Field Demonstration of the Activated Iron Technology for Removing Heavy Metals from Flue-Gas-Desulfurization Wastewater

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ABSTRACT

The Activated Iron Process (AIP) technology, which is renamed from the hybrid zero-valent-iron (hZVI) process, is a novel chemical treatment process that has shown great potential in previous laboratory and field bench-scale tests for removing selenium, mercury, and nutrients from the flue-gas-desulfurization wastewater. In this study, a pilot-scale demonstration was conducted to continuously treat 3.8-7.6 L/min (1-2 gpm) of the FGD wastewater at a coal-fired power plant for five months. Results show that the AIP process could simultaneously reduce selenate-Se from 1-3 mg/L to below 10 µg/L and mercury from over 100 µg/L to below 10 ng/L, in compliance with new stringent effluent discharge limits planned by the USEPA for Se and Hg. Moreover, the process efficiently removed a broad spectrum of heavy metals such as As(III), As(V), Cr(VI), Cd(II), Pb(II) and Cu(II) from ppm level to near or sub-ppb level. A 3-stage AIP reactor with a combined hydraulic retention time of 8-12 h was sufficient for Se treatment and a single stage for Hg and other heavy metals. The process had a competitive economics and consumed ~0.3 kg ZVI per 1 m^3 FGD wastewater treated at a cost of about \$0.6/m^3. Solid waste production and energy consumption were reasonably low. The AIP process is scalable. The successful pilot study demonstrates that the AIP technology can be a reliable, low-cost, high-performance treatment platform with numerous application potentials, particularly, for solving some of the toughest heavy metal water problems

INTRODUCTION

Flue gas desulfurization (FGD) is a process used by thermoelectric power plants to cleanse sulfur dioxide (SO_2) 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 U.S. EPA (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 NO_x 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 environments. In response to the 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 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 water industry (Chu, 2006; USEPA, 2009). Reducing selenate to µg/L level and dissolved mercury to ng/L level is of particular challenge. 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 Se^0 and removed (Doran & Alexander, 1977; Oremland et al., 1989). In recent years, biological technologies represented by GE Water's ABMet[TM] and CH2MHill's ICB[TM] 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, 2005b). Despite many promising laboratory test results, endeavors by 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/Fe_3O_4/Fe(II) (or hZVI) system by Y. Huang (patents pending), which is now renamed as the activated iron process (AIP) technology. The hybrid ZVI system employs unique roles of $Fe^{2+}_{(aq.)}$ and magnetite to overcome ZVI surface passivation, the underlying mechanisms of which were related to findings from several previous works (Huang et al., 2003; Huang & Zhang, 2004, 2006a, 2006b; Huang et al. 2012). The primary role of Fe^{2+} in the AIP 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 ~3000 µg/L to below 7 µg/L and dissolved Hg^{2+} from ~50 µg/L to below 0.005 µg/L. 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 AIP technology.

The objective of this project was to further evaluate the practicability of the AIP 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 mining and refinery industry in selenium treatment.

MATERIALS AND METHODS

THE AIP TREATMENT SYSTEM - The pilot-scale AIP treatment system was designed based on the successful bench-top prototype (Huang et al., in review). The pilot system consisted of four stainless steel AIP reactors and post-treatment units including aeration, clarification, and sand filtration, all of which were mounted on a 40-ft flat-bed trailer (Fig. 1). The four AIP reactors were arranged in hydraulic elevation that allowed incoming FGD water to gravitationally flow through in sequence without the need of an intermediate lift pump. The design also allowed the AIP 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 m×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 m^3 for R1-R4, respectively. The combined volume of the four AIP reactors was 3.93 m^3. At 3.8 L/min (1 gpm) flow rate, the total hydraulic retention time (including both reaction and solid/liquid separation time) in the AIP system was 16 hours. In each AIP reactor, an overhead mixer was used to provide mixing in the reaction zone. The rotating speed of the mixer was adjustable between 0 and 1760 rpm through a frequency controller.

The post treatment units and tanks were made from plastic (Polytanks, U.S.A.). The effective volume of the aeration basin was 0.11 m^3 and that of the settling tank was 0.45 m^3. At a flow rate of 3.8 L/min, the hydraulic retention time (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.
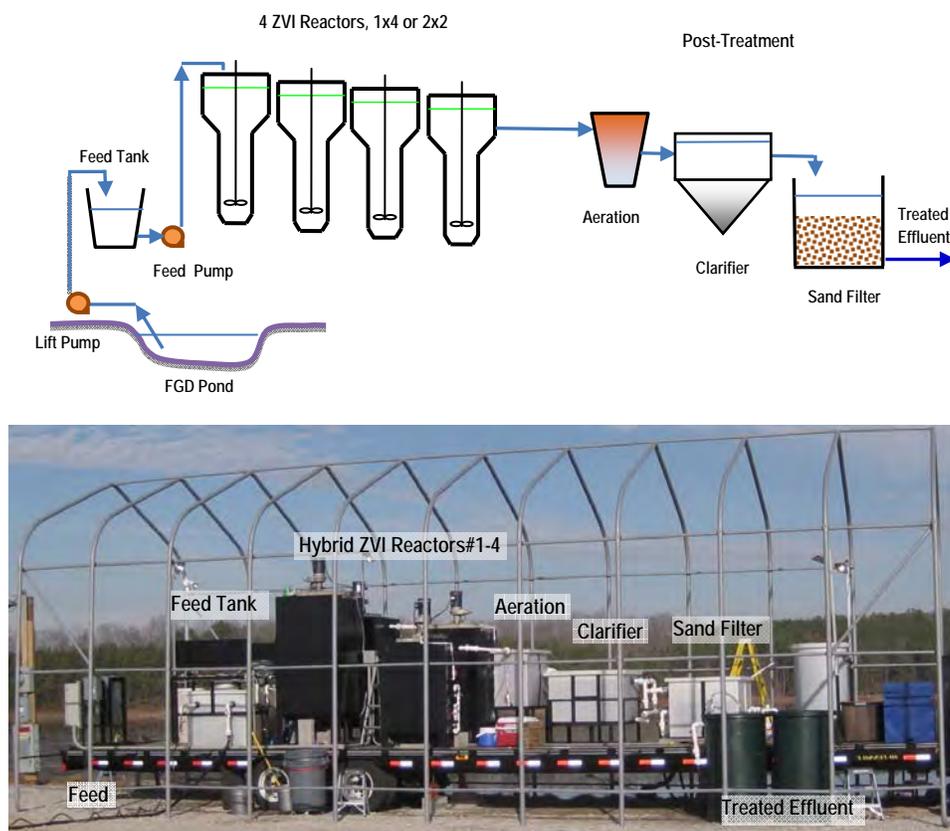
Fig. 1. Schematic representation (top) and a picture (bottom) of the hybrid ZVI treatment system. The system was mounted on a 40-ft flat-bed trailer.

