

Cementitious Stabilization of Chromium, Arsenic, and Selenium in a Cooling Tower Sludge

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INTRODUCTION

The U.S. Department of Energy Oak Ridge Operations Office has signed a Federal Facility Compliance Agreement (FFCA) with the U.S. Environmental Protection Agency Region IV regarding Oak Ridge Reservation (ORR) mixed (radioactive and hazardous) wastes that are subject to the land disposal restrictions (LDR) of the Resource Conservation and Recovery Act (RCRA). The FFCA establishes an aggressive schedule for conducting studies and treatment method development under the treatability exclusion of RCRA (treatability studies) for those mixed wastes for which treatment methods and capabilities have yet to be defined. One of these wastes is a radioactive cooling tower sludge with the waste codes D004 (arsenic), D005 (barium), D007 (chromium), D008 (lead), and D010 (selenium). This paper presents some results of a treatability study of the stabilization of this cooling tower sludge in cementitious waste forms.

The sample of the cooling tower sludge obtained for this study was found to be not characteristically hazardous [see the toxicity characteristic leach procedure (TCLP) results for the unspiked sludge in the results section] in regard to arsenic, barium, chromium, lead, and selenium, despite the waste codes associated with this waste. However, the scope of this study included spiking three RCRA metals to two orders of magnitude above the initial concentration to test the limits of cementitious stabilization. Since the sample appeared to contain little of the RCRA metals that was extractable, the decision was made to spike the sludge to an initial level and then at two more levels, each an order of magnitude above the preceding level. Based on prior characterization data of the cooling tower sludge, the metals selected for spiking were chromium, arsenic, and selenium. Chromium and arsenic were spiked at concentrations of 200, 2,000, and 20,000 mg/kg, and selenium was spiked at 100, 1,000, and 10,000 mg/kg (concentrations based on the metal in the sludge solids).

The stabilization of arsenic, chromium, and selenium, as well as other metals, can be achieved with grout.¹ The stabilization of inorganic arsenic can be achieved, even at high concentrations. Stabilization of arsenic concentrations as high as 20,000 mg/kg in arsenic sludge has been reported using Portland cement.² However, "very high levels" can be troublesome.¹ Specifically, arsenic sulfide species are soluble under high pH conditions, unlike other metal sulfides with solubilities that are usually much lower than those of the corresponding metal hydroxides. Hence, this behavior for arsenic could make ground granulated blast furnace slag (referred to hereafter as slag) an undesirable stabilizing agent for arsenic because the iron sulfide in slag can supply the problematic sulfide species. On the other hand, the use of iron salts is promising in the stabilization of arsenic,¹ so slag may be an ideal stabilizing agent if the detrimental role of iron sulfide can be controlled.

Chromium stabilization usually involves the reduction of the hexavalent state to the trivalent state and the precipitation of the chromium(III) hydroxide. The implication of this approach is that a straightforward high-pH stabilization, such as that provided by Portland cement alone, may not succeed. Stabilization of chromium concentrations as high as 16,300 mg/kg in electroplating sludge has been reported using lime-sulfide.^{3,4} Furthermore, whereas potassium silicate can stabilize similar chromium concentrations in wood-preserving waste, cement-silicate and Portland cement do not.¹ Consequently, high slag compositions were tested in the present study in order to take advantage of the reducing potential of the slag.

Selenium is rarely found in industrial wastes, it does not leach above the RCRA limit of 1 mg/L, and it

usually does not detectably leach from most cementitiously stabilized wastes. Stabilization of selenium concentrations as high as 1275 mg/kg in a mix of wastes has been reported using cement-fly ash.⁵

Based on the preceding considerations, Portland cement, Class F fly ash, and slag were selected as stabilizing agents in the present study. Perlite, a fine, porous volcanic rock commonly used as a filter aid, was used as a water-sorptive agent in this study in order to control bleed water for high water contents. The highly porous perlite dust absorbs large amounts of water by capillary action and does not present the handling and processing problems exhibited by clays used for bleed water control.

