PILOT-SCALE DEMONSTRATION OF hZVI PROCESS FOR TREATING

FLUE GAS DESULFURIZATION WASTEWATER

AT PLANT WANSLEY, CARROLLTON GA

A Thesis

by

PHANI KUMAR PEDDI

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2011

Major Subject: Biological and Agricultural Engineering

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Approved by:

Chair of Committee,   Yongheng Huang
Committee members,   Youjun Deng
                         Vijay Singh
Head of Department,   Stephen W. Searcy

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ABSTRACT

Pilot-Scale Demonstration of hZVI Process for Treating Flue Gas Desulfurization

Wastewater at Plant Wansley, Carrollton, GA. (December 2011)

Phani Kumar Peddi, B.E., Andhra University, India

Chair of Advisory Committee: Dr. Yongheng Huang

The hybrid Zero Valent Iron (hZVI) process is a novel chemical treatment platform that has shown great potential in our previous bench-scale tests for removing selenium, mercury and other pollutants from Flue Gas Desulfurization (FGD) wastewater. This integrated treatment system employs new iron chemistry to create highly reactive mixture of Fe^0, iron oxides (FeO_x) and various forms of Fe (II) for the chemical transformation and mineralization of various heavy metals in water. To further evaluate and develop the hZVI technology, a pilot-scale demonstration had been conducted to continuously treat 1-2 gpm of the FGD wastewater for five months at Plant Wansley, a coal-fired power plant of Georgia Power. This demonstrated that the scaled-up system was capable of reducing the total selenium (of which most was selenate) in the FGD wastewater from over 2500 ppb to below 10 ppb and total mercury from over 100 ppb to below 0.01 ppb. This hZVI system reduced other toxic metals like Arsenic (III and V), Chromium (VI), Cadmium (II), Lead (II) and Copper (II) from ppm level to ppb level in a very short reaction time. The chemical consumption was estimated to be approximately 0.2-0.4 kg of ZVI per $1m^3$ of FGD water treated, which suggested the

process economics could be very competitive. The success of the pilot test shows that the system is scalable for commercial application. The operational experience and knowledge gained from this field test could provide guidance to further improvement of technology for full scale applications. The hZVI technology can be commercialized to provide a cost-effective and reliable solution to the FGD wastewater and other metal-contaminated waste streams in various industries. This technology has the potential to help industries meet the most stringent environmental regulations for heavy metals and nutrients in wastewater treatment.

ACKNOWLEDGEMENTS

It is with immense gratitude that I acknowledge the support and help of my advisor Dr. Yongheng Huang and committee members, Dr. Vijay Singh and Dr. Youjun Deng throughout my Master's program at Texas A&M University. I am heartily thankful to my advisor, Dr. Huang, whose support, supervision and encouragement from preliminary to the concluding level enabled me to develop an understanding of the subject. I would like to thank him for this opportunity to face the real world of challenges and trusting me in every aspect of this project. I would like to thank Mr. Jason Teng, Southern Company Services, Al for his immense support throughout this project at Plant Wansley, Ga. I would also like to thank crew of Plant Wansley, Ga for their help in setting up the pilot scale systems.

I extend my gratitude to the department staff and faculty for their valuable help and guidance throughout my life at Texas A&M University. I would like to thank my friends and colleagues for their affection and support in every aspect of my life.

I would also like to thank my family for being with me in every phase of my life and supporting me with immense love, care and trust.

NOMENCLATURE

ABMet	Advanced Biological Metal Removal Systems.
AsO_3^{3-}	Ortho Arsenite
AsO_2^-	Meta Arsenite
B	Boron
BOD_5	5 day Biological Oxygen Demand
Br^-	Bromide Ion
Ca	Calcium
Cl^-	Chloride Ion
COD	Chemical Oxygen Demand
CrO_4^{2-}	Chromate
Cu	Copper
EPRI	Electric Power Research Institute
ERG	Eastern Research Group Inc
Fe^0	Elemental Iron
$FeCl_2$	Ferrous Chloride
FeO_x	Iron Oxide
Fe_3O_4	Magnetite
$\gamma\text{-}FeO(OH)$	Lepidocrocite
$FeSo_4$	Ferrous Sulfate
FGD	Flue Gas Desulfurization

GE	General Electric
gpm	gallon per minute
Hg	Mercury
HCl	Hydrochloric Acid
hZVI	Hybrid Zero Valent Iron
I^-	Iodide Ion
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
Mg^{2+}	Magnesium Ion
ml	millilitre
mM	millimole
Na	Sodium
Na_2CO_3	Sodium Carbonate
$NaHCO_3$	Sodium Bicarbonate
NH_4^+	Ammonium Ion
NO_3^-	Nitrate Ion
NaOH	Sodium Hydroxide
NPDES	National Pollutant Discharge Elimination System
ppb	parts per billion (µg/l)
ppm	parts per million (mg/l)
ppt	parts per trillion (ng/l)
SBR	Sequential Bioreactors
Se	Selenium

SeO_4^{2-}	Selenate
Si	Silicon
SO_4^{2-}	Sulfate Ion
SRI	Southern Research Institute
TAMU	Texas A&M University
TCLP	Toxicity Characteristic Leaching Procedure
TSS	Total Suspended Solids
USEPA	United States Environmental Protection Agency
ZLD	Zero Liquid Discharge
ZVI	Zero Valent Iron

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1. INTRODUCTION

A field study was conducted to evaluate the efficacy of the hybrid Zero-Valent Iron (hZVI) system for removing heavy metals and other pollutants in the Flue Gas Desulfurization (FGD) waste stream waters from the wet scrubbers of coal-fired power plants. A mobile pilot treatment system was installed and operated at Plant Wansley of Georgia Power, Carrollton, GA for five months between January and June 2011. The effectiveness of this hZVI system had been demonstrated through a series of continuous flow test on bench scale prototypes in our laboratories. This technology can stand as a potential and cost effective solution for current and emerging needs in the field of industrial wastewater treatment. This hZVI system can be effectively used in sectors like fossil fuel power generation sector, oil and gas sector and mining sector which are facing tough time in facing the stringent regulations levied by USEPA for toxic metals like mercury, arsenic and selenium, Bench scale prototype of this hZVI systems was operated at Plant Bowen, GA (Southern Company) and showed a consistent removal capability of reducing the selenium content in the FGD water from 2-4 ppm to below 0.01ppm and dissolved mercury from 20 ppb to blow 0.01 ppb. Fig. 1 shows the bench scale system operated at Plant Bowen.

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This thesis follows the format and style of Chemosphere.

Fig. 1. Bench Scale Prototype Operated at Plant Bowen, GA

Based on these satisfactory results produced form the bench scale systems, Southern Company decided that a scaled-up demonstration would be essential to further evaluate the feasibility of the hZVI technology. Southern Company funded Texas A&M University to conduct a pilot-scale demonstration of hZVI technology at Plant Wansley. A formal agreement was signed in November 2010 between Texas Agri Life Research and Southern Company to build a pilot scale system capable of handling about 4 gpm flow rate and operate for three months at one of their power generation site. The fabrication and installation of different elements of this pilot scale system took about two months and we were able to successfully deliver the system at Plant Wansley, Carrollton, GA on January 13, 2011 followed by installation of this system near the source of FGD water. Operation of this system had started on January 17, 2011. In late April, with support of EPRI the initially scheduled three month test period was extended by seven more weeks to conduct additional simulated tests to

investigate the adaptability of these systems in different conditions. The field demonstration was completed by June 22, 2011 and prototype was officially decommissioned on August 5, 2011. The detailed proposed treatment system is shown in Fig. 2.
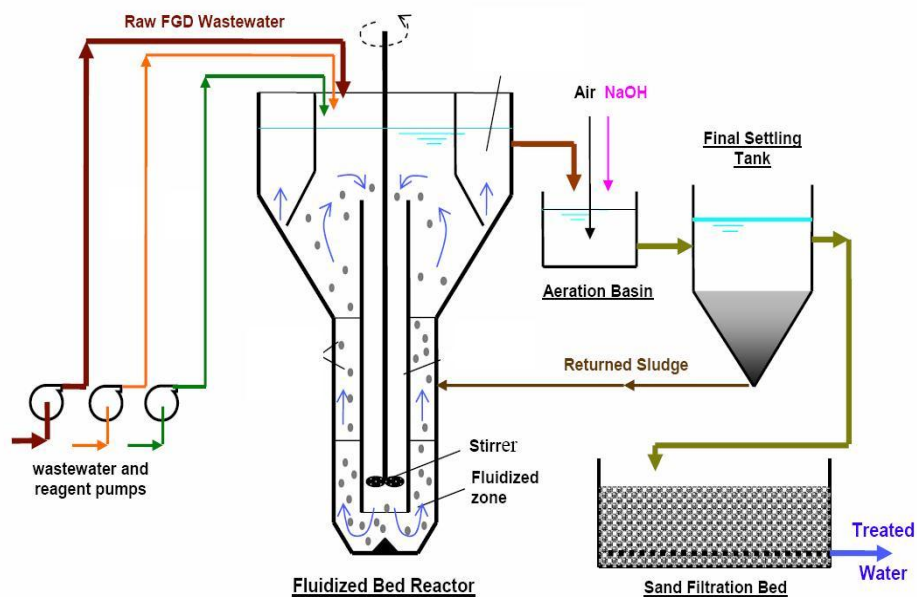
Fig. 2. Process Flow Diagram of Proposed hZVI Treatment System

1.1 Problem Statement

In this environmental conscious world, coal fired power plant operators are facing tough challenges in handling their effluents. Anticipated regulatory requirements for air and water discharge from coal-fired power generation utilities have triggered interest in the research and development of innovative treatment technologies for the remediation of process (flue gas) and waste streams. Due to heavy

negative impacts of SO_2 on human health and ecosystems, there is a huge public concern regarding SO_2. SO_2 is emitted as a byproduct of combustion of the fossil fuels. Power generation sector in USA is responsible for almost 70% of total emissions of SO_2 into the atmosphere. Due to adverse impacts of SO_2 on human health like eye, nose and throat irritations and ecosystems like acid rains, there is huge public concern regarding emission. To control SO_2 emissions into atmosphere generally the power plants adopt four main technologies. 1) Tall gas stacks in order to disperse the emissions away from immediate point of release, 2) variation of operational conditions to reduce the SO_2 emissions according to surrounding atmospheric conditions, 3) Reduction of sulfur levels in the fossil fuel before combustion and 4) removal of SO_2 using special techniques from post combustion gas stream (Margaret et al.., 2004). Power plants used to select low sulfur content fossil fuels initially and then coupled them with first three techniques as stated above. Later the focus shifted to post-combustion control technologies.

Power plants are employing FGD systems or scrubbing technologies to control SO_2 in the flue gases generated as post-combustion control technologies. The commercially available FGD systems are of two types 1) once-through and 2) regenerable processes. In once-through FGD systems, sulfur oxides are bound permanently to the sorbent and disposed later as a byproduct like gypsum, whereas in regenerable processes sulfur oxides are released from the sorbents and further processed and recovered as sulfuric acid, elemental sulfur and liquid SO_2 (Margaret et al., 2004). Both these systems can either be wet processed or dry processed based on the sulfur content of the coal. Detailed classification is shown in Fig. 3 (Srivatsava R.K, 2000).
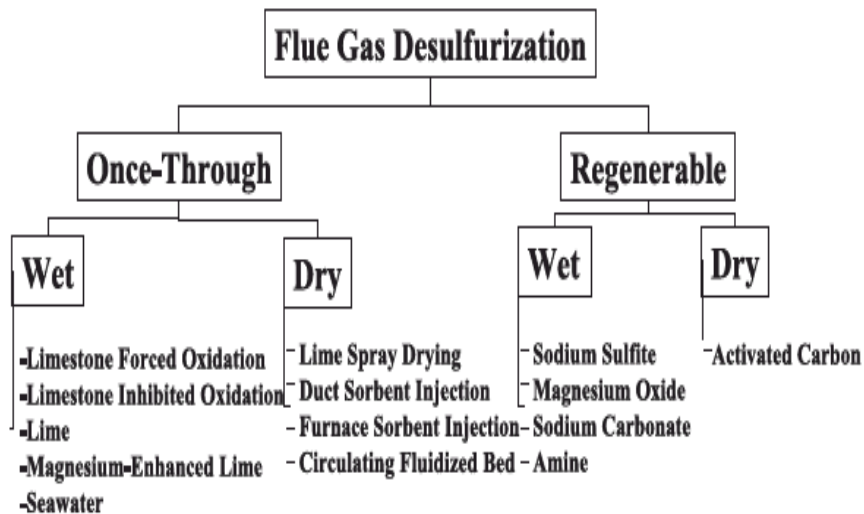
Fig. 3. Classification of FGD Systems (Srivatsava R.K, 2000)

Dry scrubbers or wet scrubbers are adopted in FGD systems based on the sulfur content of the coal burnt. Generally when coal contains lower percentage of sulfur (<2%) dry scrubbers are adopted. At higher sulfur contents wet scrubbers are constructed to effectively control SO_2 emissions. Nowadays all the power plants in USA (almost 85%) are adopting wet scrubbers irrespective of the sulfur content for future flexibility of using any type of coal.

1.2 Coal Fired FGD System Statistics

As of June 2008, about 108 power plants adopted wet FGD systems treating the flue gases from 223 power generating units. Table 1 (US DOE 2005a, US DOE 2005b, US EPA, 2008a) represents the statistics regarding the coal fired power generation associated with FGD systems. The power plants which adopt the wet FGD systems use high sulfur content coal types like eastern bituminous coal as the fuel source. About 46% of the power plants equipped with the wet FGD systems use

eastern bituminous coal which is known for its high sulfur content.

Table 1

Scrubbed Coal-Fired Steam Electric Power Generation as of June 2008 [US DOE 2005a, US DOE 2005b, US EPA, 2008a]

Industry Category	Number of Plants	Number of Electric Generating Units	Capacity (MW)
Fossil-Fueled Steam Electric Power Generation	1,120	2,450	657,000
Coal-Fired Steam Electric Power Generation	488	1,180	330,000
Coal-Fired Steam Electric Power Generation with Any FGD System (Wet or Dry)	146	280	123,000
Coal-Fired Steam Electric Power Generation with a Wet FGD System	108	223	108,000
Coal-Fired Steam Electric Power Generation with a Dry FGD System	41	57	14,900

After the revisal of effluent guide lines in 1982, installations of these FGD systems increased substantially. These installations are expected to continue till 2025. According to EPA models, it is being expected that about 60% of coal burnt power plants will operate wet scrubbers by 2020. Current and estimated use of FGD systems in future years is shown in Table 2 (ERG, 2008f) and Fig. 4 (ERG, 2008b; ERG, 2008c; ERG, 2008g; ERG, 2009s; ERG, 2009w; U.S EPA, 2009).

Table 2

Projected Future Use of FGD Systems at Coal-Fired Power Plants [ERG, 2008f]

	2009 Capacity (MW)	2010 Capacity (MW)	2015 Capacity (MW)	2020 Capacity (MW)	2025 Capacity (MW)
Wet Scrubbed	136,000	162,000	189,000	231,000	282,000
Dry Scrubbed	21,000	21,500	30,100	36,700	38,600
Total Scrubbed	157,000	184,000	219,000	268,000	321,000
Total Coal-Fired Generating Capacity	316,000	318,000	333,000	371,000	409,000
Percent Wet Scrubbed	*43%*	*51%*	*57%*	*62%*	*69%*
Percent Scrubbed (Wet & Dry Combined)	*50%*	*58%*	*66%*	*72%*	*78%*
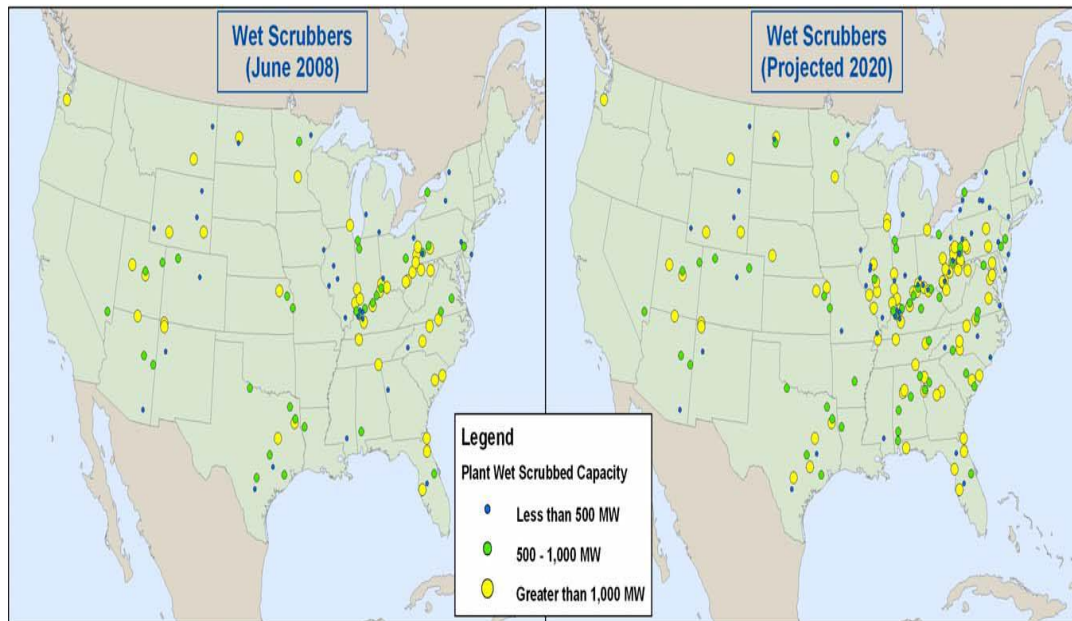
Fig. 4. Current and Projected Wet FGD Systems [ERG, 2008b; ERG, 2008c; ERG, 2008g; ERG, 2009s; ERG, 2009w; U.S EPA, 2009]

1.3 FGD Process Description and Wastewater Generation

In most of the forced oxidation FGD systems, limestone is used as the sorbent. During the process a liquid slurry stream containing limestone as sorbent comes in contact with flue gas stream resulting in mass transfer of pollutants from the flue gas to liquid stream. SO_2 in the flue gas reacts with lime stone ($CaCO_3$) and produce hydrated Calcium Sulfite ($CaSO_3$). The reaction between SO_2 and $CaCO_3$ is shown below:

$$CaCO_{3(s)} + SO_{2\,(g)} + \tfrac{1}{2}\,H_2O \longrightarrow CaSO_3.\ \tfrac{1}{2}\,H_2O_{\,(s)} + CO_{2\,(g)}$$
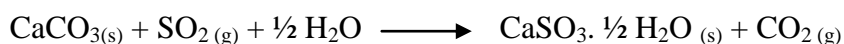
This calcium sulfite is further oxidized to calcium sulfate (gypsum) by injecting air to the calcium sulfite slurry. The oxidation reaction is shown below.

$$CaSO_3.\ \tfrac{1}{2}\,H_2O_{(s)} + \tfrac{1}{2}\,O_{2\,(g)} + 3/2\,H_2O_{\,(l)} \longrightarrow CaSO_4.\ 2H_2O_{\,(s)}$$
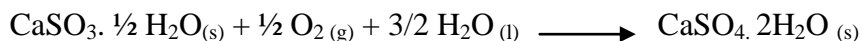
In the spray or tray tower FGD systems, limestone and flue gas are counter acted. Limestone slurry is supplied to FGD scrubber and pumped to top of the tower and then sprayed downward at different levels. The flue gas rises through the vessel, it gets counteracted with droplets of lime slurry and SO_2 gets absorbed. SO_2 reacts with limestone and water and produces calcium sulfite. After this scrubbing process, the flue gas is released into atmosphere through stacks by eliminating the mist. This slurry containing calcium sulfite falls down to the bottom of the scrubber. High pressure air is injected into the slurry and agitated vigorously to oxidize calcium sulfite to calcium sulfate (gypsum). This slurry containing gypsum is recycled using recycle pumps and pumped to different levels and sprayed down. This slurry is continuously re-circulated until the percentage of solids and chlorides concentration raises up to certain level. Then a blowdown pump is used to pump out some slurry out of the scrubber until the solids percentage decreases. In some power plants these blowdown pumps are operated continuously and slurry is removed after every cycle. The percentage of

solids and chloride content are taken as the controlling parameters to operate the wet scrubbers. The chloride concentration in the FGD systems is maintained less than maximum level to protect the scrubber materials from corrosion. Operational conditions of the wet scrubbers differ from plant to plant. Some systems operate at higher concentrations like 40,000 ppm while some operate at lower concentrations like 2000 to 3000 ppm. The percentage of solids in the slurry is also continuously monitored considering it as one of the crucial controlling parameter (EPRI, 2006a). The ejected solid rich stream is further processed depending on the intention of the power plant on marketing gypsum. This solid rich stream is passed though vacuum belt or drum filters to reduce the moisture content of the gypsum up to desired level. The gypsum is rinsed and stored until transported. If the power plant has no intention of marketing the gypsum, the slurry is discharged into disposal sites. The process flow diagram for lime stone forced oxidation system is shown in Fig. 5 (U.S EPA, 2009).

