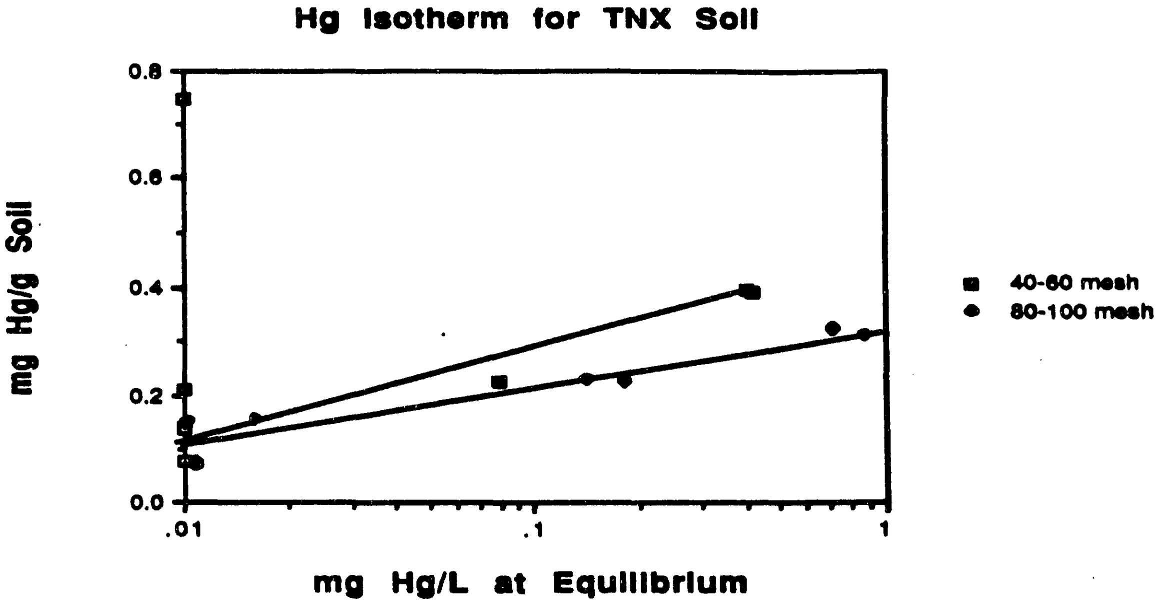

Figure 6. Hg^{2+} on TNX Soil

4.4.3 ETF Soil Isotherm

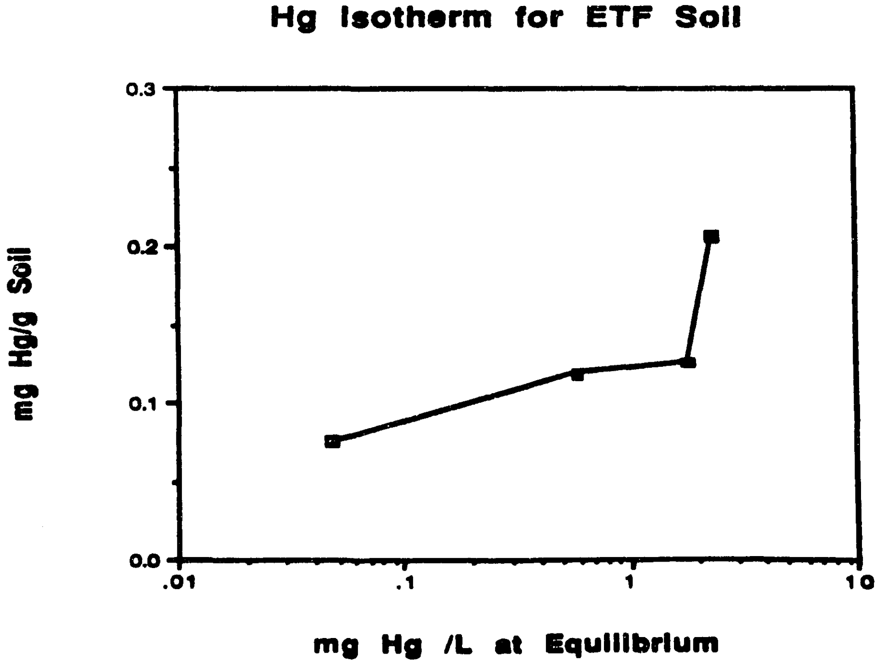

Figure7. Mercuric ion on ETF Soil

As in the case of TNX soil, the ETF soil sorbed Pb^{2+} so well that the equilibrium ion concentration was less than the detection limit of the instrument. (Table 19)

4.5 A Tabulation of Ion Exchanging Species

Table 31 contains data collected in an attempt to establish a mass balance among ion exchanging species in solution and on the soil. It was presumed that Pb^{2+} or Hg^{2+}, and possibly H^{+} in solution would exchange for Na^{+} in the kaolinite clay of the soils.