EXPERIMENTAL

The study scope included controlling the sludge water content and varying this water content over a wide range. For this reason, the cooling tower sludge was first oven dried at 105°C. The dried sludge was then sieved through 4.75-mm sieve openings and homogenized to provide the feed sludge solids for the experimental design (see Table 1). Homogeneity was tested by standard total analysis (EPA Method 3051) of a marker element (chromium) in five subsamples of the dried-sieved homogenized sludge. The percentage relative standard deviation (% RSD, i.e., standard deviation divided by the mean times 100) for chromium was 12%.

Grout Preparation

The grout preparation consisted of first mixing the sludge solids with water and the spike compounds and then mixing with the stabilizing agents. The treated sludge (grout) was cured in a humid environment at room temperature for 28 d to make the cementitious waste form. The spiking procedure consisted of mixing the spike compounds with some of the water overnight, adding this slurry to the sludge solids, rinsing the slurry container with the remainder of the water and adding this rinsate to the sludge solids, and mixing this concoction for 20 min with a model N-50 Hobart mixer using a wire whip on low speed. The spiked, wet sludge was then mixed with a dry blend of the stabilizing additives for 4 min in the Hobart mixer. The compounds used for spiking were $\text{Na}_2\text{Cr}_2\text{O}_7$, As_2O_3 , and SeO_2 .

The dry blend consisted of as many as four additives blended for 2 h in an 8-qt twin-shell blender (Patterson-Kelley Co.). The four dry blend additives consisted of (1) Type I-II Portland cement (cement) from the Dixie Cement Co., (2) Class F fly ash (fly ash) from the American Fly Ash Co., (3) ground granulated blast furnace slag (slag) (Blaine fineness of 6220 cm^2/g) from the Koch Minerals Co., and (4) perlite (Grade H-200) from the Harborlite Corp. The composition of each of these dry additives was varied over a wide range, and only cement was present in every dry blend. Slag is a cement substitute, but requires activation by a base. Thus, when slag was used as the main binder, a small amount of cement was also added to activate the slag. The grout compositions were chosen in a statistical design (mixture experiment), but this statistical approach is not discussed in this paper.

Modified TCLP Measurements

Both the sludge solids (unspiked and spiked at the three levels) and cementitious waste forms were extracted using a modified TCLP. The modifications to the TCLP consisted of (1) extracting a 10-g sample in 200 mL of extraction fluid; (2) size reduction to <4.75-mm particles; and (3) analysis of the extract for arsenic, selenium, and mercury by an inductively coupled argon plasma spectrometer (model ICAP 61E Trace Analyzer from Thermo Jarrell Ash). TCLP extraction fluid #2 (an aqueous solution of acetic acid at a pH of about 2.8) was required for all the TCLP extractions in this study.

Density Measurements

The bulk density of the as-received sludge and dried-sieved homogenized sludge was determined by weighing a known volume (using a graduated cylinder) of the granular sludge and calculating the bulk density. The bulk density of the cementitious waste forms was measured by packing a 2-in. cube mold with the freshly made grout, determining the net weight of the grout, and calculating the bulk density. The corresponding volumes of the as-received and dried-sieved homogenized sludge were calculated along with each grout volume. The ratio of each grout volume to the sludge volumes gives an estimate of the volume increase that can be expected from cementitious stabilization of the cooling tower sludge.

RESULTS

Table 1 lists the compositions (including the spike levels of chromium, arsenic, and selenium in the dried-sieved homogenized sludge solids) of the cementitious waste forms made from the cooling tower sludge. Table 2 lists the RCRA metal concentrations of the TCLP extracts for the dried-sieved homogenized sludge (unspiked, low spike, medium spike, and high spike). Table 3 lists the TCLP extract concentrations of the cementitious waste forms made from the cooling tower sludge according to the compositions listed in Table 1.

The TCLP performance of the grouts proved to be sensitive to the final extract pH. For example, the fraction of the spiked arsenic and selenium extracted in the TCLP test showed a definite correlation with the final extract pH, as illustrated in Figure 1. The chromium concentrations had no obvious correlation with pH. Figure 2 illustrates the ratio of the TCLP extract concentrations of chromium, arsenic, and selenium before and after treatment as a function of the final extract pH. These plots are quite similar to those of Figure 1. (The results for the untreated spiked sludges are plotted in Figure 1 along with the results for the grouts, but not in Figure 2.)

