DRAFT

Stabilization of Barium in Cañon de Valle Soils by Sulfate Amendments (draft of a treatability study report)

Maureen McGraw
EES-6, LANL

Los Alamos, New Mexico
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INTRODUCTION

During the 2002 calendar year a treatability notification was submitted to the New Mexico Environment Department on June 3, 2002 to study the effectiveness of aqueous sodium sulfate (Na_2SO_4) solutions at reducing barium solubility in soils and sediments from TA-16. The soils to be treated are from the alluvial system in Canon de Valle, including surface, subsurface, and overbank sediment samples. The soils are contaminated with barium derived from the outfall and drainage of the high explosives machining building in TA-16. Barium is the most abundant inorganic contaminant of potential concern in sediments, with bulk concentrations ranging up to 40,300 mg/kg (LA-UR-98-3918).

Remediation options for contaminated soils from the TA-16-260 outfall are being evaluated. Excavation would require removal of thousands of cubic yards of material, and is not considered the optimum treatment solution. One treatment method being evaluated is stabilization of barium through a reduction in solubility by chemical treatment of barium solid phase species to minerals with low solubility that will not be mobile in surface water run off or in the alluvial aquifer, such as barite and witherite. In evaluating sulfate compounds, it was determined that Na_2SO_4 was optimal because of potential regulatory concerns regarding supernatant chemistry and reaction kinetics for the other forms. For example, ammonium sulfate ($(NH_4)_2SO_4$) may cause ammonia or nitrate problems in the supernatant and both $(NH_4)_2SO_4$ and $CaSO_4$ convert witherite to barite more slowly than Na_2SO_4. The treatment technique being evaluated in this study is the initial step necessary to determine if Na_2SO_4 could be used in-situ to reduce the solubility of Ba. The results from the laboratory scale treatability study will then be used to evaluate the feasibility of the technique on the field scale.

EXPERIMENT

Description of Soil Samples

The soils to be treated are from the alluvial system in Canon de Valle, and are listed in Table 1. The geomorphic units listed in the table are the standard nomenclature used for canyon investigations by the ER project and described in ER-SOP-03.08, R1 (pg 6). The c2 unit corresponds to the youngest abandoned post 1942 channel, and the f1 unit corresponds to floodplain areas affected by post 1942 floods, but that are not part of the main channel. The soils used for this study are contaminated with barium released from the 260 outfall at the high explosives machining building in TA-16 in the form of $Ba(NO_3)_2$, which was a component of explosive processing.

Table 1: Description of Soil Samples Used in Treatability Study

Sample Name	Distance from 260 Outfall (m)	Depth of Sample (cm)	Unit
CDV-2W-16	25	0 -7	c2
CDV-2W-12	165	0 - 20	f1
CDV-2W-9	287	13 - 22	f1
CDV-2W-10	300	0 - 18	c2

Batch Experiment

Batch studies will be used to examine the effectiveness of Na_2SO_4 on reducing barium solubility. The variables for the experiment will include the soil samples (collected from different locations), soil to solution ratios, length of treatment, and Na_2SO_4 concentration. The steps of the batch experiments are: i) sieve and homogenize sample through 8 mm sieve, ii) place sample into a beaker with the Na_2SO_4 solution, iii) shake the sample for the specified time, iv) allow the sample to sit for 10 minutes, v) centrifuge sample to separate the soil and fluid, vi) pressure filter the fluid to remove particulates and include filter with the soil sample, vii) discard supernatant, and viii) dry soil sample for Toxicity Characteristic Leaching Procedure (TCLP) analysis. The treatment of the soils was done at Los Alamos National Laboratory (LANL). Both General Engineering Laboratory, Inc. (GEL) out of South Carolina and LANL did some TCLP analysis for various samples. Of the samples analyzed by the external laboratory, four of the samples were replicates of samples that were also run at LANL and four were controls (untreated samples) used to evaluate the effectiveness of the treatment for all samples. Table 2, shows the matrix of experiments conducted, including who conducted the TCLP analysis.