Table 31. A Comparison of Milliequivalents of Ions Exchanged Between Soil and Solution for 100 mg/L Pb^{2+} at Four pH's

SAMPLE	Solution pH	meq Na change per g soil	meq Pb change per g soil	meq H change per g soil
TF1-1	0.45	7.44E-03	-2.16E-03	9.62E+00
TF1-11	0.45	7.60E-03	-1.73E-03	1.30E+01
TF1-2	1.51	8.12E-03	-4.21E-03	3.77E+00
TF1-21	1.51	8.01E-03	-4.77E-03	1.97E+00
TF1-3	2.78	7.37E-03	-2.92E-02	-1.07E-01
TF1-31	2.78	1.59E-02	-3.08E-02	-1.13E-01
TF1-4	4.61	6.16E-03	-7.20E-02	-1.70E-02
TF1-41	4.61	5.80E-03	-6.73E-02	-1.60E-02
TF2-1	0.45	4.43E-03	-2.54E-03	1.49E+01
TF2-11	0.45	4.49E-03	-2.31E-03	1.88E+01
TF2-2	1.51	5.14E-03	-3.24E-03	3.63E+00
TF2-21	1.51	5.74E-03	-3.35E-03	-1.56E-01
TF2-3	2.78	4.48E-03	-1.04E-02	-5.64E-02
TF2-31	2.78	4.48E-03	-1.01E-02	-5.71E-02
TF2-4	4.61	3.66E-03	-4.71E-02	-1.44E-03
TF2-41	4.61	3.39E-03	-4.61E-02	-1.43E-03
TNX-1	0.45	6.45E-02	0.00E+00	1.75E+01
TNX-11	0.45	7.21E-02	0.00E+00	1.28E+01
TNX-2	1.51	8.36E-02	-1.76E-03	2.35E+00
TNX-21	1.51	8.36E-02	-1.60E-03	1.18E+00
TNX-3	2.78	8.26E-02	-4.46E-02	-9.93E-03
TNX-31	2.78	9.17E-02	-4.84E-02	-1.01E-02
TNX-4	4.61	6.54E-02	-7.18E-02	-1.63E-02
TNX-41	4.61	7.35E-02	-6.73E-02	-1.62E-03

A - signifies lost from solution concentration-sorbed by soil
A + signifies gained by solution - lost from soil

Table 32. A Comparison of Milliequivalents of Ions Exchanged Between Soil and Solution for Pb Ion in the Presence of 1M Ca Ion

SAMPLE	meq Na change per g soil	meq Pb change per g soil	meq Ca change per g soil	Initial Pb ppm
TF1-1	<0.100	-6.90E-03	3.57E-01	42.60
TF1-11	<0.100	-5.57E-03	3.07E-01	42.60
TF1-2	<0.100	-4.48E-03	-1.75E-02	66.80
TF1-21	<0.100	-5.49E-03	-5.53E-01	66.80
TF1-3	<0.100	-5.05E-03	-5.11E-01	86.29
TF1-31	<0.100	-4.96E-03	-4.36E-01	86.29
TF1-4	<0.100	-3.13E-03	1.16E+00	153.81
TF1-41	<0.100	-4.04E-03	-1.35E-02	153.81
TF2-1	<0.100	-2.72E-03	2.28E-01	42.60
TF2-11	<0.100	-2.67E-03	6.90E-01	42.60
TF2-2	<0.100	-2.04E-03	-1.49E-02	66.80
TF2-21	<0.100	-1.36E-03	-1.85E-01	66.80
TF2-3	<0.100	-2.21E-03	-4.40E-01	86.29
TF2-31	<0.100	-1.94E-03	-1.07E-01	86.29
TF2-4	<0.100	-1.26E-03	5.53E-01	153.81
TF2-41	<0.100	-1.58E-03	1.32E-01	153.81
TNX-1	3.62E-02	-5.46E-03	2.43E-01	35.488
TNX-11	3.65E-02	-5.52E-03	2.76E-01	35.488
TNX-2	3.41E-02	-3.25E-03	8.50E-01	55.976
TNX-21	3.52E-02	-3.07E-03	1.22E+00	55.976
TNX-3	3.56E-02	-2.98E-03	-3.70E-01	77.028
TNX-31	3.51E-02	-2.92E-03	-3.70E-01	77.028
TNX-4	3.35E-02	-1.93E-03	2.74E-01	96.556
TNX-41	3.29E-02	-1.75E-03	9.26E-01	96.556
ETF-1	<0.100	-1.00E-02	1.50E+00	42.60
ETF-11	<0.100	-9.49E-03	7.40E-01	42.60
ETF-2	<0.100	-9.48E-03	1.30E+00	66.80
TNX-21	<0.100	-9.59E-03	1.02E+00	66.80
ETF-3	<0.100	-9.18E-03	1.02E-01	86.29
ETF-31	<0.100	-1.04E-02	1.61E-01	86.29
ETF-4	<0.100	-6.17E-03	1.03E+00	153.81
ETF-41	<0.100	-6.26E-03	5.55E-01	153.81

In Table 32., a (-) number signifies concentration lost from solution to the soil and a (+) number signifies concentration lost from the soil to the solution.

Samples of TF1, TF2, and TNX soils were shaken with deionized water to determine if H^+ concentrations in solution would change in the absence of Pb^{2+}. The results of this experiment are given in Table 33.

Table 33. The Change in Solution Hydrogen Ion Concentration on Contacting Three Soils With Deionized Water.

Soil	Initial pH	Final pH	g. Soil	meq.H lost/g Soil
TF1	5.69	6.35	1.0292	1.57E-6
TF2	5.69	6.10	1.0060	1.24E-6
TNX	5.69	6.13	1.0299	1.26E-6

Samples of the same soils were also shaken with deionized water which had been pH adjusted to 4.11 using HNO_3. The amount of Na^+ liberated from the soils by the hydrogen ion is found for each soil in Table 34.

Table 34. The Change in Solution Sodium Ion Concentration on Contacting Three Soils With pH 4.11 Water

Soil	meq Na desorbed/g Soil	g. Soil	meq.H sorbed/g Soil
TF1	3.61E-3	1.0282	3.61E-3
TF2	1.47E-3	1.0160	1.47E-3
TNX	2.62E-3	1.0229	2.26E-3

4.6 Removing Ions Already Sorbed on Soils

Table 35 details the results of contacting soils, already containing a known amount of Pb^{2+}, Hg^{2+}, $UO_2{}^{2+}$, and Cs^+, with 1M $Ca(NO_3)_2$ and 0.01 M HNO_3 in order to test the kinetics of the reverse of the sorption reaction for those ions.

