Pilot-scale demonstration of the hybrid zero-valent iron process for treating flue-gas-desulfurization wastewater: Part I
Yong H. Huang, Phani K. Peddi, Hui Zeng, Ci-Lai Tang and Xinjun Teng

ABSTRACT

The hybrid zero-valent-iron (hZVI) process is a novel chemical treatment process that has shown great potential in previous laboratory and field bench-top scale tests for removing selenium, mercury and nutrients from various industrial wastewaters. In this study, a pilot-scale demonstration was conducted to continuously treat 3.8–7.6 L/min (1–2 gpm) of the flue-gas-desulfurization (FGD) wastewater at a coal-fired power plant for five months. Results show that the hZVI process could simultaneously reduce selenate-Se from 1 to 3 mg/L to below 10 μg/L and mercury from over 100 μg/L to below 10 ng/L in compliance with the new stringent effluent discharge limits planned by the U.S. EPA for Se and Hg. A three-stage hZVI system with a combined hydraulic retention time of 12 h is sufficient for Se treatment, while a single-stage system can meet Hg treatment requirement. The successful pilot study demonstrated that the hZVI process is scalable and could be a reliable, low-cost, high-performance treatment platform with many application potentials, particularly, for solving some of the toughest heavy metal water problems.

Key words | FGD wastewater, heavy metal removal, hybrid zero-valent iron (hZVI), mercury removal, selenium removal

INTRODUCTION

Flue gas desulfurization (FGD) is a process used by thermoelectric power plants to cleanse sulfur dioxide (SO₂) from the exhaust flue gas of fossil fuel combustion, particularly coal-burning. Among many FGD technologies, wet scrubber technologies are increasingly being used thanks to their higher removal efficiency in capturing both acid gases and gaseous or colloidal mercury. The USEPA (2009) predicted that 69% of coal-fired capacity will be wet scrubbed by 2025. When dirty exhaust is cleansed, various metal and non-metal pollutants as well as NOₓ gas generated during fuel combustion will be stripped off and accrue as dissolved or solid forms in liquid phase. As a result, the wet scrubber blowdown is often contaminated with harmful concentrations of heavy metals and metalloids including mercury (Hg), selenium (Se) and arsenic (As). Discharge of FGD wastewater without sufficient treatment, which unfortunately is not uncommon in the industry, poses a serious threat to the environment. In response to increasing public concern, the U.S. EPA will soon publish new effluent guidelines for FGD wastewater, which will impose much stricter discharge limits for toxic metals, e.g., to as low as 14 ng/L for Hg and 10 μg/L for Se, effective in 2014 (USEPA 2011).

FGD wastewater is extremely complex in composition (Chu 2006; USEPA 2009). Major constituents include chloride, calcium, sulfate, sodium, magnesium, nitrate as well as silicate and borate in some cases. Total dissolved solids (TDS) can be as high as 50,000 mg/L. Advanced treatment of FGD wastewater, which requires selectively removing various contaminants from such a complex matrix to an extremely low concentration, remains one of the biggest challenges to the water industry (Chu 2006; USEPA 2009). Reducing selenate to μg/L level and dissolved mercury to ng/L level is particularly challenging. Unlike selenite, selenate exhibits low affinity for most solid surfaces and cannot be easily removed by conventional adsorption-precipitation treatments. Selenate, nonetheless, may be reduced by certain microorganisms to selenite or Se⁰ and removed (Doran & Alexander 1977; Oremland et al. 1989). In recent years, biological technologies represented by GE...
Water’s ABMet™ and CH2MHill’s ICB™ processes have emerged as a viable Se solution for FGD wastewater (Sonstegard et al. 2007; Pickett et al. 2008; Munirathinam et al. 2011). Applications of these emerging technologies, however, are significantly constrained by high cost, process complexity, O&M difficulty, and other problems. Moreover, the potential formation of highly toxic organic Se or Hg compounds from biological treatment remains a concern (Amweg et al. 2003). Other potential technologies such as ion exchange, constructed wetlands, and zero-liquid discharge (ZLD) technologies have also been evaluated extensively but the prospect of success seems far from certain (Seigworth et al. 1995; EPRI 2008). As a result, the industry is still searching for a reliable, low-cost and high-performance technology for FGD wastewater treatment to comply with the upcoming new discharge limits, particularly, for Se and Hg.