Table 2: Experimental matrix of batch studies conducted for reduction in barium solubility

Ionic Strength	time (hr)	fluid:rock ratio	Soil CDV-2W-#	TCLP Analysis
No Treatment			16, 12, 9, 10	External
0.01 M	0.25	10:01	16, 10	LANL
	0.5	10:01	16, 10	LANL
	1	10:01	16, 12, 9, 10	External
	6	10:01	16, 10	LANL
	24	10:01	16, 12, 9, 10	LANL, External
	1	02:01	16, 10	LANL
	1	05:01	16, 10	LANL
	1	15:01	16, 10	LANL
	1	20:01	16, 12, 9, 10	LANL, External
	24	20:01	16, 12, 9, 10	External
0.10 M	0.25	10:01	16, 10	LANL
	0.5	10:01	16, 10	LANL
	6	10:01	16, 10	LANL
	24	10:01	16, 10	LANL

RESULTS

This treatability study examined the effect of contact time, initial soil concentration, ionic strength, and solution to soil ratio on leachable barium after soil treatment. The results for each soil type are shown in Tables 3 to 5, and differentiate who conducted the TCLP analysis. The percent reduction in barium concentration was based on the TCLP analysis done by the external laboratory on untreated samples. Tables 3 and 6 each contain two samples that were analyzed by both laboratories. In comparing the results for these samples, the difference between the results are 2-6% for Table 3 and <1% for Table 6. These numbers are reasonable variations given the heterogeneity of the soils and experimental error, so all the data will be used in the analysis of the effectiveness of the treatment which be evaluated for each of the variables considered.

Table 3: TCLP results for CDV2W-16

Ionic Strength	time (hr)	fluid:rock ratio	LANL TCLP Analysis (mg/l)	Percent Reduction	External TCLP Analysis (mg/l)	Percent Reduction
No Treatment			-	-	365	-
0.01 M	0.25	10:01	176	51.8%	-	-
	0.5	10:01	185	49.2%	-	-
	1	10:01	-	-	165	54.8%
	6	10:01	129	64.6%	-	-
	24	10:01	128	64.9%	141	61.4%
	1	02:01	293	19.7%	-	-
	1	05:01	242	33.7%	-	-
	1	15:01	152	58.4%	-	-
	1	20:01	113	69.0%	119	67.4%
	24	20:01	-	-	70.7	80.6%
0.10 M	0.25	10:01	0.65	99.8%	-	-
	0.5	10:01	0.88	99.8%	-	-
	6	10:01	0.59	99.8%	-	-
	24	10:01	0.42	99.9%	-	-

Table 4: TCLP results for CDV2W-12

Ionic Strength	time (hr)	fluid:rock ratio	External TCLP Analysis (mg/l)	Percent Reduction
No Treatment			116	-
0.01 M	1	10:01	98.8	14.8%
	24	10:01	66.4	42.8%
	1	20:01	95.9	17.3%
	24	20:01	70.0	39.7%

Table 5: TCLP results for CDV2W-9

Ionic Strength	time (hr)	fluid:rock ratio	External TCLP Analysis (mg/l)	Percent Reduction
No Treatment			597	-
0.01 M	1	10:01	351	41.2%
	24	10:01	267	55.3%
	1	20:01	323	45.9%
	24	20:01	124	79.2%

Table 6: TCLP results for CDV2W-10

Ionic Strength	time (hr)	fluid:rock ratio	LANL TCLP Analysis (mg/l)	Percent Reduction	External TCLP Analysis (mg/l)	Percent Reduction
No Treatment			-	-	58.5	-
0.01 M	0.25	10:01	4.05	93.1%	-	-
	0.5	10:01	5.95	89.8%	-	-
	1	10:01	-	-	3.4	94.2%
	6	10:01	4.14	92.9%	-	-
	24	10:01	1.85	96.8%	1.98	96.6%
	1	02:01	23.4	60.0%	-	-
	1	05:01	12.5	78.6%	-	-
	1	15:01	3.25	94.4%	-	-
	1	20:01	3.26	94.4%	3.38	94.2%
	24	20:01	-	-	2.49	95.7%
0.10 M	0.25	10:01	0.84	98.6%	-	-
	0.5	10:01	0.96	98.4%	-	-
	6	10:01	0.90	95.5%	-	-
	24	10:01	0.63	98.9%	-	-