Table 35. Effectiveness of Ion Removal from Four SRS Soils Using 2M Calcium Ion and 0.1 M Nitric Acid

	TF1	% Removed	TF2	% Removed	TNX	% Removed	ETF	% Removed
Pb								
mg Pb/g Soil, initial	1.01E-01		9.85E-02		1.01E-01		9.88E-02	
mg Pb/g Soil removed using	BDL	0	BDL	0	BDL	0	BDL	0
1M Calcium ion	BDL	0	BDL	0	BDL	0	BDL	0
mg Pb/g Soil removed using	9.84E-02	97	5.39E-02	55	9.84E-02	97	4.11E-02	42
0.1M Nitric Acid	6.09E-02	60	3.98E-02	40	6.09E-02	60	4.79E-02	48
Hg								
mg Hg/g Soil, initial	1.05E-02		7.78E-03		1.07E-02		1.04E-02	
mg Hg/g Soil removed using	BDL	0	BDL	0	BDL	0	BDL	0
1M Calcium ion	BDL	0	1.01E-03	13	BDL	0	BDL	0
mg Hg/g Soil removed using	BDL	0	BDL	0	BDL	0	BDL	0
0.1M Nitric Acid	BDL	0	BDL	0	BDL	0	BDL	0
U								
mg U/g Soil, initial	3.24E+00		6.00E-01		4.00E+00		1.31E+00	
mg U/g Soil removed using	1.20E-01	4	1.97E-01	33	6.05E-01	15	3.54E-01	27
1M Calcium ion	1.11E-01	3	1.77E-01	30	6.32E-01	16	2.13E-01	16
mg U/g Soil removed using	3.31E+00	100*	6.22E-01	100*	4.02E+00	100*	1.36E+00	100*
0.1M Nitric Acid	3.27E+00	100*	7.11E-01	100*	4.04E+00	100*	1.06E+00	81
Cs								
µCi Cs/g soil, initial	5.13E-03		4.63E-03		5.60E-03		4.94E-03	
mg Cs/g Soil, initial	5.90E-02		5.32E-02		6.44E-02		5.68E-02	
µCi Cs/g Soil removed using	3.79E-03		BDL	0	6.91E-03		2.14E-03	
1M Calcium ion	3.65E-03		BDL	0	6.44E-03		BDL	
mg Cs/g Soil removed using	4.36E-02	74	BDL	0	7.50E-02	100*	2.46E-02	43
1M Calcium ion	4.20E-02	71	BDL	0	7.40E-02	100*	BDL	0
µCi Cs/g Soil removed using	4.40E-03		2.72E-03		6.33E-03		4.19E-03	
0.1M Nitric Acid	3.60E-03		3.55E-03		4.79E-03		2.71E-03	
mg Cs/g Soil removed using	5.07E-02	86	3.13E-02	59	7.28E-02	100*	4.82E-02	85
0.1M Nitric Acid	4.14E-02	70	4.08E-02	77	5.51E-02	86	3.12E-02	55

BDL = below detection limit

100* = Measures >100% but is within 10% analytical error allowed

5.0 DISCUSSION

It must be remembered that this study was done with actual soils, made as homogeneous as possible by mixing and sieving, rather than with pure kaolinite. Therefore, Kd's are less for these samples than they would have been for the clay alone. Discrepencies in results between duplicate samples can be attributed, for the most part, to slightly different percentages of clay and sand in the samples.

5.1 Physical Behavior of Soils in Different Solutions

Although the soils were all comprised of mostly kaolinite and sand, their swelling behavior in different solutions was not uniform. For example, TF1 and TF2 soils exhibited the greatest swelling (smallest bulk density) at very low pH in the presence of mercuric ion, though they tended othérwise to increase in wet volume as pH was increased. The volume of the TNX soil, on the other hand, was at a minimum (largest bulk density) in the same mercury solution. Conversely, the uranyl ion, at nearly the same pH as the mercuric nitrate solution, had little effect on TF1 soil relative to deionized water but generated a shrinking of TF2 soil and swelling for ETF (not shown in Figure 8) and TNX soils. The bulk density of soils, thus appears to be related not only to the pH of the solution contacting the soil and the soil itself but also the contacting ion in the solution.