These blowdown streams from wet scrubbers are often laden with various toxic metals and metalloids like mercury (Hg), selenium (Se), arsenic (As) in various forms and toxic conditions. Discharge of these streams into the environment without prior treatment causes potential harm to natural environmental health, polluting the downstream waters. FGD water is characterized with a complex matrix, often complicated with high total suspended and dissolved solids. Treatment of these FGD water streams to comply with stringent discharge standards is a big challenge for the wastewater industry. In response to increasing public concern towards the FGD waste water problem, the USEPA is currently revising the effluent guidelines for coal burnt power plants which will impose more stringent discharge standards for Hg, Se and other major toxic compounds. In the past two decades, several efforts and resources were invested in this area of wastewater treatment for research and development of

innovative technologies to handle the FGD streams effectively. Most of the power plants are using settling ponds to discharge FGD water.
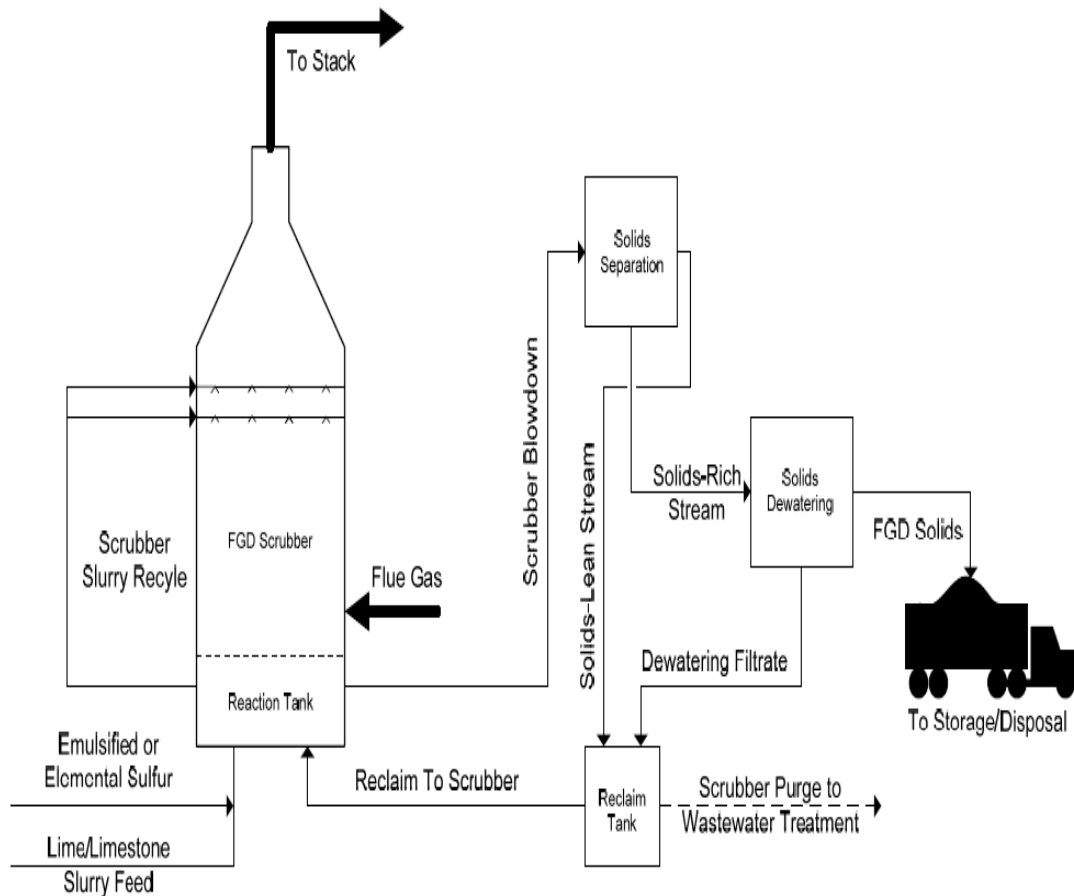
Fig. 5. Process Flow Diagram for Lime Forced Oxidation FGD System [U.S EPA, 2009]

Though these settling ponds are able to reduce TSS and some specific undissolved particulate pollutants at higher residence time, they are not able to meet the stringent discharge standards. Industry giants like GE, Siemens and Degremont

Technologies developed innovative methods like ABMet, ZLD to handle FGD water and treat pollutants like Se, Hg. Short comings like high operational costs, operational and maintenance complexities, high concentrated byproducts (brine solution) constrained these emerging technologies. So still there is a need for a technology which is reliable, economical, posing low operational and maintenance difficulties and incredible performance.

2. LITERATURE REVIEW

Many treatment technologies are adopted by coal burnt power plants to handle their FGD streams. Presently settling ponds are used to discharge FGD water by most of the power plants. The following technologies are used to discharge the FGD water.

2.1 Settling Ponds

The principle of gravity is used to remove the particulate matter from the FGD water in settling ponds by providing enough residence time. Either single settling pond or a series of ponds are used as system to reduce TSS and particulate pollutants in FGD water. pH of the FGD water is adjusted to meet National Pollutant Discharge Elimination System (NPDES) permits before it is discharged into settling pond. Additional treatment chemicals are not incorporated into FGD settling pond. These ponds are designed to provide certain residence time to reduce the suspended solids and providing specific life span for the pond considering the sludge buildup in the pond.

These ponds are not designed considering pollutants in dissolved phase. Along with particulate pollutants FGD water contains considerable amount of dissolved metals like Se, Hg, and B which are discharged without considerable reduction by settling ponds. Most plants using settling ponds as treatment systems for FGD water purge, discharge FGD water into the ponds that are also used to treat other streams like fly ash transport water. In some cases FGD water is discharged into special ponds designed for FGD water for initial settling then released into ash ponds for further settling and dilution. EPRI reported that addition of FGD water into ash pond affects the settling efficiency in ash ponds due to gypsum particle dissolution (EPRI 2006b).

FGD water increases effluent metal concentration in ash pond by loading additional volatile metals to ash pond affecting the solubility of metals in ash pond (EPRI, 2006b). Typical FGD settling pond at Plant Wansley is shown in Fig. 6.

Fig. 6. FGD Settling Pond at Plant Wansley, Carrollton, GA

According to EPA, these settling ponds are not limited to older scrubbers. 20% of power plants have adopted these settling ponds for handling their FGD water streams even after 2000 (U.S. EPA, 2009). This refers that the power plants rely on their existing settling ponds for their new FGD scrubbing units than installing more advanced treatment systems.

2.2 Chemical Precipitation

The physical state of the dissolved and suspended solids is altered using external precipitants like calcium hydroxide (hydroxide precipitation), sodium hydroxide (hydroxide precipitation) and sulfide chemicals (sulfide precipitation). These chemical precipitation techniques are used to improve the efficiency of the settling ponds by precipitating the pollutants by adding these chemicals and thus facilitating the settling process.

Ferrous salts like ferrous chloride and ferric chloride are used as co precipitants in hydroxide precipitation to precipitate additional metals and organic compounds. Ferric chloride is comparatively more insoluble than metal hydroxides. Some plants use all the three techniques in different stages to optimize the precipitation process. Sulfide precipitation is effective for precipitation of heavy metals like mercury while hydroxide precipitation is used to precipitate some metals. Accordingly, power plants select the specific precipitation depending on the targeted pollutant. Plants typically discard this treated water due to presence of high chlorides which are capable of corroding the downstream equipment. The sludge generation in this process is remarkably high due to precipitation and coagulation of the solids resulting in the problems of disposal of the sludge cake as the sludge is rich of toxic pollutants like mercury, arsenic, and selenium. The process diagram for hydroxide and sulfide chemical precipitation system is shown in Fig. 7 (U.S EPA, 2009).
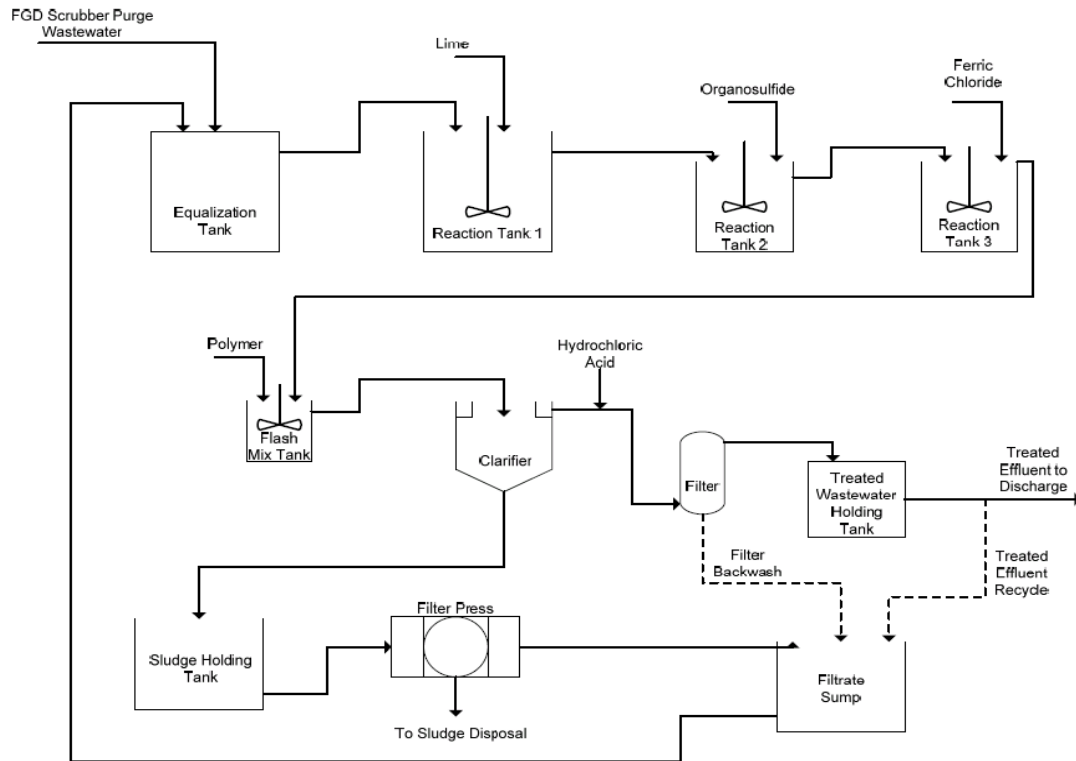
Fig. 7. Process Flow Diagram for a Hydroxide and Sulfide Chemical Precipitation [U.S. EPA, 2009]

2.3 Biological Treatment Systems

In biological processes, microorganisms are employed to consume biodegradable organic contaminants. Toxic metals can be reduced aerobically or anaerobically. Power plants use two types of biological treatment systems to treat FGD waters.

1) *Aerobic biological treatment systems:* Aerobic systems are used to reduce BOD_5. These systems can be either conventional flow through or sequential batch systems. FGD water is continuously fed into flow aerobic bioreactors in

which microorganisms use dissolved oxygen to digest organic matter thus reducing BOD_5. The sludge produced in this process is dewatered and disposed. Suspended growth bioreactors or fixed film bioreactors are used for this process. A sequential batch reactor (SBR) is operated similar to activated sludge process. FGD water is fed into the reactor containing sludge. After digestion, the sludge along with treated water undergoes settling process. During settling process air is turned off and solids are allowed to settle down. The treated water is discharged into local water bodies or transferred for additional treatment depending on the quality of water. Some of the solids from the reactor are removed and dewatered for disposal, while some are retained in the reactors as seeding agents.

2) *Anoxic or anaerobic Biological treatment systems:* Wastewater industry is focusing more on these anaerobic treatment processes compared to any other treatment systems to achieve better reductions of heavy metals. In this process selenium and other metals are reduced by anaerobic bacteria. Activated carbon bed inoculated with anaerobic bacteria is used as a fixed film bed reactor to reduce selenium and other heavy metals. This fixed film retains the bacteria and reduced metals. The anaerobic systems are generally designed as plug flow reactors. Aerobic conditions prevail in the top part of the reactor facilitating nitrification and organic carbon oxidation. As the wastewater moves downward in the reactor, denitrification occurs because typical anoxic conditions prevail in lower parts of the reactor. Chemical reduction of selenates and selinites into selenium occurs at this zone of reactor. The elemental selenium from reduction of selenates and selinites forms nanospheres and stick to cell walls of microorganisms. As the reactor retains all the microorganisms in the reactor,

the trapped elemental selenium gets adsorbed on the activated carbon. Other pollutants like arsenic, cadmium and mercury are transformed into corresponding sulfides by the bioreactor and are retained within the reactor. Some biological reactors are operated like flow through systems in which the aeration is controlled in stages to create aerobic zone for nitrification, anoxic zone for denitrification. The process flow diagram for anaerobic biological system is shown in Fig. 8 (U.S EPA, 2009).
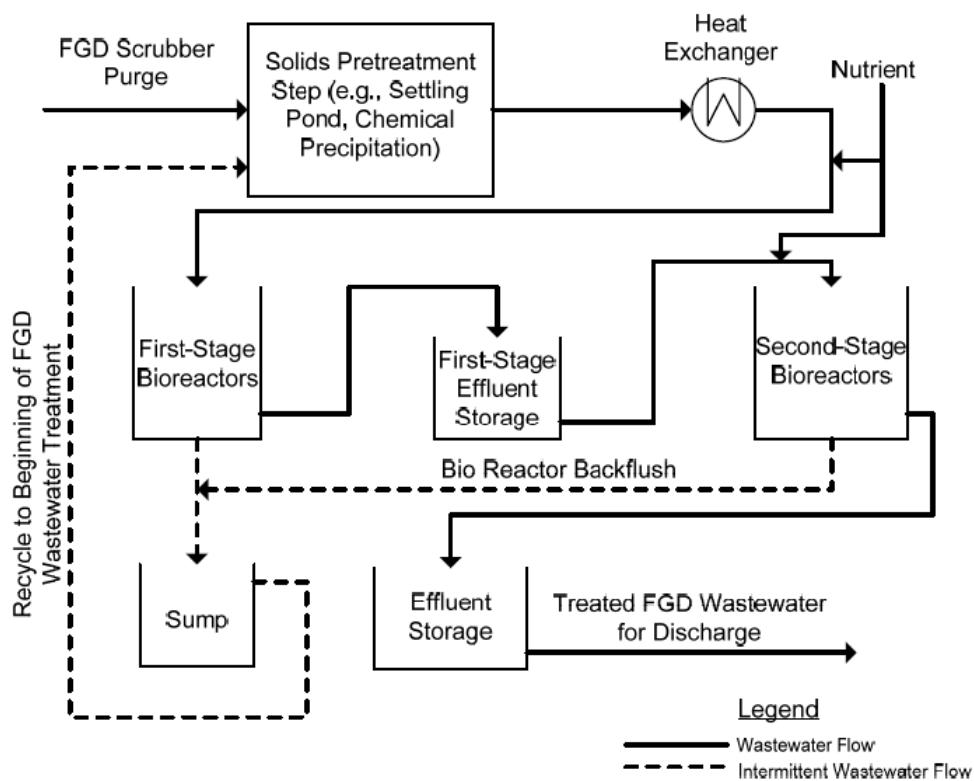
Fig. 8. Process Flow Diagram for Anoxic/Anaerobic Biological Treatment System [U.S. EPA, 2009]

Potential disadvantages of microbial systems are their consistency and operational difficulty. The bioreactor must be backwashed periodically to remove the trapped solids and other inorganic materials. These solids are flushed using high pressure jet stream which will fluidise the carbon bed dislodging the particles fixed in the carbon bed. The backwash water should be treated prior to discharge as the concentrations of the pollutants are very high. Microbes are susceptable to high temperatures, so FGD water must be cooled to desired temperature and monitored continously. The water should be pre-treated to prevent suspended solids entering into the reactors, hence these systems are operated along with a settling pond or chemical precipitation to control TSS. This SBR is able to denitryfy effectively but proved unrelaible in precipitation of metals like arseninc, mercury and cadmium. So some plants operate SBR along with chemical precipitators to enhance the treatment capacity.

2.4 Constructed Wetlands

These systems are engineered to use the natural biological processes in which wetland vegitation and microbial activities are involved. FGD water is passed through different cells of wetland treatment systems containind bacteria and natural vegetation. Bacteria reduces heavy metals like selenium and mercury into their elemental form and these metals partition into the sediments. The wetland vegitation in other cells consumes these accumulated toxic metals (Rodgers,2005).

Several factors effect these wetland treatment systems. High temperature, chlorides, sulfates, boron and nitrates in the FGD water streams adversely effect the efficiency of the treatment system. Generally powerplants dilute the FGD streams with natural waters prior to its entry into the system. Chloride levels should be below 4000 ppm in constructed wetlands. Scrubbers are typically operated by maintaining

chloride levels at 12000 to 20000 ppm. So they must dilute FGD water prior to entry or they should operate the scrubbers at lower chloride levels by using blowdown pumps frequently to discharge water from the scrubber tower.

2.5 Evaporation Systems

In several industrial applications like power plants, oil refineries and chemical plants evaporators are used to reduce the wastewater stream significantly. In brine concentrator evaporating systems, a concentrated wastewater stream called brine is produced along with distilled water which can be reused. When a crystaliser is used along with brine concentrator a solid byproduct and distillate are generated. This solid waste can be disposed in a landfill. One power plant in USA and one in Italy operate this vapor compression evaporating systems to treat their FGD streams (Veolia,2007). Detailed process diagram for vapor-compression evaporation system is shown in Fig. 9 (U.S EPA, 2009). Though this evaporation technique proved to be strong enough to handle FGD streams there are also several disadvantages associated when adopted in a commercial scale. High costs are involved in this process as lot of energy is required to raise the temperature of FGD water to its boiling point.
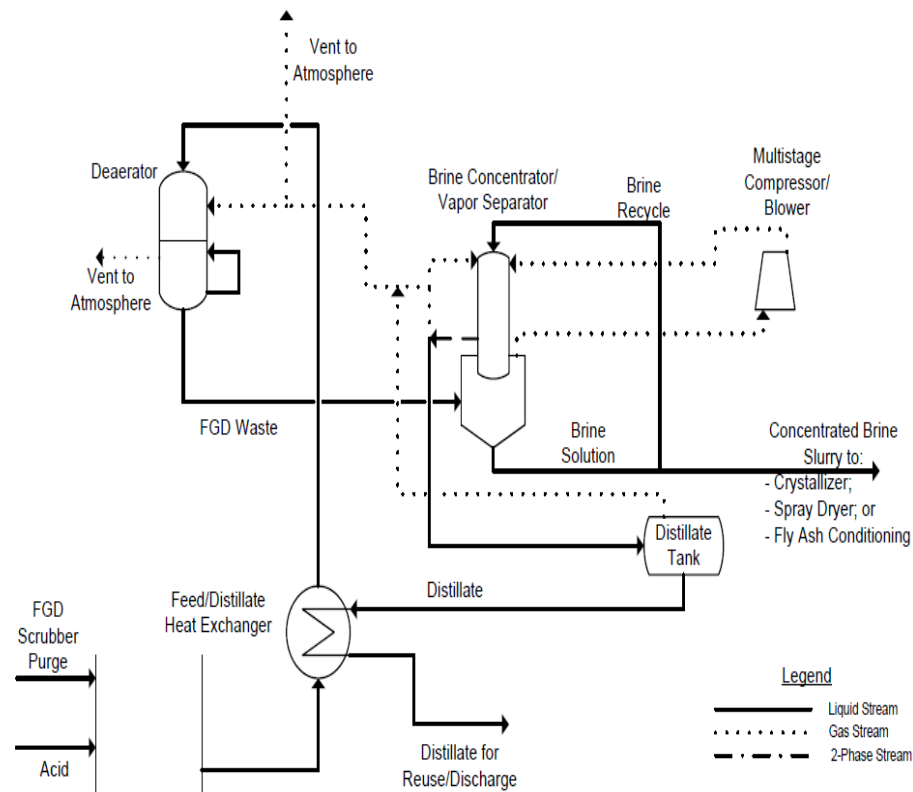
Fig. 9. Process Flow Diagram for Vapor-Compression Evaporation [U.S. EPA, 2009]

The pH of the FGD water must be adjusted around 6.5 (approximately) prior to heat exchange. Handling of concentrated brine solution posed several problems in the absence of crystalizers. Scaling within the brine concentators must be effectively controlled. Calcium sulfate is used as seeding agent to seed crystals instead of tube surfaces (Shaw, 2008).

