Combined Iron Reduction and Solidification/Stabilization Process to Immobilize Heavy Metals in Concentrated Flue Gas Desulfurization Brines

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ABSTRACT

Combination and optimization of an iron-based reduction and solidification/stabilization (S/S) processes for the immobilization of heavy metals in concentrated flue gas desulfurization (FGD) brines was investigated. The performance of aged zero valent iron (ZVI) on heavy metal removal in simulated FGD brine and real FGD brine was investigated. Batch studies were performed to evaluate the effects of temperature, pH, TDS, ZVI dosage, nitrate and sulfate on ZVI's reactivity in simulated brine. Temperature is the dominant factor on ZVI's reactivity compared to other factors being studied. At 80°C, almost 100% removal of arsenate (1 ppm) and chromate (1 ppm) can be achieved in less than 5 min using 4.17 g/L of ZVI in simulated brine, while selenate (25 ppm) and cadmium (5 ppm) could be completely removed within 30 minutes. The process of heavy metal retainment by S/S of the ZVI-pretreated or non-pretreated FGD brines was studied by using class C (subbituminous) and F (bituminous) coal fly ash, with the addition of Portland cement or lime. Leaching tests were performed to evaluate the performance of each S/S recipe by comparing the heavy metal concentrations in the leachate. The pre-treatment of brine by ZVI enhanced the retainment of heavy metals when Class F ash was used, but not when Class C ash was used since it already performed quite well without ZVI pretreatment.

INTRODUCTION

The United States coal-fired power industry faces increasing demands to improve solid waste and wastewater disposal practices ¹. Over 130 Mt of coal ash are produced annually in the U.S. and more than half are disposed in landfills or surface impoundments ². The disposal of coal ash poses environmental risks due to elevated
levels of heavy metals in these wastes and potential to leach. The ashes may become
more contaminated as the recently implemented Mercury and Air Toxics Standards
(MATS) for flue gas emissions control is expected to transfer more mercury and other
metal pollutants to fly ash. Furthermore, incidents of coal ash pond spills, such as at the
Tennessee Valley Authority’s Kingston station in 2008 and Duke Energy’s power plants
near the Dan River in North Caroline in 2014, have prompted the industry to move
toward all dry disposal of fly ash.

In addition to coal ash, the flue gas desulfurization (FGD) purge wastewaters at coal-
fired power plants contain significant concentrations of heavy metals (e.g. Se, As, Cr,
Cd and Hg) and large amounts of salts (e.g. Cl-, Ca$^{2+}$, Mg$^{2+}$, Na$^{+}$ and SO$_{4}^{2-}$), which will
contaminate receiving water bodies if discharged without proper treatment. Recently,
the USEPA released the Steam Electric Power Effluent Limitation Guidelines (ELG),
which sets stringent limits on As, Hg, Se and other pollutants’ release to the
environment from FGD wastewater.

Interest in zero liquid discharge (ZLD) for wastewater treatment has increased
significantly in recent years. This interest has been most evident in the coal-fired power
plants because it helps the plants to meet the stringent wastewater discharge
regulations and maximize water recycling at the plants. While ZLD eliminates FGD
wastewater discharge, it will likely increase pollutant strength in the solid residuals from
the wastewater, rendering these challenging solids in need of more effective
stabilization technology before disposal.

The solidification/stabilization (S/S) process includes the mixing of wastes (liquids,
sludges, or solid waste) with Portland cement, Portland cement/coal fly ash, or coal fly
ash/lime. The USEPA regards S/S to be an established treatment technology for
more than 57 wastes. S/S has been shown by many studies to be a viable
treatment process for many heavy metal bearing solid wastes. 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 its less
mobile and less toxic forms).

