Immobilization of Sb(III) and Sb(V) using Steel Slag Fines

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ABSTRACT

The immobilization potential of Sb(III) and Sb(V) by freshly crushed steel slag fines (SSF) media was evaluated. The SSF media was characterized as USCS SP type soil with <5% passing the No. 200 (0.075 mm) sieve. Despite its granular nature, the mineralogy and residual lime content make the SSF media quite reactive and there is interest in potentially using SSF media in firing range back stop berms. Accordingly, the SSF media was individually spiked Sb(III) and Sb(V) solutions having target doses equivalent to 100 mg/kg to 10,000 mg/kg to gauge the ability of the SSF media to immobilize antimony, an alloy used in munitions. After 30 days of mellowing, all samples were air-dried and tested for pH, total metal concentrations, toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP) leaching performance.

INTRODUCTION

Antimony (Sb) is a naturally occurring element, and is mainly found in two oxidation states (III and V) in the environment. The toxicity of Sb depends upon its oxidation state and Sb(III) is reported to be 10 times more toxic than Sb(V) (Smichowski et al. 1998). Sb has many applications either in its pure or alloyed form in applications and products such as, semiconductor devices, lead batteries, car brake pads, ammunition and flame-proofing materials (Herbst et al. 1985; Carlin, 2000; Filella et al. 2002a,b). Antimony releases to the environment systems can be caused by road traffic (brake pad dust and tires), older battery producing plants, secondary lead smelter sites and from ammunitions (Filella et al. 2002a,b; Scheinost et al. 2006). Sb compounds are considered to be priority pollutants by the United States Environmental Protection Agency (USEPA). The USEPA maximum contaminant level (MCL) for Sb in drinking water is 0.006 mg/L.

In the pH range 2-11, Sb(III) forms a neutral complex $Sb(OH)_3$ in aqueous solutions, whereas Sb(V) exists as a negatively charged complex, $Sb(OH)_6^-$ (Smith and Martell, 1976; Filella and May, 2005). Though the oxidation of Sb(III) to Sb(V) in the presence of oxygen is kinetically inhibited and extremely slow in aqueous systems, Sb(III) sorbed to Mn oxides tend to oxidize faster (Blay, 2000; Belzille et al. 2001 Leuz and Johnson, 2005). Removal of Sb from drinking water/waste streams by natural sorbents was reported by Filella et al. (2002b) and Blay (2000) and their references, where Sb(III) and Sb(V) appear to bind strongly to Fe and Mn hydroxides and weakly to clay minerals. Depending on the testing conditions, Sb(V) is almost completely sorbed at pH values below 7, while Sb(III) sorbs up to pH values of 10.

Soils at small army firing ranges (SAFRs) are frequently contaminated with Cu, Ni, Pb, Sb, W and Zn because of spent bullet loading, which is estimated to be on the order of 80,000 tons per year (Dermatas et al. 2004a-c; Larson et al. 2005; Bednar et al. 2009). Moreover, the application of phosphate to stabilize Pb in SAFRs was reported to have enhanced the mobilization of toxic oxyanions such as Sb and W by factors up to 100, depending on soil conditions (Koutsospyros et al. 2006; Chrysochoou et al. 2007; Griggs et al. 2011). The primary ammunition used in SAFRs (M855, 5.56 mm bullets) contains approximately 3% Sb (Defense Ammunition Center, 2005), and the maximum concentration of Sb observed in SAFR soils was 486 mg/kg (Griggs et al., 2011). Remediation technologies are needed to immobilize multiple metals, in SAFR soils and DoD is currently evaluating alternative berm media to mitigate the potential migration of heavy metals which comprise munitions.

Grubb et al. (2010a,b) reported that SSF media successfully immobilized up to 10,000 mg/kg of numerous heavy metals at the 10,000 mg/kg dosing level and 100,000 mg/kg of Pb. This study presents the immobilization of antimony (Sb) by SSF media. Despite the granular nature of the SSF media, its mineralogy and residual lime content enabled high removals of different anionic and cationic metals (Grubb et al. 2010b).