2.6 Evaporation Ponds

Power plants adopt these evaporation ponds in the regions with warm and dry climate to handle their FGD streams. Plants discharge their FGD stream into a pond or series of ponds and allow to evaporate under natural conditions till it attains zero discharge. These ponds should be designed such that the evaporation rate and discharge rate are well balanced thus increasing the foot print of evaporation ponds in the power plants working at higher flow rates of the FGD water.

2.7 Conditioning Fly Ash

In the process of handling dry fly ash, water is added to fly ash for dust suppression, compaction and to transport flyash. Some power plants use FGD water to condition this flyash. Power plants use a combination of vapor-compression and fly ash conditoning to dispose their FGD streams. Vapor-compression is used to reduce the quantity of FGD water and then the effluent form brine concentrator is mixed with flyash and disposed onto landfil. By addition of FGD water to ash ponds, the settling characterstics of the pond are effected due to dissolution of gypsum in FGD pond. This will increase the load of volatile metals on ashponds impacting the solubility of metals in ash ponds resulting in increase of effluent metal concentrations from ashponds.

2.8 Underground Injection

In this technique FGD water is injected into underground water as an alternative for discharging into surface waters. FGD water is subjected to pre treatments like chemical precipitation, prior to injection into underground. Power plants which have adopted this technique have experienced pressure issues. Developments of wells are observed due to geological formations. Other treatment technologies like ***reverse osmosis sytems, sorption media, ion exchange, electro***

coagulation etc are also considered for small scale treatment facilities.

As of june 2008, among 108 plants about 84 plants are operating wet FGD scrubber systems. These FGD srcubber represent 175 coal-fired electric generating units out of 223 wet scrubbers. Of these 84 plants, 38 % (32 plants) achieved zero discharge either by recycling the water or by using evaporation ponds, or underground water injection. 34% of plants use settling ponds for handling their FGD water. Chemical prescipitation is used for treating FGD waters in 20% of plants. About 2% of plants are using biological (aerobic/anaerobic) treatment systems to handle their effluents (U.S. EPA 2009). Distribution of FGD waste water treatment systems is shown graphically in Fig. 10 (U.S EPA, 2009).
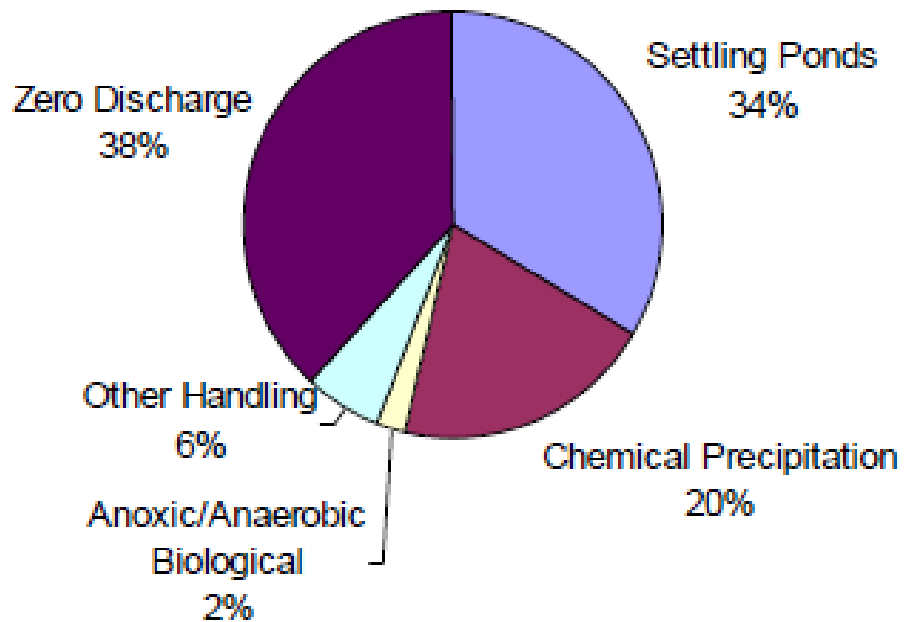
Fig. 10. Distribution of FGD Wastewater Treatment Systems [U.S. EPA, 2009]

2.9 Other Technologies under Consideration

Several other technlogies like polymeric chelate, taconite tailings and nano-scale iron reagents are under lab scale study to develop effective method to treat FGD water (EPRI, 2007a). Among several remediation agents, zero valent iron (ZVI) is receiving more attention because of its strong potential to abate several contaminants like halogenated hydrocarbons, azo dyes, nitrate, perchlorate, hexavalent chromium, nitroaromatic compounds and heavy metals like selenium, arseninc, lead, copper and mercury. Several investigations showed that Fe^0 is a very effective medium to treat heavy metals like selenium, mercury, arsenic, lead, copper, cadmium and chromium under laboratory scale investigations. ZVI due to its lower cost and reuse of solid waste observed to be more advantageous than other media like granular ferric hydroxide (Driehaus et al., 1998; Boller and Steiner, 2002).

The reaction of different heavy metals with ZVI involves three predominant stages: Cementation, adsorption and metal hydroxide precipitation (Blowes et al., 2000; Cantrell et al., 1995; Fiedor et al., 1998; Gu et al., 1998; Shokes and Moller, 1999; Smith, 1996). The iron cementation process involves reduction of redox sensitive metals into their insoluble forms. This cementation process is shown to be very effective at acidic pH range and lower dissolved oxygen content (Annamalai and Murr, 1979; Biswas and Reid, 1972; Huang et al., 1998; Ku and Chen, 1992; Nadkarni et al., 1962; Nadkarni and Wadsworth, 1967; Strickland and Lawson, 1971). Several pollutants can be reduced by the redox reactions involving metallic iron and Fe^{2+} on the surface of iron. Fe(II) adsorbed on the surface of iron in different forms like Fe_3O_4, FeOH(OH), α-FeO(OH) plays a key role in reduction of many pollutants (Klausen et al., 1995). Microscopic and spectroscopic studies proposed that ZVI in aqueous environment has core iron material covered by layer of iron oxide (Martin et al..,

2008; Nurmi et al., 2005; Sun et al., 2006). This oxide layer is a mixture of Fe(II) and Fe(III). Fe(II) and Fe(III) mixture is present near to iron surface and mostly Fe(III) oxides near to water interface (Signorini et al., 2003; Wang et al., 2009). This defective and disordered nature of oxide layers renders to high reactivity of iron species compared to normal oxide layer on the surface of the bulk iron (Wang et al., 2009). The presence of these two different constitutents in the core structure impart different properties to ZVI material. The inner core material facilitates the redox reaction by acting like electron source whereas the outside oxide layer facilitates the adsorption of reduced metals and metal ions through electrostatic interactions and surfacial complexation. The corrosion mechanism and formation of magnetite can be shown as below .

$$Fe_{(0)} + 2H_2O \ (l) \longrightarrow Fe^{2+} + 2OH^- + H_2 \ (g) \qquad (1)$$

$$3Fe^0 + 4H_2O \longrightarrow Fe_3O_4 + 8H^+ \qquad (2)$$

$$3Fe^{2+} + 4H_2O \longrightarrow Fe_3O_4 + 8H^+ \qquad (3)$$

In the above two reaction though final product is magnetite the number of electrons released are different changing the reduction capability of the reaction occurred. The continued corrosion results in saturation and precipitation of $Fe(OH)_2$. In the absence of oxygen, $Fe(OH)_2$ is predicted to be converted into magnetite thermodynamically (Huang et al., 2005).

$$3Fe(OH)_2 \ (s) \longrightarrow Fe_3O_4 \ (s) + H_2 \ (g) + 2H_2O \ (l) \quad (4)$$

Structure of ZVI particle coated with FeO_x layer is shown in Fig. 11 and sequential conversion of Fe^0 and Fe^{2+} to Fe^{3+} is shown in Fig. 12.
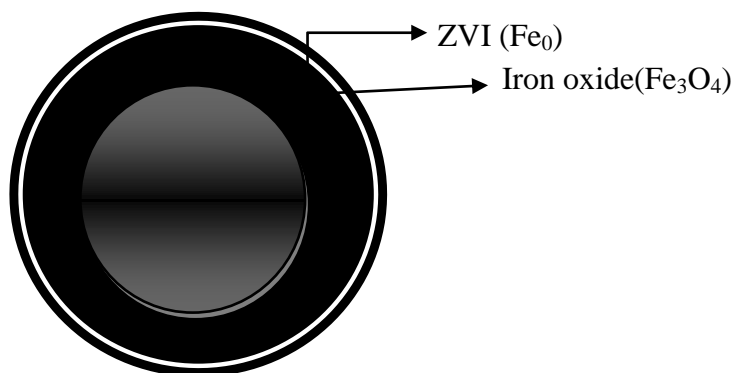
Fig. 11. ZVI Particle with Iron Oxide Layer on the Surface
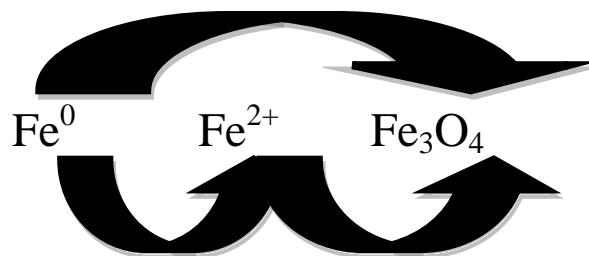
Fig. 12. Sequential Formation of Magnetite

ZVI can be effectively used to treat Se(VI) in the water through chemical reduction followed by adsorption. There are two possible mechanisms suggested by Zhang et al., that states either Se(VI) is reduced to either Se(IV) or Se(0) based on the reduction environment followed by adsorbtion onto the surface of ZVI or Se(VI) is adsrobed directly onto the surface of ZVI (In-Ho et al., 2011). X-ray studies showed that Se(VI) is reduced to Se(IV)/Se(0) prior to adsroption on ZVI surface (S.R.Qui et al.,2000). Inorganic reduction of Se(VI) and Se(IV) using iron containing materials

like green rust, pyrite, iron carbide and NiFe particles (Myeneni et al., 1997; Scheinost et al., 2008; Gehin et al., 2007;) have been investigated and satisfactory results are reported. Fe^{2+} can also reduce nitrate in presence of several strong catalysts. Remediation techniques involving ZVI permeable reactive barriers are developed to treat contaminants in underground water. There is a growing interest in studying the usage of ZVI in treating nitrate. In general, nitrate is realtively non-toxic, but upon microbiological reduction into nitrite, it poses severe health problems like methemoglobinemia, liver damage and can cause alagal blooms in the settling ponds due to eutrification. Studies demonstrated the potential of metallic iron to reduce nitrate under anoxic and aerobic conditions to ammonia (Huang et al., 1998; Huang et al., 2004). ZVI of various sizes are packed in columns and used in situ under ground water treatment to treat nitrate.

Mercury in the form of Hg(II) is one of the most notorious contaminant in wastewater from several industries like power generation, metal plating, industrial manufacturing and mining. ZVI can reduce Hg(II) to insoluble Hg(0) which can be removed by surface adsorption or filtration.

Previous studies showed effective results in treating heavy metals using nZVI and failed in using mZVI as treatment soltion as they posed a problem of decrease in the reactivity of ZVI due to formation of a passive oxide layer on the surface of ZVI. Several operational difficulties are reported for usage of ZVI such as reduced reaction kinetics, blockage of pores and cementation of the iron particles when used as a packed column due to precipitation of metal oxides (Furukawa eet al., 2002; Wilkin et al., 2003).

3. OBJECTIVES

This proposed project is to develop a pilot-scale system and use the system to conduct long-term demonstrations under various field conditions to further evaluate the performance and cost-effectiveness of the hZVI process for removing toxic metals and other pollutants from the FGD wastewater.

This pilot project aimed to further improve our understanding of the basic chemistry, mechanisms and kinetics of pollutant removal by the system under various field conditions. The project helps to accumulate more operational experience, estimate basic operation parameters, optimize reactor and process design, develop a solid waste management plan, and evaluate economy of the process. The project will provide key information essential for designing and executing a successful full-scale application of the new technology. A successful pilot project is the key in our effort to commercialize the technology within four years to meet industry's need. The specific objectives of this field demonstration are:

1. To significantly reduce the concentration of the pollutants of major concern such as mercury and selenium in the FGD waste water so that the treated effluent can comply with the discharge limits that may be enforced by the federal and local governments in the coming years. Specifically, the target is to reduce total mercury in the treated effluent to below 12 ppt and total selenium to below 50 ppb.

2. To determine the lower range of hydraulic retention time required for achieving desired removal efficiency for the target pollutants.

3. To evaluate the effects of various constituents present in the FGD water on

the hybrid ZVI systems and how to operate the system more effectively under different water matrix.

4. To evaluate the impact of various types of commercial ZVI supplies on the system performance and process economics.

5. To evaluate the capability of system to treat other pollutants and impurities likely present in the FGD streams like lead (Pb), copper (Cu), cadmium (Cd), arsenic (As), Chromium, nutrients like nitrate and phosphate, boron, and dissolved silica and various oxyanions.

6. To develop a detailed design of a full scale treatment system capable of handling the whole facility based on the results and operational data yielded.

4. MATERIALS AND PILOT SCALE SYSTEM

4.1 Treatment System

The treatment system was designed by Dr. Huang based on the successful bench-top prototype. The pilot treatment system consisted of four stainless ZVI reactors and post-treatment units including aeration, clarification and sand filtration. Fabrication of the prototype had started on November 5, 2010 and was completed on January 8, 2011.

The four ZVI reactors were arranged in hydraulic elevation that allowed the incoming FGD water to gravitationally flow through the four reactors in series without the need of an intermediate lifting pump. The design also allows the ZVI reactors to operate as a single train, four-stage reactor in series or as a duplex, each with two-stage reactors. This flexible configuration is needed for different tests. The dimension of ZVI reactors measures about 0.9m × 0.9m in horizontal cross section (a square) with 1.2-1.6m in height. The effective volume of the ZVI reactors ranges from about 200 gallons to 300 gallons. The combined volume of the four ZVI reactors are about 1000 gallons, out of which the reaction zone (the internal mixing zone) accounts for about 700 gallons and the internal settling zone (separated by a hanging hood from the mixing zone) about 300 gallons. For treating 1 gpm flow, the total hydraulic retention time (including both reaction time and settling time) in the ZVI reactive system is about 16 hour. In each ZVI reactor, an overhead mixer is used to provide mixing power in the reaction zone. The rotation speed of mixer can be adjusted between 0-1760 rpm through a frequency controller.

The post treatment units were made using plastic tanks. The effective volume of aeration basin is about 30 gallons. The effective volume of settling tank is about 100 gallons. At a flow rate of 1 gpm, the hydraulic retention time will be 30 min in the aeration basin and 100 min in the settling basin. The reaction time will be shortened by half when operated at 2 gpm. Two sand filtration basins are used, each with 5 sqft surface area. The treated final effluent was discharged into the adjacent ash pond. All these reactors and units were fastened and secured on the 40' flat-bed trailer. A schematic diagram of designed flow system is shown in Fig. 13.
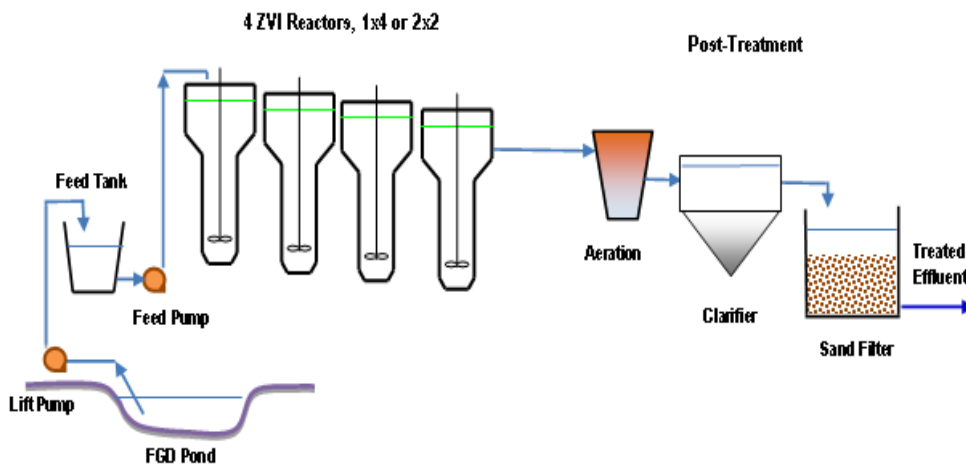
Fig. 13. A Schematic Diagram of the Complete Treatment Train of the Pilot-Scale hZVI Treatment Prototype.

Fig. 14. The Pilot-Scale Prototype of hZVI System.

The system includes four ZVI reactors for removing pollutants and post-treatment units of aeration, settling and filtration to further polish the effluent from the ZVI reactors by removing residual iron and suspended solids. The system was mounted on a 40 ft flat-bed trailer as shown in Fig. 14 that was set up on the embankment between the FGD pond and ash pond at Plant Wansley. The FGD water was initially pumped into a 45 gallon feeding tank at a rate of 3-5 gpm. A second pump was used to pump the water from the feeding tank into the treatment system at a desired flow rate (0.5-2.0 gpm). The excess water in the feeding tank was allowed to overflow and return back to the FGD pond. Centrifugal magnetic drive polypropylene pumps (1/16hp feeding pump, 1/4hp backwash pump and 1/4hp lift pump) were purchased from Cole-Parmer. Four peristaltic pumps (Masterflex, Cole–Parmer) were

used to deliver the reagents to reactors. List of all tanks and respective purposes are shown in Table 3.

Table 3

List of Tanks and Basins Used in the Treatment System

Tanks/Basins	Volume	Purpose
Equalization Tank (1)	45 gal	This tank was used to trap any solids that were pumped out from FGD pond and also to equalize the flow, thus serving both the tasks. This tank was cleaned once a month.
Reagent Tanks (4)	30 gal	These tanks were used to prepare necessary reagents and store them.
Aeration Tank (1)	45 gal	This tank was used as aeration tank to which high power aerator was fixed. The effluent coming out of the final reactor enters into this tank to which $NaHCO_3 + Na_2CO_3$ mixture solution or NaOH solution was supplied to precipitate residual Fe^{2+} ions.
Settling Tank (1)	165 gal	This tank was used to trap the sediments and suspended solids in the effluent after precipitation of residual Fe^{2+} ions in aeration tank. The solids trapped in settling tank were pumped out when required.

Table 3 (continued)

Tanks/Basins	Volume	Purpose
Filtration Tank (2)	45 gal	These filtration tanks were connected in parallel, so that they divide the flow from the settling tank thus reducing sudden load on them. These tanks were filled with gravel to a height of 10-12 inches and rest of the space is filled with pool filter sand available locally (Home Depot, LOWES and Walmart). This filtered beds were periodically backwashed (approximately once in a week)
Effluent Tank (2)	135 gal	These tanks were used to collect the final effluent coming out of sand filtration beds.

Note: The listed volume is the maximum capacity of the tanks. Only a fraction of the total volume is effective when used in the treatment system. All plastic tanks were purchased from Polytanks Inc MN.

