

US EPA ARCHIVE DOCUMENT

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October 9, 1996

Via Hand Delivery

Ms. Anita Cummings
Office of Solid Waste (5303W)
U.S. Environmental Protection Agency
401 M Street S.W.
Washington, D.C. 20460

Re Requested Sample Influent/Effluent Data on Chemical
Slag Stabilization at Secondary Smelters

Dear Ms. Cummings:

Appended are the requested TCLP data results from six sets of influent (untreated) and effluent (treated) slag samples taken at GNB's Frisco, Texas secondary smelter. Three sample sets (three influent, three effluent) were taken on September 13, 1996, followed by three more on September 16, 1996. All six sample sets were analyzed using EPA's SW-846 test methodology, with appropriate quality controls.

The assay and TCLP numbers shown here represent the lead, selenium, and other metals present in the six slag sample sets both before (influent) and after (effluent) chemical stabilization treatment was performed. The influent samples were taken of crushed solidified slag just before the slag was chemically stabilized (i.e., after removal from the blast furnace, solidification into button molds, and crushing in preparation for stabilization); a total assay and TCLP were performed on these influent samples. The subsequent chemical stabilization process mixes the crushed slag with cement, phosphate chemicals, and water. The effluent samples were taken of the resultant slag slurry mix. The samples were cured prior to performing the TCLP.

Nonetheless, the "before" samples do not directly match the "after" samples. Crushing and mixing are separate steps in the treatment process. Crushed material is placed into a surge hopper, from which it is fed over the course of an eight-hour shift into

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the mixing equipment. Some portions of the crushed material may be fed into the mixer soon after they are crushed; other portions may not reach the mixer for hours. There is no way to predict or control for this variability.

Furthermore, a limited number of influent samples such as these are not likely to be broadly representative of precrusher feed materials. This is due to the manner in which feed-stocks are introduced to the furnace. Specifically, the materials sampled were produced in a furnace designed to be fed using "charge boards." Input material is placed on the charge boards in layers. It is not unusual, therefore, to find in a single input slag sample a disproportionate quantity of what amounts to one layer from the charge.

Indeed, the sample set analysis presented in the appended Tables 1-3 appears to demonstrate this phenomenon. Each sample has a relatively low proportion of iron. This low level of iron is indicative of a high level of silicates. Accordingly, it is likely that the samples were taken from slag that was disproportionately impacted by a layer of sand on a charge board. If it were possible to "match" this sample to a corresponding sample of stabilized material, the high level of silicates likely would make the lead in the sample less detectable using the TCLP test.

Thus, while the Battery Council International (BCI) and Association of Battery Recyclers (ABR) have agreed to submit these samples at the request of the Agency, the Associations caution EPA that this data is grossly insufficient to support any decision regarding the appropriate treatment of D008 materials. To the contrary, this is an extremely limited set of data points derived from sampling at only one plant during a brief two day period. Accordingly, the data points, taken alone, lack the statistical significance necessary to an informed evaluation.

In contrast, BCI and ABR provided the Agency with statistically significant effluent data in comments submitted on the August 22, 1995, proposed rule. That data reflects a total of 276 samples (the attached data must be viewed in the context of this larger data set) and conclusively demonstrates that the slag treatment process used by the majority of smelters in the United States -- chemical stabilization -- results in a 2.97 mg/l TCLP lead level and 2.48 mg/l TCLP selenium level (using the 99 percentile confidence interval required by EPA's testing methodology).

TABLE 6

TOTAL ASSAY AND TCLP ANALYSIS
OF SAMPLE SET #6 TAKEN ON
SEPTEMBER 16, 1996

	Total Assay, mg/kg		TCLP, mg/l	
	Untreated Slag Duplicate Samples ¹		Untreated Slag	Treated Slag
	Sample A	Sample B		
Aluminum	6,230	6,860		
Antimony	1,410	1,280		
Arsenic	1,540	734	0.148	<0.005
Barium	699	696	11.4	2.6
Beryllium	0.5	0.5		
Cadmium	189	201	1.27	<0.005
Calcium	29,500	33,600		
Chromium	432	415	<0.02	<0.02
Cobalt	56	50		
Copper	4,330	4,140		
Iron	450,000	449,000		
Lead	47,800	48,400	393	<0.1
Magnesium	2,430	2,820		
Manganese	1,820	1,910		
Mercury			<0.002	<0.002
Molybdenum	68	75		
Nickel	667	487		
Potassium	1,700	1,840		
Selenium	276	241	0.10	0.09
Silver	<0.5	<0.5	<0.01	<0.01
Sodium	32,400	34,900		
Sulfur	75,600			
Thallium	<0.3	<0.3		
Tin	9,250	9,160		
Titanium	446	449		
Vanadium	200	206		
Zinc	2,740	3,270		

¹ Duplicate analysis were performed on the untreated sample.