Zero-valent iron (ZVI), a relatively inexpensive reducing agent, was demonstrated capable of removing selenate from water via reduction, co-precipitation and adsorption (Roberson 1999; Qiu et al. 2000; Mondal et al. 2004; Zhang et al. 2005a, b). Despite many promising laboratory test results, endeavors by the water industry to develop the ZVI technology into a selenium solution have generated disappointing results so far, largely due to the lack of a viable method to overcome the ZVI passivation (Roberson 1999). When ZVI particles contact wastewater, iron corrosion will start and subsequently form an iron oxide coating on the ZVI surface. The nature of the iron oxide coating formed depends largely on the aquatic chemistry. Under most wastewater conditions, the resulting corrosion coating is chemically passive and could significantly diminish ZVI reactivity with respect to target contaminants.

The practicability of ZVI technology takes a major step forward with the invention of the hybrid zero-valent iron (hZVI)/Fe₃O₄/Fe(II) system by Y.H. Huang (patents pending). The hZVI system employs unique roles of Fe²⁺(aq.) and magnetite to overcome ZVI surface passivation, the underlying mechanisms of which were related to findings from several previous works (Huang et al. 2003, 2012b; Huang & Zhang 2004, 2006a, b). The primary role of Fe²⁺ in the hZVI system was to regulate the interfacial iron chemistry towards forming magnetite, a mixed Fe(II) and Fe(III) oxide, as the iron corrosion product. As an electron-conducting iron oxide, magnetite could mediate rapid redox reactions between ZVI and pollutants. A bench-scale treatment prototype was successfully demonstrated in a five-week continuous-flow field test in 2009 at a power plant, consistently reducing selenate-Se from ~3,000 μg/L to below 7 μg/L and dissolved Hg²⁺ from ~50 μg/L to below 0.005 μg/L (Huang et al. 2012a). Because of the promising results, the host utility company decided that a scaled-up long-term demonstration at another plant was essential to further verify the hZVI technology.

The objective of this project was to further evaluate the practicability of the hZVI technology as a cost-effective solution to the FGD wastewater problem. The scaled-up demonstration aimed to gather more operational experiences and insights to help optimize reactor and process design, develop a solid waste management plan, and evaluate the process economics. A successful pilot demonstration would be a major milestone to commercialize the technology within a short time span to meet the urgent needs of the power industry as well as those of the mining and refinery industry in selenium treatment.

**MATERIALS AND METHODS**

**The hZVI treatment system**

The pilot-scale hZVI treatment system was designed based on the successful bench-top prototype (Huang et al. 2012a). The pilot system consisted of four stainless steel hZVI reactors and post-treatment units including aeration, clarification, and sand filtration, all of which were mounted on a 40-ft flat-bed trailer (Figure 1). The four hZVI reactors were arranged in hydraulic elevation that allowed incoming FGD water to gravitationally flow through in sequence without the need for an intermediate lift pump. The design also allowed the hZVI reactors to be operated either as a single-train, four-stage system or as a dual-train system with two stages in each train. The flexible configuration was necessary for this test. The dimension of the ZVI reactors measured a 0.9 × 0.9 m square in horizontal cross section and 1.2–1.6 m in height. The effective volumes of the ZVI reactors were 1.13, 1.06, 0.91, and 0.83 m³ for R1–R4, respectively. The combined volume of the four hZVI reactors was 3.95 m³. At 3.8 L/min (1 gpm) flow rate, the total hydraulic retention time (HRT) (including both reaction and solid/liquid separation time) in the hZVI system was 16 h. In each hZVI reactor, an overhead mixer was used to provide mixing in the reaction zone. The rotating speed of the mixer was adjustable between 0 and 1,760 rpm through a frequency controller.

The post-treatment units and tanks were made from plastic (Polytanks, USA). The effective volume of the aeration basin was 0.11 m³ and that of the settling tank was...
0.45 m$^3$. At a flow rate of 3.8 L/min, the HRT was 30 min in the aeration basin and 120 min in the settling basin. R4 effluent entered the aeration tank, in which residual Fe$^{2+}$ was oxidized and precipitated to become ferric oxide precipitates at pH 7.5–8.5 adjusted by adding NaOH. Suspended solids were removed in the settling tank, and then further polished by two sand filters operated in parallel, each with a surface area of 0.45 m$^2$ and an effective volume of 0.13 m$^3$. The filtration media consisted of a 30-cm support layer of pea gravel at the bottom and a 25-cm top layer of pool filter sand (Home Depot store). These filter beds were backwashed once a week.