4.2 Chemicals

The main chemicals used for the field test include:

1. Zero Valent Iron (ZVI): Three types of ZVI powder were used in this field demonstration to evaluate the effective of different ZVI powder.

   a. H200 Plus: The H200 Plus ZVI powder was procured from Hepure Technologies, CA. This ZVI has about 95.5% of iron and other impurities comprising of Carbon (1.75 – 4.50%), Silicon (1.0-2.50%), Sulfur (0.01-0.15%) and Oxygen (2.5% max). This iron powder size varies from 5-100 microns and has a specific gravity of 2.8 – 3.2 g/cm^3. The BET surface area of H200+ was measured as 1.14 m^2/g (compared to 1.55 m^2/g for HC15 ZVI used in Plant Bowen's demonstration).
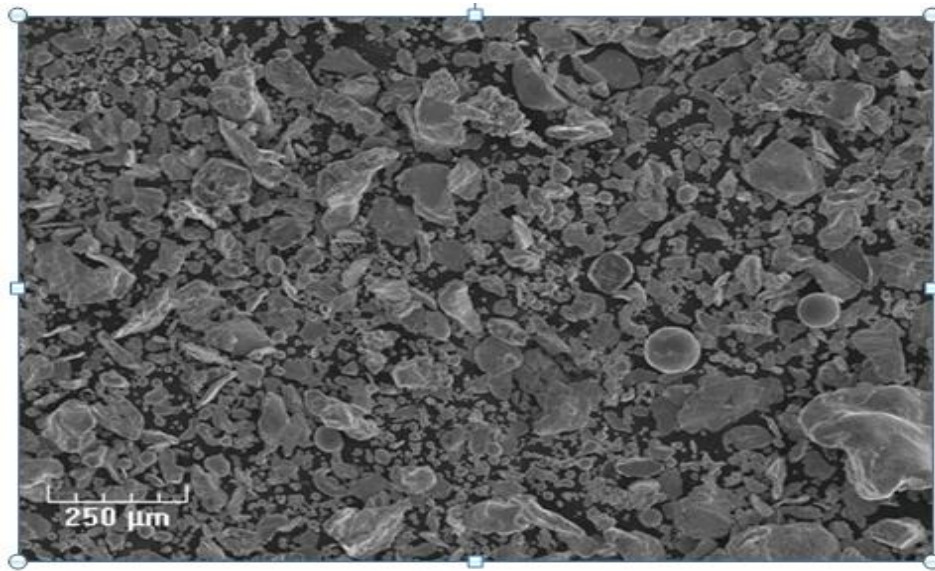
Fig. 15. Micrograph of HC200+ ZVI Used for the Pilot Tests.

Micrograph of HC200+ in Fig. 15 shows that HC200+ ZVI powder has various sizes of particles ranging from a few microns to over 100 microns.

b. -325 meshes: This H_2-reduced Iron powder was supplied by Sunlight Solutions, NY.

2. 5 microns: This H_2-reduced iron powder was supplied by Sunlight Solutions, NY. The mean particle size is between 4.5 and 6.0 micron, with 95% mass below 15 micron and 99% mass below 20 micron. The purity of iron is 99.0%, much higher than H200+.

3. HCl (1M) solution: was prepared on site from concentrated HCl (36.5% or 6N) supplied by VWR international, Radnor, PA.

4. Pre-acidified $FeSO_4$ solution, 400mM $FesO_4$ + 20mM HCl. Industrial grade

$FeSO_4$ was supplied by Capitol Scientific, Austin, TX.

5. Pre-acidified $FeCl_2$ solution, 400mM $FeCl_2$ + 20mM HCl. Reagent grade $FeCl_2$ was supplied by VWR International, Radnor, PA.

6. Na_2CO_3 + $NaHCO_3$ solution, 400mM $NaHCO_3$ + 200mM Na_2CO_3. Industrial grade chemicals were supplied by Fox Scientific, Alvarado, TX.

7. NaOH (2M) solution, prepared from NaOH pellet supplied by VWR International, Radnor, PA.

8. $Ca(ClO)_2$: A small amount of calcium hypochlorite (known commonly as bleaching powder) was used to test ammonium removal for three days supplied from VWR International, Radnor, PA.

In addition, the following compounds were purchased from VWR International, Radnor, PA. to conduct spike tests that tested the performance of the hZVI system under elevated loading of various toxic metals.

Sodium Selenate (Na_2SeO_4),

Sodium Arsenate (Na_2HAsO_4),

Sodium Arsenite ($NaASO_2$),

Potassium Chromate (K_2CrO_4),

Mercury Chloride ($HgCl_2$),

Lead Chloride ($PbCl_2$)

Cupric Chloride ($CuCl_2$)

Cadmium Chloride ($CdCl_2$)

For spike tests, concentrated stock solutions of toxic metal were prepared from the selected metal salts.

Stock Solution A

6000 mg/L selenate-Se + 150 mg/L arsenite-As + 150 mg/L arsenate-As +1500 mg/L chromate-Cr. 25 gallons of stock solution A was prepared and added into ZVI Reactor 1 at a rate of 12.6 ml/min for 5 days.

Stock Solution B

2000 mg/L Lead(II) + 2000 mg/L Copper(II) + 1000 mg/L Cadmium (II) + 400 mg/L Hg(II). 20 gallons of stock solution was prepared and feed at a rate of 9.45 ml/min for 5 days.

4.3 Sampling and Analysis

4.3.1 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. Systematic and rigorous sampling was done twice a week, typically on Monday and Thursday, to collect water samples for trace toxic metal analysis at SRI (Southern Research Institute, Birmingham, Al). The collected water samples were sent to SRI overnight in a cooler filled with ice. Sampling kits were supplied by SRI upon request, including 0.45 micron filter discs, 30ml syringes, gloves, 125ml glass bottles for mercury sampling, and 125ml plastic bottles for analysis of heavy metals. For three times, split samples were sent to Brooks Rand Laboratory (Seattle, WA) to verify the analysis of the SRI. The results from the two labs were generally in good agreement. For this reports, we used the metal analysis result from SRI to assess the performance of the system.

In addition to SRI samples, separate water samples were collected daily and shipped in batch to Dr. Huang water quality laboratory at TAMU campus for various analyses and backup sample storage. Reactive solid samples were collected once a month to estimate status of FeOx present in the reactors. The silt content of reactors was monitored regularly.

4.3.2 Water Analysis

Water samples sent to SRI were analyzed with an ICP-MS to perform an elemental scan to quantify toxic metals and metalloids of major concern present in the raw and treated FGD water. The SRI results were used to assess the performance of the system in removing toxic metals and metalloids. For most trace metals, the SRI analytical method had a detection limit of 1.0 ppb or lower. For Hg analysis, the SRI method could detect as low as 1.0 ppt Hg. In addition, the results of Si, B, and Fe are also used in conjunction with our own analysis results to evaluate the performance of the system.

Common cations and anions were analyzed in Dr. Huang's water quality lab. We used an Ion Chromatographer (Dionex DX500) to analyze major cations and anions in the water samples, including Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, Br^-, and I^-. The DX 500 IC system is equipped with a CD20 conductivity detector, an AD20 absorbance detector, an AS50 auto sampler. The available IC separation columns included IonPac 4-mm AS22, AS16, AS18, CS5 and CS12 columns, the selection of which depends on the target ions and the water matrix. The detection limits for these common ions are about 0.1 ppm for the IC method. Dissolved Silica in the water was analyzed using standard molybdosilicate method. A well mixed sample was filtered through 0.45μm membrane filter. The filtrate upon addition of molybdate ion in acidic solution, develop a greenish-yellow color complex proportional to

dissolved silica in the sample. This color sample was measured spectrometrically and compared with standards to estimate the dissolved silica content (APHA, 2005). Dissolved Fe^{2+} was analyzed using standard phenanthroline method (APHA, 2005). Phenanthroline chelates with ferrous ion to form an orange red complex. The color intensity is proportional to ferrous ion concentration, which can be measured spectrometrically. We also used the IC to analyze selenate and selenite concentration in the water using an AS22 column. Total dissolved solids were measured by evaporating a well-mixed filtered sample at 180^0C. The increase in the weight of the dish represents the amount of total dissolved solids (APHA, 1998). Acidity and alkalinity were analyzed using titration methods, by titrating against standard titrants (APHA, 1998).

Water pH and dissolved iron (Fe^{2+}) at various treatment stages were analyzed routinely as the key operating and control parameters. Dissolved silica was analyzed intermittently when there was a need. Temperature in the ZVI reactor were recorded, but the data was incomplete unfortunately.

4.3.3 Solid Analysis

Solid substances in the hZVI process include fresh ZVI, iron corrosion product, spent solids, and inert solid accumulated in the reactors. Scanning electron microscopy was used to discern the morphology of solid particles. X-ray diffraction spectroscopy was used to characterize the crystalline of iron oxides generated from iron corrosion particles. The toxicity of spent reactive solid is to be analyzed through the TCLP process defined by the USEPA. Detailed list of the methods adopted to estimate the specified parameters are shown in Table 4.

Table 4

List of Analytical Methods

Parameter	Method (performer)	Reported Results
Nitrate	Ion Chromatography (Huang)	Huang
Se (total, dissolved, selenate)	ICP-MS (SRI), AAS-Hydride (Huang)	SRI
Hg (total, dissolved)	ICP-MS (SRI), AAS-Hydride (Huang)	SRI
Ca^{2+}, Mg^{2+}, K^+, NH_4^+	ICP-MS (SRI), IC (Huang)	SRI
Cl^-, SO_4^{2-}, $S_2O_8^{2-}$, Br^-	IC (Huang)	Huang
Total Dissolved Solid	EPA method (Huang)	Huang
pH, ORP, Temp	Probe (Huang)	Huang
Alkalinity/Acidity	Titration (Huang)	Huang
Silica (dissolved)	ICP-MS (SRI), UV-VIS (Huang)	Huang
ZVI and Iron Oxide	SEM, XRD (Huang)	Huang
Silica (dissolved)	ICP-MS (SRI), UV-VIS (Huang)	Huang
ZVI and Iron Oxide	SEM, XRD (Huang)	Huang

4.3.4 Project Tasks and Milestones

Project Tasks:

1. Design and fabrication of a pilot-scale treatment system with a treatment capacity of 1 to 2 gpm. The system would be mounted on a flat-bed trailer and delivered to Plant Wansley.

2. Conduct a long-term field test at Plant Wansley to demonstrate the feasibility of the hZVI process for treating the FGD pond water to meet the required discharge limits for Se, Hg, and other toxic metals and concerned pollutants.

Project Milestones:

The major milestones to be achieved in this pilot scale demonstration are

1. Setup of pilot scale system at Plant Wansley and trail operation of the system.

2. 4-stage operation of system to treat FGD water at a rate of 1 gpm.

3. 2-stage treatment configuration setup and operation to treat FGD water at a rate of 2 gpm

4. To conduct spike test by spiking the influent FGD water with known concentrations of targeted toxic metals.

5. To replace the ZVI reaction mixture in the system and to evaluate the performance of different kinds of ZVI selected.

5. RESULTS AND DISCUSSIONS

5.1 Characteristics of Raw FGD Water

Raw FGD pond water (most time in clarified form) was lifted first and fed into the reactor directly without any pretreatment. A 45 gallon feeding tank as preliminary settling tank was used to provide the sediments and prevent them from entering into reactors. The temperature of the FGD water varied from 40^0F in mid-January to 90^0F during last end of May. We didn't observe any impact of temperature variation on system performance. Proper care was taken during startup weeks to prevent formation of ice in the reactors, as this may affect the propellers and overhead mixers. We observed a huge variation in pH of FGD water. During the startup weeks the pH used to be near neutral (~6.80). We observed a substantial drop in pH to about 4.0 in the month of June. pH varied from 3.5 to 7.7 throughout the test period. Detailed pH variation of raw FGD water throughout the operation period is shown in Fig. 16. TDS varied between 7,500 mg/l and 15,000 mg/l during the test period. Concentration of dissolved solids in FGD water during the test period is shown in Fig. 17. The major cations include 1300 ~ 2600 ppm Ca2+ and 145~360 ppm Mg2+. The major anions include 1400~4900 ppm Cl- and 750~1400 ppm sulfate. Concentrations of measured cations are shown in Appendix 1.
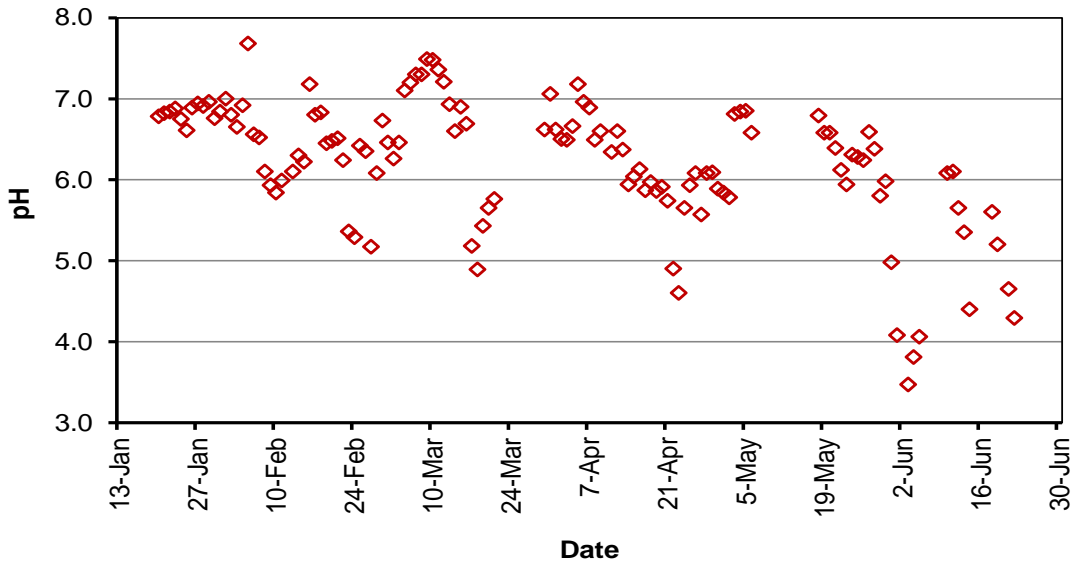
Fig. 16. pH of the Raw FGD Pond Water
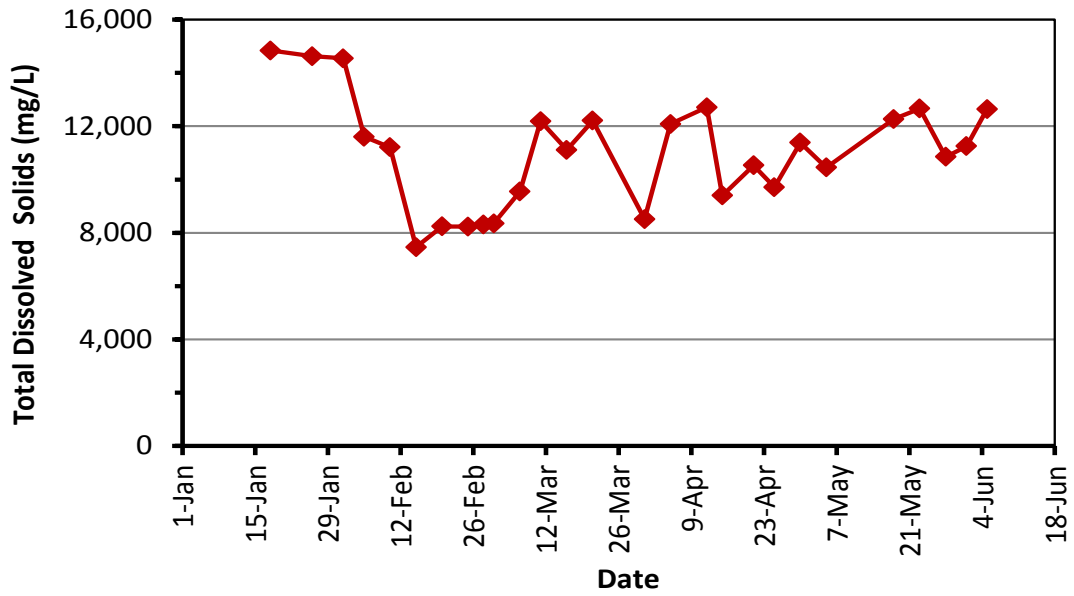
Fig. 17. Concentration of Total Dissolved Solids (TDS) in the FGD Pond Water
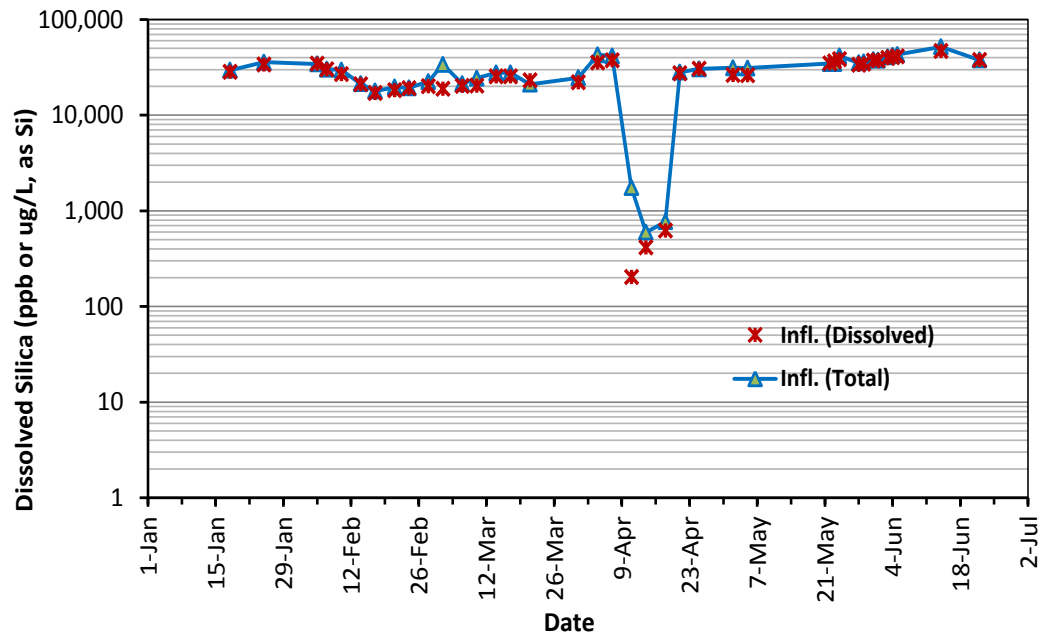
Fig. 18. Dissolved Silica Concentration (Reported as Si) in the FGD Pond

Dissolved silica content varied between 8 ppm and 40 ppm during the test period as shown in Fig. 18. Most of selenium was present in dissolved form, almost all as selenate during the test. Total Se varied between 909 and 3220 ppb. Fig. 19 shows variation of concentration of dissolved and total selenium throughout the testing period.
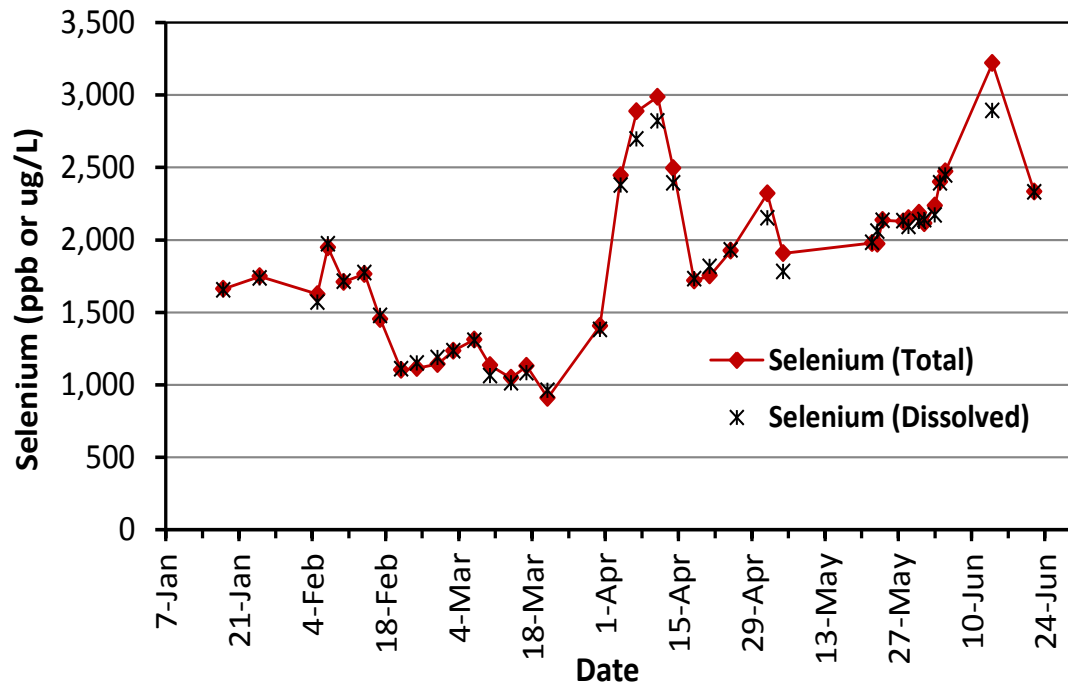
Fig. 19. Concentrations of Total and Dissolved Selenium in the Raw FGD Pond Water.
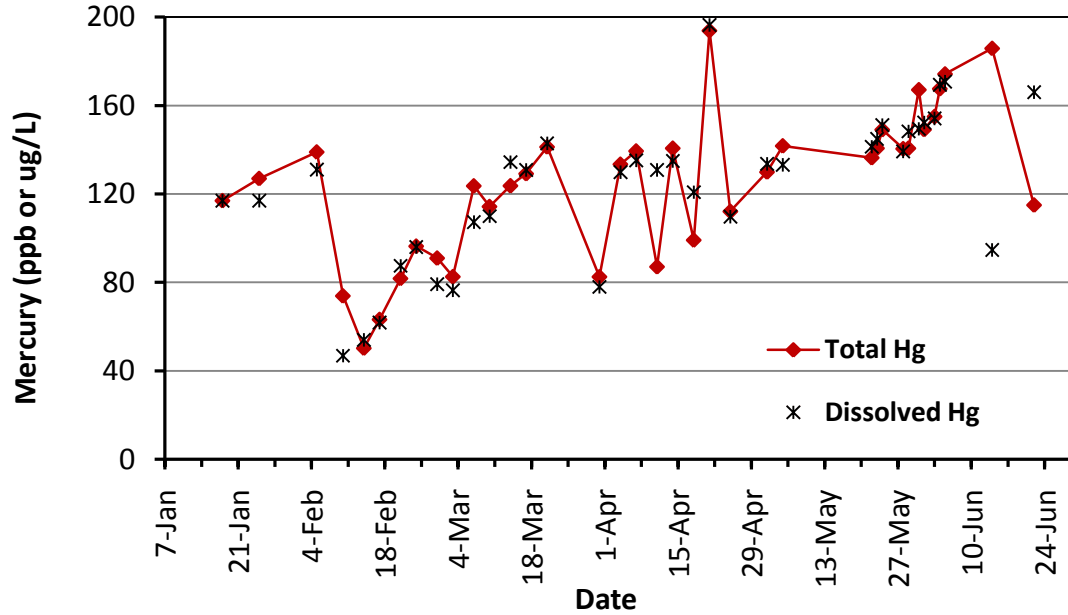
Fig. 20. Total and Dissolved Mercury Concentration in the Raw FGD Pond Water.