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 Fig. 2). Raw FGD pond water (most time in a clarified form) was fed directly into the AIP reactors without any pretreatment. 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 (Fig. 2). Total dissolved solids (TDS) varied between 7,500 and 15,000 mg/L (Fig. 2). The major cations included 1300–2600 mg/L Ca^{2+} and 145–360 mg/L Mg^{2+}; the major anions included 1400–4900 mg/L Cl^- and 750–1400 mg/L SO_4^{2-}. The FGD wastewater at this power plant contained a much higher concentration of persulfates (represented by $S_2O_8^{2-}$, up to 400 mg/L), a highly reactive strong oxidant, relative to all other FGD wastewaters we had tested previously.

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

Pollutant	Conc. in raw FGD wastewater	
Selenium	909 to 3220	µg/L
Mercury	50 to 194	µg/L
Arsenic	3.5 to 21.1	µg/L
Cadmium	2.1 to 12	µg/L
Copper	<1.0 to 100.4	µg/L
Lead	< 0.1	µg/L
Chromium	25 to 50	µg/L
Zinc	34 to 196	µg/L
Nitrate-N	10 to 38	mg/L
Silica	17 to 45	mg/L
Boron	37 to 194	mg/L
pH	3.5 to 7.7	
TDS	7,500 to 15,000	mg/L

TIMELINE - The pilot test lasted about five months. The AIP 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-May 6. After the test with raw FGD water, a spike test treating FGD water with artificially-elevated concentrations of selected toxic metals was conducted on 4-stage configuration in phase I (May 22-29) and phase II (May 31-Jun 5) (more details in Section "Spike Test").

SPIKE TEST - A spike test was conducted to evaluate performance of the AIP system for treating artificially-elevated concentrations of selected toxic metals including Se(VI), As(III), As(V), Cr(VI), Hg(II), Pb(II), Cu(II), and Cd(II). The list was determined in consultation with the host utility company as these metals

represented some of the most immediate and biggest concerns among a long list of potential metal pollutants in
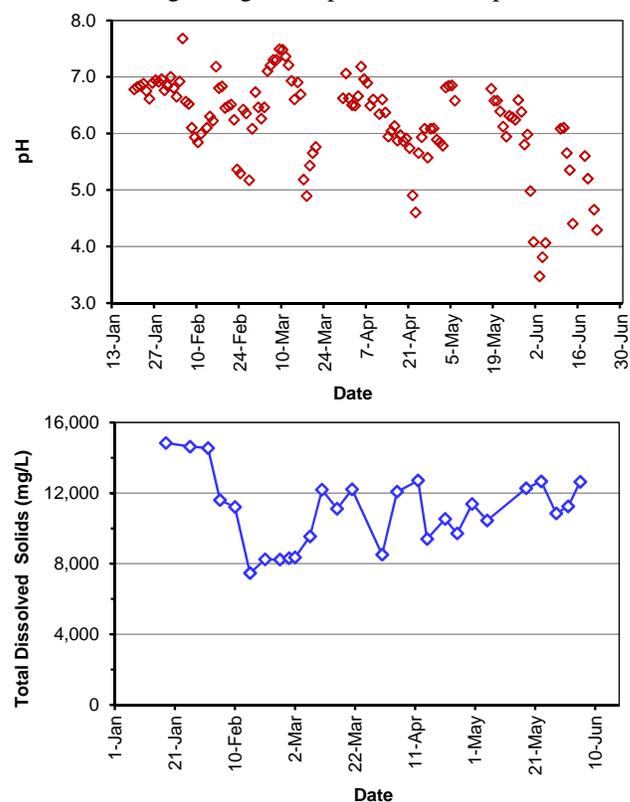
Fig. 2. pH and total dissolved solids in the raw FGD wastewater during the test.