Table 4 lists two ratios for each grout composition: (1) the grout volume to the volume of the as-received sludge and (2) the grout volume to the volume of dried-sieved homogenized sludge. The measured bulk densities (standard deviations of 0.02 kg/L for both) were 0.81 and 1.07 kg/L for the as-received sludge and the dried-sieved homogenized sludge, respectively. The as-received sludge experienced a 24.9 wt% mass loss on drying, implying an initial water content of 24.9 wt% in the as-received sludge. Typically, the waste consists of the solids plus water and the volume increase over this combination would be reported. The bulk volume of this combination was not measured, and the air voids in the granular as-received and dried sludge made estimation of this volume inaccurate. Hence, the volume increases over the combination of sludge solids plus water were not obtainable. The volume ratios listed in Table 4 overestimate the volume increase for high water contents because the water volume is included in the grout and not the waste solids, but the ratios also underestimate for low water contents because of the air voids present in both the as-received and dried sludge.

DISCUSSION

The compositions of the grouts in this study were intentionally varied over a wide range, including variations from high waste loadings to low waste loadings and from high water contents to low water contents. Most of the grouts listed in Table 1 formed relatively weak waste forms. Only a few with higher binder content formed strong cementitious monoliths. The grouts with high waste loadings resulted in wet, soft products that flowed under their own weight, even after a 28-d cure. The higher

water content resulted in considerable bleed water in some grouts, but perlite did prove capable of handling high water content. In accord with these considerations, the TCLP performance of these widely varying compositions also varied widely.

One of the more important results is that many of the treated samples did meet the TCLP LDR limits for chromium, arsenic, or selenium, even at the highest spike levels. For example, Grout No. 18 (Table 1) passed the TCLP LDR for all three of these RCRA metals, even though the chromium was spiked in the sludge solids to 20,000 mg/kg. Grout Nos. 5, 7, 13, and 17 passed the TCLP LDR limit for arsenic, even though the arsenic was spiked in the sludge solids to 20,000 mg/kg. Grout Nos. 1, 5, 10, 15, and 19 passed the TCLP LDR limits for selenium, even though the selenium was spiked in the sludge solids to 10,000 mg/kg.

The untreated sludge solids, unspiked and low spike, met the TCLP LDR limits for the RCRA metals, while the medium- and high-spiked sludges greatly exceeded these limits (see Table 2). Thus, only the medium and high spiked sludges were characteristically hazardous and would have required treatment. Treatment always improved the TCLP performance, except for two grouts: Grout Nos. 2 and 14. The TCLP concentrations of arsenic and selenium were higher for these two grouts than for the untreated sludge spiked to the corresponding level of the RCRA metals (see the two points above 0.0 in Figure 2). These two grouts performed similarly because Grout No. 14 was a true replicate of Grout No. 2. This particular grout composition had a high sludge solids loading, which helps explain its poor TCLP performance but does not explain why the treated sludge performed worse in the TCLP test than did the untreated sludge. In general, the TCLP performance for arsenic and selenium improved (that is, the extract concentration decreased) with increasing extract pH (see Figures 1 and 2). The chromium results were more scattered, relative to the extract pH. Except for Grout No. 17, the low TCLP extract concentrations of chromium (<0.1 mg/L) were for grouts that used slag, rather than cement, as the main binder (Grout Nos. 1, 3, 6, 10, 14, and 20). This is consistent with the approach of using the reduction potential of slag to reduce the chromium to a more insoluble valence state [the sludge was spiked with chromium(VI), that is, a chromate].

The observed TCLP behavior may be explained thermodynamically by the speciation of the RCRA metals with pH. The solid RCRA metal compound may be speciating into two or more species in solution, whose concentration depends on the equilibrium pH. Even the behavior of the chromium may be amenable to such an analysis, though the chromium behavior may be complicated by the reduction potential of the waste form and the possible valence conversion of the chromium.