Most of the mercury in the water was present in dissolved form. Total mercury varied from 50 ppb to 194 ppb. Fig. 20 shows influent dissolved and total mercury concentrations during the test period.
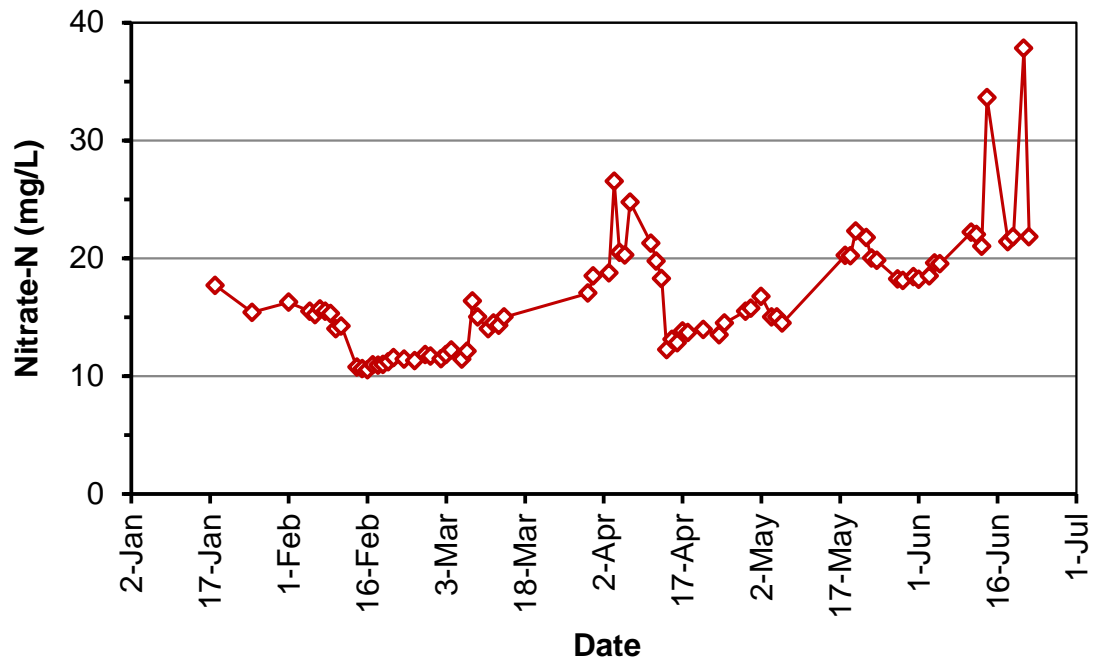
Fig. 21. Nitrate Concentration in the Raw FGD Pond Water

The nitrate concentration varied between 10.5 mg/L and 37.8 mg/L and had an average of 16.5mg/L. Variation in nitrate concentrations in FGD water is showed in Fig. 21. Concentration ranges of different pollutants present in the FGD water of Plant Wansley are shown in Table 5.

Table 5

Concentrations of Major Contaminants in the FGD Water at Plant Wansley

Pollutant	Concentration Ranges
Selenium	909 to 3220 ppb
Mercury	50 to 194 ppb
Arsenic	3.5 to 21.1 ppb
Cadmium	2.1 to 12 ppb
Copper	up to 100 ppb
Zinc	up to 200 ppb
Lead	< 0.1 ppb
Chromium	25 to 50 ppb
Nitrate-N	10 to 38 ppm
Silica	17 to 45 ppm
Boron	37 to 194 ppm

5.2 Operation and Maintenance

The feeding was started on Jan 15, 2011.The initial feeding rate was 0.5 gpm, but was increased to 1 gpm in the following day. First sample was taken on Jan 20, 2011 and sent to SRI (Southern Research Institute, Birmingham, Alabama) for analysis. The main problem during the startup was that the settling property of the reactive solid was not as good as we expected. We observed that a significant amount (> 150 mg/L) of dissolved Fe^{2+} was released from ZVI Reactor 1 upon the feeding of the FGD at 1 gpm. As the released Fe^{2+} cascade through the following ZVI reactors, the reactors started to accrue a hue of green color and the reactive solids in the ZVI became fluffy and settled much slower. Overtime, the reactive solid particles blanket

reached to the top of settling zone and started to bleed. As the solid bleeding might potentially affect the reactors, the feeding to reactors was stopped on Jan 20, 2011. Subsequently, the reactor was operated for three days under batch mode under a special condition to improve the reactivity and density of the FeOx phase. The feeding was restarted at a rate of 1gpm as the targeted secondary iron species was observed in the reactors.

The sludge bulking problem appeared to relate to the unique reactive characteristic of the FGD ponder water at Plant Wansley. Upon entering Reactor 1, certain constituent(s) of the FGD water reacted with ZVI and released significant amount of both Fe2+ and acidity. The pH of reaction zone in R1 dropped below 5.5, accompanied with a release of over 100 mg/L Fe^{2+}. To control this condition sodium bicarbonate solution was introduced into the reactor-1 to raise the pH of reaction zone to near neutral pH. As excessive release of ferrous ions was observed from the reactor-1, aeration was introduced into the reaction chamber at a depth of about 1.5 ft, which could help to oxidize excess ferrous ions and thus improve the settling property of the solids. Though this bleeding of reactors seemed like a hard shell to break in initial stages, by proper study of FGD characteristics, ZVI response to those suspicious ions and several other factors we were able to control the bleeding to a large extent. In prior laboratory tests using simulated FGD waters and supplied FGD waters from Plant Bowen, the sludge characteristics were quite different to that of Plant Wansley. Through a series of laboratory screening test, we identified that the FGD water at Plant Wansley contained high concentration (up to 400mg/l) of persulfate (compared to Plant Bowen's FGD water) and that the excess release of Fe^{2+} and acidity was due to the reaction between persulfate and ZVI, which is able to oxidize ZVI particles and release excessive amount of H+, ferrous ions and Mn ions. The high concentration of

Mn^{2+} (up to 13 mg/L) in conjunction with high concentration of dissolved Fe^{2+} at certain pH may cause the sludge bulking and bleeding problem during the first week. The ZVI iron powder used in this test could be another reason. Some potential suppliers of ZVI were selected and two new kinds of ZVI were ordered to check the response of different kinds of ZVI to raw FGD water.

5.2.1 Chronology of Field O&M Events

(Jan-24 to April-3) Four-stage single train treatment at 1 gpm: During one week of operation after January 24, it was observed the settling properties improved and loss of iron particles through bleeding was arrested upto a large extent. These improved operational conditions might be due to formation of a protective coat on the ZVI particles resisting further corrosion. We observed that the strength of the FGD water started slowly swooping down from mid-February by over laboratory analysis. We were informed that the FGD units are shut down for general maintenance thus resulting in less amount of discharge into FGD pond. The tranquility of the FGD pond was continuously interrupted by blowing winds resulting in increase of solids concentration in FGD water. As our intention was to feed raw FGD water into the reactor-1 without any prior treatment, we observed the FGD water entering the reactor was laden with considerable amount of slit which may cause potential threat to reactor-1, as there was continuous accumulation of silt in the reactor. Increase in percentage of silt will result in treatment capability of the reactor by hindering the interaction of FGD water with reactive FeO_x particles. So we expected to release the sludge from reactor-1 in near future to maintain better performance of the system.

We tried to alter the mixing conditions to check the treatment efficiency of the systems at a different mixing intensity. During these conditions we observed relatively fewer amounts of dissolved ferrous ions released from each reactor thus decreasing the

consumption of ZVI. It is one of our crucial objectives to evaluate the impact of agitation power employed in the reactors on its treatment capabilities of different elements. Reactor-3 was being bypassed in order to reduce retention time and culture the ZVI in the reactor-3 to study the response of well-aged ZVI particles to FGD water. The settling conditions and effluent quality (physical) from each reactor resembled near to laboratory conditions. The laboratory results showed that the efficiency of reactors to treat selenium been decreased due to this condition, so on February 23rd we changed the agitation conditions in all the reactors to regain treatment efficiency. Removal of mercury still remained unaffected. This study helped us to assess the treatment and operational conditions of systems at different mixing conditions showing a considerable impact on ZVI texture. Meanwhile the water level in FGD pond was observed to be continuously receding, so the feed pump was adjusted to arrest silting in reactor-1 to the maximum possible extent.

During the first week operation of systems a rise in pH was observed in reactors due to variation in strength of FGD water. Dissolved Ferrous content in all the reactors considerably decreased which showed a change in FGD water matrix. Reactor-3 was again made to work along the remaining treatment system. The mixing conditions of all the reactors were altered and corresponding treatment efficiencies were checked through this period.

The systems were operated without any major problems till second week of March. During our daily assessment of silt to ZVI ratio in reactor-1, we observed huge accumulation of silt in reactor-1. From analysis reports we observed that efficiency of reactor-1 to handle toxic metals was dropped. So we restored reactor-1 by replacing about 80% of solids in reactor with about 58kg of Fresh ZVI and reactor-1 was restarted and fed at a rate of 0.5gpm on March 11th and flow rate raised back to 1gpm

on the following day. The systems were partially suspended on March 21st due to insufficient water in FGD pond. Operation under this condition results in silt accumulation in reactors due to high solid contents in FGD water. During this suspended period the mixers were run at a very low speed just to keep the particles in suspension else there might be a chance of cementation of particles. The systems were restarted on March 29th and fed at a rate of 1gpm. We observed no major impact of this partial suspension of operation on the efficiency or operational conditions of the system. During this suspension necessary plumbing work was done in order to operate the system as a two stage treatment facility thus reducing the retention time by half.

(April 4th – May 6th) *Two-stage, duel train treatment at 2 gpm:* During this period the systems were aligned to run as two different 2-stage treatment systems. Reactors 1 and 4, Reactors 2 and 3 were coupled together by proper plumbing work. The final effluent from reactors 3 and 4 were combined together and combined flow was subjected to post treatment so that the final effluent has a mixture of effluents from 3&4. As the designed post treatment might not handle the high flow rate discharging from reactors 3&4, about 50% of the effluent was discharged before entering into the aeration tank to the ash pond.

The mixing conditions of all the reactors were altered in order to achieve better treatment efficiency in shorter span. The flow rate of FGD water was slowly raised to 2gpm allowing enough time to the reactors to accommodate higher flow rate at that vigorous mixing conditions. On Feb 4th the reactors 1&2 were fed at a rate of 0.5gpm each separately (total flow of 1gpm). On the following day the flow rate was increased to 0.6gpm (total flow of 1.2gpm). It was observed better settling properties of FeO_x particles in reactors 1&4 series compared to reactors 2&3. This was mainly because reactor 1 was already been under effect of Raw FGD water and got adjusted to it. As

reactors 2&3 series had been newly exposed to raw FGD water, it required a specific amount of time for the iron particles in the reactor 2 to withstand high strength FGD water. So reactor 1&4 series was fed at a rate of 0.8gpm and reactors 2&3 series at a rate of 0.6 gpm (total flow rate of 1.4gpm) It was observed that silt percentage in reactor-1 increased, therefore about 50% of solids from reactor 1 were pumped to FGD pond. Well conditioned FeO_x particles were pumped from reactors 3&4 to reactor 1 (about 25% of R-3 and 25% of R-4). Apart from this about 20 kg of fresh ZVI was added to R-1 and 10kg each to remaining three reactors. The reactor 2&3 series was fed at a rate of 0.8gpm from April 15th (total flow rate of 1.6gpm) as better operational qualities were observed in this series.

Starting from April 17th the systems were fed at a rate of 2gpm thus decreasing the retention time to half of the initial (8h approx). These feeding conditions were maintained till May 6th with minimal operational variation. About five sets of samples were collected. The systems were suspended from May 6th to May 16th due to lack of required chemicals for starting spike tests.

(May 17th – June 5th) Elevated toxic metal loading test: On May 17th the systems were realigned to 4-stage treatment system and feeding started at a rate of 1gpm. The systems were run for 4 days (till May 21st) to check the functioning and were readapted to FGD water. Then spike test was started on May 21st to study the fate of different contaminants like Lead, Copper, Mercury, Selenium, Cadmium, Chromate, Arsenate and Arsenite when present in higher concentrations. These ions are grouped into two batches based on their chemical behavior. A strong spiking solution is prepared and supplied to Reactor-1 along with FGD water at a calculated flow rate so that desired amount of these toxic metals are supplied. The whole spike test had been conducted till Jun 5th without any change in operational conditions. During these days,

a drop in pH of FGD water was observed thus decreasing the pH in all the reactors result in increase of dissolved ferrous ions.

(Jun 9th - June 22nd) ZVI sources and reactivity test: On Jun 6th the systems were configured into two-stage duel train treatment system (R1-R4 and R2-R3) to conduct parallel tests on two treatment train and compare the reactivity of two different types of ZVI sources. Both Reactor 1 and 2 were emptied before adding new ZVI power. Reactor 1 and Reactor 2 were replaced with two different kinds of ZVI and were run by maintaining similar conditions to compare the treatment capacity and handling ease of those ZVI powders. R1 was filled with 90kg of 5 micron ZVI powder and R2 was filled with 100kg of 325 meshes ZVI powder. Systems were fed with FGD water at a rate of 1 gpm to each treatment train, starting from Jun 9th till Jun 14th. During this period it was observed significant loss of reactive particles from all the reactors. So after sampling on 6/14/2011 feeding into the reactors was stopped and ageing process was employed to cultivate the iron powder in both R1 and R2 till 6/17/2011. The reactors were fed with FGD water at a rate of 1gpm to each series and samples were collected on Jun 22nd then systems were completely suspended and demonstration was wrapped.

5.2.2 Incidents

The treatment system was operated without any major equipment failures or operational accidents. After startup of the system, in the first week of February we observed a sudden shutdown of overhead mixer due to loss of the power supply. The power loss occurred when a thunder storm passed the area overnight. The mixers were restarted by switching on the frequency regulators. Similar events of power loss and temporary shutdown of the mixers occurred two more times throughout the demonstration period, all related to thunder storm activities passed through the field

site. When a power loss occurred within 24 hr for the planned SRI sampling time, sampling was deferred for one day. The temporary power supply appeared not able to handle well the thunder storm conditions very well. Such disruptions, however, didn't affect the operation of the treatment system in a significant way.

Metal corrosion was another minor problem identified during the test. Some of the metal fittings and valves used were observed to corrode rapidly and had to be replaced every two months to ensure proper functional and preventing any major leaks in the system. Those fittings and valves were obtained from local home-improvement stores (Lowe's or Home Depot) and could not handle the corrosive nature of the FGD water. On the last week of operation (Jun 20) the coil carrying power to the feed pump was burnt due to exposure to FGD water. This coil was replaced and pump was started. The main body of the reactor, which was made of stainless steel, showed no sign of any corrosion. The stainless mixer had no corrosion problem.

5.3 Performance and Discussions

5.3.1 Performance of hZVI System and Pollutants

Selenium removal was evaluated under different test conditions and configuration, including 4-stage ZVI reactor configuration at 1 gpm, 2 stage ZVI reactor configuration, and a spike test with elevated-loading of selenate. While it is inevitable that under certain conditions Se removal was not as good as we expected, the test results in general demonstrate that the hZVI/FeOx process could reliably achieve excellent Se removal and reduce selenate-Se from ppm level to below the anticipated effluent limit of 50 ppb. From Plant Wansley's FGD water, a three-stage ZVI treatment with a combine HRT of 12 hr would be sufficient to secure Se reduction from a few ppms to below 20 ppb.

4-stage ZVI treatment: The test was conducted between January 15 and April 4, 2011. The system was fed with the FGD water at a rate of 1 gpm, corresponding to a combined hydraulic retention time of 16 h.   Most times Se in the treated effluent was below 10 ppb with some exceptions due to our effort to test certain operating conditions.

For example, the high total Se concentrations detected in the effluent between February 14 and February 21 was caused by insufficient mixing of reactor solid in the hZVI reactors. During this period, we conducted a test to evaluate the minimum mixing condition required for sustaining the reactivity of the reactor. The mixing power was reduced by more than 50% of the designed value. The resulting poor performance indicated that the design speed and power of propeller is essential for achieving high reactivity in the hZVI reactor. Once the mixing speed was increased (after February 23), the performance of the hZVI returned to normal.