Our group previously demonstrated that coupling concentrated FGD brine with a S/S
process by mixing and co-disposing the concentrated brine with coal fly ash (CFA) and
Portland cement (PC) is a promising ZLD method for effective heavy metal
immobilization. However, oxidized forms of heavy metals, such as selenate and
chromate, remain challenging to treat due to their high mobility. By adding ferrous
sulfate into this S/S process, the retainment of selenate and chromate could be
enhanced, but selenate immobilization was still not ideal. These results motivated us to
couple this S/S process with an iron-based reduction process to develop an effective
ZLD method for heavy metal immobilization.

Zero valent iron (ZVI) has been shown to effectively remove a variety of contaminants
such as selenate, chromate, nitrate, phosphate and chlorinated hydrocarbons. ZVI
is a moderately strong reducing agent which is readily available, non-toxic and
inexpensive. Although the reactivity of ZVI on heavy metal removal has been well studied by many researchers, to our knowledge, it was limitedly tested in concentrated FGD wastewater brines. Huang et al. demonstrated a successful field study using their hybrid ZVI system to immobilize heavy metals and nitrate in FGD wastewater, however, the chemistry between FGD wastewater and its concentrated brines are quite different due to the significantly higher concentrations of salts and other components in the brines. Therefore, evaluating the effectiveness of ZVI on heavy metal removal in real FGD wastewater brines is an important study for the development of a successful ZLD method for the FGD waste brines.

In this study, the chemistry, speed and effectiveness of ZVI reduction processes in the treatment of simulated FGD brines were optimized first. Then, the impact of ZVI reduction process on the S/S process in terms of heavy metal immobilization was evaluated by conducting 2 different EPA leaching tests. Last, the mineral formation in the S/S solids which were responsible for the immobilization of heavy metals was characterized by X-ray diffraction (XRD). In addition, real FGD wastewater was collected from a local coal-fired power plant and the brine generated from this wastewater was also tested in this study.

METHODOLOGY

Chemicals:
ZVI spherical particles of size ranges in 1-3 micron were purchased from Alfa Aesar. ZVI particles were stored at ambient air condition; therefore, the particles were aged. All chemicals were of analytical grade and used as received. Sodium selenate (Na2SeO4), sodium arsenate heptahydrate (Na2HAsO4·7H2O), cadmium chloride (CdCl2), sodium chromate (Na2CrO4), barium chloride dihydrate (BaCl2·2H2O), and mercuric chloride (HgCl2) were purchased from VWR. Calcium chloride dihydrate (CaCl2·2H2O), sodium chloride (NaCl), magnesium nitrate hexahydrate (Mg(NO3)2·6H2O), magnesium chloride hexahydrate (MgCl2·6H2O), magnesium sulfate heptahydrate (MgSO4·7H2O), sodium bromide (NaBr) and ferrous sulfate heptahydrate (FeSO4·7H2O) were purchased from Fisher Scientific. The Se(IV) and Se(VI) analytical standards (1000 mg/L) were purchased from High-Purity Standards (Charleston, SC, USA). All the solutions used in the experiments were prepared by dissolving the corresponding salts in ultrapure water generated from a Milli-Q nanopure water purification system.

Preparation of Simulated Brine:
The simulated brine was prepared by mixing and dissolving various salts in Milli-Q water. The simulated brine without the addition of any heavy metals is named “metal-free brine”. The simulated brine with the addition of selenate, arsenate, cadmium and chromate is named “metal brine”. The concentration of each component in the simulated brines is shown in Table 1. The total dissolved solid (TDS) was around 125,000 ppm, and the pH was 5.9.

Preparation of Real Brine:
Real FGD wastewater collected from a coal-fired power plant in the Southeast of U.S. was used in this part of study. The brine was generated by heating (160-220 °C) the FGD wastewater. The volume of the final brine was about 10% of the original wastewater. During the process of concentrating the FGD wastewater into its brine through heating, the colorless FGD wastewater became yellow to brownish, with the formation of precipitates and crystal solids at the bottom. The TDS, nitrate, sulfate, chloride, pH, total organic carbon, and heavy metal concentrations in the produced brine were measured. The resulting characteristics of the real brine sample are shown in Table 1.