the FGD wastewater. Soluble metal salts Na_2SeO_4, Na_2HAsO_4, $NaAsO_2$, K_2CrO_4, $HgCl_2$, $PbCl_2$, $CuCl_2$ and $CdCl_2$ (VWR) were used to prepare two stock solutions: A) 6000 mg/L selenate-Se + 150 mg/L arsenite-As + 150 mg/L arsenate-As +1500 mg/L chromate-Cr; and B) 2000 mg/L Pb(II) + 2000 mg/L Cu(II) + 1000 mg/L Cd(II) + 400 mg/L Hg(II). Separation of the cationic metals from the oxyanionic metals was to avoid potential chemical precipitation in their co-presence. The spike test was conducted in two phases on a 4-stage configuration at a flow rate of 3.8 L/min and a combined hydraulic retention time (HRT) of 16 h. In phase I of the test, stock solution A was pumped into the first AIP reactor (R1) at a rate of 12.6 mL/min, resulting a spike of 20, 0.5, 0.5, and 5.0 mg/L for Se(VI), As(III), As(V), and Cr(VI), respectively. Among many FGD wastewaters surveyed by the Electric Power Research Institute (Chu, 2006) and the U.S. EPA (2009) as well as a dozen samples from various sources tested by this project team's laboratory, none contained a selenium concentration higher than 10 mg/L. Therefore, the spiked concentration of 20 mg/L selenate-Se represented an extremely high level for FGD wastewater. In phase II, solution B was pumped at a rate of 9.45 mL/min into R1, resulting a spike of 5.0, 5.0, 2.5, and 1.0 mg/L for Cu(II), Pb(II) , Cd(II) and Hg(II), respectively. The spiked concentrations of these metals

were relatively high compared to their respective typical concentration ranges in FGD wastewaters.

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 m^2/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, U.S.A. or reagent grade, VWR) was pre-acidified by 0.02 M HCl. Solutions of 2 M NaOH (VWR) or 0.4 M $NaHCO_3$ + 0.2 M Na_2CO_3 (industrial grade, Fox Scientific, U.S.A.) were used for pH adjustment. Calcium hypochlorite [$Ca(ClO)_2$] (VWR) was used in post-treatment to conduct ammonium removal test 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 hours. For three times, a full set of split samples were sent to Brooks Rand Laboratory (Seattle, Washington) to corroborate the analyses of SRI. The results from the two 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 AIP system. Common cations and anions were analyzed in this project team's laboratory. An Ion Chromatography (IC) (DX-500, Dionex) with an IonPac AS22 or AS18 or CS12A 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-}, $S_2O_8^{2-}$, 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. Total dissolved solids, 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.

SOLID SAMPLE ANALYSIS - Solid substances in the AIP process include fresh ZVI, iron corrosion products and inert solids accumulated in the reactors. Scanning electron microscopy (SEM) was used to discern the morphology of the solid particles. Powder X-ray diffraction (XRD) spectroscopy was used to characterize the crystalline of iron oxides generated from ZVI corrosion. In addition, secondary ion mass spectroscopy (SIMS) was used to perform depth profiling of the spent solids and to analyze the distribution of removed heavy metals in the iron oxide minerals. Toxicity of the spent solids was analyzed through the toxicity characteristic leaching procedure (TCLP) (USEPA Method 1311).

RESULTS AND DISCUSSION

REMOVAL OF SELENIUM AND MERCURY BY A FOUR-STAGE SINGLE-TRAIN SYSTEM – 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 (Fig. 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 AIP 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 Feb. 14 and 21 were caused by insufficient mixing of solids in the AIP reactors. During this period, we reduced the mixing speed from about 800 rpm to ~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. pH in R1 varied

between 6.0 and 7.7, but mostly around 7.0; pH in R2-R4 was mostly 7.5-8.3.

The results showed that the system could consistently reduce dissolved Hg to below 10 ng/L
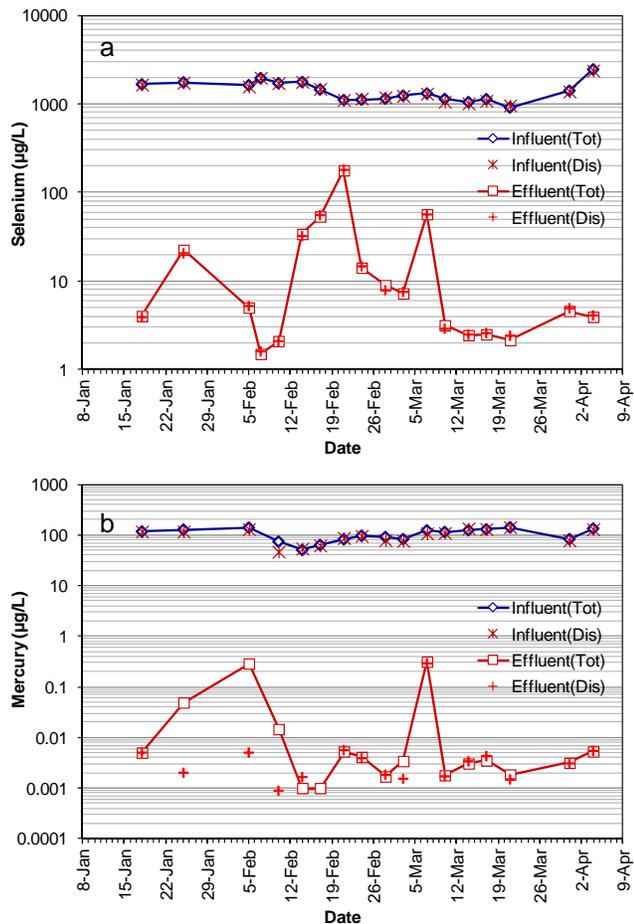
Fig. 3. Removal of a) total and dissolved selenium, and b) total and dissolved mercury by the AIP system operated as a four-stage single-train system for treating 3.8 L/min (1 gpm) FGD wastewater with a combined HRT = 16 h.