<u>Effect of Contact Time</u>

Figure 1 shows a histogram of the reduction in barium leachability for the four different soil samples at a solution to soil ratio of 10:1. The duplicates at 24 hours reflect the samples analyzed internally and externally. The figure indicates that a longer contact time between the soil and Na_2SO_4 solution helps improve the reduction in barium leachability. It is interesting to note that the percent reduction in barium leachability is different for the four soils tested. In addition, the degree improvement based on contact time is also variable.

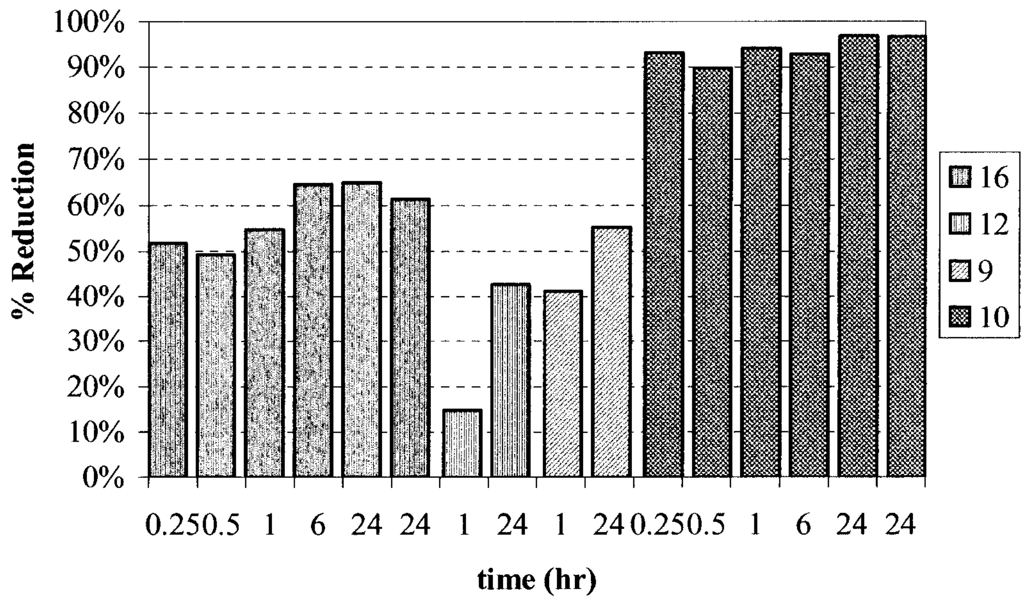

Figure 1: Percent reduction in Ba leachability for experiments with a 10:1 solution to soil ratio at different times

Effect of Initial Soil Concentration

Since the percent reduction in barium leachability varies between soil types, the question was whether it was a function of initial concentration. Figure 2 shows a plot of the 1 and 24 hour results at a solution to soil ratio of 1:10. For samples 10, 16, and 9 as the initial concentration in the soil increases the effective of the treatment decreases. For sample 12, the initial concentration does not seem to affect the effectiveness of the treatment. This is likely due to the barium speciation for the samples.

Barite ($BaSO_4$) is less soluble than whitherite ($BaCO_3$), and sorbed species can readily be released from the surface of the soil samples. So a sample that starts off with a higher barite concentration will not be as reactive as a sample with whitherite or sorbed barium. Table 7 shows XRF results for total barium for the samples treated. This data indicates that sample 12 has the highest total barium concentration, despite the relatively low TCLP value. This strongly suggests that the barium in this sample is already in a reduced state, which would explain why the barium leachability was not further reduced by treatment. In contrast, sample 9 has the lowest barium of the four samples, and has the highest leachability. This indicates that the barium in this sample is in a more soluble form. Therefore, although the initial concentration of barium in the soil does affect the effectiveness of the treatment, the speciation of the barium is also an important variable that can affect the results.