Table 1. Characteristics of real FGD brine and simulated brine (concentrations in ppm)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Simulated Brine</th>
<th>Real FGD Brine</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.9</td>
<td>6.5</td>
</tr>
<tr>
<td>TDS</td>
<td>126,000</td>
<td>133,000</td>
</tr>
<tr>
<td>Chloride</td>
<td>80,000</td>
<td>77,800</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0-600</td>
<td>1,300</td>
</tr>
<tr>
<td>Sulfate</td>
<td>0-1200</td>
<td>1,390</td>
</tr>
<tr>
<td>Bromide</td>
<td>1,312</td>
<td>240</td>
</tr>
<tr>
<td>Ca</td>
<td>57,580</td>
<td>38,439</td>
</tr>
<tr>
<td>Na</td>
<td>990</td>
<td>1,801</td>
</tr>
<tr>
<td>Mg</td>
<td>9,340</td>
<td>3,727</td>
</tr>
<tr>
<td>Se</td>
<td>25</td>
<td>3.1</td>
</tr>
<tr>
<td>As</td>
<td>1.0</td>
<td>ND</td>
</tr>
<tr>
<td>Cd</td>
<td>5.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Cr</td>
<td>1.0</td>
<td>0.09</td>
</tr>
<tr>
<td>Fe</td>
<td>NA</td>
<td>0.7</td>
</tr>
<tr>
<td>Cu</td>
<td>NA</td>
<td>0.30</td>
</tr>
<tr>
<td>Hg</td>
<td>1.0</td>
<td>0.14</td>
</tr>
<tr>
<td>Pb</td>
<td>NA</td>
<td>0.08</td>
</tr>
<tr>
<td>Zn</td>
<td>NA</td>
<td>3.82</td>
</tr>
<tr>
<td>Mn</td>
<td>NA</td>
<td>12.5</td>
</tr>
</tbody>
</table>

Optimization of ZVI Reduction:
The effects of temperature, pH, TDS, ZVI dosage, nitrate and sulfate on selenium removal by ZVI was evaluated within the metal-free brine. Selenate stock was spiked into a 100-mL glass bottle containing 60 mL of metal-free brine (100%, 50% or 10%) to have a starting concentration of 40 ppm as Se. The starting pH (2.5, 3.0, 4.0, or 5.9) was adjusted by adding HCl. The pH throughout the reaction was not controlled. The solution was preheated in a heating bath at constant temperature (25, 40, 60 or 80°C) and the constant temperature was maintained throughout the reaction. Nitrate concentration (0, 300, or 600 ppm) and sulfate concentration (0, 300, 600, or 1200 ppm) was adjusted by changing the amount of magnesium nitrate or sulfate added into the brine. ZVI powder (0.10, 0.25, 0.50 or 1.00 g) was added into the solution and the mixture was stirred by a magnetic stir bar (1.5” × 0.312”) at 550 rpm. At this speed, most of the ZVI added was observed to be well dispersed in the mixture. Samples aliquots
were taken at 0, 5, 10, 20, 30, and 60 min, filtered using a syringe filter (0.22 µm) to remove solids in the mixture, and then diluted 10 times with 5% trace metal grade nitric acid for heavy metal measurement. The effect of temperature, TDS, nitrate, sulfate and ZVI dosage on selenate, arsenate, cadmium and chromate removal was tested within the metal brine under the same conditions mentioned above. Once the reaction condition was optimized, the brine generated from real FGD wastewater was also tested at the optimized condition.

Combined Iron reduction with S/S process:
The ZVI treated or non-treated simulated brine was mixed with bituminous coal fly ash (BCFA, class F) or sub-bituminous coal fly ash (SCFA, class C), plus Portland cement or lime. The overall performances by the different S/S methods were compared in terms of heavy metal immobilization efficiency using the four different S/S recipes shown in Table 2. The chemical composition of both types of CFAs and PC can be obtain from the study by Renew at al.