The volume of the final waste form is important because the space available for land disposal at permitted facilities is scarce. A major expense of waste disposal is the lifetime costs associated with permitted land disposal, which are based on waste volume. The true volume increase for each grout could not be estimated because the bulk density of the wet sludge (sludge solids plus water) was not measured. Only the bulk density of the as-received sludge and dried-sieved homogenized sludge was estimated. Thus, the volume increase over these two initial states were estimated and listed in Table 4, but the limitations of these listed volume ratios must be recognized and used with care.

The as-received cooling tower sludge had a relatively low water content (24.9 wt%) for a sludge. The bulk densities of both the as-received and the dried sludge incorporated numerous air voids. The scope of this study included exploring stabilization of a wide range of sludge water contents. Hence, the effect

of water on the bulk density of the sludge was not measured; however, the volume of the sludge initially decreases as the air voids are filled and the dry sludge absorbs water and collapses. Then, the volume increases as more water is added. These sludge volume fluctuations are not taken into account using the two fixed bulk densities for the estimated ratios listed in Table 4. For this reason, volume decreases from the as-received sludge are implied for Grout No. 2 and for its true replicate Grout No. 14, high-sludge solids and low-water grouts. Although these are low-water grouts (see Table 1), they contained more water than would have come from the as-received sludge (33.2 wt% water in the sludge solids plus water as compared with the 24.9 wt% water in the as-received sludge). Apparently, this wet sludge had fewer air voids and a higher bulk density than the as-received sludge. Although the reported ratios are a true reflection of the actual volumes of the grout and as-received sludge, a wet sludge with this water content (33.2 wt%) would most likely experience a volume increase when stabilized into a grout. Since the sludge made up 89.8 wt% (sludge solids plus water) of this grout, the volume increase would be small, perhaps less than 10 vol%.

By the same token, the high ratios listed in Table 4 ignore the volume contribution of the large amounts of water in the initial sludge. The ratios for the dried sludge are accurate if the sludge is dried prior to stabilization. However, if the sludge is not dried prior to stabilization, then only enough water would be added to properly process the sludge, not the large amounts of water tested in some of the grouts listed in Table 1. In view of the fact that the water content can vary considerably in wastes, a wide range of sludge water contents was considered in the present study. A considerable volume increase can be expected for those grouts with a waste (sludge solids plus water) loading less than 40 wt%, but not as much as Table 4 implies with the volume contribution of the water in the initial waste ignored. The waste loadings in Table 1 of about 40 wt% may have grout-to-waste volume ratios of less than 3.0, with higher waste loadings having smaller ratios.

CONCLUSIONS

The most significant finding was that cementitious waste forms can stabilize chromium, arsenic, or selenium to meet TCLP LDR limits, even at concentrations as high as 20,000, 20,000, and 10,000 mg/kg, respectively. The final extract pH proved to be a good predictor of the TCLP performance for arsenic and selenium, relative to the concentration of these two RCRA metals in the sample. While arsenic and selenium can be stabilized by pH control, chromate can be stabilized by using ground granulated blast furnace slag. The correct blend of cement, slag, fly ash, and perlite can stabilize this cooling tower sludge for a wide range of water contents and concentrations of chromium, arsenic, and selenium. The free water can be controlled, even if the sludge contains high levels of water. Chromium, arsenic, and selenium can be stabilized, even if the final waste form is relatively weak physically; however, a physically stronger waste form can be produced, if desired, by adding more binder to increase the volume of the final waste form. Therefore, once the composition required to stabilize the RCRA metals is determined, choosing how much blend to use in treating a given waste means balancing the physical strength desired against the volume increase allowed.

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Table 1. Composition of the cementitious waste forms for the cooling tower sludge.

