Immobilization of Heavy Metals by Solidification / Stabilization in Co-Disposed Coal Fly Ash and Concentrated Flue Gas Desulfurization Wastewater Brines

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ABSTRACT

Increasingly stringent regulations to control heavy metals in flue gas desulfurization (FGD) wastewater could result in the implementation of zero liquid discharge (ZLD) treatment systems at coal-fired power plants. One option for FGD wastewater ZLD treatment is the coupling of a brine concentrator with a solidification / stabilization (S/S) process. This S/S process could include the mixing of the concentrated brine with coal fly ash / lime, coal fly ash / cement, or a novel binder. A research project is currently being conducted at the Georgia Institute of Technology on the development of S/S technology for the co-disposal of concentrated FGD wastewater brines with coal fly ash. The primary research objectives of the project are to evaluate (i) the immobilization of heavy metals in co-disposed fly ash and concentrated FGD brines, (ii) the impact of coal fly ash properties and brine chemistry on the S/S, and (iii) the predominant minerals formed during the S/S. The first phase of the project will focus on the optimization of S/S recipes. The second phase of the project will evaluate the impact of coal fly ash properties (by varying the source of the ash) and brine chemistry (by varying brine composition) on the S/S process and heavy metal immobilization. The immobilization of heavy metals will be correlated to fly ash properties, brine chemistry, and characteristics of the S/S solids to identify critical factors in the effectiveness of this process.

INTRODUCTION

The coal-fired power industry faces increasing solid waste challenges. The central solid waste issue facing the industry is the immobilization of heavy metals. Coal fly ash may contain significant concentrations of heavy metals including arsenic, cadmium, chromium, mercury, and selenium (*Federal Register: Hazardous and Solid Waste Management System; Identification and Listing of Special Wastes; Disposal of Coal Combustion Residuals From Electric Utilities; Proposed Rule*, 2010). The release of these metals into the environment through leaching can have significant negative impacts.

Flue gas desulfurization (FGD) purge brines also contain significant concentrations of arsenic, cadmium, chromium, mercury, and selenium (*Steam Electric Power Generation Point Source Category: Final Detailed Study Report*, 2009). The United State Environmental Protection Agency (USEPA) is in the process of revising the current Steam Electric Power Generation Effluent Guidelines for FGD purge brines. Thus, safe disposal of FGD brines is another environmental challenge that the coal-fired power industry is currently facing.

Among various treatment options for FGD brines, zero liquid discharge (ZLD) approaches are gaining significant interest by eliminating discharge of waste liquid completely. Traditional ZLD methods that have been employed include evaporators / crystallizers and spray dryers. However, these ZLD methods are costly due to high energy and maintenance costs. Furthermore, the solid wastes generated by the above systems are not suitable for direct landfill disposal because the produced residuals contain high concentrations of salts, which readily leach. Alternatively, ZLD can be achieved by coupling a brine concentrator with a solidification/stabilization (S/S) process by mixing and co-disposing the concentrated brine with coal fly ash and Portland cement. This alternative ZLD method is highly attractive due to several potential advantages: (1) lower costs due to lower energy demands than traditional ZLD methods; (2) enhanced immobilization of metals and salts in the generated solid wastes; (3) generation of a safer solid waste for landfill disposal; and (4) co-disposal of an abundant solid waste material, i.e., fly ash, with FGD waste brines from the coal-fired power plants.

The S/S process includes the mixing of wastes (liquids, sludges, brines, or solid waste) with Portland cement, Portland cement/coal fly ash, or coal fly ash/lime ("25 Pennsylvania Code Chapter 95: Wastewater Treatment Requirements," 2010; Batchelor, 2006; Kameswari, 2001; Kamon, 2000; Keller, 2002; Kumpienem, 2007b; Qian, 2006; Ramgobeen, 2010; T. S. Singh, K. K. Pant, 2006; Terzano, 2005). The USEPA regards S/S to be an established treatment technology for more than 57 wastes (Mickley, 2008; Paria, 2006). S/S has been shown by many studies to be a viable treatment process for many heavy metal bearing solid wastes (Akhter, 1997; Batchelor, 2006; Kameswari, 2001; Kamon, 2000; Kumpienem, 2007b; Li, 2001; Mangialardi, 1999; Mickley, 2008; Moon, 2009; Paria, 2006; Pereira, 2001; Qian, 2006; T. S. Singh, K. K. Pant, 2006; Solem-Tishmack, 1995; Su, 2003; Terzano, 2005; Valls, 2002; Yilmaz, 2003). S/S consists of two processes: solidification (producing a solid product with improved physical properties) and stabilization (process of converting a contaminant of concern to it's less mobile and less toxic forms) (Batchelor, 2006).