Table 7: Total XRF Barium

Sample Name	Total XRF Barium
CDV-2W-16	7910
CDV-2W-12	20900
CDV-2W-9	1860
CDV-2W-10	5210

*Data from Jerden, 2000.

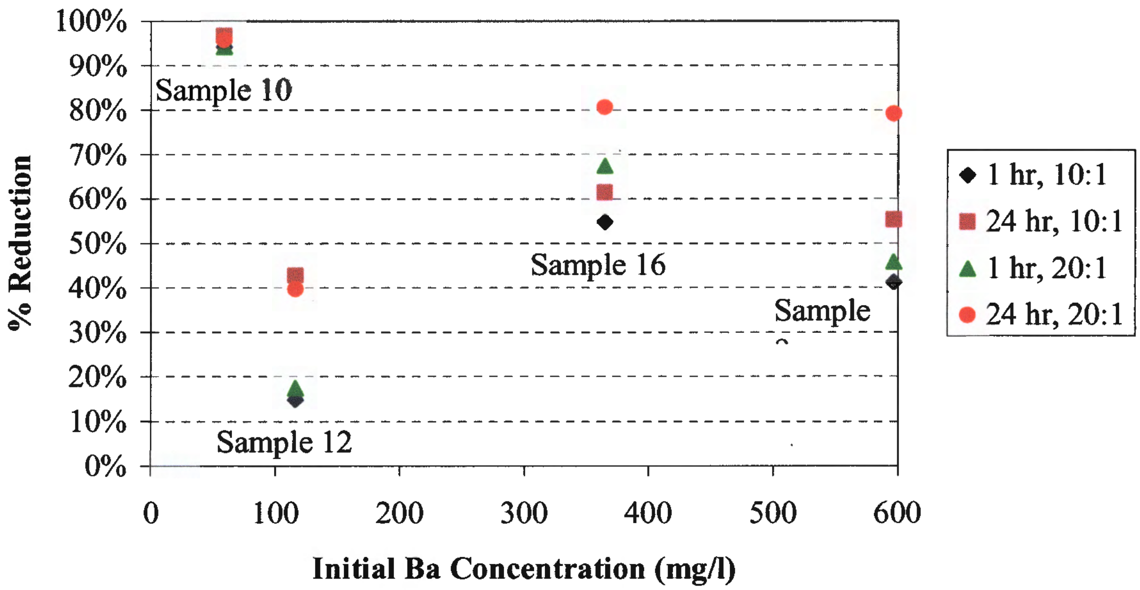

Figure 2: Effect of initial soil concentration on percent reduction in Ba leachability

<u>Effect of Ionic Strength</u>

A third variable considered in the experiments was the effect of ionic strength on treatment. Figure 3 shows the experimental results for variations in the ionic strength of the solution. For sample 10, there is improvement for the 0.10 M Na_2SO_4 solution over the 0.01 M solution, but given the low initial leachability the affect is small. For sample 16, the percent reduction in barium leachability increased from 35 - 50%, with the increase in ionic strength. This is a significant improvement. These results indicate that if feasible treating with a higher ionic strength improves the results.