(Fig. 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 suspend 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 NH_4^+ to N_2 via the reaction $2NH_4^+ + 3ClO^- \rightarrow N_2 + 3H_2O + 2H^+ + 3Cl^-$, 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 returned soon to normal levels. Notably, although $Ca(ClO)_2$ was added according to the reaction stoichiometry, less than 70% of NH_4^+ was removed, which suggested that some hypochlorite might have been consumed by other potential reductants such as residual ZVI, dissolved Fe^{2+}, iodide, and bromide. Therefore any $Ca(ClO)_2$ application for NH_4^+ removal should be added after sand filtration.

REMOVAL OF SELENIUM AND MERCURY 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.

As demonstrated in Fig. 4, train B consistently outperformed train A, reducing selenate from over 1500 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 4-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 2-stage dual-train test indicated that a two-stage AIP 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 AIP 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.
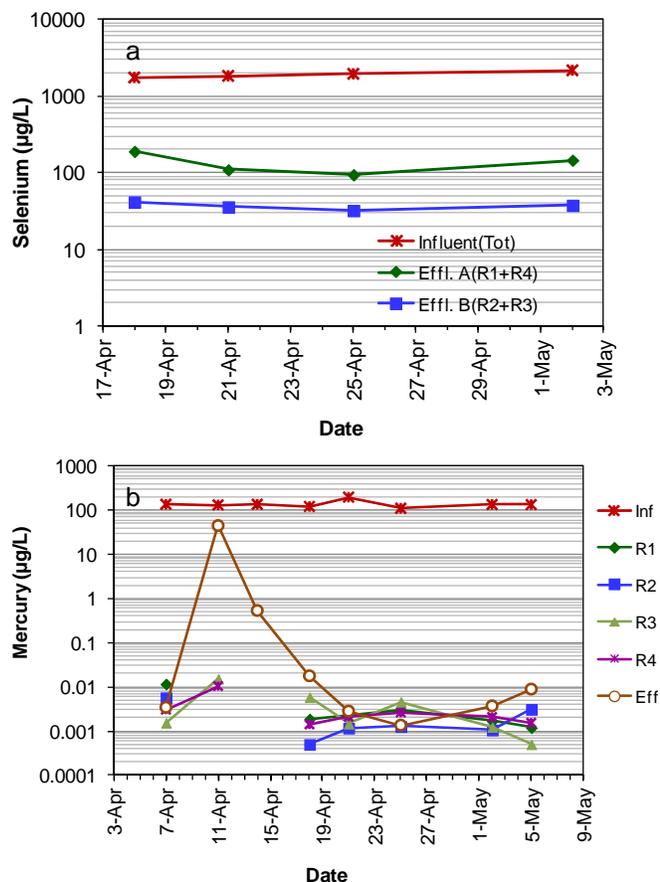
Fig. 4.   Removal of dissolved a) selenium and b) mercury by the AIP system operated as a two-stage, dual-train system with train A consisting of R1 and R4 and train B consisting of R2 and R3.   The feed flow rate for each train increased gradually from initial 1.8 L/min on April 4 to 3.8 L/min on April 17 and remained so until May 6 with an HRT of ~8 h in each train.

Even at a double FGD wastewater flow rate, the AIP 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 (Fig. 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)$_2$, as explained above.

REMOVAL OF SELENIUM AND MERCURY IN SPIKE TEST - The FGD wastewater was spiked with 20 mg/L selenate-Se before being fed into R1. With ~2 mg/L selenate-Se in the raw FGD wastewater, the combined concentration was ~22 mg/L for selenate-Se after spiking. As shown in Fig. 5, R1 reduced selenate from 22 to 8-17 mg/L Se and R2 further reduced to below

4 mg/L (~1 mg/L on the last three days).   The results indicated that under a loading as high as 22 mg/L Se, the first stage could no longer achieve a removal of over 90%; R2, the second stage, could achieve a reduction of over 90% selenate from over 10 mg/L to ~1 mg/L Se. R3 and R4, each achieving about 90% removal, further reduced selenate to about 10 µg/L Se. The results showed that the AIP process with a multiple-stage configuration could handle high concentration selenate and still met the required discharge limit. Se in the final effluent was significantly higher than in R4 on June 3-5, possibly due to errors or sample contaminations made during the external analyses by Southern Research Institute (Birmingham, AL); our own analyses showed that Se in the final effluent was in agreement with those in R4 during these days.
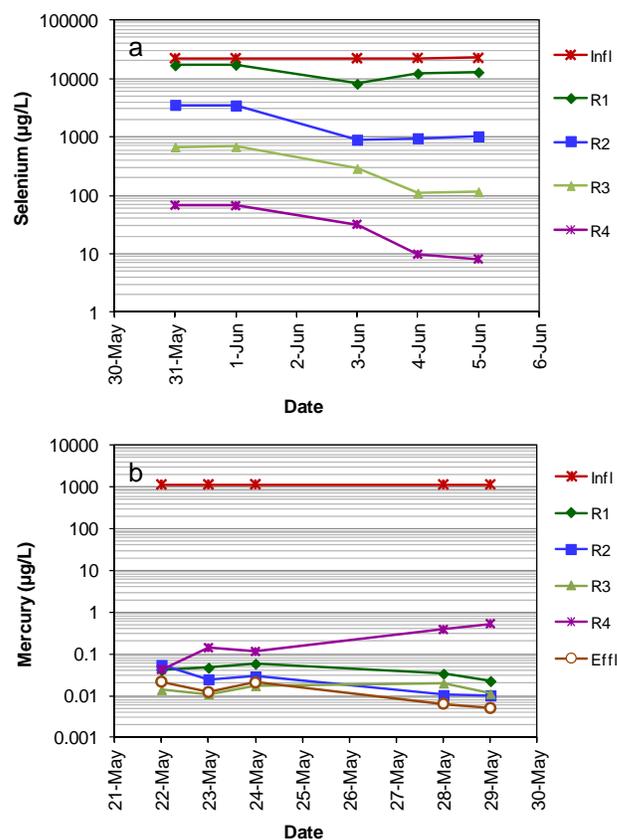
Fig. 5. Removal of dissolved a) selenium and b) mercury during the spike test with artificially elevated heavy metal loadings. The AIP system was operated as a four-stage system with a combined HRT = 16 h.