Table 2. Four recipes for the S/S process

<table>
<thead>
<tr>
<th>Recipe</th>
<th>Coal Fly Ash</th>
<th>Stabilizing Agent</th>
<th>Simulated or Real Brine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Class F (90 g)</td>
<td>Portland cement (15 g)</td>
<td>45 g</td>
</tr>
<tr>
<td>2</td>
<td>Class F (90 g)</td>
<td>Lime (15 g)</td>
<td>45 g</td>
</tr>
<tr>
<td>3</td>
<td>Class C (90 g)</td>
<td>Portland cement (15 g)</td>
<td>45 g</td>
</tr>
<tr>
<td>4</td>
<td>Class C (90 g)</td>
<td>Lime (15 g)</td>
<td>45 g</td>
</tr>
</tbody>
</table>

Solid samples were prepared in duplicate using the recipe shown in Table 4. Coal fly ash and Portland cement/lime were first added into the mixer, then brine sample was poured into the mixer and the slurry was mixed for 20 min. Simulated and real brine (60 mL) was treated by 0.25g of 1-3 µm ZVI at 80°C using a magnetic stirrer. Different brine samples added were:
1. Simulated heavy metal free brine (untreated)
2. Simulated heavy metal free brine (treated, reacted ZVI was not filtered out)
3. Simulated heavy metal brine (untreated)
4. Simulated heavy metal brine (treated, reacted ZVI was not filtered out)
5. Real brine (untreated)
6. Real brine (treated, reacted ZVI was not filtered out)

The slurry was poured into a plastic mold and placed in humid environment for curing for exactly 28 days before the leaching tests.

Leaching tests

USEPA 1311:
For USEPA 1311 leaching test (i.e. TCLP), each solid was crushed by a hammer into small pieces which were then sifted by a 0.95 cm sifter. Pieces greater than 0.95 cm was further crushed until all the pieces could go through the sifter. For each solid, 50 g was added into 1.0 L of extraction fluid in a plastic bottle. The extraction fluid was prepared by diluting 5.9 mL of acetic acid into 1.0 L of Milli-Q water. The mixture was
then rotated at 30 rpm for 18 h. After settling down, each sample was vacuum filtered through 0.45 µm acid-washed glass fiber filters. All the glassware was rinsed with 5% nitric acid and Milli-Q water before use. The filtered extraction fluid was acidified by nitric acid (5 mL of nitric acid into 95 mL of filtered extraction fluid) and the sample was stored in refrigerator before analysis.

*Modified USEPA 1313* 41:

The method applied in this modified USEPA 1313 leaching test was similar to that of USEPA 1311, with the only difference in the amount of acetic acid added in the extraction fluid. The goal of this modified leaching test was to have similar final leachate pH (around 7) among all the S/S solids.

*Analytical Methods:*

The pH was measured by an Orion Star™ A111 bench-top pH meter. The concentrations of heavy metals were detected by ICP-OES 8000 (Perkin Elmer). The washing solution used was 5% trace metal grade nitric acid. The chloride, bromide, sulfate and nitrate concentrations were measure by IC (Dionex).

*RESULTS AND DISCUSSION:*

**Optimization of ZVI Reduction:**

The higher temperature, lower pH, and lower TDS gave rise to higher heavy metal removal rates by using a fixed dosage of ZVI. Temperature was the dominant factor on ZVI’s reactivity compared to other factors being studied. At 80°C, almost 100% removal of arsenate (1 ppm) and chromate (1 ppm) could be achieved in less than 5 min using 0.25 g of ZVI in 60 mL of simulated brine. Selenate (25 ppm) and cadmium (5 ppm) could be completely removed within 30 min under the same condition, as shown in Figure 1. At 80°C, the effect of pH (2.5-5.9), TDS (12,500-125,000 ppm), nitrate (0-600 ppm), sulfate (0-1,200 ppm), and even ZVI dosage (0.25-1.00 ppm) was not evident (data not shown).
The real FGD brine was filtered before being tested. The initial pH was 6.5 which was similar to the pH of the simulated brine. However, the matrix of the real FGD brine was very different from that of the simulated brine. Also, the color of the real FGD brine was yellowish brown while the simulated brine was clear. In the real FGD brine, the arsenate concentration was not detectable.

