

REMOVAL OF SELENIUM FROM WASTEWATER USING ZVI AND HYBRID
ZVI/IRON OXIDE PROCESS

A Thesis

by

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ABSTRACT

Selenium (Se), often in form of selenocyanate (SeCN^-), which present in some of refinery process wastewater known as stripped sour water. As Se discharge is increasingly regulated, the industry struggles to find a cost-effective technology for SeCN^- treatment. Zero-valent iron (ZVI) technology, with some successes in remediating toxic-metal contaminated groundwater remediation, emerges as a potential solution for addressing SeCN^- problem.

In this study, bench scale tests were conducted to investigate the removal of SeCN^- from wastewater with ZVI. The removal efficiency was evaluated by a series of tests under different conditions such as initial pH, various ions, ZVI particle size, dissolved oxygen (DO) and iron oxide. Results showed that SeCN^- was effectively removed from wastewater with ZVI and Fe(II) filings when the water pH was controlled at approximately 6 with sufficient DO.

The further evaluate of treating SeCN^- using hybrid zero valet iron (hZVI) system has also been conducted in this study. The hZVI system process is a novel chemical treatment that has shown valuable potential for removing several heavy metals from wastewater. This study concluded that at bench scale, the removal efficiency of SeCN^- in the wastewater is over 99% with 2-steps of hZVI reactors and a HRT of 12 hours.

In essence, this study concluded that ZVI is a highly valuable potential cost-effective treatment for SeCN^- removal from wastewater and the results from bench scale

hZVI system can be effectively used to scale up the system to serve the industrial needs in the future.

DEDICATION

To Hongliang Zhang, my beloved husband and my best friend.

To Elena Yiran Zhang, my baby girl and my wonder of wonders.

To Yang Gaihe and Shen Yunxia, my parents and my foundation.

Words cannot express how much I love you all.

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Finally, thanks to my mother and father who always support and love me. Thanks to my husband for standing by my side all the way through. Thanks to my sweet baby girl Elena, your smile can delight me anytime, anywhere.

NOMENCLATURE

AAS	Atomicabsorption Spectrophotometer
ABMet	Advanced biological metal removal systems.
BDAT	Best Demonstrated Available Technology
Ca	Calcium
CaSO ₄	Calcium sulfates
Cl ⁻	Chloride Ion
CN	Cyanide
COD	Chemical oxygen demand
DO	Dissolved Oxygen
ELM	Emulsion Liquid Membranes
EPRI	Electric power research institute
ERG	Eastern Research Group Inc
Fe ⁰	Elemental Iron
Fe(II)	Ferrous ion
FeCl ₂	Ferrous Chloride
FeO _x	Iron Oxide
Fe ₃ O ₄	Magnetite
γ -FeO(OH)	Lepidocrocite
FeSO ₄	Ferrous Sulfate
Gpm	gallon per minute

HCl	Hydrochloric Acid
HRT	Hydraulic Retention Time
hZVI	Hybrid Zero Valent Iron
IC	Ion Chromatographer
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
mM	Millimole
Na	Sodium
Na ₂ CO ₃	Sodium Carbonate
NaHCO ₃	Sodium Bicarbonate
NH ⁴⁺	Ammonium Ion
NO ³⁻	Nitrate Ion
NaCl	Sodium chloride
NaNO ₃	Sodium nitrate
NaOH	Sodium Hydroxide
ppb	Parts per billion(μ g/l)
ppm	Parts per million(mg/l)
Se	Selenium
SeCN-	Selenocyanate
Se(IV)	Selenite
Se(VI)	Selenate
SO ₄ ²⁻	Sulfate Ion
SSW	Stripped Sour Water