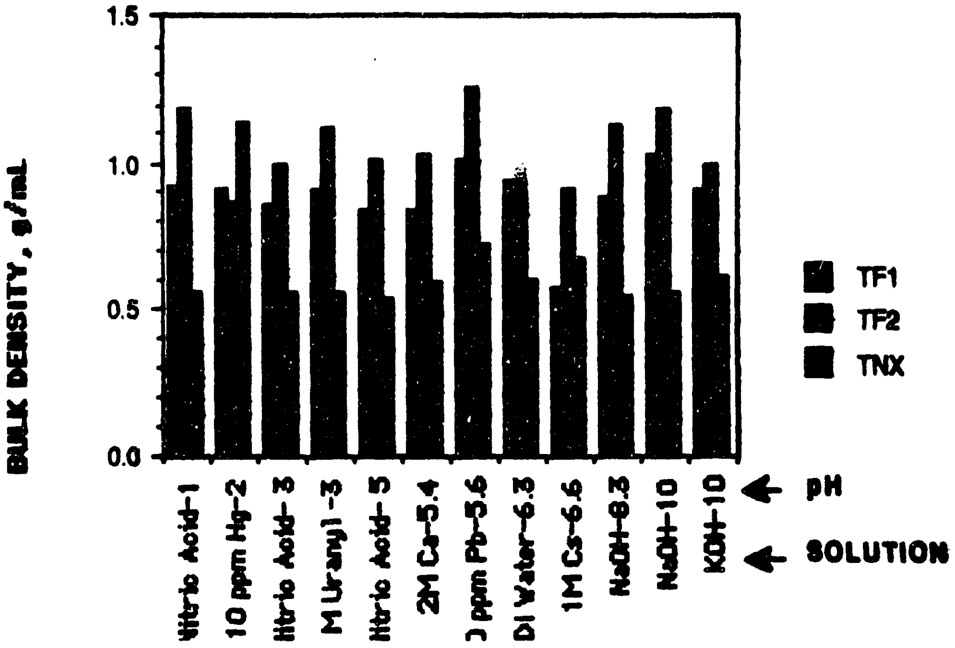

Figure 8. Bulk Densities of TF1, TF2, and TNX Soils

Although the X-ray diffraction data did not identify the presence of iron in the soils, the rust colored appearance of TF1, TF2 and the ETF soils would indicate that iron is, indeed, present. It may exist as an amorphous FeO(OH) species that would not generate any peaks in the X-ray spectrum. Or, the concentration of a crystalline compound may be too small to detect.

5.2 The Kd Values

Kd values, when an ion was removed from solution by the soil, were positive numbers. When the ion concentration change on contact with the soil was negligible, the sign of Kd was negative. Very small or negative Kd's indicated little or no attraction for the ion by the soil.

In general, it may be said that the magnitude of the sorption Kd could be controlled for any given metal ion by the concentration of competing ions, such as H^+ or Ca^{2+}. Kd's for heavy metal ions were reduced as the concentration of H^+ or Ca^{2+} was increased in the same solution because of competition for sorption sites. For example, Kd for Pb^{2+} on TF1 soil was lowered by a factor of 1,000 in the presence of 1M Ca^{2+} and varied from 8E-1 mL/g to ≥1E+5 mL/g at pH 0.46 and 4.6, respectively. Figure 9. graphically shows the differences in Pb^{2+} Kd that competing ions can impose on sorption. It also shows, since Kd is much lower (2 mL/g) in 0.1M HNO_3 than in 1M $Ca(NO_3)_3$ (120 mL/g), that concentration is not the only parameter involved. The Law of Mass Action for equilibria is most certainly at work in this effect, but other factors such as zeta potential, selectivity,

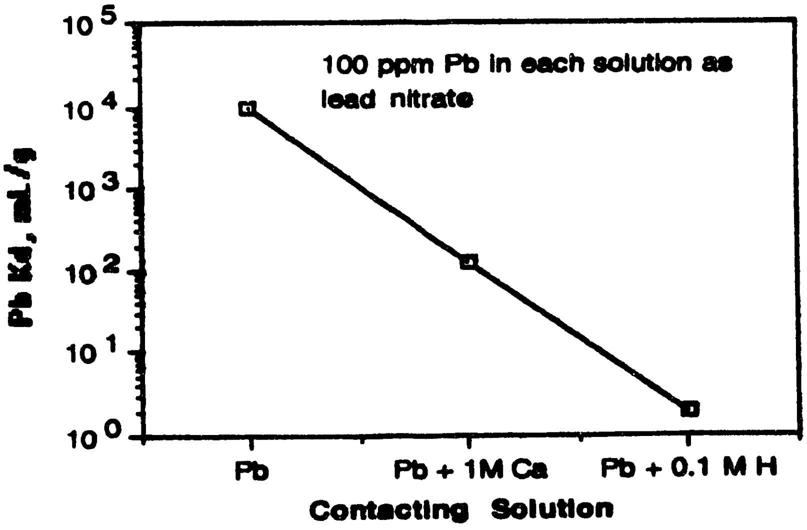

Figure 9. The Effect on Pb^{2+} Kd With Competing Ions Present

and swelling of the matrix may also play a role in the ability of the soil to sorb certain ions. It is of interest to note that, even in the presence of a large excess of H^+ or Ca^{2+}, all four soils showed a selective preference for Hg^{2+} and Pb^{2+}.
Decreasing the particle size of a soil increased its ability to sorb ions from solution. (See Figures 2,4, and 6) This result is expected because increased surface area for smaller particles means more sorption sites. However, the soil samples of smaller particle size also contained 20-40 percent more kaolinite, the expected primary sorbing component of the soils, and should exhibit greater capacity and larger Kd's for that reason as well. The relationship between amount of kaolinite and Kd was not linear, however. Kd values did not increase 20-40% on going from 40-60 mesh to 80-100 mesh soil particle size.

Kd's measured for pure silica sand (Table 31), the other soil component, showed that the "hard",i.e. small, slightly polarizable, ions, Cs^+ and $UO_2{}^{2+}$ were not sorbed. The larger, more polarizable, or "soft" Lewis acids [1] , Hg^{2+} and Pb^{2+}, however exhibited Kd's of 13 and 34 mL/g, respectively. Such sorption of metallic ions by silica sand is well-documented in the literature.[2,3] This study did not determine whether the uptake of metal ion on the sand was due to true adsorption on the surface of the sand or to precipitation of an oxy- or hydroxy-metal species at the solvated surface.

Sorption Kd values for all four ions were larger with TNX soil than for the other soils. This may, in part, be attributed to the fact that TNX soil was often composed of a larger percentage of kaolinite than the other soils (Figure 1). A comparison of Hg^{2+} Kd's, however, between 80-100 mesh TF1 soil (65% kaolinite) and 40-60 mesh TNX soil (45% kaolinite) shows that the TNX soil sorbed more mercuric ion at equilibrium than the TF1 soil. Similarly, 40-60 mesh TNX soil generated larger Kd values for Hg^{2+} than the 80-100 mesh TF2 soil (50% kaolinite). Thus, the amount of kaolinite in the soil cannot be the only factor in metal ion uptake by the soil. The TNX soil was the only soil with any residual organic matter associated with it and the added capacity of TNX soil for metal ions is attributed to the chelating ability of that organic matter.