Grout No.	Spike Concentration in Waste Solids (mg/kg)			Mass Fraction in Waste Form					
	Chromium	Arsenic	Selenium	Waste Solids	Water	Cement	Fly Ash	Slag	Perlite
1	200	20,000	10,000	0.100	0.583	0.029	0.000	0.288	0.000
2	200	2,000	10,000	0.600	0.298	0.009	0.000	0.093	0.000
3	200	200	1,000	0.100	0.574	0.009	0.000	0.091	0.226
4	20,000	2,000	10,000	0.100	0.583	0.115	0.000	0.000	0.202
5	200	20,000	10,000	0.100	0.286	0.112	0.503	0.000	0.000
6	2,000	2,000	1,000	0.100	0.286	0.111	0.000	0.503	0.000
7	20,000	20,000	1,000	0.100	0.583	0.317	0.000	0.000	0.000
8	2,000	200	1,000	0.324	0.576	0.044	0.000	0.056	0.000
9	20,000	20,000	1,000	0.600	0.286	0.087	0.012	0.014	0.000
10	2,000	20,000	10,000	0.100	0.286	0.009	0.514	0.091	0.000
11	2,000	200	100	0.100	0.414	0.100	0.386	0.000	0.000
12	2,000	2,000	1,000	0.302	0.422	0.092	0.068	0.076	0.041
13	20,000	20,000	1,000	0.100	0.583	0.317	0.000	0.000	0.000
14	200	2,000	10,000	0.600	0.298	0.009	0.000	0.093	0.000
15	2,000	200	10,000	0.100	0.286	0.614	0.000	0.000	0.000
16	2,000	2,000	100	0.317	0.583	0.100	0.000	0.000	0.000
17	200	20,000	100	0.100	0.286	0.614	0.000	0.000	0.000
18	20,000	200	100	0.100	0.286	0.056	0.000	0.558	0.000
19	2,000	200	10,000	0.100	0.286	0.614	0.000	0.000	0.000
20	2,000	20,000	100	0.173	0.533	0.009	0.000	0.091	0.194

Table 2. TCLP extract concentrations for the dried-sieved homogenized cooling tower sludge, mg/L.

Analyte	Unspiked	Low Spike ¹	Medium Spike ²	High Spike ³	TCLP LDR Limits
Arsenic	0.2	2.83	30.4	210	5
Chromium	0.3	1.43	31.6	400	5
Selenium	<0.05	2.65	13.2	70.8	5.7
Silver	<0.03	<0.003	<0.003	<0.003	5
Barium	4.1	1.19	1.47	0.721	100
Cadmium	<0.02	0.004	0.003	<0.002	1
Mercury	<0.10	<0.011	<0.011	<0.011	0.2
Lead	<0.05	0.007	0.008	<0.006	5
Extract pH	N/A ⁴	5.36	5.55	5.46	

¹Values of 200, 200, and 100 mg/kg, respectively, of arsenic, chromium, and selenium in dried-sieved homogenized sludge.

²Values of 2,000, 2,000, and 1,000 mg/kg, respectively, of arsenic, chromium, and selenium in dried-sieved homogenized sludge.

³Values of 20,000, 20,000, and 10,000 mg/kg, respectively, of arsenic, chromium, and selenium in dried-sieved homogenized sludge.

⁴Not applicable. Filter was rinsed with acid prior to filtering extract, biasing the pH measurement.

Table 3. Concentrations in the TCLP extract of the cementitious waste forms, mg/L.

Grout No.	Chromium	Arsenic	Selenium	Extract pH
1	0.003	18.5	3.4	9.39
2	0.104	43	216	6.6
3	0.084	0.617	0.364	6.85
4	83.1	0.458	8.97	7.88
5	0.14	0.608	1.17	8.3
6	0.008	0.022	0.275	11.02
7	7.47	0.012	0.026	12.36
8	8.8	1.48	1.33	6.73
9	290	48.9	3.11	6.81
10	0.042	67.8	0.998	6.61
11	6.04	0.127	0.16	8.57
12	3.53	3.64	0.32	8.72
13	7.68	0.224	0.083	11.88
14	0.063	38.9	185	6.96
15	0.448	<0.006	0.305	11.93
16	10.1	8.03	0.25	8.11
17	0.032	0.031	0.011	11.8
18	0.121	0.02	0.053	9.35
19	0.344	<0.006	0.307	12.06
20	0.062	101	0.215	6.42
TCLP LDR limit	5	5	5.7	

Table 4. Ratio of the bulk volume of each grout to the bulk volumes of the cooling tower sludge.