Fly ash has successfully replaced a portion of Portland cement in several S/S mixture applications (Kaplan, 2008; Kumpienem, 2007b; J. S. Mahlaba, 2006; J. S. Mahlaba, E.

P. Kearsley, and R. A. Kruger, 2011; J. S. Mahlaba, P. C. Pretorius, and M. P. Augustyn 2006; J. S. Mahlaba, E. P. Kearsley, R. A. Kruger, and P. C. Pretorius, 2011; J. S. Mahlaba, E.P. Kearsley, and R. A. Kruger, 2011; Pereira, 2001; M. Singh, and M. Gart, 1999; T. S. Singh, K. K. Pant, 2006; Solem-Tishmack, 1995; Su, 2003; Terzano, 2005). The combination of Portland cement and coal fly ash appears to optimize the S/S process. Portland cement/coal fly ash S/S mixtures trap metals into the matrix better than purely pozzolanic processes (i.e. fly ash and lime) (J. R. Connor, and S. L. Hoeffner, 1996). Replacement of a portion of Portland cement with fly ash has been shown to enhance S/S mixtures versus pure Portland cement mixes by forming a less permeable solid (Batchelor, 2006; J. R. Connor, and S. L. Hoeffner, 1996; Dhir, 2006). Coal fly ash has been utilized in S/S mixtures to immobilize numerous waste streams which include significant concentrations of heavy metals typically found in fly ash including arsenic, mercury, selenium, cadmium, and chromium (Akhter, 1997; J. R. Connor, 1997; Kameswari, 2001; Kumpienem, 2007a; Pereira, 2001; T. S. Singh, K. K. Pant, 2006; Solem-Tishmack, 1995). In addition, cement based S/S has been successfully utilized to treat municipal solid waste incineration (MSWI) fly ash (Kamon, 2000; Keller, 2002; Lombardi, 1998; Mangialardi, 1999; Qian, 2006).

A research project on developing S/S technology for the co-disposal of concentrated FGD brines and coal fly ash has been initiated at the Georgia Institute of Technology. This paper provides an update on the initial progress of the project. The objective of this project is to develop S/S technology with Portland cement in order to immobilize heavy metal contaminants to co-dispose coal fly ash and concentrated FGD brine. If successful, S/S can simultaneously address the problems presented by disposal of fly ashes and FGD brines in minimizing their potential to release heavy metals to the environment and protecting human health and the ecosystem.

EXPERIMENTAL

COAL FLY ASH - The coal fly ash utilized in the project is Type F, which is not self cementing. Physical and chemical properties of the fly ash are shown in Table 1 (Yeboah, 2012 (In Preparation)).

Table 1. Chemical and Physical Properties of Fly Ash (Yeboah, 2012 (In Preparation)).

Chemical or Physical Property	**Value**
Mean Particle Size (µm)	16.2
Total Organic Carbon (%)	1.1
Total Inorganic Carbon (%)	0.0
Silicon (%)	55.28
Aluminum (%)	27.21
Iron (%)	7.98
Calcium (%)	1.26
Potassium (%)	3.02
Magnesium (%)	1.23
Titanium (%)	1.41
Sulfur (%)	0.07
Phosphorous (%)	0.19
Sodium (%)	0.47
Manganese (%)	0.06

PORTLAND CEMENT - Cemex Type I/II Portland cement was utilized in the project.