The spike of both total and dissolved Se on March 7 (similar to the Hg results on the date) were caused by our trial test of adding bleaching powder ($Ca(ClO)_2$) in the aeration tank for verifying its capability in removing NH_4^+. The spike of Se due to application of $Ca(ClO)_2$ indicates that $Ca(ClO)_2$ may cause the release of adsorbed Se from the reactive solid accumulated in the aeration tank. The result suggests that $Ca(ClO)_2$ application for NH_4^+ removal should be added after sand filtration. It needs to be noted that the treatment system was shut downed for six days during the week of Mar 26 due to the inadequate water level in the FGD pond. Once the system came back to operation, the system immediately produced excellent results. This episode demonstrated that the hZVI system is robust and flexible. Fig. 22 and Fig. 23 show the treatment results. Selenium analysis reports are shown in Appendix 2.
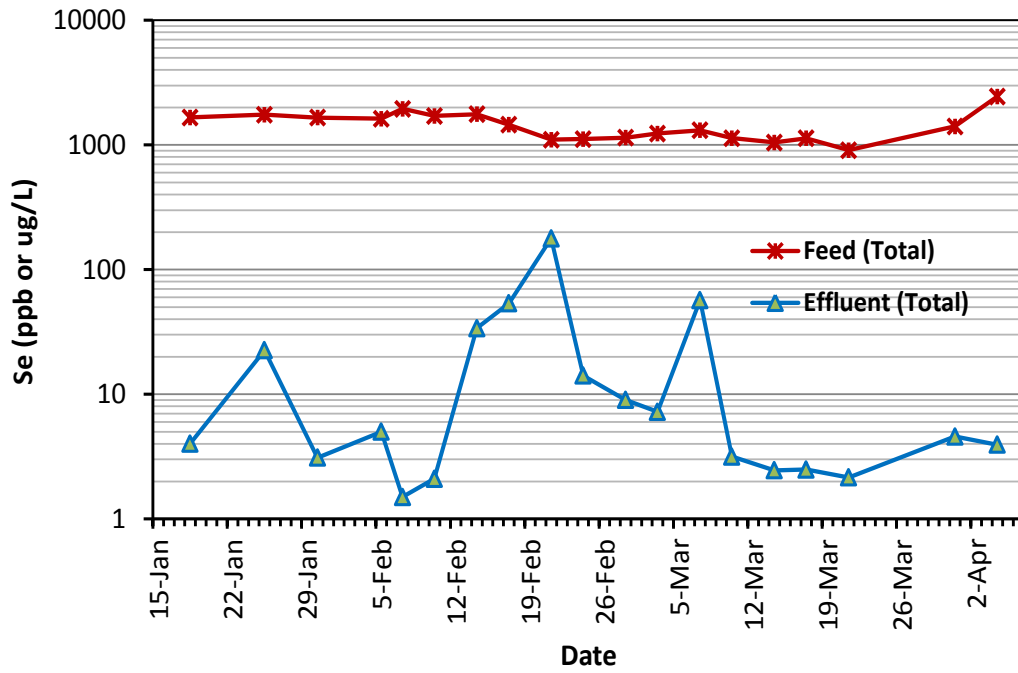
Fig. 22. Influent and Effluent Concentrations of Total Selenium for 4 Stage System.
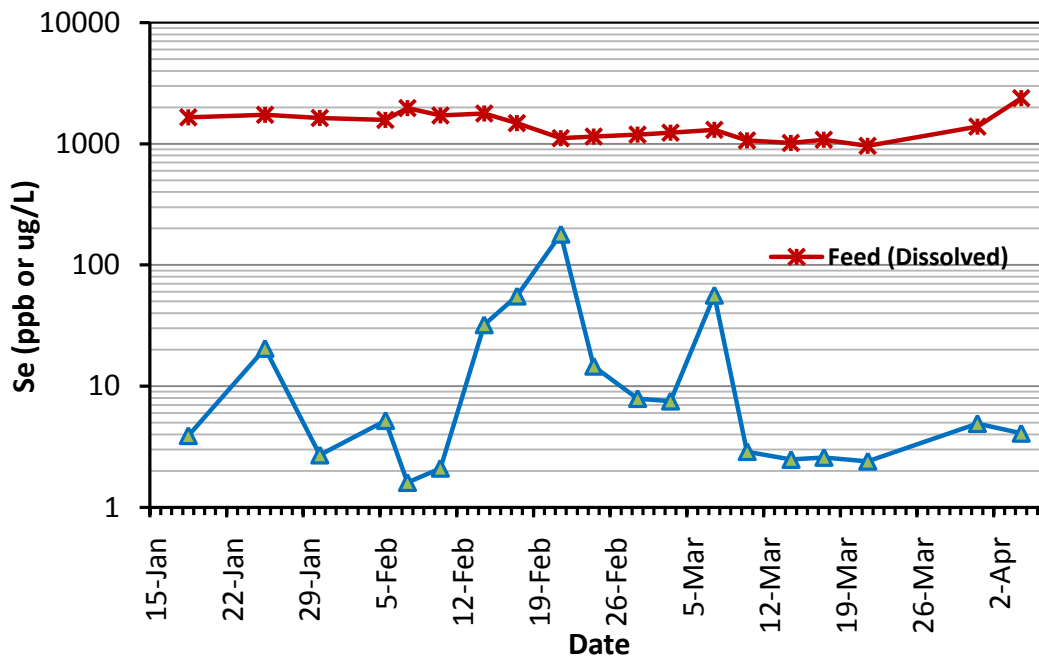
Fig. 23. Influent and Effluent Concentrations of Dissolved Selenium for 4 Stage System.

2-stage ZVI treatment test: During this test between April 4 and May 5, 2011. (4/4/2011 to 5/5/2011), the system was operated as duel trains, each with 2-stage ZVI reactors (Train A: R1->R4; Train B: R2->R3). Each Train started with 0.5 gpm and stepped increased to receive 1 gpm FGD wastewater by April 17, and thus the system treated 2 gpm in total between April 17 and May 5 with a hydraulic retention time of 8 hr. Train B (R2+R3) consistently outperformed Train A (R1+R4), reducing selenate from over 1500 ppb to mostly below 50 ppb. Treatment train A's performance was not as good, mostly reducing Se to 100-200 ppb. Further examination showed that the performance of R2 was substantially better than R1 and thus responsible for the difference between Train A and B. The difference between R1 and R2 might be attributed to the different composition of FeOx in the two reactors. As the second stage, R2 had accumulated substantial high quality magnetite particles during the previous 4-stage test. In contrast, R1 always served as the first stage and thus was exposed to high concentration of persulfate carried in the raw FGD pond water. Overtime, the iron oxide phase had been altered and become completely oxidized to ferric (oxyhydr) oxides, which according to our previous laboratory tests, was less reactive than well crystallized magnetite.

Results of this test demonstrates that a two-stage ZVI system may be able to achieve reduction of selenate from a few ppm level to below 50 ppb with a reaction time as short as 8 hr, but such a good removal efficiency can be ensured only when the system was under very favorable conditions. The significant performance gap between the two treatments trains operated under parallel conditions suggests that the composition and quality of reactive solid phase has great impact on the overall system efficiency. The performance of the two treatment trains is reported in Fig. 24.
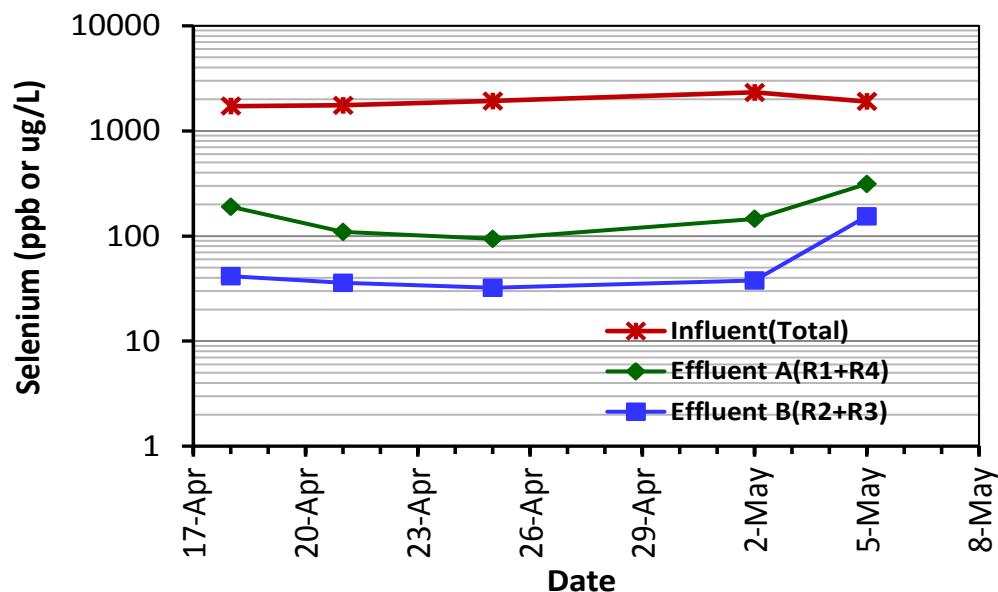
Fig. 24. Influent and Effluent Concentrations of Total Selenium for 2 Stage System.

Treatment train B (R2+R3) achieved much better Se removal than train A (R1+R4), possibly due to the higher quality reactive solids in R2. Both train A and B were operated to treat 1 gpm, corresponding to HRT of 8 h. The results indicate that with high quality solids (well-coated ZVI powder and sufficient highly reactive FeO_x) a two stage system with retention time about 8h may be able to meet the discharge limit of 50 ppb for Se.

Spike test with elevated Se loading: On the week between May 29 and June 5, a spike test was conducted to assess the capacity of the system in handling very high concentrations of selenate selenium. The test was conducted under 4-stage ZVI treatment configuration with a constant flow rate of 1 gpm and a combined HRT of 16 hr. During the week, the FGD pond water was spiked with 20 ppm of selenate-Se by pumping a stock solution of sodium selenate (in conjunction with other selected toxic

metals including chromate, arsenate, arsenite) along with 1 gpm FGD pond water into reactor 1.With about 2 ppm selenate-Se in the FGD pond water, the combined concentration after spike was about 22 ppm for selenate-Se. R1 reduced selenate-Se from 22 ppm to 8-17ppm. In R2, selenate was reduced to below 4 ppm (for June 3, 4 and 5, dissolved Se in R2 effluent was about 1 ppm).The results indicate that under a loading as high as 22 ppm, the first stage may not be able to achieve over 90% removal as it was observed when dealing with low ppm Se concentration. The second stage could achieve the maximum Se removal, e.g., reducing selenate from about 13 ppm to below 1 ppm with over 90% removal. At high concentration, selenate reduction of over 10 ppm in a single stage was possible.   In June 4 and 5, R3 and R4 could further polish selenate to about 10 ppb, each stage achieve about 90% removal efficiency. Such robustness was previously demonstrated through various laboratory tests. The success of this spike test demonstrates that a scaled-up system is as flexible and robust as a bench-top system.

Concentration of selenium can vary greatly from facility to facility depending on different wet-scrubber technologies and operating conditions and the types and sources of coals used by the power plants. Within Southern Company's facilities, for example, the FGD wastewater at Plant Bowen and Plant Wansley were typically in 1-4 ppm concentration for Se, while the FGD water at Plant Barry could often be higher than 10 ppm. The capability of a treatment system to adapt to different Se concentrations can be a major advantage of the technology.   The multi-stage hZVI process demonstrated its robustness in handling extra-high selenate loading with a great flexibility. What is needed for the hZVI to handle extra high strength FGD water is the addition of one extra stage and extension of the HRT for a few more hours. For

Plant Barry's water, we project that a 4-stage system with an HRT of 16 h can ensure
high quality effluent of < 20 ppb Se. The treatment efficiency is shown in Fig. 25.
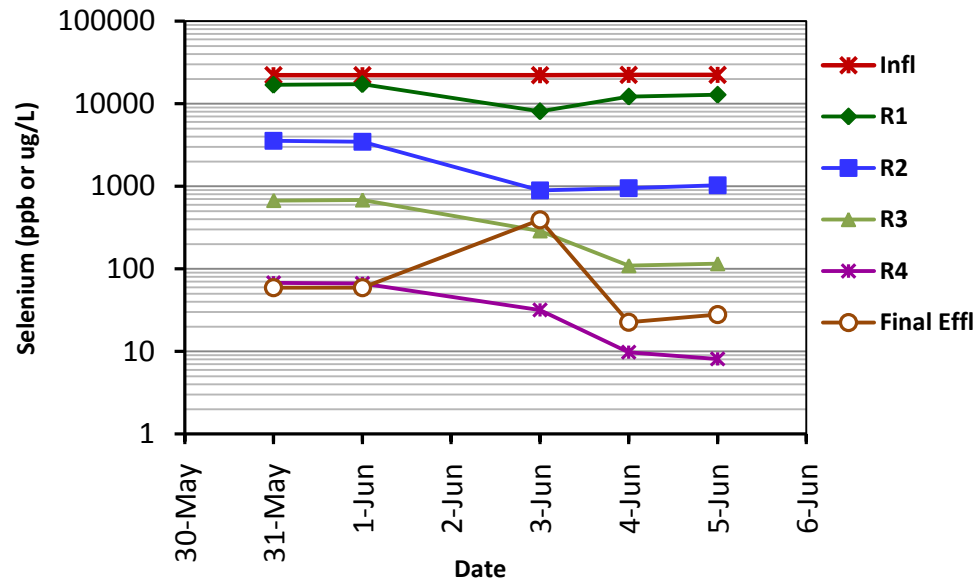
Fig. 25. Influent and Effluent Concentrations of Total Selenium for Spike Test.

The results in general show that the hZVI process with 4 stage configuration
can handle extremely high concentration of Se and still meet the required discharge
limit for Se. The final effluent was significantly higher than R4 in June 3, 4 and 5,
which is hard to explain. We are trying to verify those results by re-analyzing the
samples in our storage.

Mercury removal was estimated under the same test conditions. During the
five month test period, the hZVI treatment system showed extraordinary removal
efficiency for mercury treatment. The FGD pond water contained about 50-190 ppb of
total Hg, mostly in dissolved form. The hZVI system consistently reduced total Hg to

below 10 ppt meeting the stringent effluent standards for Hg. A spike test showed that hZVI system can treat about 1150 ppb of dissolved Hg^{2+} without much difficulty. Evidences suggest that Hg removal may follow a very fast reaction kinetic, thus requiring much less reaction time than Se removal. There were a few exceptions when Hg in the effluent was higher than the limits but the anomaly was clearly attributable to certain controllable O&M conditions. Similar to our discussion on selenium treatment, the mercury treatment performance will be discussed below based on the test phases.

4-State ZVI treatment: As mentioned above, the first phase between Jan. 15 and April 4, 2011, the system was operated as a single-train 4-stage treatment system for treating 1 gpm at a HRT of 16 hr. The results showed that the system can consistently reduce dissolved Hg to below 10ppt. In most samples, we observed that R1 reduced dissolved Hg from over 100 ppb to below 0.01 ppb (or 10 ppt), which was an extraordinary removal rate of over 99.99% in a single stage. In the initial weeks of test before February 5, we noticed that while dissolved Hg was as low as a few ppt, total Hg could be much higher at over 100 ppt in the final effluent. We concluded that the problem was due to the breaching of suspended particle through the sand filter. The leaked suspended particles (mainly FeOx) carried Hg and caused unusual high total Hg when the sample was digested and measured. The problem of rapid sand filtration bed was fixed in February 7 by adding a steel girder to strengthen the plastic tank so that the tank would not bulge as it was filled up with water and create a crevice for suspend particle to breach the sand bed. Thereafter, the total Hg concentrations in the final effluent were comparable with dissolved Hg concentration, both below our target level of < 0.012 ppb.

Hg result on Mar 7 was abnormal. The spike of both dissolved Hg and total Hg was caused by our trial test of adding bleaching powder ($Ca(ClO)_2$) between the aeration tank and settling tank for ammonium control. The test is to verity that breakpoint chlorination can be an effective method if there is a need to remove NH_4^+ that was produced as a result of nitrate reduction by Fe^0. The result showed that $Ca(ClO)_2$ could be a potential method for NH_4^+ control. $Ca(ClO)_2$ as a strong oxidant can oxidize NH_4^+ to N_2. Unfortunately, $Ca(ClO)_2$ can also react with ZVI or certain iron oxides, and thereby release Hg that was otherwise locked within the FeOx phase. The spike of Hg due to application of $Ca(ClO)_2$ pointed out that $Ca(ClO)_2$ can cause secondary release of adsorbed Hg from the FeOx particles and that any $Ca(ClO)_2$ application for NH_4^+ removal should be added after sand filtration when there is negligible iron reactive material to react with $Ca(ClO)_2$. After the stop of $Ca(ClO)_2$ addition, Hg results returned to normal. It has to be noted that during this $Ca(ClO)_2$ episode, dissolved Hg in the effluents of R1 –R4 were normal, all in low ppt level. Influent and effluent concentrations of total and dissolved mercury are shown in Fig. 26 and Fig. 27 respectively. Detailed analysis report by SRI is shown in Appendix 3.
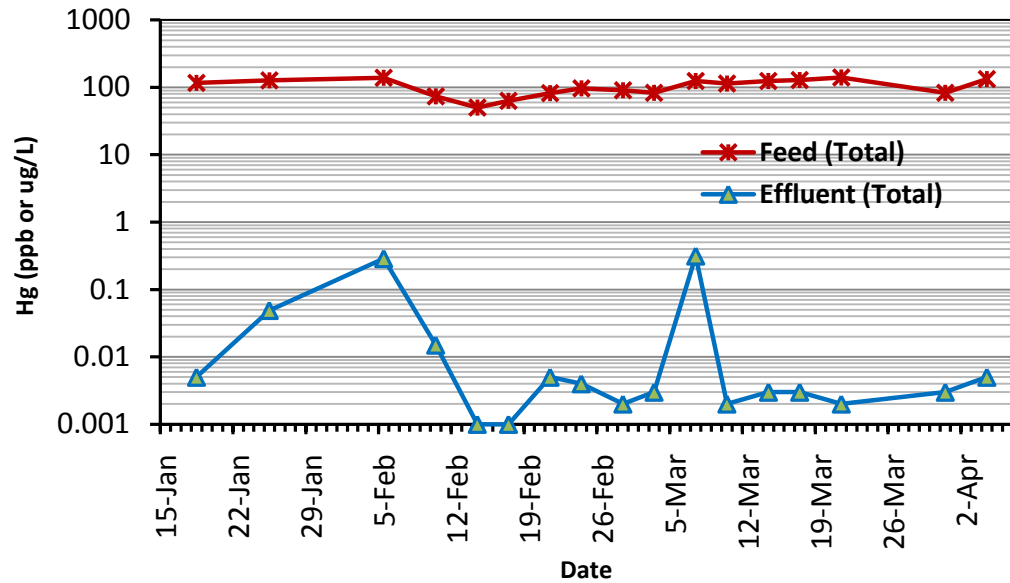
Fig. 26. Influent and Effluent Concentrations of Total Mercury for 4 Stage System
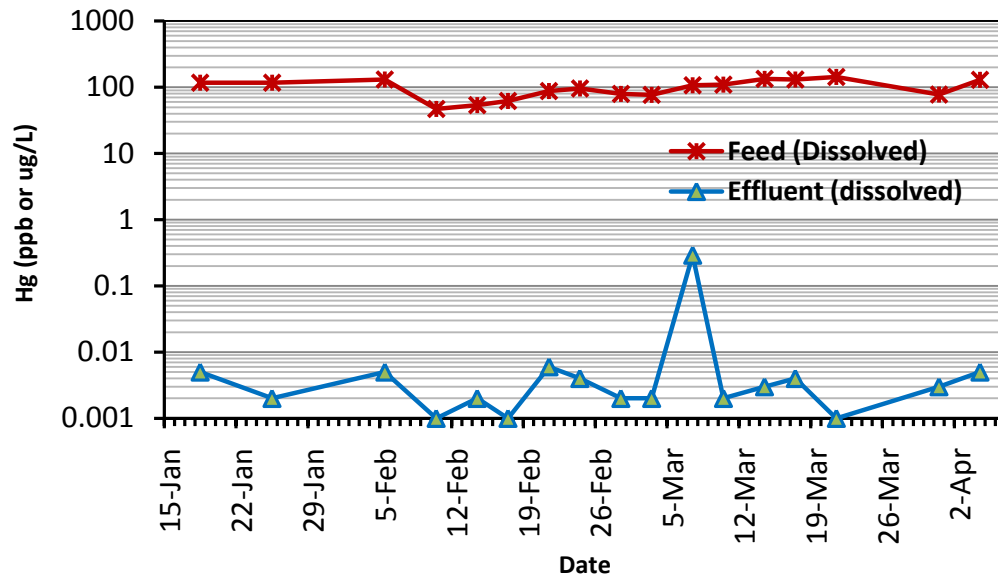
Fig. 27. Influent and Effluent Concentrations of Dissolved Mercury for 4 Stage System

2-stage ZVI treatment test: During the second stage (4./4/2011 to 5/5/2011), the treatment system was configured as a duel train, two-stage treatment system (Train A: R1+R4; Train B: R2+R3) and the flow rate was doubled to 2 gpm to reduce the retention time to 8 hr.   Even at this higher flow rates, the ZVI reactors were found capable of reducing Hg to below 12 ppt. In fact, both R1 and R2 showed that a single stage would be able to reduce dissolved Hg to below 12 ppt, achieving a removal rate of over 99.99% for dissolved Hg reduction. The abnormal results on the date of April 11, 2011 with high dissolved Hg in the final effluent was due to our trial test of using $Ca(ClO)_2$ as an oxidizing agent for ammonia removal through break-point chlorination. This $Ca(ClO)_2$ is strong enough to cause a secondary release of mercury form the sediments in aeration and settling tank, which explains why effluents from the ZVI reactors contained low ppt Hg while final effluent had much higher Hg. Influent and effluent concentrations of total mercury for two stage treatment system are shown in Fig. 28.
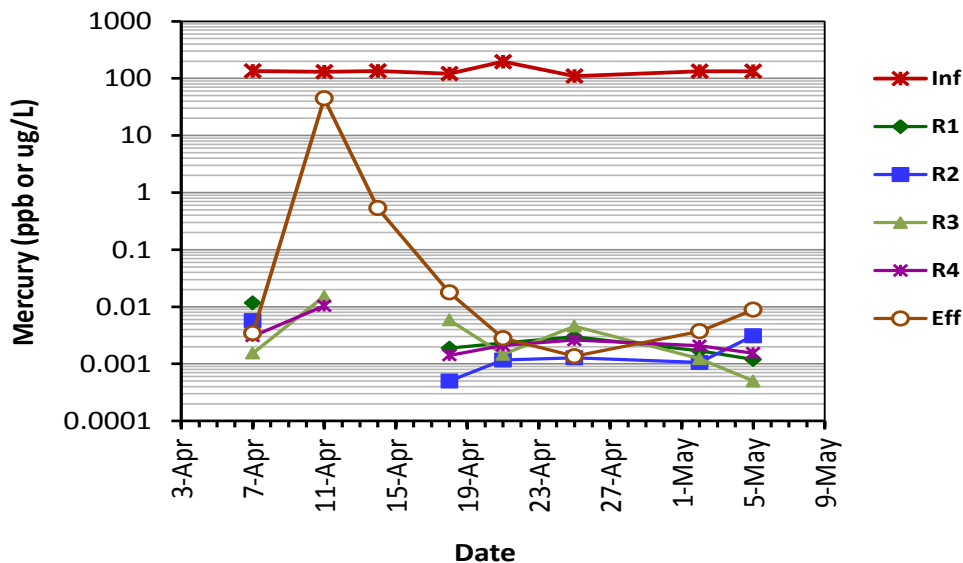
Fig. 28. Influent and Effluent Concentrations of Total Mercury for 2 Stage System

The results show that the hZVI reactor can reduce dissolved Hg from over 100 ppb to below 0.01 ppb level. The spike of final effluent on April 7 was not related to the performance of the hZVI reactors, but resulted from the addition of $Ca(ClO)_2$ in the aeration tank that might have dissolved Hg from the reactive ZVI/FeOx solids in the aeration tank and the bottom sludge in the settling tank.