The heavy metal removal by 0.25 g of ZVI in the real FGD brine at 80°C was tested. Figure 2a shows the removal of selenium and cadmium in real FGD brine compared to that in simulated brine (Figure 2b). Note that chromium was nearly completely removed within the first five minutes in both cases so it is not shown.

It can be seen that the removal rates of both selenium and cadmium were slower in the real brine compared to that in the simulated brine. This difference was primarily due to the different matrix of the real brine and some other competing or inhibiting species in the real brine that were absent in the simulated brine.

Combined Iron reduction with S/S process:

USEPA 1311 and modified USEPA 1313 leaching test:
The pH of leachate after 18 hours of rotation in both the EPA 1311 and modified 1313 leaching tests is shown in Table E. It can be seen that the final pH of leachate from the modified 1313 leaching test had been lowered to around 7 by the addition of extra acetic acid in the extraction fluid.

Table 3. The pH of leachate after 18 h rotation

<table>
<thead>
<tr>
<th>Type of S/S solid</th>
<th>1311</th>
<th>Modified 1313</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class F + cement</td>
<td>6.6-7.3</td>
<td>6.6-7.3</td>
</tr>
<tr>
<td>Class F + lime</td>
<td>9.8-10.2</td>
<td>6.8-7.2</td>
</tr>
<tr>
<td>Class C + cement</td>
<td>9.7-10.1</td>
<td>7.1-8.1</td>
</tr>
<tr>
<td>Class C + lime</td>
<td>11.5-11.9</td>
<td>6.9-7.5</td>
</tr>
</tbody>
</table>

The heavy metal concentrations in the leachate from both leaching tests were compared among the samples from different S/S recipes. Figure 3 shows the results of selenium removal.

Figure 3. Selenium concentration in the leachate among different S/S recipes and leaching tests. “MB” represents simulated metal brine without ZVI treatment, “MB+ZVI” represents simulated metal brine treated with ZVI which was mixed into the S/S process. Real brine (RB) followed the same case.

From the results in Figure 3, it can be concluded that recipes using the Class C ash (i.e. SCFA) performed better in terms of selenium removal. Overall, the Class C ash with lime had the best performance among the 4 recipes. The pre-treatment of brine by ZVI enhanced the retainment of heavy metals when Class F ash (i.e. BCFA) was used, but not when Class C ash was used since it already performed quite well without ZVI.
pretreatment. The final pH of the leachate was the dominant factor. As shown in Table 5, after the 1311 leaching test, the leachate of Class C ash with lime had the highest final pH at 11.5-11.9. However, after the modified 1313 leaching test, the leachate pH dropped to around 7, which led to more selenium leaching, as seen in Figure 3. This trend was most obviously observed for the MB sample since it had the highest starting heavy metal concentration. A similar trend could also be observed with the RB and ZVI treated samples, but the differences not as obvious as those from the MB samples since the concentration of selenium in the leachate was lower in the RB samples. The other heavy metals (As, Cr and Cd) had much lower concentration levels in the leachate, but mostly follow the same trend as Se in terms of immobilization efficiency by the different S/S recipes (data not shown).

CONCLUSION:
Temperature was the dominant factor on ZVI's reactivity compared to other factors being studied. At 80°C, almost 100% removal of arsenate (1 ppm) and chromate (1 ppm) could be achieved in less than 5 min using 0.25 g of ZVI in 60 mL of simulated brine. The S/S recipes using the Class C ash (i.e. SCFA) performed better in terms of selenium removal. Overall, the Class C ash with lime had the best performance among the 4 recipes. The pre-treatment of brine by ZVI enhanced the retainment of heavy metals when Class F ash (i.e. BCFA) was used, but not when Class C ash was used since it already performed quite well without ZVI pretreatment.

REFERENCE:


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