Another factor that appeared to have an effect on the Kd's for these soils was the zeta potential, a measure of the net charge on the surface of the soil particles. The isoelectric point for SiO_2 in nitrate solutions occurs at a pH of about 2.78.[4] Kaolinite's isoelectric point is reported to range from 3.3 to 4.6.[5] In pH-regulated experiments in this study, all ions tested (UO_2^{2+} was not tested) registered greater Kd values as the pH increased. This has already been discussed as the result of a competition with H^+, but it is important to note that a decided elevation in the Kd value occurred at pH 3-4. Figure 10 shows the change in Pb^{2+} Kd as a function of pH for TF1, TF2, and TNX soils.

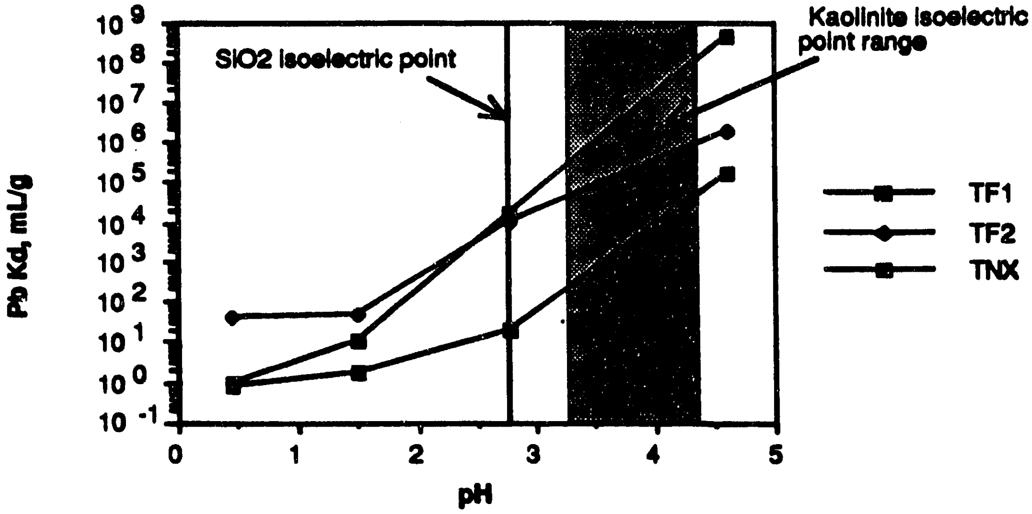

Figure 10. Pb^{2+} Kd for Three Soils Showing Isoelectric Regions for Kaolinite and SiO_2

In the region of the isoelectric point (at the zeta potential), the surface of the soil, which had been positively charged, achieves a net negative charge. This leads to greater attraction for and more sorption of the metal cations onto the surface. It may also lead to precipitation of the cation at the surface. In either case, the ion was removed from solution and became associated with the soil. The pH of the contacting solution can be directly regulated by addition of a known amount of acid or base or it can be indirectly regulated by hydrolysis of salts dissolved in it.

It would appear that sorption of counterions by these soils is also a function of the cation concentration in the contacting solution. The greater the total cation concentration in the solution, the lower the observed value for Kd. Although the Kd was less, the isotherms indicate that, for lead and mercuric ions, the amount of ion sorbed continued to increase with initial metal ion concentration until the soil was saturated. This appeared to be the case for the Cs^+ Kd's for all of the soils. Kd values for the more concentrated 1M and 0.1M solutions were negative whereas the more dilute 0.05M and 0.01M solutions were positive. But, no sorption of cesium ion occurred at the two higher solution concentrations. A rationale suggested for that observation is that, for the more concentrated Cs^+ solutions, the surface of the soil may have become quickly saturated with a small amount of counterion, screening any further sorption.

5.3 Ion Exchange

Kaolinite is not known as a good ion exchanger. Studies with lead ion (Tables 32 and 33) indicate that Na^+ is readily exchanged for H^+, though the milliequivalents of Na^+ released did not equal the milliequivalents of Pb^{2+} and H^+ sorbed. Further, the amount of Na^+ was essentially constant for TF1, TF2, and TNX soils while the amount of Pb^{2+} sorbed varied as a function of solution pH. When a large amount of Ca^{2+} was present initially, the amount of Pb^{2+} sorbed was constant. Measurable Na^+ given up by soil was noted only for the TNX samples. It is expected that this sodium ion was primarily associated with the organic matter in the TNX soil rather than with the clay portion. TF1 and TF2 soils did liberate small quantities of Na^+ in weakly acidic deionized water, and that small amount may have been difficult to detect in the presence of 1M Ca^{2+}. The Na^+ liberated did not result from dissolution of the soil.

5.4 Desorption

Equilibrium sorption studies do not generate data that can be reproduced for the reverse, desorption, process. The four ions studied can be easily kept from sorbing on the soils by decreasing the pH or adding Ca^{2+} ion. Using H^+ or Ca^{2+} to remove ions already sorbed on the soils showed that only H^+ was effective and it was efficient for $UO_2{}^{2+}$ and Cs^+ only (Table 35).

6.0 CONCLUSIONS

Results of this study indicate that sorption of ions by these soils is not accomplished by a single mechanism. Several sorption processes appeared to be simulatneously at work, those being adsorption, chelation (for TNX soil), and a small amount of ion exchange. Regulating these processes were competing ions and their concentrations, surface area, pH, the nature of the sorbing ions, and the presence of organic matter. Although it was not addressed in this study, the effect of iron oxides or iron oxyhydroxides present in some soils may also be significant.