R1	Reactor 1
R2	Reactor 2
RO	Reverse Osmosis
ZVI	Zero Valent Iron

TABLE OF CONTENTS

	Page	
ABSTRACT	(0000)ki	
DEDICATION	iv	
ACKNOWLEDGEMENTS	(0000)v	
NOMENCLATURE	(0000)vi	
TABLE OF CONTENTS	(0000)x	
LIST OF FIGURES	(0000)zi	
LIST OF TABLES	(0000)zii	
 CHAPTER		
I" INTRODUCTION	(0000)3	
3.1 "Selenium Chemistry	1	
1.2 Selenium Toxicity	2	
1.3 Regulations of Selenium Removal	3	
1.4 Oil Refining Stripped Sour Water	4	
1.5 Objectives of the Study	6	
 II" AVAILABLE TECHNOLOGIES FOR THE REMOVAL OF SELENIUM IN THE WASTEWATER		8
2.1 Biological Treatments	8	
2.2 Membrane Filtration	9	
2.3 Adsorption	10	
2.4 Chemical Oxidation/Reduction	12	
2.5 Constructed Wetlands	13	
2.6 ZVI Corrosion and Iron Oxide Formation	15	
 III" MATERIALS AND METHODS		16

3.1	Materials	16
3.2	hZVI System	18
3.3	Sampling	19
3.4	Analysis	21
IV	RESULTS AND DISCUSSIONS	22
4.1	Effect of ZVI Corrosion and Fe^{2+}	22
4.2	Effect of Initial pH	25
4.3	Effect of Different Electrolyte.....	26
4.4	Effect of ZVI Particle Size	28
4.5	Effect of Dissolve Oxygen	29
4.6	Removal of SeCN^- Using hZVI System	30
V	CONCLUSIONS	33
	REFERENCES	34
	APPENDIX	40

LIST OF FIGURES

FIGURE	Page
1. Selenium-Water System Pourbaix Diagram	2
2. Bench Scale Prototype Operated for Treating FGD Wastewater.....	18
3. Concentration of SeCN^- and Fe(II) Formation	22
4. Effect of Fe(II) on SeCN^- Removal.....	24
5. Effect of Initial pH on SeCN^- Removal	25
6. Effect of Different Electrolyte on SeCN^-	26
7. Effect of ZVI Particle Size on SeCN^- Removal	28
8. Removal Effect of Dissolved Oxygen on SeCN^- Removal	29
9. Influent and Effluent pH of the hZVI System.....	31
10. Influent and Effluent C_{SeCN^-} of hZVI System	32

LIST OF TABLES

TABLE	Page
1. Selenium Speciation Distribution.....	5
2. Particle Size Distribution of HC15 ZVI Powder.....	16
3. Particle Size Distribution of H200 Plus ZVI Powder	17

CHAPTER I

INTRODUCTION

1.1 Selenium Chemistry

Selenium is widely distributed in soils and natural waters resources through variety of species that are linked by many biogeochemical transformation reactions (Chapman et al., 2010). Different species of selenium have been found including inorganic selenium, volatile and methylated selenium, protein and amino acid selenium and non-protein amino acids and biochemical intermediates. In environment, selenium usually occurs in one of four oxidation forms including Se(VI), Se(IV), Se(0) and Se(-II). Oxyanions selenite(SeO_4^{2-}) and selenite (SeO_3^{2-}) are usually found in oxidized systems, while the other two states in anaerobic zones and unweathered mineral formations.

Figure 1 shows the pourbaix diagram of selenium in water. The reduction potential/pH existence range in water solution of inorganic selenium species is shown. Within the normal physiological pH range of 0-14, Se, H_2Se , HSe^- , H_2SeO_3 , SeO_3^{2-} , HSeO_3^- , HSeO_4^- , and SeO_4^{2-} are the species that can exist at equilibrium. However, within the pH range of 5-7 in waste water from industrial activities, Se, HSe^- , HSeO_3^- , and SeO_4^{2-} are the four species that can exist(Williams et al., 1998).