Spike test with elevated Hg loading: During the third stage between May 22 and May 29, 2011, the system was subjected to a spike test to assess its performance under high loading of dissolved Hg^{2+}. The system was operated as a 4-stage configuration with a flow rate of 1 gpm with a HRT of 16 h. For the spike test, a concentrated stock solution with Hg^{2+} was pumped at a controlled rate to spike the feeding FGD water with about 1000 ppb of Hg (II). During this period, the raw FGD pond water (before spike) contained about 150 ppb dissolved Hg. Thus the total Hg concentration loading was about 1150 ppb. Overall the results showed that the systems

were able to handle extra high concentrations of mercury. For example, the final effluents were below 10 ppt on May 28 and 29 and below 25 ppt on the other days. For unknown reason, samples from 4 were significantly higher than both previous reactors (R1, R2 and R3) and the final effluent. We could not provide any more reasonable explanation for this discrepancy other than that Hg contamination might have occurred during R4 sampling, handling or analysis. During this period, Se removal in R4 was normal. Dissolved Se concentrations in R4 were all below 5 ppb during this week.

Further examination of the Hg results showed that R1 was able to reduce dissolved Hg from 1150 ppb to below 0.05 ppb. We would expect that R2 and R3 could further reduce dissolved Hg at a substantial rate to low ppt level, but the fact was that R2 and R3 only achieved marginal further reduction of dissolved Hg. One explanation to the apparent Hg removal efficiency between R1 and R2 (or R3) was that Hg removal requires certain supplementary substance(s) and these substance(s) is present in the raw FGD pond water but will be consumed in R1. From our previous laboratory tests, we confirmed that addition of I^-, phosphate, and sulfide can greatly improve Hg removal. The limited presence of these supplemental chemicals may not be able to support the full mineralization of the extra high concentration of high Hg^{2+} and other toxic metals (e.g., ppm level Cu^{2+}, Cd^{2+}, Pb^{2+}) during the spike test.

During the final three days of the Hg spike test, we conducted additional test to assess how sulfide addition will affect the performance of the system. Sulfide ions were supplied at a concentration of 1-2 ppm (normal to 1 gpm feeding rate) to R2 using a slow-leaching process (passing 5 mM HCl through a FeS cartridge) developed by Dr. Huang. The corresponding samples dated 5/28 and 5/29 showed that after addition of S^{2-}, R2 was able to improve dissolved Hg^{2+} removal (to about 10 ppt)

relative to the prior dates without addition of sulfide. Such improvement, however, appeared not enough to reduce dissolved Hg^{2+} to 1-3 ppt we regularly achieved. Se removal and other toxic metal removals during this period of sulfide addition were not affected. The results showed that sulfide is compatible with the hZVI system and that addition of sulfide could be a viable option if there is a need. Due to the time limit of this spike test, we were only able to conduct some preliminary test. If there is an opportunity, we would like to additional test to assess the effectiveness of other supplementary agents (such as I^- and phosphate) that may help co-mineralization of various toxic metals with FeOx.
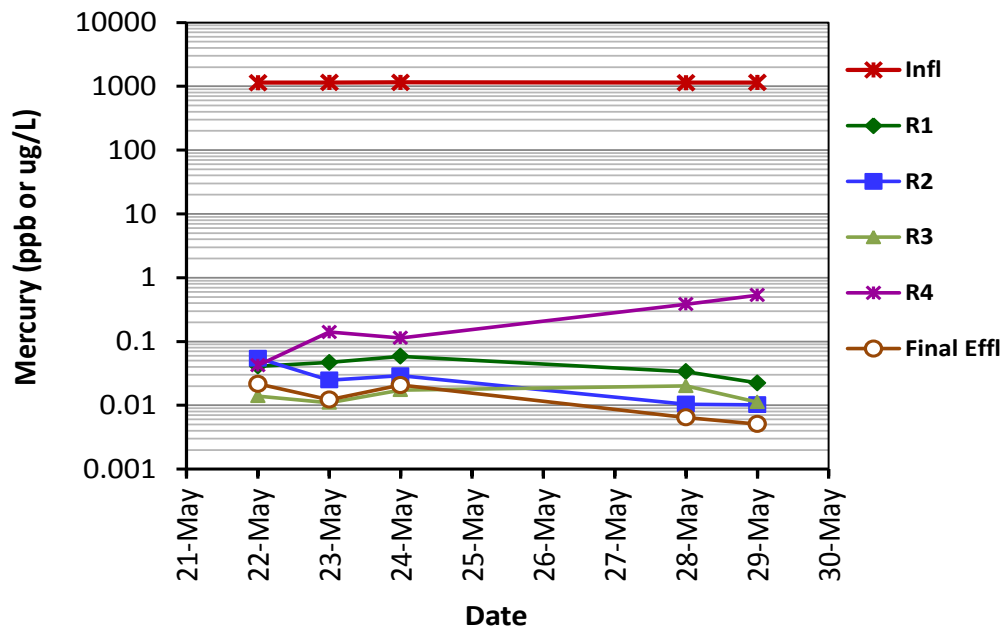
Fig. 29. Influent and Effluent Concentrations of Total Mercury for Spike Test.

Performance of the treatment system under this elevated mercury concentrations is shown in Fig. 29. The concentration in the feed contained about 1140 ug/L dissolved Hg after the FGD pond water influent was spiked with 1000 ug/L dissolved Hg^{2+}. The results show that the hZVI can handle high concentration of dissolved Hg^{2+}. Pond water influent was spiked with 1000 ug/L dissolved Hg^{2+}. The results show that the hZVI can handle high concentration of dissolved Hg^{2+}. Dissolved Hg was rapidly reduced from over 1000 ppb to below 0.1 ppb in the first ZVI reactor. R4 behaved abnormally with higher dissolved Hg in its effluent than in the influent water it received from R3. The inconsistency could not be explained.

Nitrate: Throughout the test period (except for the last few samples in June), the hZVI was able to reduce nitrate from over 10 ppm to near or below detection limits (0.1 ppm), thus consistently achieving over 99% removal rate. The concentration of nitrate varied greatly over time between about 10 ppm and 38 ppm. The hZVI system appears to handle such variation without problem. With a reaction time of 4 h, R1 typically achieved 85% to 95% reduction of nitrate from the feed. After the second reactor, nitrate was further reduced to mostly below 0.5 ppm. Reduction of nitrate occurred simultaneously with reduction of selenate. While nitrate and selenate will compete for the electron sources released from iron corrosion process, we didn't observe any sign of mutual exclusive inhibition between nitrate and selenate.

During the test, we observed that almost all nitrate was converted to ammonium. So there is a need of a secondary post treatment to complete the removal process. Break point chlorination is a proved technology that uses hypochlorite to oxidize ammonia to nitrogen gas. During the field test, we made an attempt on March 6 to oxidize ammonia to nitrogen gas by adding $Ca(ClO)_2$ between aeration and final

settling tank. The results shows that more than 50% ammonium was removed upon the addition of $Ca(ClO)_2$. The results showed that chlorination could be an effective method for nitrogen removal. The results were further verified by additional tests in our laboratories. To ensure high removal of ammonia, we need to apply the dosage of $Ca(ClO)_2$, which may be assisted by the use of an in-line probe that can give the concentration of ammonia on a real time basis. One problem we discovered is that $Ca(ClO)_2$ may react with 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, we suggest that chlorination should be added only to the treated effluent after filtration bed. We will continue to evaluate breakpoint chlorination and other methods for nitrogen control.

Removal of Other Toxic Metals: In previous laboratory tests and the bench-scale field test at Plant Bowen, the hZVI process had demonstrated its great removal efficiency for a variety of toxic metals in addition to Hg and Se. For example, the Plant Bowen test proved that the hZVI was very effective in reducing a broad spectrum of toxic metals including Zinc, Copper, Nickel, Vanadium, Cadmium, Arsenic and Chromium to near or sub ppb level. One goal of this pilot scale demonstration is to further demonstrate and verify such capability/versatility of the hZVI process. Concentrations of these toxic metals common in the FGD wastewater were generally low in the Plant Wansley's FGD water. As such, we decided that a spike test was necessary to evaluate the performance of the hZVI for removing high concentration of selected toxic metals augmented by dripping concentrated toxic metal solution.

The spike tests were conducted in two phase. In phase I, we spiked a group of cations including Cu^{2+}, Hg^{2+}, Pb^{2+} and Cd^{2+}. In phase II, we spiked a group of metal

oxyanions including SeO_4^{2-}, CrO_4^{2-}, AsO_3^-, and AsO_2^-. The separation of cation and oxyanion species prevented the incompatibility (precipitation) of these compounds. The concentrations we added were extremely high compared to the typical ranges of these toxic metals in the FGD or other wastewater. The test was conducted under 4-stage ZVI configuration with a flow rate of 1 gpm and a combined HRT of 16 h. Concentrations of different ions spiked into the FGD water are shown in Table 6 and Table 7.

Table 6
Phase One of the Spike Test (5/22/2011 to 5/29/2011) with Selected Cations

Toxic Metal	Concentration Spiked
Lead(II)	5000 ppb
Copper(II)	5000 ppb
Cadmium(II)	2500 ppb
Mercury (II)	1000 ppb

Table 7
Phase Two of the Spike Test (5/30/2011 to 6/5/2011) with Selected Oxyanions

Toxic Metal	Concentration Spiked
Selenate	20,000 ppb
Chromate	5000 ppb
Arsenate	500 ppb
Arsenite	500 ppb

Table 8 shows the spiked concentrations and effluent concentrations from reactor-1 and sand filtration (final effluent) of different ions spiked.

Table 8
Conditions and Results of the Spike Test (5/22/2011 to 6/5/2011)

Heavy Metal	Conc. Spiked (Dissolved)	Conc. after R1 Treatment (Dissolved)	Conc. In Final Effluent (Total)	Removal Efficiency (%)
Lead(II)	5,000 ppb	<1ppb	<1ppb	>99.9%
Copper(II)	5,000 ppb	<3ppb	~1ppb	>99.9%
Cadmium(II)	2,500 ppb	<10ppb	<1ppb	>99.9%
Chromium(VI)	5,000 ppb	<10ppb	<2ppb	>99.9%
Arsenic(III)	500 ppb	<1ppb	<1ppb	>99.8%
Arsenic(V)	500 ppb	<1ppb	<1ppb	>99.8%

Pb (II): The hZVI system was able to reduce dissolved lead from 5000 ppb to below 1 ppb in R1 during the spike test period. All the effluents were below 1 ppb for both total and dissolved Pb. Like mercury removal, a single stage ZVI treatment was able to reduce such high concentration of Pb^{2+} to near or below 1 ppb. The result shows that the hZVI is extremely effective for lead removal.

Cd (II): The hZVI system was able to reduce dissolved Cd^{2+} from 2500 ppb to below 1 ppb during the spike test period. All the effluents were below 1 ppb for both total and dissolved Cd(II). The first stage ZVI treatment, R1, was able to reduce

Cd^{2+} from 2500 ppb to about 10 ppb. R2 continued to reduce Cd^{2+} to below 1 ppb. The result shows that the hZVI is extremely effective for Cd^{2+} removal.

Cu (II): The hZVI system was able to reduce dissolved Cu^{2+} from 5000 ppb to near 1 ppb during the spike test period. The first stage ZVI treatment, R1, was able to reduce Cu^{2+} from 5000 ppb to low ppb (1-3 ppb) concentration. Cu^{2+} concentration in R2, R3, and R4 effluent were not much different from R1. The result shows that the hZVI is highly effective for Cu^{2+} removal. A single stage with short HRT will be sufficient to achieve low (low ppb level) Cu concentration in the effluent. In laboratory test, Cu^{2+} was found to be rapidly reduced to elemental Cu in a ZVI system. Removal of Cu^{2+} does not depend on other supplementary compounds present in the FGD pond water.

As: Both As(III) and As(V) were removed efficiently by the hZVI system. During the spike test, the dissolved As in R1 were never higher than 1 ppb. Similar As removal results were obtained in laboratory test on a bench-scale prototype that used DI water and synthetic wastewater. Unlike Hg^{2+}, arsenic removal does not depend on any other supplementary compounds.

Cr (VI): The hZVI system was very effective for removing hexavalent Cr. During the spike test between May 31 and June 5, R1 was able to reduce dissolved Cr (chromate) from 5000 ppb to mostly below 10 ppb (137 ppb June 1 was an exception for unknown reason). Removal mechanism of chromate in a ZVI system is similar to selenate, both depend on effective reduction of the oxyanions by the reducing agents in the system. Rapid reduction of chromate from 5 ppm to below 10 ppb in a single stage showed that chromate can be reduced faster than selenate. Dissolved Cr was present in the raw FGD pond water at a concentration of about 50 ppb. Prior to the spike test, dissolved Cr in all intermediate samples (filtered effluents from R1-R4) and

final effluent samples were found to be reduced to mostly below 2 ppb (with a few exceptions on April 11 and 14). The maximum contaminant level of drinking water for Cr in California is 5 ppb. This result shows that the hZVI system can meet the most stringent water quality limit for Cr.

Dissolved Silica: Dissolved silica in the FGD water was effectively removed by the hZVI system, often reducing dissolved silica from over 40 mg/L (as Si) to below 1 mg/L. Over 95% removal efficiency was achieved most of the time. Most of the removal occurred within the first hZVI reactor. The result is consistent with our previous laboratory and field test results obtained from our bench-scale treatment system. These results further demonstrate that the hZVI system is highly effective for removing dissolved silica from a liquid stream with complex water matrix. The results showed that throughout the demonstration period the dissolved silica content in the final effluent was never greater than 3 ppm (except one case).

In our previous laboratory test, we observed that the presence of high concentration of dissolved silica may interfere with iron corrosion process thus reduce the removal rate of target pollutants such as nitrate and selenate. The effect was more obvious when insufficient Fe^{2+} was provided in the ZVI system. During this test, we didn't observe a major interference from the presence of dissolved silica on the removal of selenate and nitrate. Most time we observed good Se and nitrate removal (e.g., 80~90%) achieved in the first reactor, suggesting that the presence of dissolved silica and its removal in the R1 didn't cause major slowdown in iron corrosion and selenate/nitrate reduction. One reason could be that in this test, the FGD water was able to react with ZVI and released a substantial amount of Fe^{2+}, and therefore we have never experienced the situation of inadequate supplies of Fe^{2+}. Influent and effluent concentrations of dissolved silica are shown in Fig. 30.
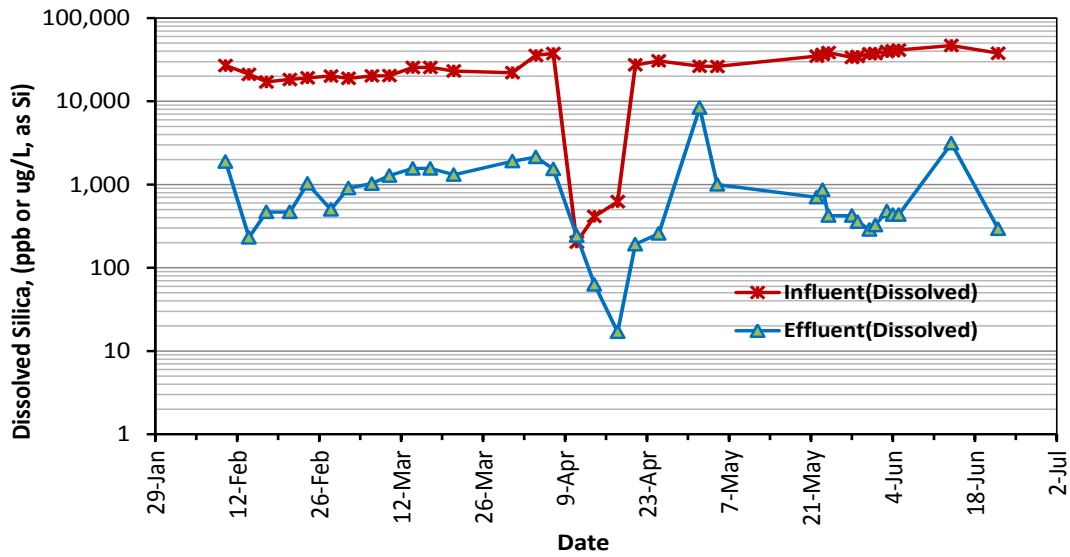
Fig. 30. Influent and Effluent Concentrations of Dissolved Silica

Except for a few days, the hZVI system removed over 95% of dissolved silica in the feed to below 2 ppm. In general, most of dissolved silica reduction (typically >80%) was achieved in the first ZVI reactor.

5.3.2 Corrosion and Removal Mechanism

The above mentioned short falls of the permeable reactive barriers, packed beds like mixing, passive oxide layer, transport of contaminants to ZVI and control of pH can be nullified in this fluidized bed reactors. Designed fluidized ZVI bed is capable to maintain the high reactivity of ZVI particles by conditioning the surface of ZVI particles and facilitating corrosion. The continuous oxidation of the ZVI can thicken the oxide layer on the surface of ZVI and thus inhibits the passage of electrons from inner core material. This will result in decrease in the redox capacity of system. The mechanical force applied on the iron materials in the reactors through the overhead mixers is able to prevent the thickening of the iron oxide layer on the ZVI

surface thus facilitating the electron transfer from inner ZVI through the thin oxide layer on the surface. By altering the agitation intensity of overhead mixers through frequency controllers, we are able to control and manage the thickness of the oxide layer on the surface of ZVI.