MATERIALS AND METHODS

The characterization and metals immobilization potential of steel slag fines (SSF) taken from the Sparrows Point Steel Mill (Baltimore, Maryland, USA) was evaluated in prior studies (Grubb et al. 2010 a,b; 2011). The SSF media were classified as a SP type soil (9.5 mm minus fraction) by the Unified Soil Classification System (USCS) with <5% passing the 0.075 mm sieve. The maximum threshold concentration (or mass) that is immobilized against a regulatory criterion or objective can be determined for certain leaching conditions (TCLP, SPLP, DI water, etc.) based on the initial constituent of concern (COC) concentration and a prescribed liquid:soild (L:S) ratio (here, 20:1). The metals evaluated in this study were Sb(III) and Sb(V) at doses between 100 and 10,000 mg/kg to evaluate the potential for Sb immobilization from SAFR soils and possible concentrated industrial sources.

Procedurally, the aqueous Sb(III) solutions were individually prepared by dissolving antimony(III) chloride ($SbCl_3$) in a 2N HCl solution to achieve the target doses. Upon contact with water, $SbCl_3$ forms an antimony oxychloride precipitate and releases hydrogen chloride, hence a 2N HCl solution was used to dissolve $SbCl_3$ salt. The SSF media was first individually wetted (sprayed) with the Sb(III)-salt solution, and then was mixed using a stainless steel spoon to achieve a moisture content of 16%. The Sb(III)-spiked SSF media was then stored in sealable plastic bags and allowed to mellow for 30 days. The amount of acidity induced by 2N HCl solution to the SSF media was negligible (~1.33 eq[H^+]/kg).

For the Sb(V)-spiked SSF media, an aqueous solution of Sb(V) was prepared by dissolving potassium antimonite [$KSb(OH)_6$] in DI water to achieve target doses of 100 and 500 mg/kg. To batch sufficient SSF media at the 1,000 to 10,000 mg/kg Sb(V) level, equivalent aqueous solutions of Sb were prepared based on the solubility of the $KSb(OH)_6$ salt (20 g/L at 20^{o}C). Due to the volume required, the Sb(V) solution was contacted with the SSF media in a 500 mL polypropylene bottle that was rotated for 18 hours in a standard TCLP tumbler. The mixture was then transferred to an open stainless steel bowl in a vacuum hood for approximately 24 hours until the free liquid evaporated. Using a spatula, the moist Sb(V) spiked SSF media was then returned to its polypropylene bottle, and was mellowed for the balance of the 30 days. A totals analysis of the process revealed negligible loss of Sb.

After mellowing, all the samples were air-dried and subjected to analytical testing. The sample size for the TCLP and SPLP analyses was reduced to 25 g. Three replicates were prepared for each target dose for totals, TCLP and SPLP analyses followed by ICP-OES analysis for Sb. Prior to analysis, the solutions were acidified using 1% concentrated HNO_3.

RESULTS AND DISCUSSION

Table 1 presents the pH and concentrations of Sb measured from the TCLP and SPLP analyses. The pH of the raw SSF media was approximately 12. The initial pHs of the Sb(III) and Sb(V) solutions (at 500 mg/L) were 0.38 and 10.61, respectively, but the $SbCl_3$ solution had minimal buffer capacity. As such, Table 1 shows that the mellowed pH (pre-TCLP) of the spiked SSF media (5,000 and 10,000 mg/kg) decreased by approximately by 1~2 units after 30 days mellowing. The TCLP solution typically reduced the aqueous pH by 3-4 units, but the SPLP-pH remained above 11, indicative of the high buffering capacity of the SSF media. Oxidation of Sb(III) to Sb(V) during the mellowing of Sb(III)-spiked SSF media was considered to occur, however, the oxidation of Sb(III) to Sb(V) in the presence of oxygen is kinetically inhibited and extremely slow in aqueous systems (Blay, 2000; Belzille et al., 2001 Leuz and Johnson, 2005). Also Sb(III) appears to persist in oxic waters (Filella et al. 2002a,b)

SSF media expressed the ability to immobilize Sb(III) and Sb(V) at elevated dosing concentrations. The percent removal of Sb(III) based on the TCLP and SPLP tests was approximately 90 and 99%, respectively for doses up to 10,000 mg/kg. The percent removal of Sb(V) ranged from 75 to 93% and 86 to 99+% under TCLP and SPLP testing conditions, respectively. The removal of Sb(III) is likely due to the formation of $Sb(OH)_3$ (Smith and Martell, 1976; Filella and May, 2005). The

Table 1. SSF Thresholding results for Sb(III) and Sb(V) spiked SSF media.