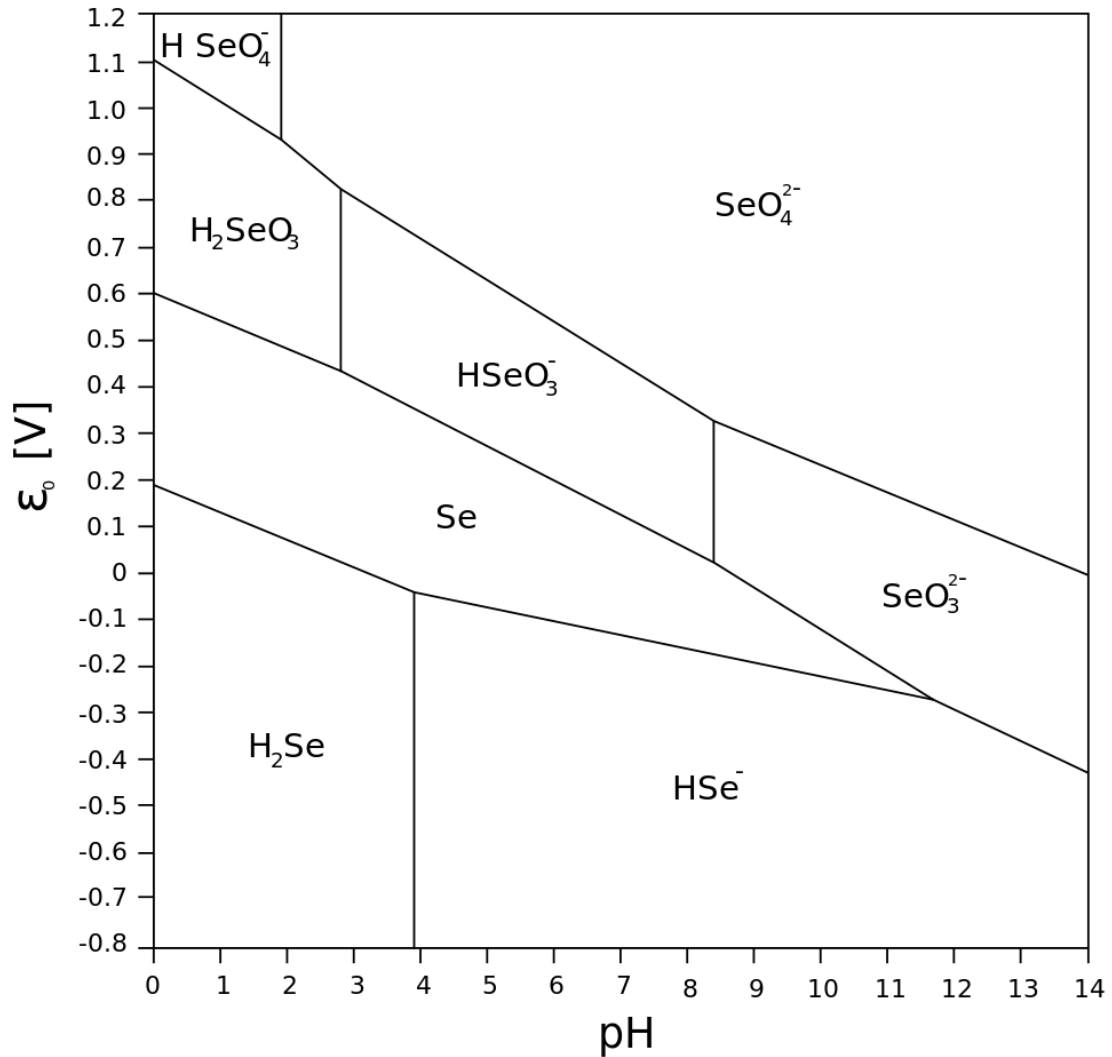


Fig. 1 Selenium-Water System Pourbaix Diagram

1.2 Selenium Toxicity

Selenium is an important trace nutrient for human beings and animals. In humans, selenium helps in the daily functioning of the thyroid gland. Lack of selenium can lead to Keshan disease which is potentially fatal.