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Accordingly, the principal value of the appended data is in illustrating the considerable variability characterizing the chemical composition of influent slag material. The lead content of the pre-treatment slag samples ranged from <0.1 mg/l TCLP to 393 mg/l TCLP. Pre-treatment selenium levels ranged from <0.05 mg/l TCLP to 0.13 mg/l TCLP. In just this limited sampling exercise, a number of pre-treatment slag samples passed the TCLP for lead, while others were well above the TCLP cutoff. In the case of selenium, while none of the pre-treatment samples failed the TCLP in this instance, further sampling would just as likely produce sample sets that do fail.

As explained during your visit to GNB's facility, efforts to decrease the TCLP levels of lead and selenium in post-treatment smelter slag by increasing the amount of cement added to the slurry mix have not proved successful. In fact, because of the high pH levels present in the cement, increasing the proportion of cement in the slurry mix will actually counteract the stabilization provided by the phosphate chemicals. Nor, as we explained in our comments on the proposed rule, is the industry aware of any feasible method to decrease the variability of lead and selenium levels in untreated smelter slag. Indeed, it is common to find widely variant levels of lead, selenium and other elements in even a single button of solidified slag. The fluctuating solubility of lead and selenium in slag is caused by a number of variables, such as the layering of input charges described above and the unpredictable presence and concentration of an almost infinite number of elements/substances in the slag (e.g., sulfur, sodium, etc.) -- variables that are impossible, in any practical way, to control.

Finally, although the emphasis in recent communications has been on lead, BCI and ABR want to make certain that selenium stabilization limitations not be overlooked. As with lead, the proposed LDR concentration for selenium has been established at too low a level. The aqueous chemistry of cationic or positively charged metal ions such as lead and the chemistry of cationic or negatively charged metal ions such as selenium are substantially different. A fixation chemistry which may be suitable for lead may not be as effective for selenium. An optimum fixation chemistry for lead or other cations may even increase the leachability of

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selenium.^{1/} Thus, the selection of a fixation chemistry for secondary lead slag requires a balance between the competing and different chemistries of lead and selenium.

If you have any questions about this data or our position, please contact BCI's Washington counsel, David B. Weinberg of Weinberg, Bergeson & Neuman at (202) 962-8566, or Counsel for the ABR, Robert N. Steinwurtzel of Swidler & Berlin, Chtd. at (202) 424-7830.

Sincerely,

Steve Emmons/Sem

Steve Emmons
BCI Environmental Committee Chair

Earl Cornette/SJP

Earl Cornette
Chairman, Association of
Battery Recyclers, Inc.

Attachments

^{1/} See Zingaro, Ralph A. and W. Charles Cooper, *Selenium*, Van Nostrand Reinhold Company, New York, NY (1974); Merrill, D.T., et al. (1986). *J. Water Pollut. Control Fed.* 58: 18-26; Stumm, W. *Chemistry of the Solid-Water Interface*, John Wiley: New York (1992); Bagby, E. L. "Treatment of an Anionic Metal by Adsorption." *Engineering Technologies in Hazardous Waste Management V*, 64-71.

TABLE 1

TOTAL ASSAY AND TCLP ANALYSIS
OF SAMPLE SET #1 TAKEN ON
SEPTEMBER 13, 1996

	Total Assay, mg/kg		TCLP, mg/l	
	Untreated Slag Duplicate Samples ¹		Untreated Slag	Treated Slag
	Sample A	Sample B		
Aluminum	6,970	5,960		
Antimony	723	819		
Arsenic	695	696	0.198	<0.005
Barium	687	516	10.2	2.5
Beryllium	0.6	0.5		
Cadmium	393	404	2.32	<0.005
Calcium	30,100	25,700		
Chromium	619	690	<0.02	<0.02
Cobalt	54	55		
Copper	7,330	7,250		
Iron	152,000	175,000		
Lead	42,700	44,800	374	<0.1
Magnesium	2,670	2,340		
Manganese	2,530	2,420		
Mercury			<0.002	<0.002
Molybdenum	77	70		
Nickel	669	749		
Potassium	1,790	1,590		
Selenium	464	531	0.11	<0.05
Silver	1.1	1.5	<0.01	<0.01
Sodium	34,700	32,300		
Sulfur	61,800			
Thallium	3.1	2.1		
Tin	10,100	9,810		
Titanium	606	574		
Vanadium	243	243		
Zinc	1,970	1,750		

¹ Duplicate analysis were performed on the untreated sample.