Concentration of selenium in the FGD wastewater can vary significantly depending on wet-scrubber technology, operating conditions, and the type and source of coal used by the power plant. The multiple-stage AIP process demonstrated its robustness and flexibility in handling extra-high selenate loadings. When there is a need to treat high concentrations of selenium, the AIP system can be upgraded simply by adding one more stage to the existing treatment train and extending the HRT for a few more hours.

With 1000 µg/L Hg^{2+} spiked, the feed water contained a total of 1150 µg/L dissolved Hg. The spike test result showed that the AIP process can handle high concentration mercury (Fig. 5). Dissolved Hg in the final effluent was below 10 ng/L on May 28 and 29, and below 25 ng/L on the other days. For unknown reason, samples from R4 contained significantly higher Hg than all previous reactors (R1-R3) and the final effluent. This abnormality was possibly due to sampling contamination.

Further examination showed that R1 reduced dissolved Hg from 1150 to below 0.05 µg/L. Accordingly, it was expected that R2 and R3 could further reduce dissolved Hg substantially, but the fact was that R2 and R3 only achieved a marginal further reduction. One explanation to the apparently different Hg removal efficiency between R1 and R2 (or R3) was that Hg removal in the AIP reactor required certain supplementary chemicals that were present in the raw FGD wastewater but were consumed in R1. From our previous laboratory tests, it was confirmed that the addition of I^-, PO_4^{3-}, or S^{2-} into the AIP reactor could improve Hg removal. The hypothesis is that the co-mineralization of Hg with iron oxides in the AIP reactor might be responsible for achieving the extremely low level of Hg in the treated water and that such co-mineralization might be more effective in the presence of certain constituents in the raw FGD wastewater. The concentrations of these supplementary constituents may not be adequate to support the full mineralization of the extra high Hg^{2+} during the spike test. Co-mineralization refers to the process in which the removed Se and Hg and other toxic metals (initially surface-adsorbed/precipitated) would gradually occupy certain lattice and become a part of the iron oxide structures and thus be encapsulated in the spent iron oxide minerals.

REMOVAL OF OTHER HEAVY METALS IN SPIKE TEST - The spike results showed that the AIP system was highly effective for lead, cadmium, copper, arsenic and chromium removal.

The AIP system reduced dissolved Pb^{2+} from 5000 to below 1 µg/L in R1 effluent. All effluent total and dissolved Pb were below 1 µg/L. Similar to mercury removal, a single-stage AIP treatment can decrease high concentration Pb^{2+} to near or below 1 µg/L.

Cd^{2+} was decreased from 2500 to ~10 µg/L in R1 and to below 1 µg/L in R2. All effluent total and dissolved Cd were below 1 µg/L.

The system decreased dissolved Cu^{2+} from 5000 to near 1 µg/L. Dissolved Cu^{2+} was decreased from 5000 to 1-3 µg/L in R1 effluent. The results showed that a single stage with a relatively short HRT was sufficient to achieve a low Cu concentration that is far lower than the maximum contaminant level (MCL) of 1.3 mg/L for Cu enforced by the USEPA. In our laboratory test, Cu^{2+} was found to be rapidly reduced to elemental Cu in an AIP system.

Both As(III) (arsenite) and As(V) (arsenate) were removed efficiently by the AIP system. During the spike test, dissolved As in R1 effluent was never higher than 1 µg/L, the method detection limit. The AIP process is superior to the conventional coagulation-precipitation processes in As removal that typically reduce As to a few µg/L level. The AIP process could be a viable technology for As-contaminated groundwater treatment if the maximum contaminant level (MCL) for As is further lowered from the current limit of 10 µg/L to below 1 µg/L.

R1 reduced dissolved chromate from 5000 µg/L to mostly below 10 µg/L Cr (137 µg/L on June 1 was an exception for unknown reason). Chromate was reduced more rapidly than selenate under comparable conditions. For both chromate and selenate, their removal depends on the effective reduction of the oxyanions to lower oxidation state(s). Prior to the spike test, dissolved Cr in all intermediate samples (filtered effluents from R1-R4) and final effluent samples were found to be decreased to mostly below 2 µg/L from ~50 µg/L in the raw FGD wastewater. These results suggested that the AIP process will likely meet the California recommended guideline for Cr treatment, which, at 5 µg/L, is probably the most stringent one in the US.

REMOVAL OF NITRATE - Throughout the test, the AIP process was able to reduce nitrate from over 10 mg/L to near or below the method detection limit (0.1 mg/L), thus consistently achieving over 99% removal. The concentration of nitrate varied greatly over time between ~10 mg/L and 38 mg/L. The AIP system appeared to handle such variation without problem. With an HRT of 4 h, R1 typically achieved 85% to 95% reduction. Nitrate was further reduced to mostly below 0.5 mg/L in R2. Reduction of nitrate occurred simultaneously with reduction of selenate. While nitrate and selenate may compete for electrons released from iron corrosion process, we did not observe any sign of mutual exclusive inhibition between them.