The toxic effects of selenium have been studied since 1842 (Moxon et al., 1943; Nelson et al., 1943). According to the Office of Dietary Supplements of National Institutes of Health, Selenosis may develop in concentrations greater than 400 micrograms per day. The symptoms may including gastrointestinal disorders, hair loss, sloughing of nails, fatigue, irritability and neurological damage for human beings.

Research in this area shows that a high concentration of selenium in natural environment may cause many problems. For example, in the Kesterson Reservoir located in the heart of the San Joaquin Valley in central California, selenium was transported into the reservoir through the drainage tiles installed in 1971 to maintain water tables for agricultures demand in the vally. The Kesterson Reservoir supported a wide varity of life including several species of fish. After 1981, only the most saline tolerant mosquito fish was found in the reservoir. A high concentration of selenium of more than 1400 micrograms per liter was found responsible for the fact according to the study completed by the United States Fish and Wildlife Service.

1.3 Regulations of Selenium Removal

In United States, selenium is included in the “priority pollutants” that USEPA is required by federal Clean Water Act to design criteria for. The national recommended criteria or their own criteria must be adopted by states and tribes. Based on the adopted criteria, point source dischargers with reasonable potential to cause exceedance of criteria re given specific effluent limits. In addition, waters listed as “impaired” limited to a total maximum daily load on both point and nonpoint sources.

In 1987, a criterion based on total recoverable selenium concentrations in water, with a chronic value of 5 ug/L for selenium was designed as National Recommended Water Quality Criteria by USEPA.

In 2004, USEPA published a draft criterion that included chronic exposure limits due to selenium concentrations in fish body.

In Canada, the federal regulation of the Fisheries Act partly protects aquatic ecosystems. It prohibits the deposit of substances that are deleterious to fish into waters where fish lives. Some provinces are delegated that they can authorize the deposits of deleterious substances through various effluents after being processed. Permits are negotiated by stakeholder, government and contain specific limits on toxic chemical pollutants, and directions on monitoring and compliance requirements. These permits require stakeholders to monitor levels of selenium in water, possibly comply with the Canadian Water Quality Guideline of 1 ug/L total selenium in surface waters.

1.4 Oil Refining Stripped Sour Water

Some crude oil from certain geological formations can contain large amount of selenium.

The major form of selenium is hydrogen selenocyanate (HSeCN) in the stripped sour water (SSW) at acidic to neutral pH. Table 1 shows the distribution of selenium species in the SSW and the oil refinery wastewater treatment plant effluent (Brown and Caldwell, 1994).

Selenium Species	Stripped Sour Water (ppb)	Refinery Wasterwater Treatment Plant Effluent (ppb)
Total selenium	170-4,870	11-300
Particulate selenium	<5-33	<5
Dissolved selenium	141-4,700	16-290
Volatile selenium	<0.3	0.3-15
Selenocyanate	84-4,800	<10
Selenite	<10	13-171
Selenite	<10	<10-46

Table 1: Selenium Speciation Distribution

Source: Adapted from Brown and Caldwell, 1994

Notes: These values were sampled and tested from San Francisco Bay Area refineries performed as part of a study for the WSPA (Brown and Caldwell, 1994).

Most refineries use biological treatment to remove contaminants, which is efficiency for selenite and selenite removal. But removal of SeCN^- is always a challenge

task. In several treatment approaches are all either expensive (costs over \$15 million in 1995) or the removal is not satisfied (the highest efficiency is 68% of total selenium removal). (Sandy et al., 2010)

1.5 Objectives of the Study

The objective of this study is to characterize removal of SeCN^- in wastewater by ZVI by different factors as pH, electrolyte, particle size of ZVI, DO, iron oxide, and develop a proper method that can strip off Se from SeCN^- to form elemental Se crystalline without post-treatment.