Oxidation of ZVI occurred in the reactors during the treatment process. In presence of oxygen and water two possible reactions occurred contributing to corrosion of ZVI and abatement of contaminants. In the first reaction dissolved oxygen is reduced by ZVI producing Fe^{2+} ions (eq. 5). In the second reactions the released Fe^{2+} ions are further oxidized to Fe(III) in the forms of different iron minerals like Lepidocrocite (γ- $FeOOH_{(s)}$) (iron hydroxide material) and Magnetite (iron oxide material) (eq. 6&7). Aqueous Fe^{2+} can further reduce this lepidocrocite layer into magnetite lowering the electron transfer barrier through this oxide layers on the core material. . So Lepidocrocite (γ- $FeOOH_{(s)}$) can undergo auto reduction to form magnetite in presence of Fe^{2+} (eq.8).

$$2Fe^0 + O_2 + 2H_2O \longrightarrow 2\ Fe^{2+} + 4OH^- \qquad (5)$$

$$2Fe^{2+} + \tfrac{1}{2}\,O_2 + 3H_2O \longrightarrow 2\gamma\text{- }FeOOH_{(s)} + 4H^+ \qquad (6)$$

$$3Fe^{2+} + O_2 + 2H_2O \longrightarrow Fe_3O_4 + 4H^+ \qquad (7)$$

$$2\gamma\text{- }FeOOH_{(s)} + Fe^{2+} \longrightarrow Fe_3O_4 + 2H^+ \qquad (8)$$
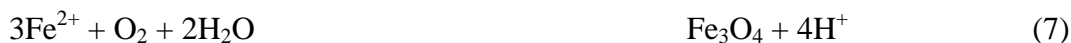
Formation of magnetite can also be possible during the redox reaction between the contaminants and ZVI.

Nitrate present in the FGD water is reduced to ammonia (eq. 9, 10, 11, 12, and 13). Our previous laboratory studies showed the presence of free Fe^{2+} ions in the solution promoted the reduction of nitrates into ammonia. In anaerobic conditions and absence of Fe^{2+} ions nitrate reduction was not observed, showing that Fe^{2+} ions are required for reduction of nitrate and in absence of DO oxygen ZVI cannot reduce

nitrate. During the reduction of nitrate, Fe^{2+} ions are further oxidized into magnetite and get deposited on the ZVI surface. Batch scale laboratory studies conducted at TAMU laboratories showed a thin layer of black coating (magnetite layer) over the surface of ZVI particles which are exposed to nitrates in presence of added Fe^{2+} ions. Formation of magnetite over the surface of ZVI increased the further reduction of nitrate and other potential contaminants like selenium and mercury due to its high conductivity. Magnetite accelerated the electron transfer from the core material, facilitating the redox reactions and removal of contaminants. ZVI by itself cannot reduce nitrate until unless there is enough amount of DO present in the system facilitating the corrosion of ZVI. Presence of aqueous Fe^{2+} ions can also trigger the reduction of nitrate near neutral conditions. Strong acidic conditions can also increase the reduction of nitrate by corroding the ZVI particles in the system and releasing Fe^{2+} ions.

$$NO_3^- + 10H^+ + 8e^- \longrightarrow NH_4^+ + 3H_2O \tag{9}$$

$$3Fe^0 + 4H_2O \longrightarrow Fe_3O_4 + 8H^+ + 8e^- \tag{10}$$

$$3Fe^{2+} + 4H_2O \longrightarrow Fe_3O_4 + 8H^+ + 2e^- \tag{11}$$

$$NO_3^- + 3Fe^0 + H_2O + 2H^+ \longrightarrow Fe_3O_4 + NH_4^+ \tag{12}$$
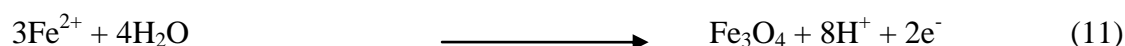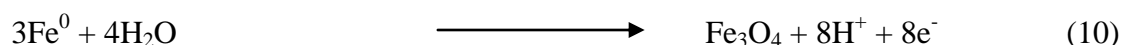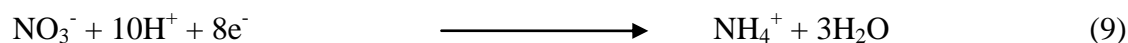
Huang et al., proposed a combined reaction involving Fe^0 and Fe^{2+} contributing nitrate reduction

$$NO_3^- + 2.82Fe^0 + 0.75Fe^{2+} + 2.25H_2O \longrightarrow NH_4^+ + 1.19Fe_3O_4 + 0.50OH^- \tag{13}$$

Removal of **Selenium** is due to reduction of Se(VI) to Se(IV) and Se(0) followed by adsorption (eq.14 and 15). Reduction of selenates also results in corrosion of ZVI and forms secondary iron oxide minerals like lepidocrocite.

$$Fe^0 \longrightarrow Fe^{2+} + 2e^- \tag{14}$$

$$HSeO_4^- + 3H^+ + 2 \longrightarrow H_2SeO_{3\,(aq)} + H_2O \tag{15}$$

$$H_2SeO_{3\,(aq)} + 4\,H^+ + 4e^- \longrightarrow Se_{(s)} + 3H_2O \qquad (16)$$

$$HSeO_4^- + 3Fe^0 + 7H^+ \longrightarrow Se_{(s)} + Fe^{2+} + 4H_2O \qquad (17)$$
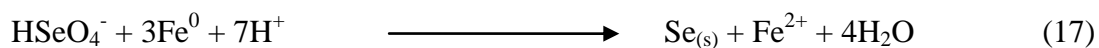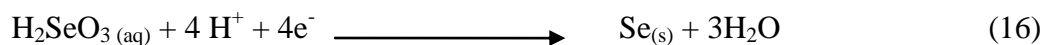
Our previous batch scale studies at TAMU labs showed no considerable reduction of selenate in anaerobic conditions and absence of added aqueous Fe^{2+} ions. Thus reduction of selenate showed similar mechanism like nitrate reduction. Dissolved oxygen plays a crucial role in the reduction mechanism of selenate facilitating iron corrosion. The reduction products Se (IV) and Se (0) are adsorbed onto this lepidocrocite layer (eq.18). This layer on further reduction in presence of Fe^{2+} converts to magnetite in absence of DO.

Reduction of mercury using hZVI system resembles similar redox reactions in which the mercury in Hg(II) form is reduced to elemental mercury Hg(0) (eq.18 and 19). This elemental mercury is removed through either surface adsorption or filtration. Prior to sand filtration in the field site, it was observed mercury in undissolved form releasing from reactor-4 (last stage of treatment)

$$Hg^{2+} + Fe^0 \longrightarrow Hg^0 + Fe^{2+} \qquad (18)$$

$$Hg^{2+} + 2Fe^{2+} \longrightarrow Hg^0 + 2Fe^{3+} \qquad (19)$$

Similar redox mechanisms are possible with other heavy metals like Zn(II), Pb(II), Cd(II) and Cr(VI) in which the ions are reduced to their corresponding elemental forms and removed from water either by precipitation or surface adsorption.

5.4 Oxidation-Reduction Potential (ORP)

The hZVI system is a reducing reactive system that depends on various redox reactions to transform and remove nitrate, selenate and other oxidizing contaminants from wastewater. Therefore, the ORP in the ZVI reactor is often considered one of the key parameters in predicting and evaluating the effectiveness of a ZVI system for removing a specific contaminant. We took samples from each of the ZVI reactors and

used an ORP probe to measure the ORP readings of the mixed liquid of each of the four ZVI reactors. The system was operated under a 4-stage single train configuration. The ORP in R1 was about -370 mV; the ORP readings in R2, R3, and R4 were measured as -412 mV, -422 mV, and -420 mV respectively. The results showed that all reactors were operated under very reducing environment which is adequate for thermodynamically reducing the selenate and nitrate in the FGD water. R2, R3, and R4 were more negative in ORP than R1, which was expected since R1 received the raw FGD water that contained various oxidants (such as nitrate, persulfate, and other oxyanions) that increases the ORP of the water to as high as +480 to +510 mV. The high oxidizing power of the raw FGD wastewater has a major impact on the operating condition and the composition of the reactive materials in R1. After R1, most of these oxidants had been consumed (reduced) and as such, R2 was allowed to operate at a more reducing environment with lower ORP.

5.5 Chemical Consumption

Throughout the field demonstration period, usage of all major chemicals was calculated to estimate operational costs of this system. Employed chemicals and corresponding consumptions are shown in Table 9.

Table 9

Chemicals and Corresponding Consumption

Chemicals	Consumption
ZVI	850 kg (125 kg in each reactor during startup, 20kg to R-1 on 2/23, 2/26. 58kg to R-1 on 3/11, 20 kg to R-1 and 10 kg each to R-2,3,4 on 4/10, 10 kg to R-4 on5/28, 90kg (5 micron) to R-1 and 100 kg (325 mesh) to R-2 on 6/9
$FeSO_4$	40 lbs
$FeCl_2$	11 lbs
NaOH	110 lbs
$NaHCO_3$	100 lbs
Na_2CO_3	45 lbs
HCl	27.5 gal
$NaNO_3$	40 lbs

The consumption of ZVI is more difficult to estimate due to the fact that (1) during the pilot test, there were bleeding of reactive solids of various degree from the reactors; (2) the test duration was not sufficiently long in comparison with the life-span of the amount of the ZVI powder we added at the beginning of the test to reach a steady state condition that is most reliable for estimating long-term steady consumption rate of ZVI powder; (3) the difficulty to estimate the amount of ZVI remained in the reactors after the test period. Some of the estimates have to base on best guess. Despite the difficulty, we still can have a reasonable estimate of the range of consumptions for ZVI.

For the FGD wastewater, the process consumed about 0.3 kg ZVI per 1 m^3 water treated at a cost of $0.6/m^3$ water treated. Assuming the average FGD pond

water 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. To treat 1L of this FGD pond water, ZVI will need to provide 14.4 mM electron (the sum 8.6 mM for nitrate + 3.1 mM for persulfate + 2.5 mM for dissolved oxygen + 0.2 mM for selenate). It takes 5.4 mM Fe^0 (i.e., 0.30 g Fe^0) to provide 14.4 mM electron upon oxidation to form magnetite. Reductions of nitrate and persulfate were responsible for much of the ZVI consumption. The actual use of ZVI was observed to be in line with the best estimate based on the stoichiometry of the involved redox reactions between ZVI and major pollutants. Wasteful consumptions of ZVI reacting with H_2O, O_2, or acid were limited due to an effective reactor design and the near neutral pH the hZVI process was operated.

Consumption of other chemicals include occasional use of HCl to adjust the pH of the ZVI reactor and addition of NaOH or $NaHCO_3$ to the aeration tank to maintain a favorable pH for facilitating the oxidative precipitation of residual dissolved Fe(II) in the effluent from the ZVI reactors. These chemical consumptions were relatively limited in comparison with the use of ZVI. Overall, for treating a FGD waste stream flow of 400 gpm, which is a typical flow rate, the chemical cost of the hZVI process can be controlled within $500,000 USD, which would be considered very competitive and acceptable to the power industry in comparison with other alternative solutions.

5.6 Solid Waste Production and Disposal

Waste produced during this operation was mainly in form of thick slurry which was pumped out into FGD pond periodically. The main constituent of this waste is precipitated iron oxides formed during operation or added externally into the reactors. The residual Fe^{2+} ions are precipitated in aeration tank by adding NaOH or Na_2CO_3.

The settling tank was cleaned once in a month during the entire operation period accumulating about 825 gal of liquid waste (thick slurry). Dewatering of this slurry can decrease the amount of this waste by about 50 – 60%. Another potential source for this waste was bleeding of the reactors as we experienced a startup problem of losing solids from the reactors. About 25% of this waste was due to loosing of the solids from rectors which can be restricted by optimizing the operational parameters.

Various forms of iron minerals present in this solid waste are nontoxic and chemically stable. Our prior Leaching tests according to USEPA TCLP showed very few amounts of toxic metals in this solids and which are well below regulatory limits.

6. CONCLUSIONS

The 5-month pilot-scale field test demonstrated that :

- The hZVI process can reduce selenate-Se from low ppm concentration to below 10 ppb and mercury from over 100 ppb to below 10 ppt, thus comply with the most stringent discharge limits for Se and Hg in the coming years. In addition, the process can efficiently remove various heavy metals of concern such as As(III), As(V), Cr(VI), Cd(II), Pb(II), and Cu(II) from ppm level to sub-ppb level in a short reaction time.

- A 3-stage ZVI reactor treatment with a combined hydraulic retention time of 12 hour will be sufficient for Se treatment for the FGD wastewater of the host site; for Hg and other heavy metals treatment, a single stage with a reaction time of no more than 4 hour will be adequate.

- The process economics of the hZVI can be very competitive.

- The current design of ZVI reactor and process configuration works well for the FGD application. Scaling up over 100 times from a bench-top system to mobile pilot-scale system was not a problem. The treatment system is robust and flexible.

The results from the five-month test confirm that the hZVI process can be a cost-effective solution to selenium and mercury pollution for the FGD wastewater problem. The overall performance of the pilot-scale system is comparable to or even better in some aspects than the bench-scale system, indicating that the process is scalable.

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APPENDIX 1

MAJOR CATIONS IN RAW FGD WATER (ppb)

Date	Na+	Mg++	Ca++	K+
2/7/2011	27920	303961	2317144	14686
2/10/2011	26224	251103	1783904	13826
2/14/2011	22395	183411	1490982	10935
2/17/2011	19938	153363	1361234	10105
2/21/2011	20045	150904	1340401	10338
2/24/2011	18864	146163	1421735	10500
2/28/2011	19266	148461	1476793	11699
3/3/2011	20987	154743	1603679	13347
3/7/2011	23101	186031	1791398	12696
3/10/2011	24582	224902	2289265	13628
3/14/2011	28236	275410	2491588	13999
3/17/2011	31627	313704	2807866	14786
3/21/2011	24246	241657	2159994	11472
3/31/2011	26211	226699	1345844	13070
4/4/2011	32980	291290	1747467	18275
4/7/2011	32663	291188	1960147	18736
4/11/2011	35724	317323	2235365	40645
4/14/2011	35111	305912	2334394	40454
4/18/2011	24512	202452	1733841	29723
4/21/2011	23987	195497	1671014	14649
4/25/2011	27282	216322	1890191	16096
5/2/2011	35239	280386	2133083	21265
5/5/2011	29700	223679	1705380	17788
5/22/2011	31810	204526	297137	135669
5/23/2011	33445	291044	1544457	18545
5/24/2011	32381	286509	1697317	18522
5/28/2011	40978	268842	1691888	18280
5/29/2011	41877	283169	1790652	19316
5/31/2011	4984097	<100000	1222439	2665145
6/1/2011	39222	283625	1852008	19574
6/3/2011	40976	295567	1882864	20492
6/4/2011	46439	327296	2000142	23061
6/5/2011	47461	329130	2051784	23815
6/14/2011	223286	1402280	8911322	104850
6/22/2011	41534	359179	2588895	22259

APPENDIX 2

INFLUENT AND EFFLUENT SE (VI) CONCENTRATIONS (ppb)

	Total Se			Dissolved Se		
Date	Influent	Effluent	Removal%	Influent	Effluent	Removal%
1/18/2011	1661	4.02	99.76	1655	3.9	99.76
1/25/2011	1748	22.5	98.71	1737	20.5	98.82
2/5/2011	1625	5	99.69	1570	5.2	99.67
2/7/2011	1948.1	1.5	99.92	1972.7	1.6	99.92
2/10/2011	1710.1	2.1	99.88	1713.4	2.1	99.88
2/14/2011	1765.1	33.9	98.08	1773.2	32.1	98.19
2/17/2011	1453.1	53.5	96.32	1478.1	55.4	96.25
2/21/2011	1103.0	177.9	83.87	1110.5	179.6	83.82
2/24/2011	1114.0	14.1	98.73	1149.3	14.6	98.73
2/28/2011	1143.7	9.0	99.21	1186.3	7.9	99.34
3/3/2011	1235	7.23	99.41	1233	7.53	99.39
3/7/2011	1312	56.8	95.67	1307	56.3	95.69
3/10/2011	1134	3.16	99.72	1063	2.88	99.73
3/14/2011	1047	2.45	99.77	1014	2.48	99.76
3/17/2011	1130	2.49	99.78	1082	2.58	99.76
3/21/2011	909	2.15	99.76	960	2.40	99.75
3/31/2011	1407	4.58	99.67	1381	4.91	99.64
4/4/2011	2446	3.94	99.84	2379	4.08	99.83
4/7/2011	2887	84.5	97.07	2696	79.4	97.05
4/11/2011	2988	44.5	98.51	2819	44.5	98.42
4/14/2011	2496	37.1	98.51	2392	33.6	98.60
4/18/2011	1718	63.5	96.30	1731	62.5	96.39
4/21/2011	1754	56.7	96.77	1817	54.5	97.00
4/25/2011	1925	50.3	97.39	1931	52.1	97.30
5/2/2011	2320	88.3	96.19	2151	85.8	96.01
5/5/2011	1907	201.5	89.44	1782	196.0	89.00
5/22/2011	1978	8.55	99.57	1983	8.60	99.57
5/23/2011	1973	5.93	99.70	2060	5.94	99.71
5/24/2011	2136	4.50	99.79	2133	4.56	99.79
5/28/2011	2127	9.17	99.57	2133	9.33	99.56
5/29/2011	2148	7.23	99.66	2092	7.30	99.65
5/31/2011	22186	58.9	99.73	22126	59.4	99.73
6/1/2011	22114	59.0	99.73	22140	59.3	99.73
6/3/2011	22237	386	98.26	22172	392	98.23
6/4/2011	22401	22.4	99.90	22393	22.6	99.90
6/5/2011	22472	27.7	99.88	22449	28.0	99.88
6/14/2011	8974	368	95.90	8739	370	95.76
6/22/2011	2334	149	93.60	2331	149	93.59

APPENDIX 3

INFLUENT AND EFFLUENT MERCURY CONCENTRATIONS (ppb)

	Total Hg			Dissolved Hg		
Date	Influent	Effluent	Removal%	Influent	Effluent	Removal%
1/18/2011	117	0.005	100.00	117	0.005	100.00
1/25/2011	127	0.049	99.96	117	0.002	100.00
2/5/2011	139	0.288	99.79	131	0.005	100.00
2/7/2011	n/a	n/a	n/a	n/a	n/a	n/a
2/10/2011	73.9	0.015	99.98	46.8	0.001	100.00
2/14/2011	50.3	0.001	100.00	54.0	0.002	100.00
2/17/2011	63.3	0.001	100.00	61.8	0.001	100.00
2/21/2011	81.8	0.005	99.99	87.5	0.006	99.99
2/24/2011	96.4	0.004	100.00	96.0	0.004	100.00
2/28/2011	91.0	0.002	100.00	79.2	0.002	100.00
3/3/2011	82.6	0.003	100.00	76.4	0.002	100.00
3/7/2011	124	0.315	99.75	107	0.290	99.73
3/10/2011	114	0.002	100.00	110	0.002	100.00
3/14/2011	124	0.003	100.00	134	0.003	100.00
3/17/2011	129	0.003	100.00	131	0.004	100.00
3/21/2011	141	0.002	100.00	143	0.001	100.00
3/31/2011	82.6	0.003	100.00	78.0	0.003	100.00
4/4/2011	133	0.005	100.00	130	0.005	100.00
4/7/2011	139	0.007	100.00	135	0.003	100.00
4/11/2011	87.1	46.5	46.56	131	44.6	65.92
4/14/2011	141	0.592	99.58	135	0.533	99.60
4/18/2011	99.2	0.0215	99.98	121	0.0177	99.99
4/21/2011	194	0.0035	100.00	196	0.0028	100.00
4/25/2011	112	0.0015	100.00	110	0.0014	100.00
5/2/2011	130	0.0041	100.00	134	0.0037	100.00
5/5/2011	142	0.0091	99.99	133	0.0089	99.99
5/22/2011	1,136	0.0259	100.00	141	0.0217	99.98
5/23/2011	1,141	0.0129	100.00	145	0.0122	99.99
5/24/2011	1,149	0.0180	100.00	151	0.0207	99.99
5/28/2011	1140	0.0053	100.00	139	0.0064	100.00
5/29/2011	1141	0.0053	100.00	148	0.0051	100.00
5/31/2011	167	0.0081	100.00	149	0.0090	99.99
6/1/2011	149	0.0079	99.99	152	0.0089	99.99
6/3/2011	155	0.0118	99.99	154	0.0130	99.99
6/4/2011	168	0.0249	99.99	169	0.0272	99.98
6/5/2011	174	0.0264	99.98	171	0.0307	99.98
6/14/2011	186	0.0275	99.99	94.6	0.0301	99.97
6/22/2011	115	0.0173	99.98	166	0.0177	99.99

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