During the test, almost all nitrates were converted to ammonia, which necessitated an additional post treatment to complete the nitrogen removal if required. Break-point chlorination is a proved technology that uses hypochlorite or chlorine to oxidize ammonia to nitrogen gas. On March 6, an attempt was made to oxidize ammonia to nitrogen gas by adding $Ca(ClO)_2$ into the aeration basin. More than 50% ammonium was removed upon the addition of $Ca(ClO)_2$. The effectiveness of the method was further verified by additional tests in our laboratory. To ensure a high removal of ammonia, an in-line probe that can measure the real-time concentration of ammonia should be used to help determine the application rate of $Ca(ClO)_2$. One potential problem is that $Ca(ClO)_2$ may react with the iron sludge accumulated in the aeration tank or settling basin and result in a release of toxic metals such as Hg^{2+} through unknown mechanism(s). Therefore,chlorination should be applied only to the filtered effluent after sand filtration.

CHEMICAL AND ELECTRICITY CONSUMPTION - Throughout the field demonstration,

chemical usages were recorded to estimate operational costs of this AIP process (Table 2). We tried to make a reasonable estimation of the ZVI consumption, despite the difficulties: (1) there were bleedings of solids of various degrees from the reactors during the start-up period; (2) the test duration was not sufficiently long, relative to the life span of the ZVI powders added at the beginning of the test, to reach a steady state that is more reliable for estimating the long-term steady consumption rate of ZVI powder; and (3) the amount of ZVI residue in the reactors was difficult to estimate accurately.

Table 2. Chemical usages during the pilot field test.

Chemicals	Consumption (kg or L)*
ZVI powder**	670
$FeSO_4$	18
$FeCl_2$	5
NaOH	50
$NaHCO_3$	45
Na_2CO_3	21
6 N HCl	104
$NaNO_3$	18

* All chemical consumptions are in kg, except for HCl, which is in L. **The total ZVI usage included: 125 kg in each reactor during startup; 20 kg to R1 on 2/23, 2/26; 58 kg to R1 on 3/11; 20 kg to R1 and 10 kg each to R2-4 on 4/10; 10 kg to R4 on 5/28. Only a fraction of 670 kg added into the system over time was actually consumed: some unused ZVI were discharged when the silted reactors were decanted; and a large quantity of unused ZVI still remained in the system at the end of the test.

Assuming that the average FGD wastewater contains 15 mg/L nitrate-N, 300 mg/L $S_2O_8^{2-}$, 5.0 mg/L dissolved oxygen, and 2.5 mg/L selenate-Se, ZVI will need to provide 8.6, 3.1, 0.6, 0.2 mmol e⁻ (12.5 mmol in total), respectively, to reduce these oxidants in 1 L of this FGD wastewater. Assuming Fe_3O_4 as the iron corrosion product, 4.7 mmol Fe^0 (0.26 g) will be needed to provide 12.5 mmol e⁻. Note that much of the consumption resulted from nitrate reduction. The actual consumption rate appeared close to this estimate. At a rate of 0.3 kg/m³, the system will consume 818 kg/d ZVI (or 300 ton/yr) for treating a 2725 m³/d (or 500 gpm) FGD wastewater stream (a representative full-scale flow rate). For a weaker strength waste stream like ash transport water of a power plant or none-FGD wastewater applications (e.g., refinery stripped sour wastewater, or mining drainage), the ZVI consumption could be much lower.

The main electricity consumption came from the four mixers. At a full speed of 1800 rpm, the mixer was rated at 1 hp (0.735 kW). A frequency controller was used to reduce the speed of the mixing propeller to ~600-900 rpm. The actual power usage was estimated at ~0.5 hp, which translates to 0.37 kW/m³ reactor volume. For a full-scale reactor, it was estimated that 0.1-0.2 kW/m³ power input will be enough to provide mixing. For treating a stream of 2725 m³/d with an HRT of 12 h, the total reactor volume will be about 1363 m³ and the total power consumption by the AIP reactors will be about 136-272 kW, the cost of which would be considered moderate for a power plant.   Other minor power consumption sources include lifting pump(s) and aerator.

SOLID WASTE PRODUCTION AND CHARACTERIZATION - During this operation, solid waste was released mainly in form of thick slurry. The main constituent was iron oxides formed as iron corrosion products or as precipitate of residual Fe^{2+} ions in the aeration tank upon addition of NaOH.   At a consumption rate of 0.3 kg ZVI per m³ treated water, the system will produce 0.42 kg of Fe_3O_4 (or 0.39 kg Fe_2O_3) per m³ treated water.   SEM images (Fig. 6) illustrated that besides iron oxides, there was a substantial presence of inert solids, mainly gypsum ($CaSO_4$). The SEM-EDS elemental scan confirmed that Ca and S were present in substantial fractions in R1 spent solids, but not as much in R2-R4 spent solids. The XRD results (Fig. 7) showed that R1 solids were dominated by gypsum, suggesting that there was not much magnetite accumulated in R1. Magnetite could be oxidized in the presence of strong oxidizing agents, e.g., persulfate in high concentrations. R2 solids (as well as R3 and R4 solids) from the 4-stage operation were clearly dominated by magnetite crystalline. Elemental iron was also detected. R2 solids from the 2-stage configuration showed that magnetite phase was phasing out and gypsum was starting to accumulate. R2 in the two-stage configuration received raw FGD wastewater, just like R1 in the 4-stage configuration, which might explain why gypsum started to accumulate.