(1) Further develop optimize the efficiency of SeCN^- removal from water with ZVI and iron oxide. The parameters to be tested include pH, electrolyte, particle size of ZVI and DO.

(2) Understand the mechanism of oxidation from $\text{Se}(-\text{II})$ to $\text{Se}(0)$ and the formation of iron oxide. The various selenium and iron species generated in the processed will be characterized using different instruments such as Atomic Absorption Spectrophotometer(AAS), ion chromatographer (IC) and spectrophotometer.

(3) Elucidate the mechanism of how various selenium and iron species interact with each other and whether during the formation of iron oxides the selenium species in the water can be co-precipitate. Redissolution of selenium (if occur) will be studied. Also Different conditions that can reduce or prevent redissolution will be explored.

(4) Estimate the feasibility and performance of using ZVI and iron oxide for removing SeCN^- in wastewater. Oil refinery wastewater with various contaminations

will be used. The cost of the process and consumption of chemicals will be compared with current SeCN- treatment processes.

CHAPTER II

AVAILABLE TECHNOLOGIES FOR THE REMOVAL OF SELENIUM IN THE WASTEWATER

2.1 Biological Treatments

Biological processes are potential selenium removing technologies which interest researchers because they use bacteria to transfer selenium from aqueous solutions to elemental selenium. Various bacteria have been tested such as *Pseudomonas stutzeri*, Bacterial inoculum, and clostridium bacteria (Adams et al., 1996; Koren et al., 1992; Altringer et al, 1989; Kauffman et al., 1986; Altringer et al, 1991).

P. Stutzeri appears to offer great promise because it can reduce both Se(IV) and Se(VI) species. *P. stutzeri* is known to be effective under aerobic conditions. 98% removal rate was obtained in an 18 hour residence time (Adams et al., 1996;). Enzymatic bioremediation can work together with *P. stutzeri* and continuous selenium removal to less than 10 ug/L is possible within four month long time. Koren et al. also validated the effectiveness of *P. stutzeri* to convert selenium to elemental selenium (Koren et al., 1992). Maximum reduction rates were demonstrated to happen in pH of 7 to 9.5 and optimal temperature was around 25-35 degree. Furthermore, the presence of impurities such as sulfate and nitrate has no adverse effect on selenium reduction.

Anaerobic bacterial reactors are also a successful way to remove selenium from agricultural waters. Laboratory scale and pilot-scale study in California for water form

agricultural drainages with pH of about 8 show selenium can be effectively removed (Ergas et al., 1990; Owens et al., 1991).

A process which can treat selenium when nitrate and sulfate are present was patented by Oremland (Oremland, 1991). At first stage, an aerobic bioreactor was used to remove nitrate to the upper limit. Then nitrate free water is treated in the second stage. The biomass from first stage is a nutrient source for microorganisms at the second stage so that the removal rate is optimized.

2.2 Membrane Filtration

Membrane technologies are useful to remove pollutants from aqueous solutions. Reverse osmosis, emulsion liquid membranes, and nano-filtration are among various separation methods.

Reverse osmosis (RO) is listed by U.S. EPA as one of the BATs to remove selenium (Pontius, 1995). The removal effectiveness is above 80% for all valence states. RO requires that the solutions should be diluted for solids. Thus, pretreatments are needed to avoid polluting the membranes. RO is now readily applicable for drinking waters.

Emulsion liquid membranes (ELM) is based on the transfer of selenium from the aqueous phase to a liquid extractant phase which is contained inside organic droplets (Gleason et al., 1996). During the processing steps, selenium is transferred from the bulk wastewater to organics. ELM has been shown to be an effective method, Se(VI) can be extracted rapidly even in the presence of sulfate at all pH values larger than 2.

Nano-filtration is similar to reverse osmosis but based on the use of membranes constructed of a porous inert layer of polysulfone and a negatively charged hydrophobic rejection layer. These membranes reject multivalence anions, sulfate included. Nano-filtration system is operated at pressures that are about one-third of that required for reverse osmosis (Kharaka, et al., 1996).