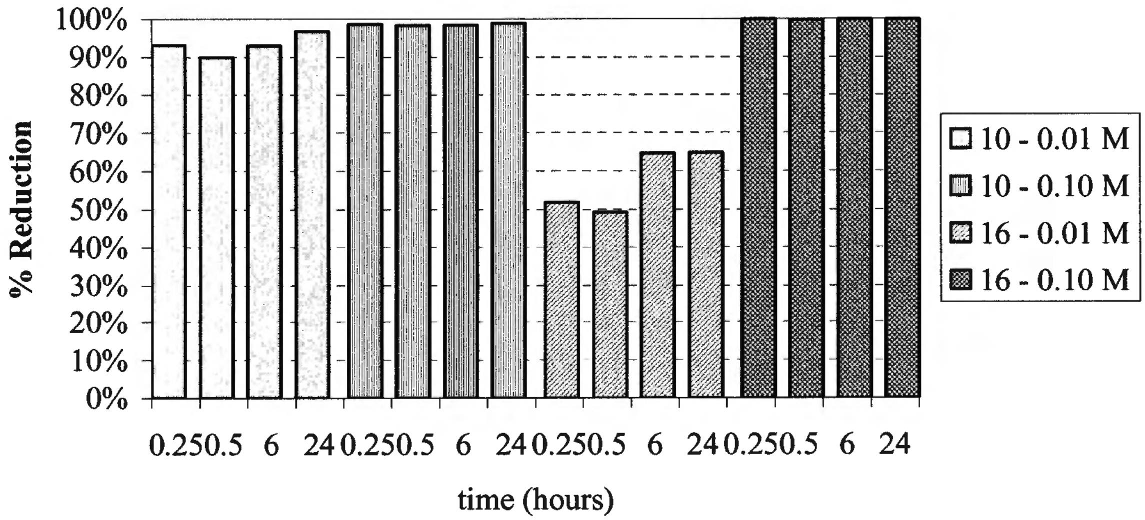

Figure 3: Percent reduction in Ba leachability for experiments with a 10:1 solution to soil ratio at different ionic strengths

<u>Effect of Solution to Soil Ratio</u>

The final variable considered was the solution to soil ratio. Figure 4 shows the results as a function of soil to solution ratio. For all four soils, increasing the solution to soil ratio improved the percent reduction in barium leachability. Therefore, higher ratios will improve the reduction in barium leachability.

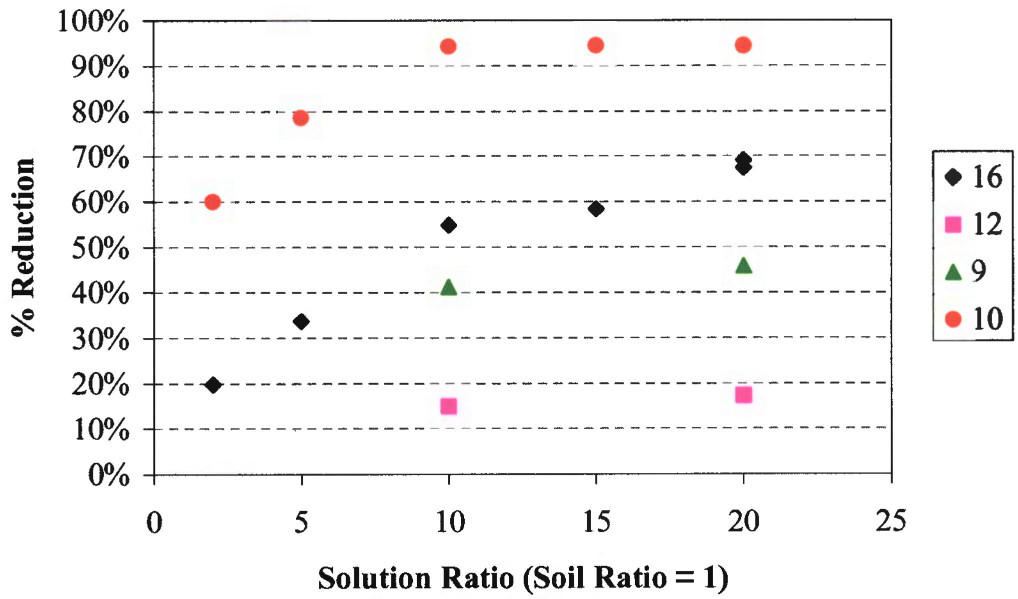

Figure 4: Effect of solution to soil ratio on percent reduction in Ba leachability

CONCLUSION

This treatability study indicates that Na_2SO_4 solution is an effective batch treatment technique for reducing the leachability of barium in the Canyon de Valle soils examined. Additional information about the species of barium in the soils and the soil mineralogy could provide additional insight into the mechanism affecting the reduction in barium leachability. Based on this study, treatment of the soil at higher ionic strength, higher solution to soil ratios, and longer contact times help to decrease the soil leachability.