The spent FeOx solids collected from R1 and R2 were analyzed using secondary ion mass spectroscopy (SIMS). The results showed that selenium and mercury were distributed rather evenly within the entire iron oxide crystalline. The co-mineralization of heavy metals with iron oxides could stabilize the removed heavy metals and reduce the risk of their leaching from the spent solids.

TOXICITY AND DISPOSAL OF SPEND SOLIDS - Spent solid samples were analyzed following TCLP test protocols to determine whether the spent solids could be designated and disposed as non-hazardous waste. The spent solids were generally pH neutral in water. Two batches of samples were obtained from each AIP reactor for TCLP tests. The first batch was obtained on April 5 at the end of the 4-stage test after nearly 3 months operation. The second batch was obtained on June 22 just before the pilot test was terminated. The second batch of samples had experienced the spike tests under the high loadings of externally-added toxic metals (Hg, Se, As, Cd, Cr, Cu and Pb). As such the toxic metals accumulated in these samples could be very high.
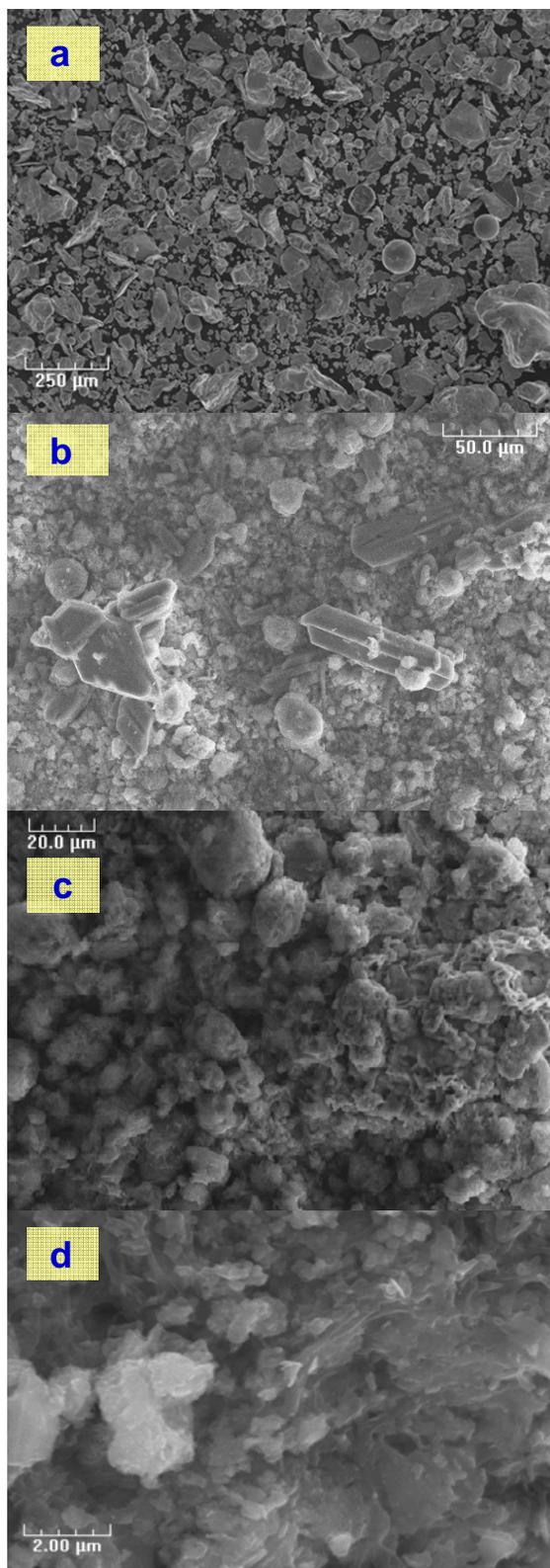
Fig. 6.   SEM images of a) raw ZVI powders; b) suspended solids from R1 that contained some large gypsum crystallines; c) solids from R2, mostly magnetite crystalline; and d) solids from aeration tank, a mixture of magnetite and probably lepidocrocite.
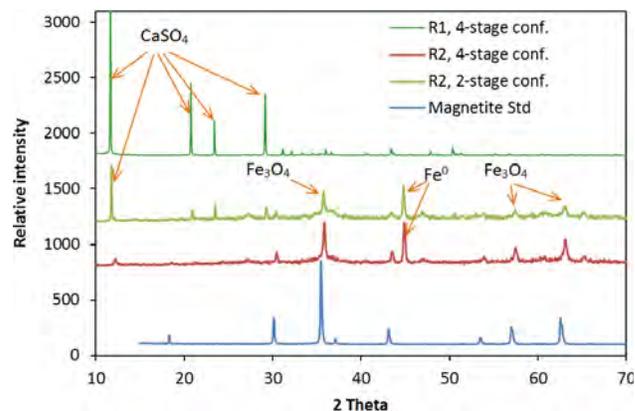
Fig. 7. Powder X-ray diffraction spectra of solid particular matters collected from the AIP reactors under different operational stage.   The XRD spectrum confirmed that gypsum ($CaSO_4$) was the dominant crystalline in the first AIP stage. The iron oxide in the first stage was poorly crystallized. Magnetite crystalline dominated the second and the subsequent stages.