2.3 Adsorption

A lot of investigations have been performed on surface adsorption because it can remove multi-pollutants simultaneously, e.g., not only selenium but also metals, and arsenic can be removed from aqueous phase solutions. Absorbents studied include ferric hydroxides, aluminum hydroxides, alumina, activated carbon and clays.

Ferrihydrite adsorption is the one has been the emphasis of most of the investigations and U.S. EPA has selected it as the Best Demonstrated Available Technology (BDAT) for selenium removal from waterwater (L. Rosengrant, L. Fargo, A Final Best Demonstrated Available Technology (BDAT) Background Document for K031, K084, K101, K102, Characteristic Arsenic Wastes (D004), Characteristic Selenium Wastes (D010), and P and U Wastes Containing Arsenic and Selenium Listing Constituents. Volume 1, @ (EPA/530/SW-90/059A, 1990) 124 p). Studies have shown that Selenium (IV) is effectively removed at pH less than 8 and this technology is not effective for Se(VI), thus reduction of Se(VI) prior to adsorption is required in order to get high removal rate. Moreover the presence of other aqueous species in the solution may influence the removal of Se(IV). (Balistrieri et al., 1987, 1990; Brown et al., 1980; Hayes et al., 1987; Manning et al., 1995; Isaacson et al., 1994). Whether the wasterform

product will be stable or not when the removal process is conducting outdoor which will be exposed to air is a key issue.

Aluminum hydroxide is also studied for selenium adsorption. Trussell et al. found that the adsorption of Selenium (IV) was effective over the pH range of 3-7 while selenium (VI) adsorption was much less effective. In addition, sulfate and bicarbonate had no effect on Se(IV) but greatly affected Se(VI) adsorption. Studies conducted on both groundwaters and mine waters show that aluminum hydroxide adsorption of selenium can be widely applied.

Activated carbon adsorption is the most universally absorbent to clear drinking water and also been studied to remove selenium. It is widely used in treatment of wastewater from mining industries. However, it is not effective, for example, only less than 4% removal rate of Se(IV) or Se(VI) at concentrations around 30-100 ug/L was observed using dosages of active carbon up to 100 mg/L (Sorg et al., 1978). Other absorbents are performed as well such as peat impregnated with ferric oxyhydroxide (Chamberlin, 1996). In studies by USBM (Corwin et al., 1994; Jeffers et al., 1991), ferric oxyhydroxide and peat were mixed into beads of polysulfone resin and the resin with Se of 1700 mg/L was loaded together with solutions containing both Se(IV) and Se(VI). The removal rate of Se(IV) can be higher than 95% while that of Se(VI) is about 80%. Absorbing selenium onto a lanthanum oxide substrates was also investigated by researchers (Adutwum, 1995). The adsorption is effective for both Se(IV) and Se(VI).

Sulfate is acting as hamper and should be removed before going this process. pH range can be 3 to 10.

2.4 Chemical Oxidation/Reduction

Reductants such as ferrous hydroxide, iron, zinc, and aluminum can be used to produce elemental selenium or metal selenides.

Ferrous hydroxide has been developed by U.S. Bureau of Reclamation (BOF) as a process for selenium form surface and agricultural waters (Murphy, 1988). Reduction of selenium can happen at a pH range of 8.8-9.2 and nitrate, dissolved oxygen (DO) and bicarbonate are interferences to the process. Costs can be increased when nitrate concentration is high. However, it is difficulty to be widely applied because the generation of large volumes of iron sludge and the relatively high cost of reagents(Murphy, 1989).

Iron power has been tested as well to be a reductant in a selenium recovery process (McGrew et al., 1996) when copper ions present. The elemental iron reduces both selenium and copper to produce a copper selenide on the iron surface. In mining wastewaters, sulfate is always extremely high compared to selenium, thus, preliminary process is required to remove sulfate. Presence of copper acts as a catalyst to the Se(VI) reduction by iron to selenium and increases the removal rates. Little is known about the applicable pH range and more test work is needed before the application of this method.