SIMULATED CONCENTRATED BRINES - Simulated concentrated FGD brines were prepared based on concentrations of heavy metals (arsenic, cadmium, chromium, and selenium) and ions (calcium, chloride, fluoride, and magnesium). Sulfate was not included because it is believed that most of the sulfate in FGD brines will precipitate as insoluble gypsum during the evaporation process. Nitric acid was added to the simulated brine to decrease the pH to the level expected for an actual concentrated brine leaving an evaporator. Typical metal concentrations of the simulated brine in the experiments are shown in Table 2. Metal concentrations in the simulated brine were determined using inductively coupled plasma – mass spectrometry (ICP-MS).

Table 2. Typical Heavy Metal Concentrations in Simulated Concentrated Brine

Heavy Metal	Concentration (ppm)
Arsenic	2 – 3
Cadmium	0.4 – 16
Chromium	5 – 7
Mercury	44 - 63
Selenium	63 - 90

S/S OF BRINES - The simulated FGD brines, coal fly ash, and Portland cement were mixed at mass ratios of 30%, 60%, and 10%, respectively, for twenty minutes. The mixture was then added to cylindrical tubes and allowed to cure for 14 to 28 days.

TOXIC CHARACTERISTIC LEACHING PROCEDURE (TCLP) - After curing, the solidified samples were crushed and subjected to the TCLP per USEPA Method 1311. Following the TCLP, samples were digested per USEPA Method 200.8. Heavy metal concentrations were determined using ICP-MS.

RESULTS AND DISCUSSION

Figure 1 shows the mixing of the brines, fly ash, and Portland cement. Figure 2 shows a picture of the final S/S solid.

Figure 1. Mixing of coal fly ash, simulated brine, and Portland cement.

Figure 2. Picture of S/S solid. Coal fly ash is shown on the left.

RETAINMENT OF HEAVY METALS - The percentage of the heavy metals retainment on the S/S matrix during the TCLP test was calculated as follows:

$$\%\ \boldsymbol{Retainment} = \frac{MB - (ME - MFA)}{MB}\ x\ 100$$

MB is the mass of the heavy metal added to the S/S mixture from the simulated brines. ME is the mass of the heavy metal detected in the TCLP extract. MFA is the background mass of the heavy metal leaching from the fly ash and/or Portland cement. MFA was determined by conducting the similar experiment with a simulated brine that contained salts, but did not include any heavy metals. MFA was assumed to be the mass leaching from the coal fly ash and/or Portland cement.

Figure 3 shows the typical retainment values from the S/S experiments in the project.

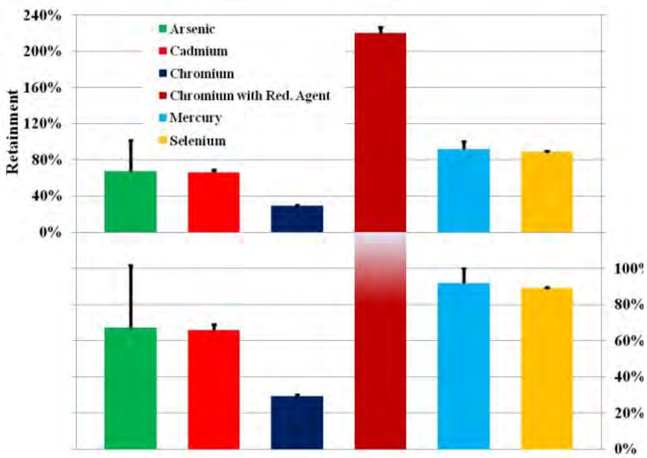

Figure 3. Typical retainment results for heavy metals.

The results show good retainment for selenium, mercury, arsenic, and cadmium. Average selenium retainment was over 89%, even at very high selenite concentrations (>60 ppm). Average mercury retainment was over 90% at very high mercury concentrations (>44 ppm). Average arsenic and cadmium retainment were over 60%. The results for arsenic did have a greater standard deviation. Average chromium retainment was fairly low; however, the addition of a reducing agent significantly increased the chromium retainment to over 220%. The retainment increased to over 100% because the reducing agent actually decreased leaching of chromium from the fly ash, not just the brine.

CONCLUSIONS

S/S technology in co-disposed coal fly ash and FGD waste brines holds great promise for the immobilization of heavy metals including arsenic, cadmium, chromium, mercury, and selenium. This process should be further developed for the coal-fired power industry in managing fly ash and FGD waste brines to decrease the release of heavy metals to the environment.

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