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TABLE 3

TOTAL ASSAY AND TCLP ANALYSIS
OF SAMPLE SET #3 TAKEN ON
SEPTEMBER 13, 1996

	Total Assay, mg/kg		TCLP, mg/l	
	Untreated Slag Duplicate Samples ¹		Untreated Slag	Treated Slag
	Sample A	Sample B		
Aluminum	5,920	5,750		
Antimony	848	970		
Arsenic	575	733	0.400	<0.005
Barium	904	627	24.1	3.9
Beryllium	0.5	0.4		
Cadmium	159	160	0.040	<0.005
Calcium	28,600	28,000		
Chromium	555	725	0.21	<0.02
Cobalt	42	54		
Copper	4,420	5,910		
Iron	179,000	245,000		
Lead	30,900	38,900	<0.1	<0.1
Magnesium	2,160	2,300		
Manganese	2,250	2,490		
Mercury			<0.002	<0.002
Molybdenum	68	74		
Nickel	409	545		
Potassium	1,680	1,880		
Selenium	324	386	<0.05	0.06
Silver	<0.5	<0.5	<0.01	<0.01
Sodium	38,500	37,600		
Sulfur	60,300			
Thallium	1.9	2.6		
Tin	10,800	11,500		
Titanium	535	615		
Vanadium	281	282		
Zinc	2,290	2,560		

¹ Duplicate analysis were performed on the untreated sample.

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TABLE 4
TOTAL ASSAY AND TCLP ANALYSIS
OF SAMPLE SET #4 TAKEN ON
SEPTEMBER 16, 1996

	Total Assay, mg/kg		TCLP, mg/l	
	Untreated Slag Duplicate Samples ¹		Untreated Slag	Treated Slag
	Sample A	Sample B		
Aluminum	7,890	8,180		
Antimony	634	1,090		
Arsenic	495	447	0.185	<0.005
Barium	1,220	1,850	16.9	2.4
Beryllium	0.6	0.6		
Cadmium	72.8	212	1.06	<0.005
Calcium	35,600	36,400		
Chromium	413	295	<0.02	<0.02
Cobalt	49	27		
Copper	2,460	2,220		
Iron	456,000	403,000		
Lead	28,600	48,000	282	0.8
Magnesium	2,950	3,090		
Manganese	2,100	1,980		
Mercury			<0.002	<0.002
Molybdenum	88	66		
Nickel	236	204		
Potassium	1,780	2,060		
Selenium	167	168	0.11	0.05
Silver	<0.5	<0.5	<0.01	<0.01
Sodium	81,600	88,600		
Sulfur	88,800			
Thallium	<0.8	<0.3		
Tin	6,580	6,270		
Titanium	508	485		
Vanadium	230	222		
Zinc	2,880	2,560		

¹ Duplicate analysis were performed on the untreated sample.

TABLE 5

TOTAL ASSAY AND TCLP ANALYSIS
OF SAMPLE SET #5 TAKEN ON
SEPTEMBER 16, 1996

	Total Assay, mg/kg		TCL
	Untreated Slag Duplicate Samples ¹		Untreated Slag
	Sample A	Sample B	
Aluminum	4,520	5,420	
Antimony	1,030	909	
Arsenic	1,050	517	0.159
Barium	501	579	13.4
Beryllium	0.3	0.4	
Cadmium	174	170	1.46
Calcium	24,000	25,800	
Chromium	640	557	<0.02
Cobalt	44	40	
Copper	5,240	4,980	
Iron	515,000	500,000	
Lead	39,900	36,200	215
Magnesium	1,980	2,340	
Manganese	2,000	1,920	
Mercury			<0.002
Molybdenum	58	58	
Nickel	575	476	
Potassium	1,540	1,600	
Selenium	394	359	0.13
Silver	<0.5	<0.5	<0.01
Sodium	31,800	31,900	
Sulfur	68,900		
Thallium	<0.5	<0.3	
Tin	8,260	7,780	
Titanium	445	440	
Vanadium	214	210	
Zinc	2,180	2,390	

¹ Duplicate analysis were performed on the untreated sample.

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