2.5 Constructed Wetlands

Constructed wetlands are complex biological and physical reactors that collectively change the chemical nature of contaminants by immobilizing and/or transforming pollutants to be less toxic. Both vegetation and microorganisms play vital role in the wetlands. The effectiveness have been observed in different places.

Ye et al. (2003) used wetland microcosms to evaluate the ability of constructed wetlands to remove high concentrations of SeCN-, arsenic, and boron in wastewater from a coal gasification plant in Indiana. The microcosms were found to be able to reduce concentrations of selenium (Se), and cyanide (CN) by 64% and 30%, respectively. Hansen et al. (1998) analyzed data collected from in wetland located adjacent to San Francisco Bay, California. Biological volatilization may have accounted for as much as 10-30% of a total Se removal of 89%. The effectiveness of biological processes to remove selenium was also observed by Lin et al. (2003) vegetated wetlands in Corcoran, California and found 69.2% of the total Se mass can be removed.

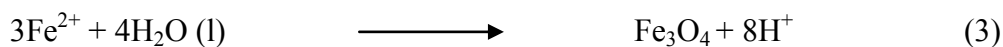
Sediment is the suggested primary sink of Se by wetlands. The accumulation in plant tissues is less than 5%. Biological volatilization, accounting for as much as 10-30%, is the secondary important process especially in spring and summer. Cattail, thalia, saltmarsh bulrush and rabbitfoot grass are the best choice of plants to establish in the wetlands. Further investigation on the feasibility of using constructed wetlands for Se remediation, methods for the enhancement of Se volatilization, and the potential Se ecotoxicity is still needed.

Several factors effect wetland treatment systems. High temperature, chlroides, sulfates, boron and nitrates in the polluted water streams adversely affect the efficiency of the treatment system. Effluents from industries are usually preprocessed with natural waters prior to its entry into wetland system. Certain levels of some species such as Chloride should be maintained in constructed wetlands. For example, scrubbers are typically operated by maintaining chloride levels at 12000 to 20000 ppm.

2.6 ZVI Corrosion and Iron Oxide Formation

ZVI has been reported very effective to treat heavy metals like mercury, arsenic, selenium, lead and copper under bench scale investigations. ZVI can be easily oxidized in aqueous environment with oxygen forms a ZVI and iron oxide system. The reaction of treating heavy metals using ZVI generally involved with three parts: cementation, adsorption and chemical reduction (Smith, 1996; Shokes et al., 1999; Blowes et al., 2000). Cementation of ZVI has been reported highly effective under low pH and anoxic conditions (Huang et al., 1998; Nadkarni et al., 1967; Ku et al., 1992). During this process, redox sensitive inorganic compounds can be reduced to insoluble forms.

Iron oxide generated in the corrosion process always forms a layer covering the iron material surface. This oxide layer including different forms of Fe(II) and Fe(III). Mostly with Fe(III) near the water surface and Fe(II) near the iron surface. Fe(II) generated in the ZVI CORROSION process can appear in the forms of Fe₃O₄, FeOH(OH), α -FeO(OH). These compounds play a key role during the adsorption of contaminants (Klausen et al., 1995). The corrosion formation can be shown as below:



The final product of corrosion is magnetite (Eric, 1995). With dissolved oxygen (DO) and water in the system, magnetite is formed with Fe(II) and redox reaction of contaminants.

CHAPTER III
MATERIALS AND METHODS

3.1 Materials

The main chemical used for this research include

3.1.1. Zero Valent Iron (ZVI): three types of ZVI powder were used in this research:

a. HC15 Zero valent Iron Powder provided by Hepure Technologies: The HC15 is atomized powder with at least 91.35% with main size from 5 microns up to 50 micron.