The FGD pond water was pumped first into a feeding tank (0.13 m$^3$) at a rate of ~15 L/min. A second pump was used to pump the water from the tank into the treatment system at a desired flow rate (e.g., 3.8 L/min). The excess water would overflow and return to the FGD pond. Centrifugal magnetic-drive polypropylene pumps (1/16 hp feeding pump, 1/4 hp backwash pump and 1/4 hp lift pump) were purchased from Cole-Parmer. Four peristaltic pumps (Masterflex, Cole-Parmer) were used to deliver reagent solutions to the reactors. Four 110 L plastic tanks were used as reagent tanks.

**Timeline of the pilot-scale field test**

The pilot test lasted about five months. The hZVI system was started up on January 15, 2011 with 125 kg ZVI powder added into each of R1–R4 and then entered a trial operation for 10 days. The treatment prototype was first configured as a single-train, four-stage system to treat 3.8 L/min FGD wastewater between January 24 and April 3 and then as a dual train, two-stage system to treat 7.6 L/min (2 gpm) FGD water during April 4 to May 6.

**Characteristics of raw FGD wastewater**

The characteristics of the FGD pond water at this field site were typical among 22 coal-fired power plants operated by the host utility company (Table 1 and Figure 2). Raw FGD pond water (usually in a clarified form) was fed directly into the hZVI reactors without any pre-treatment. The
The temperature of the FGD wastewater varied from ∼5°C in mid-January to ∼30°C in June. Proper care was taken to prevent formation of ice in the reactors during the initial weeks. The pH of the FGD wastewater varied significantly from near neutral (∼6.8) during the startup weeks to ∼4.0 in June (Figure 2). TDS varied between 7,500 and 15,000 mg/L (Figure 2). The major cations included 1,500–2,600 mg/L Ca<sup>2+</sup> and 145–360 mg/L Mg<sup>2+</sup>; the major anions included 1,400–4,900 mg/L Cl<sup>−</sup> and 750–1,400 mg/L SO<sub>4</sub><sup>2−</sup>. The FGD wastewater at this power plant contained a much higher concentration of persulfates (represented by S<sub>2</sub>O<sub>8</sub><sup>2−</sup>, up to 400 mg/L), a highly reactive strong oxidant, relative to all other FGD wastewaters we had tested previously.

### Chemicals

ZVI powder used in this field demonstration was purchased from a commercial vendor. The ZVI powder, rated as ∼95.5% in purity, contained various impurities comprising carbon (1.75–4.50%), silicon (1.0–2.50%), sulfur (0.01–0.15%), and oxygen (2.5% max). The powder had a specific surface area of 1.14 m²/g and a specific gravity of 2.8–3.2. Particle size ranged from 5 to ∼100 μm. Hydrochloric acid of 1 M was prepared from concentrated HCl supplied by VWR. Ferrous sulfate of 0.4 M (industrial grade, Capitol Scientific, USA or reagent grade, VWR) was pre-acidified by 0.02 M HCl. Solutions of 2 M NaOH (VWR) or 0.4 M NaHCO<sub>3</sub> + 0.2 M Na<sub>2</sub>CO<sub>3</sub> (industrial grade, Fox Scientific, USA) were used for pH adjustment. Calcium hypochlorite [Ca(ClO)<sub>2</sub>] (VWR) was used in post-treatment to conduct ammonium removal testing for three days.

### Sampling

Water samples were collected from various points of the treatment train, including both filtered and unfiltered samples of influent, final effluent and intermediate water samples from various ZVI reactors and post-treatment stages. Comprehensive sampling was done twice a week, typically on Monday and Thursday, to collect water samples for trace toxic metal analysis at Southern Research Institute (SRI) (Birmingham, Alabama). Sampling kits were supplied by SRI upon request, including 0.45 μm filter discs, 30 mL syringes, 125 mL glass bottles for mercury sampling and 125 mL plastic bottles for analysis of other heavy metals. For dissolved metals, samples were filtered through 0.45 μm filters. For total metals, samples were collected without filtration. No acid preservation was applied to the samples. Water samples were sent in a cooler filled with ice to SRI within 24 h. Three times, a full set of split samples was sent to Brooks Rand Laboratory (Seattle, WA) to corroborate the analyses of SRI. The results from the two