Sorption of mercuric and lead ions by the hydrated sand in these soils should not be ignored. This indicates that the sand cannot be considered uncontaminated after exposure to solutions of certain metal cations.

The use of equilibrium data from Kd experiments should not be used to predict the desorption of ions from these soils. The kinetics of the reverse of the sorption processes must be understood before any *a priori* predictions can be made.

7.0 QUALITY ASSURANCE

All data from this study are recorded in WSRC-NB-90-345 and WSRC-NB-90-346. Standard solutions were prepared with reagent grade chemicals to check analytical methods. Reagent grade chemicals were used for all pH adjustments. Analyses were performed by the SRL Analytical Development Section (ADS) for the following "customer assisted" analyses: gamma counting for Cs-137, cold vapor atomic absorption for mercury and cesium, total uranium, and inductively coupled plasma atomic emission spectrometry for lead, calcium, and sodium. An Orion pH meter, Model 701A, was used to measure hydrogen ion concentration.

8.0 REFERENCES

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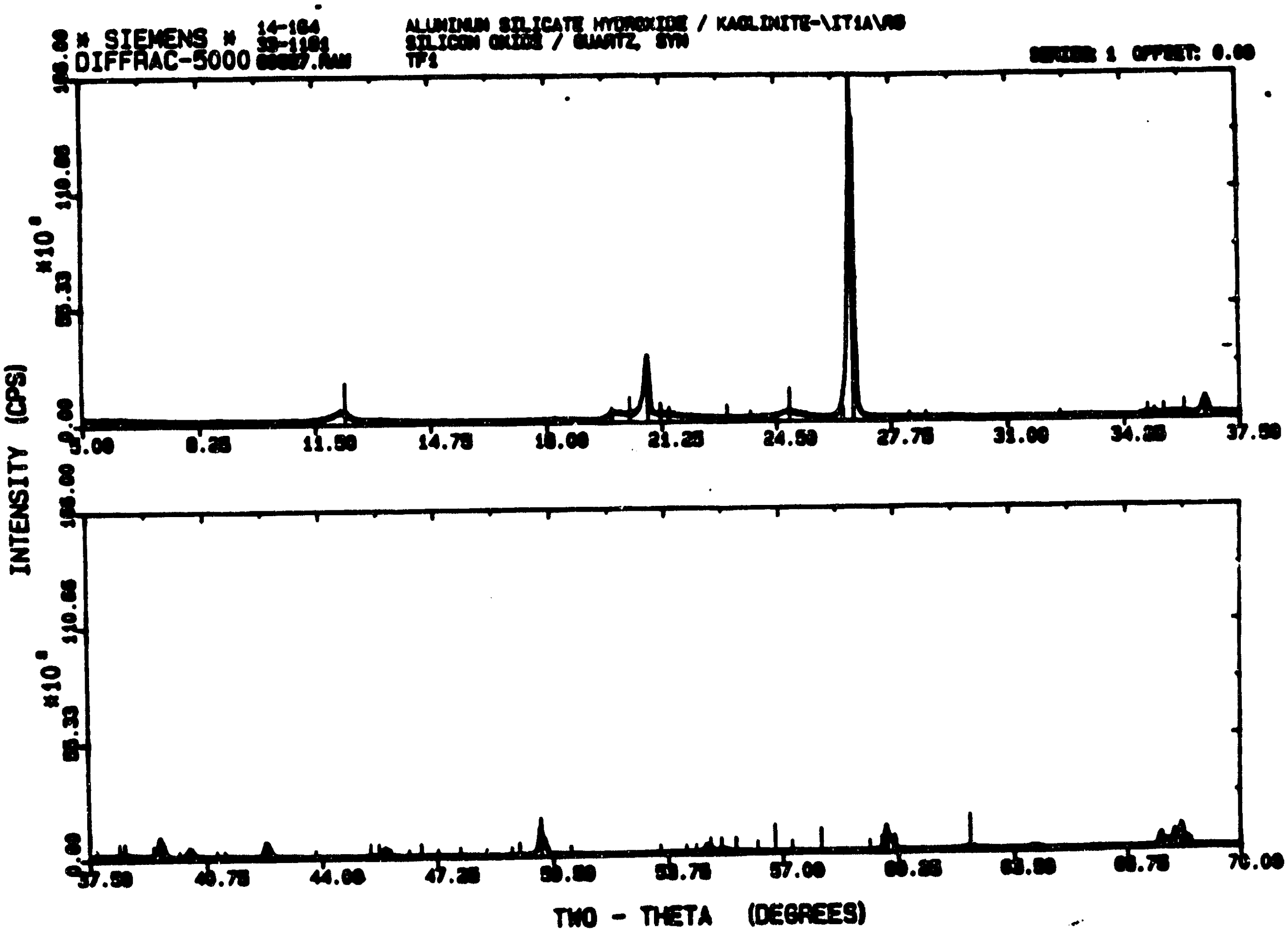
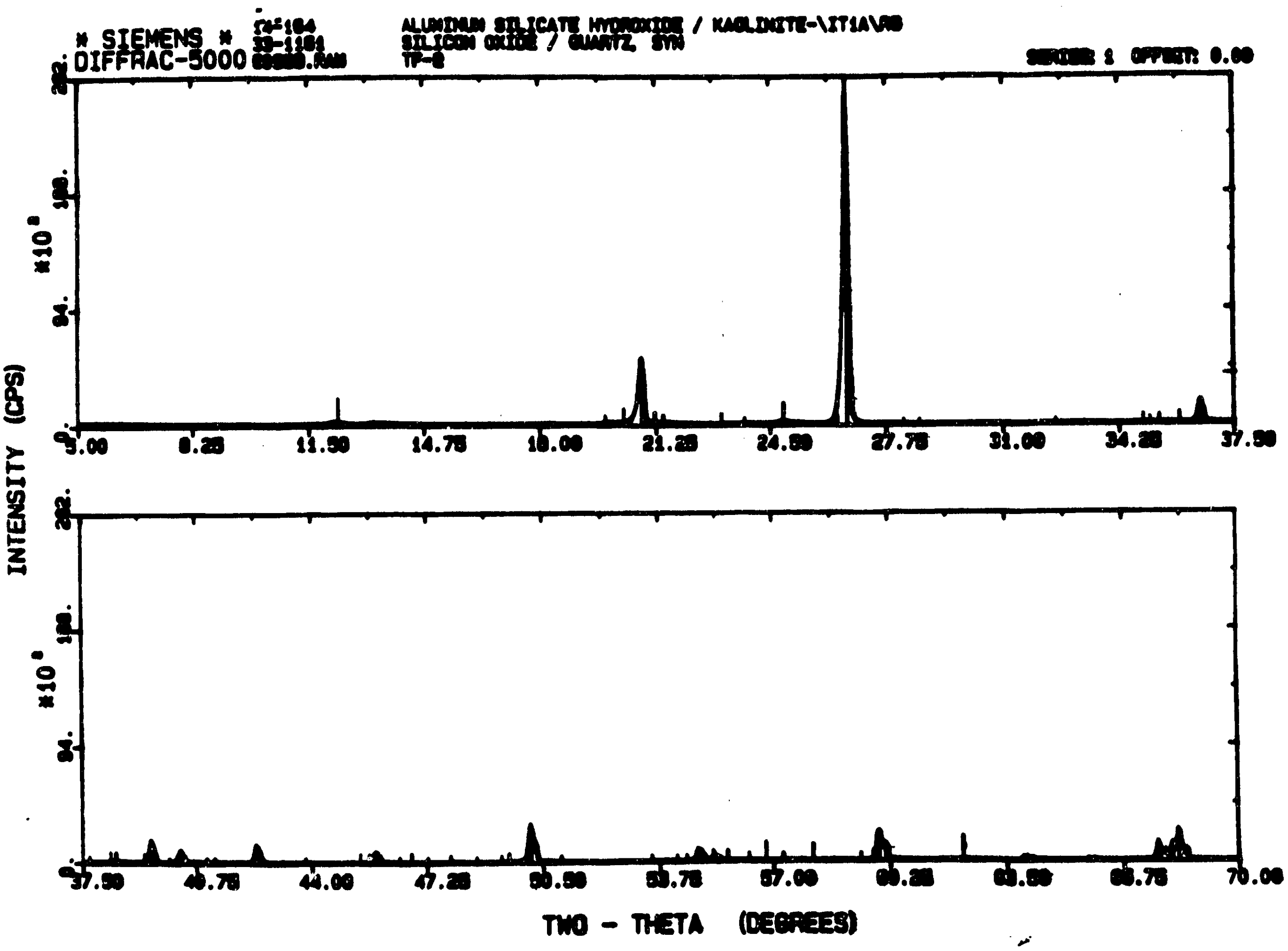
APPENDIX 1