Grout No.	Grout Volume/Sludge Volume	
	As-Received	Dried
1	4.67	8.18
2	0.63	1.10
3	4.81	8.43
4	4.85	8.50
5	3.60	6.30
6	3.45	6.05
7	4.67	8.18
8	1.42	2.48
9	0.61	1.07
10	3.82	6.69
11	4.25	7.44
12	1.36	2.38
13	4.74	8.30
14	0.69	1.21
15	3.30	5.79
16	1.58	2.77
17	2.83	4.96
18	3.43	6.02
19	3.30	5.79
20	2.68	4.69

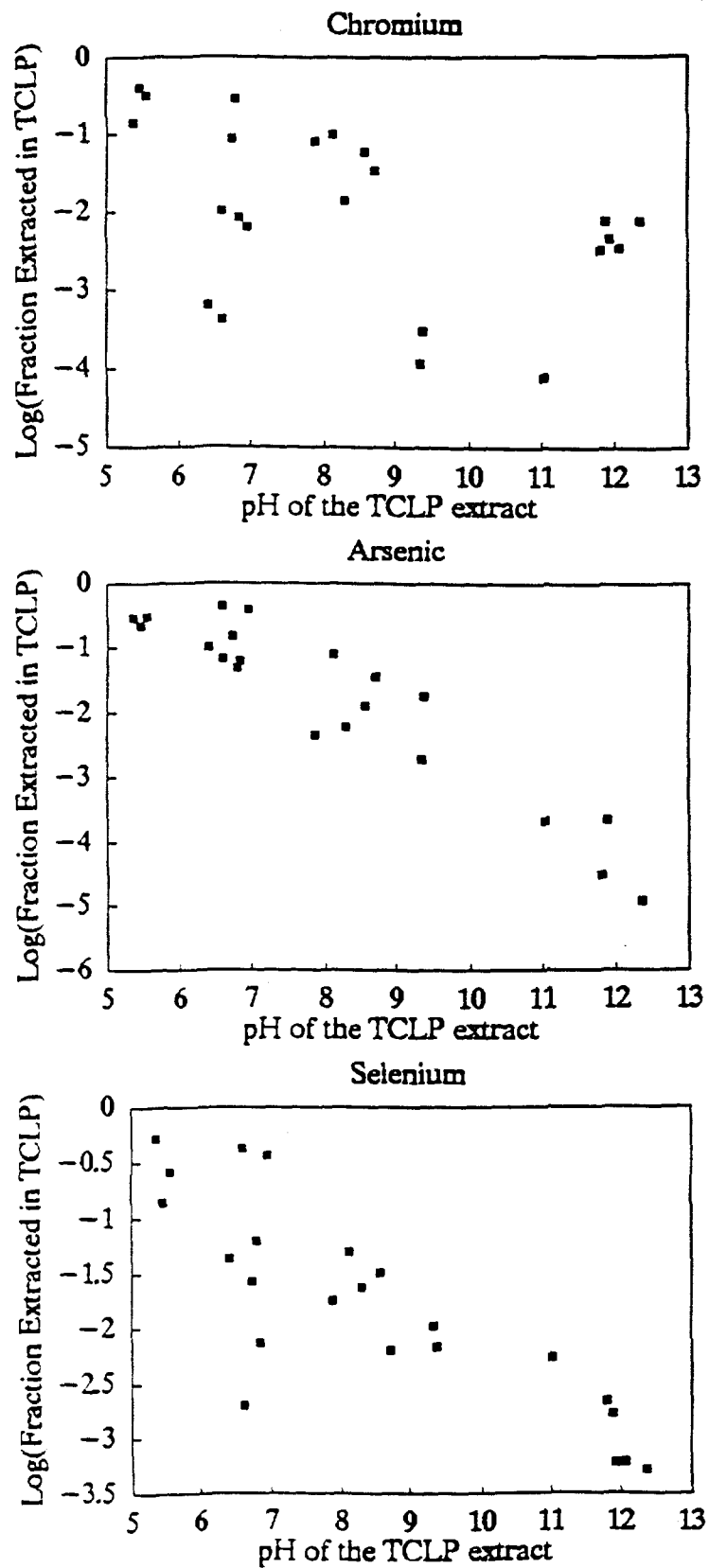


Figure 1. The logarithm of the fraction of chromium, arsenic, and selenium extracted in the TCLP versus the final extract pH.