### Table 1 | Concentrations of major contaminants (total) in the raw FGD wastewater

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Conc. in raw FGD wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenium</td>
<td>909–3,220 μg/L</td>
</tr>
<tr>
<td>Mercury</td>
<td>50–194 μg/L</td>
</tr>
<tr>
<td>Arsenic</td>
<td>3.5–21.1 μg/L</td>
</tr>
<tr>
<td>Cadmium</td>
<td>2.1–12 μg/L</td>
</tr>
<tr>
<td>Copper</td>
<td>&lt;1.0–100.4 μg/L</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;0.1 μg/L</td>
</tr>
<tr>
<td>Chromium</td>
<td>25–50 μg/L</td>
</tr>
<tr>
<td>Zinc</td>
<td>34–196 μg/L</td>
</tr>
<tr>
<td>Nitrate-N</td>
<td>10–38 mg/L</td>
</tr>
<tr>
<td>Silica</td>
<td>17–45 mg/L</td>
</tr>
<tr>
<td>Boron</td>
<td>37–194 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>3.5–7.7 mg/L</td>
</tr>
<tr>
<td>TDS</td>
<td>7,500–15,000 mg/L</td>
</tr>
</tbody>
</table>

Figure 2 | pH and TDSs in the raw FGD wastewater during the test.
laboratories were generally in good agreement. In this paper, we presented the metal analysis results from SRI.

In addition to SRI analyses, separate water samples were collected daily and shipped to this project team’s water quality laboratory for various analyses and sample storage. The supplementary analysis was conducted mainly to monitor the day-to-day status of the system and to optimize the operation. Reactive solid samples were collected once a month to investigate the status of FeOx present in the reactors. The silt content of reactors was monitored regularly.

**Water sample analysis**

Water samples sent to SRI were analyzed with a Dynamic Reaction Cell Inductively Coupled Plasma Mass Spectrometry (DRC-ICP-MS) to quantify toxic metals and metalloids of major concern present in the raw and treated FGD water. For most trace metals, the SRI method (EPA method 1638) had a detection limit of 1.0 μg/L or lower. For Hg, the SRI method (EPA method 1631-E) could detect as low as 1.0 ng/L Hg. In addition, the results of Si, B and Fe were also used in conjunction with this project team’s own analysis to evaluate the performance of the hZVI system.

Common cations and anions were analyzed in this project team’s laboratory. An ion chromatograph (IC) (DX-500, Dionex) with an IonPac AS22 or AS18 separation column was used to analyze major cations and anions in the water samples, including Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, NH$_4^+$, NO$_3^-$, PO$_4^{3-}$, SO$_4^{2-}$, S$_2$O$_8^{2-}$, Cl$^-$, Br$^-$ and I$^-$. The IC detection limits for these common ions were about 0.05–0.2 mg/L. Dissolved silica and Fe$^{2+}$ were analyzed colorimetrically on a UV-Vis spectrophotometer (T80, PG Instruments) following the ammonium molybdate method (U.S.EPA Method 370.1) and the 1,10-phenanthroline method (APHA-AWWA-WEF 2005), respectively. TDS, acidity and alkalinity were routinely analyzed. Water pH and dissolved iron (Fe$^{2+}$) at various treatment stages were measured routinely as key operating and control parameters.

### RESULTS AND DISCUSSION

**Removal of Se and Hg by a four-stage single-train system**

**Selenium**

During the four-stage single-train test, the system was fed with 3.8 L/min FGD water, corresponding to a combined HRT of 16 h. Se in the effluent (Figure 3) was mostly below 10 μg/L. Additional analysis on the intermediate samples showed that dissolved selenium had been reduced to below 10 μg/L by the third hZVI stage (R3) effluent after 12 h total reaction time. Some exceptions were caused by specific trial tests in our effort to optimize the system performance. For example, the high total Se concentrations detected between February 14 and 21 were caused by insufficient mixing of solids in the hZVI reactors. During this period, we reduced the mixing speed from about 800–300 rpm to assess the minimum mixing speed required for sustaining the reactivity of the reactors. The resulting poor performance indicated that the designed speed and power of the propellers were essential for achieving good system performance. Selenium removal returned to normal once the mixing speed was increased after February 23. Throughout the test, we did not observe an obvious impact of temperature variation on the system performance.

![Figure 3](https://iwaponline.com/wst/article-pdf/67/1/16/441341/16.pdf)
The pH in R1 varied between 6.0 and 7.7, but was mostly around 7.0; pH in R2–R4 was mostly 7.5–8.3.

**Mercury**

The results showed that the system could consistently reduce dissolved Hg to below 10 ng/L (Figure 3). In most aqueous samples, we observed that R1 reduced dissolved Hg from over 100 μg/L to below 0.01 μg/L, which was an extraordinary removal efficiency of over 99.99% in a single stage. In the initial weeks from January 15 to February 5, we noticed that while dissolved Hg was as low as a few ng/L, total Hg could be much higher at over 100 ng/L in the final effluent. We concluded that the problem was caused by the breaching of suspended particles through the sand filter. The leaked suspended particles (mainly FeOx) released Hg when acid-digested, resulting in unusually high total Hg concentrations. The problem of rapid sand filtration was fixed on February 7 by adding a steel girder to strengthen the plastic tank so that the tank would not bulge when it was filled up with water and create crevices in the sand media that allowed suspended particles to penetrate. Thereafter, the total Hg concentration in the final effluent was comparable with dissolved Hg, both below our target level of 0.010 μg/L.