X-RAY SPECTRA FOR FOUR SRS SOILS

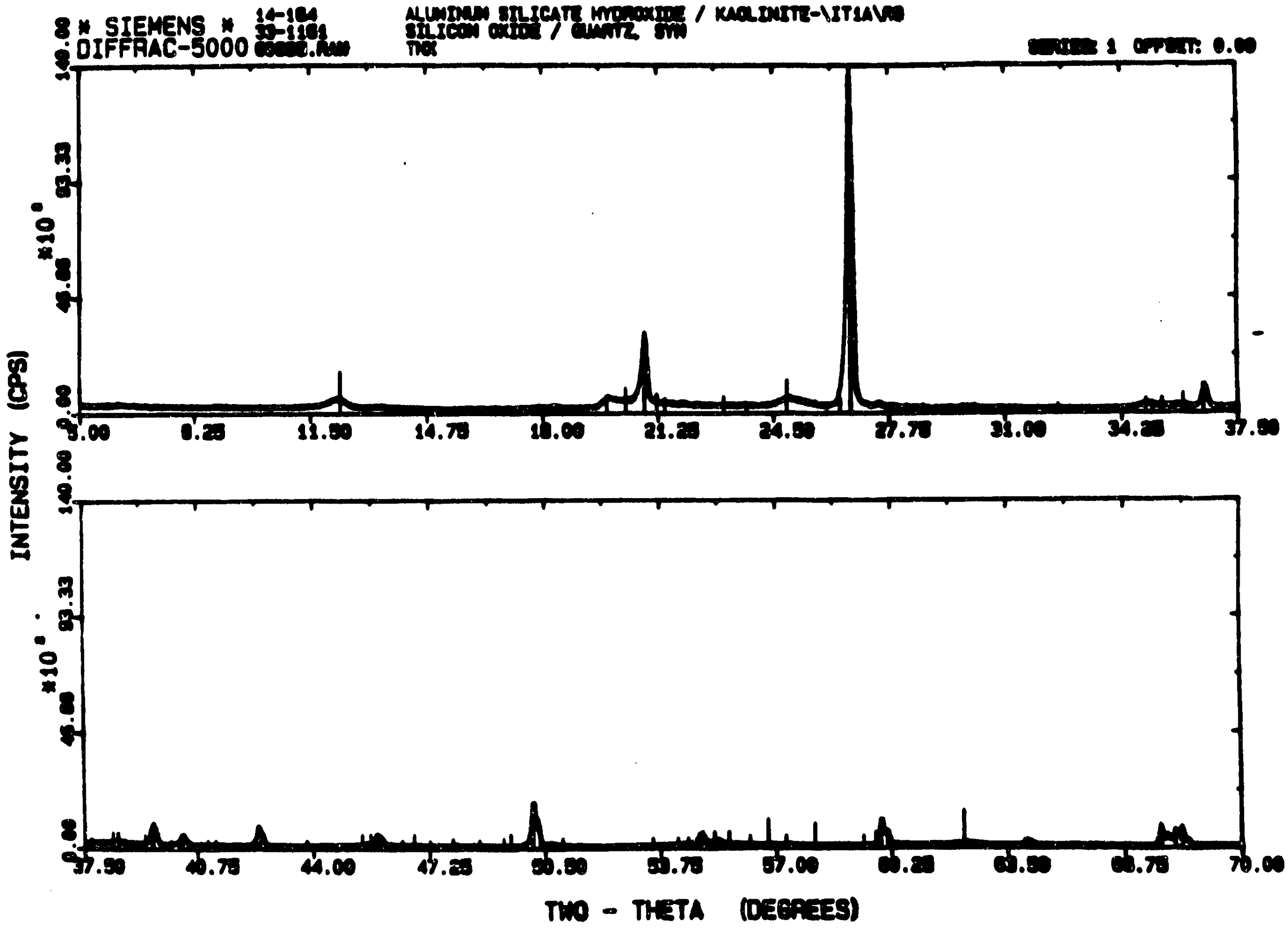
SPECTRUM FOR TF1 SOIL



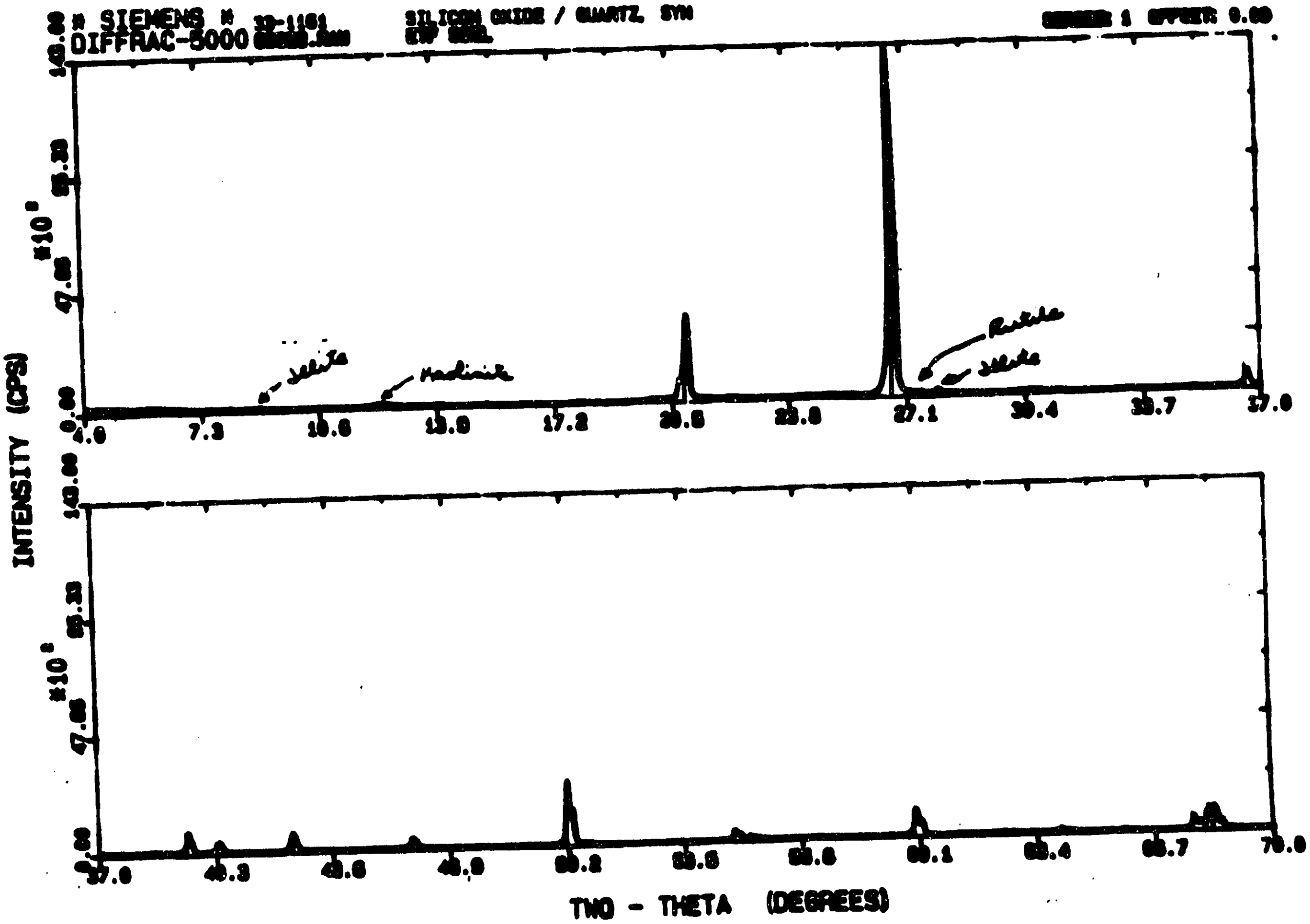
SPECTRUM FOR TF2 SOIL



SPECTRUM FOR TNX SOIL



SPECTRUM FOR ETF SOIL



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SPECTRUM FOR ETF SOIL