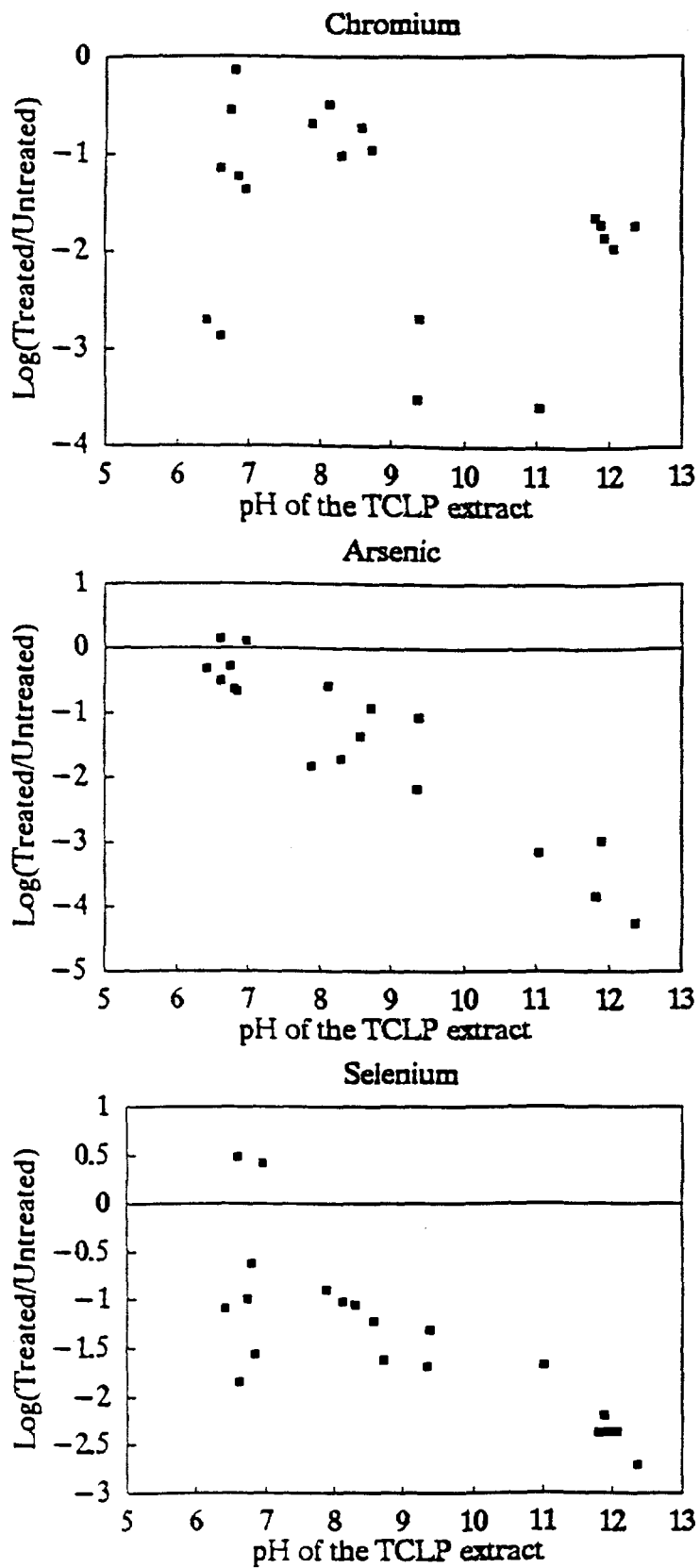


Figure 2. The logarithm of the ratio of the TCLP extract concentrations of chromium, arsenic, and selenium for the treated sludges (grouts) to the untreated sludges versus the final extract pH.