The sudden increase of both Se and Hg on March 7 was caused by the trial test of adding bleaching powder (Ca(ClO)₂) into the aeration tank to verify its capability of oxidizing NH₄⁺ to N₂ via the reaction 2NH₄⁺ + 3ClO⁻ → N₂ + 3H₂O + 2H⁺ + 3Cl⁻, which is better known as break-point chlorination. It has to be noted that during this Ca(ClO)₂ episode, dissolved Hg and selenate in the R1–R4 effluents were normal, all in low levels. The incident suggested that Ca(ClO)₂ could react with ZVI or the iron oxides and release Hg and Se in the spent solids. After stopping Ca (ClO)₂ addition, Hg and Se in the final effluent soon returned to normal levels. Notably, although Ca(ClO)₂ was added according to the reaction stoichiometry, less than 70% of NH₄⁺ was removed, which suggested that some hypochlorite might have been consumed by other potential reductants such as residual ZVI, dissolved Fe²⁺, iodide, and bromide. Therefore any Ca(ClO)₂ application for NH₄⁺ removal should be added after sand filtration.

**Removal of Se and Hg by a two-stage, dual-train system**

During this test between April 4 and May 5, 2011, the system was operated as a two-stage, dual-train system consisting of train A (R1 + R4) and train B (R2 + R3). The purpose of the test was to evaluate whether or not a two-stage system with a higher treatment flow rate and shorter total reaction time can meet the treatment target for Se and Hg. Each train started by receiving 1.9 L/min FGD wastewater and the flow rate gradually increased to 3.8 L/min (1 gpm) by April 17. Thus the system treated 7.6 L/min (2 gpm) in total between April 17 and May 5 with an HRT of 8 h.

**Selenium**

As demonstrated in Figure 4, train B consistently outperformed train A, reducing selenate from over 1,500 μg/L to mostly below 50 μg/L, while train A mostly reduced Se to 100–200 μg/L. Further examination revealed that the performance of R2 was substantially better than that of R1 and thus was responsible for the difference between trains A and B. The difference between R1 and R2 might be attributed to their different compositions of FeOx. During the previous four-stage test, R2, as the second stage, had accumulated a substantial amount of well crystallized...
magnetite particles. In contrast, R1 always served as the first stage and thus was exposed to high concentrations of persulfate carried in the raw FGD wastewater. Overtime, the iron oxide phase had been altered and become oxidized to ferric (oxyhydr)oxides, which were less reactive than well-crystallized magnetite according to our previous laboratory tests.

Results of this two-stage dual-train test indicated that a two-stage hZVI system, with a combined HRT as short as 8 h, might achieve a reduction of selenate from low mg/L level to below 50 μg/L; however, such good removal efficiency can be ensured only when the system is under favorable conditions. The significant gap in performance between the two trains operated under parallel conditions indicated that the composition and quality of the reactive solid phase had a great impact on the overall system efficiency. A two-stage hZVI system with an HRT of 8 h will be difficult to meet the target 10 μg/L for total Se in the treated effluent, which was set by the host company of this project.

**Mercury**

Even at a double FGD wastewater flow rate, the hZVI system was found capable of reducing dissolved Hg to below 10 ng/L. In fact, a single stage (R1 or R2) was able to reduce dissolved Hg to below 10 ng/L, achieving over 99.99% removal (Figure 4). The cause of abnormally high dissolved Hg in the final effluent on April 11, 2011 was also caused by our additional trial test of break-point chlorination using Ca(ClO)\textsubscript{2}, as explained above.

**CONCLUSIONS**

The pilot study demonstrated that the hZVI process is an effective treatment platform for removing selenium and mercury from the FGD wastewater. The hZVI process can simultaneously reduce selenate-Se from 1 to 3 mg/L to below 10 μg/L and mercury from over 100 μg/L to below 10 ng/L in compliance with the new stringent effluent discharge limits. While a three- or four-stage hZVI system with a reaction time of 12 h or more may be needed for meeting the Se treatment requirement, a single-stage hZVI reactor with a relatively short reaction time can meet the Hg treatment requirement. The study shows that the hZVI process is scalable and could be a low-cost, high-performance treatment platform with numerous application potentials, particularly, for solving some of the toughest heavy metal water problems.

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