	Target Dose		Sb(III)				Sb(V)			
	Totals mg/kg	Equivalent mg/L	Conc. mg/L	Removal %	Mellowed pH	Extracted pH	Conc. mg/L	Removal %	Mellowed pH	Extracted pH
TCLP	100	5	0.58	88.44	11.4	7.39	0.37	92.52	11.62	7.18
	500	25	2.89	88.46	11.5	7.19	5.64	77.43	11.5	7.92
	1,000	50	5.30	89.41	11.52	7.29	12.68	74.63	11.32	8.22
	5,000	250	20.00	92.00	10.91	7.16	39.12	84.35	10.66	6.95
	10,000	500	49.46	90.11	10.84	6.43	66.00	86.80	10.43	6.83
SPLP	100	5	0.06	98.71	Same As Above	11.86	0.05	98.98	Same As Above	11.95
	500	25	0.08	99.66		11.74	0.09	99.63		11.98
	1,000	50	0.08	99.85		11.78	0.12	99.77		11.98
	5,000	250	2.70	98.92		11.56	19.96	92.01		11.06
	10,000	500	7.60	98.48		11.44	68.81	86.24		11.21

prevailing species of Sb in SAFR soils is Sb(V), which is produced from the weathering of metallic Sb (Scheinost et al., 2006). Johnson et al. (2005) suggested that a calcium antimonate mineral, $Ca[Sb(OH)_6]_2$ would control dissolved Sb(V) concentrations in soils at elevated concentrations. Since SSF media contains high Ca concentrations (26,000 mg/kg) the formation of calcium antimonate mineral appears possible.

The SPLP-pH values were approximately 3.5 to 4 units higher than TCLP-pH which resulted in lower extractable Sb concentrations. Also, Quentel et al. (2004) showed that neutral $Sb(OH)_3$ species are unreactive, whereas the presence of $Sb(OH)_4^-$ results in the formation of Sb(V) through H_2O_2 oxidation.

Griggs et al. (2011) observed maximum Sb concentrations in outdoor SAFR soils containing spent M855 (5.56 mm) rounds to be on the order of 486 mg/kg. At this dosage, the thresholding results (Table 1) show that SSF was able to immobilize 99% of the Sb(III) and Sb(V) based on the SPLP results. Since the SPLP solution is mildly acidic and is intended to simulate metals leaching under acid rain conditions, it appears that SSF would perform well as a SAFR backdrop berm media. As the SSF media weathers and pH drops, the TCLP results (Table 1) indicate that the berm media would have to be changed out when the pH approaches 8. These results show the broad applicability of SSF media to successfully immobilize Sb (this study) and other metals found in SAFR soils such as, Pb, W, Cu, Ni, Zn and phosphate (Grubb et al. 2010a,b).

CONCLUSION

The main environmental motivation for performing the thresholding experiments was to gauge the ability of SSF media to immobilize significant concentrations of Sb(III) and Sb(V) that accumulate in firing range soils. For doses up to 10,000 mg/kg, the Sb(III) removal efficiency of the SSF media under TCLP and SPLP conditions was approximately 90% and almost 99%, respectively. Likewise, the Sb(V) removal efficiency of the SSF media for TCLP and SPLP conditions varied from 75 to 93% and 86 to >99%. The immobilization of Sb(III) and Sb(V) may be due to the formation of $Sb(OH)_3$ and $Ca[Sb(OH)_6]_2$, respectively, as suggested by literature. Based on the current and previous studies conducted by the authors, recycling based (green) remediation could be undertaken by using SSF media as firing range berm media to immobilize an array of heavy metals.

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