The results were summarized in Table 3. Key toxic metals levels in the leachate were generally below the regulatory limits set by the U.S. EPA. We were not able to quantify silver in the leachates. There was one sample (R1 collected on June 22) that failed to meet the EPA regulation for Cd. However, R1 collected on April 5 was well below the limit for Cd. One possible factor is the spike test. Results from these two TCLP tests are in agreement with previous findings (Huang et al., in review).

OPERATION AND MAINTENANCE - During start-up, the four ZVI reactors were preconditioned for 4 days to seed the system with some initial Fe_3O_4 mass using a nitrate-Fe^{2+} method that was described in a previous bench-scale test (Huang et al., in review). Upon continuously feeding the FGD wastewater, it was observed that a significant amount of dissolved Fe^{2+} (>150 mg/L) and acidity (pH <5.5) were released in R1. During the transition period, the settling property of the reactive solids was not as good as those in our prior laboratory tests on simulated wastewaters or in the bench-top scale field test (Huang et al., in review). The problem appeared related to the unique compositions of the FGD wastewater at this power plant, which contained a much higher concentration (up to 400 mg/L) of persulfate than several other FGD wastewaters this project team had previously evaluated. Rapid reduction of persulfates in R1 might play a role in the release of Fe^{2+} (often >100 mg/L). High Fe^{2+} in conjunction with a relative high pH (~8.0) in R2-R4 during the transition phase might cause the sludge bulking and bleeding problems during the startup week.   To mitigate the poor sludge settling problem, $NaHCO_3$ solution was introduced into R1 to adjust the pH to near neutral while aeration was introduced into R1 to remove some of Fe^{2+} and thus improve the settling of the solids in R1

Table 3. Heavy metal content in the leachate samples from the TCLP tests on the solid samples collected from the AIP system.

Heavy Metal	Concentration (µg/L)						Max. Conc. allowed by USEPA Reg. (µg/L)
	Sample Set#1		Sample Set#2				
	R1	Composited R2+R3+R4	R1	R2	R3	R4	
Arsenic	305.8	289.1	<5	<5	<5	<5	5,000
Barium	187.1	46.7	118.1	53.7	32.3	31.4	100,000
Cadmium	17	14.1	2043	28.5	143.0	139.3	1,000
Chromium	<5	<5	23.1	107.3	153.8	148.1	5,000
Lead	<5	<5	<5	<5	<5	<5	5,000
Mercury	<1	<1	11.6	5.2	6.4	<5	200
Selenium	818	632.7	2.7	45.5	36.4	36.6	1,000
Silver	n/a	n/a	n/a	n/a	n/a	n/a	1,000
Molybdenum	54.7	54.7	<5	<5	<5	<5	N/A

Note: Sample Set#1 was collected at the end of the 4-stage single-train test on April 5.   Sample Set#2 was collected at the end of the entire demonstration on June 22, 2011.

as well as in the downstream reactors. The reactive solid bleeding problem gradually subsided as the reactors reached a new equilibrium after a few days. Overall, the presence of high persulfate had complicated the operation of the AIP system in several aspects; with a multiple-stage configuration, however, the problem was manageable since persulfate was removed in R1.

The strength of the FGD wastewater started to weaken in mid February as both salinity and the concentrations of all major pollutants (Se, Hg and nitrate) dropped considerably. It was found that the wet scrubbers were shut down for general maintenance; thus no liquid was discharged. As the pond became shallower, wind/wave agitation substantially increased the concentration of solids (e.g., gypsum silts) pumped into the treatment train. The continuous accumulation of inert solids started to disrupt the normal operation of the system, particularly R1. With excess inert solid buildup (e.g., silts accounted for over 50% of total solids in R1), the mixing power became inadequate and the heavy ZVI particles appeared to settle at the bottom without being fluidized fully. To solve the problem, we released the excess sludge from R1 and replenished with some new ZVI powder.

During the entire pilot test, the treatment system was operated without any major equipment failure or operational incidents. Overnight power outage due to passing thunder storms happened a few times, but the disruptions didn't significantly affect the performance of the system. A one-week complete shutdown of the system for a personnel break did not result in cementation of reactive solids nor affect the system performance subsequently. Some metal fittings and valves corroded rapidly and had to be replaced. The main body of the reactor, made of stainless steel, showed no sign of corrosion. The stainless mixers had no serious corrosion or abrasion problem.

CONCLUSIONS

The five-month project demonstrated that the AIP technology is an effective treatment platform for removing selenium and mercury from the FGD wastewater. The AIP process can simultaneously reduce selenate-Se from 1-3 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 AIP system with a reaction time of 12 hours or more may be needed for meeting the Se treatment requirement, a single-stage AIP reactor with a relatively short reaction time can meet the Hg treatment requirement.   The process was also very effective at decreasing As(III), As(V), Pb(II), Cr(VI), Cu(II) and Cd(II) from over 1000 µg/L to near or below 1.0 µg/L in a single-stage treatment system with a relatively short reaction time.   The consumption of chemicals and solid waste production were moderate.   At 0.3 kg ZVI consumed per 1 m^3 FGD wastewater treated, the chemical cost was estimated at about \$0.6-1.0 per 1 m^3 FGD wastewater treated. The production of total solids was estimated to be around 0.9-1.5 kg/m^3 water treated. Electricity consumption accounted for a relatively small fraction in total operational cost.   The pilot study shows that the AIP process is a scalable, robust, and versatile technology and could be a simple, low-cost, high-performance treatment platform with numerous application potentials, particularly, for solving some of the toughest heavy metal water problems.

Acknowledgment

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