Particle Size	Percentage/%
+40 Mesh (>420 microns)	0.1% Max
+60 Mesh (>250 microns)	1.0% Max
-60/+100 Mesh (150-250 microns)	25% Max
-100/+325 Mesh (45-150 microns)	Report
-325 Mesh (<45 microns)	15-40%
Apparent Density	3.0 g/cm ³

Table 2. Particle Size Distribution of HC15 ZVI powder

b. H200 Plus provided by Hepure Technologies: This ZVI product contains about 95.5% of iron. The sizes varies from 5-100 microns as showed in table 3.

Particle Size	Percentage
+60 Mesh (>250 microns)	1.0% Max
-100/+325 Mesh (45 - 150 microns)	Report
-325 Mesh (<45 Microns)	15-40%
Apparent Density	2.8-3.2g/cm ³

Table 3. Particle Size Distribution of H200 Plus ZVI Powder

c. 20 mesh ZVI purchased from VWR.

3.1. 2. SeCN- stock solution was prepared with Phenyl Selenocyanate (SeCN- at 98%) provide by Alfa Aesar with deoxygenated DI water. Dissolved oxygen (DO) was removed from the DI water by nitrogen gas purging and stored in anaerobic chamber for 24 hours. The anaerobic chamber maintained an atmosphere of approximately 95% N₂/5% H₂ using a catalytic O₂ removal system (Coy Laboratory Products, Grass Lake, MI).

3.1.3.Pre-acidified FeCl₂ solution, 400mM FeCl₂ + 20mM HCl. Reagent grade FeCl₂ was purchased from VWR International.

3.1.4. HCl (1 mol/L) solution: was prepared on site from concentrated HCl (6N) purchased from VWR International.

3.1.5. NaOH (1M) solution: was prepared on site from NaOH purchased from VWR International.

3.1.6. In addition ,the following compounds used in this research were purchased from VWR International.

sodium nitrate (NaNO_3)

calcium sulfate (CaSO_4)

sodium chloride (NaCl)

3.2 hZVI System

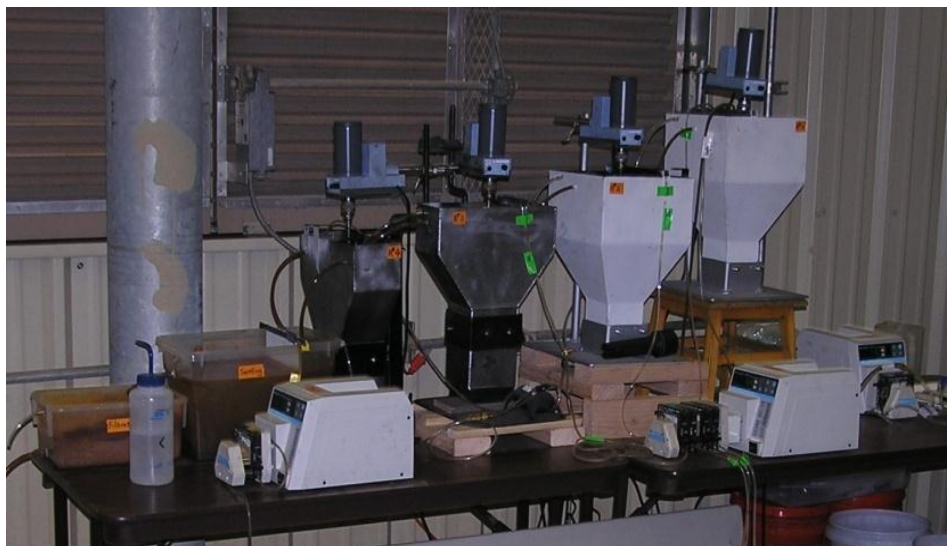


Fig. 2 Bench Scale Prototype Operated for Treating FGD Wastewater

The treatment hZVI system was designed by Dr. Yongheng Huang based on the successful bench and pilot scale system for treating FGD wastewater in fig.2.

The system contained a two-stage ZVI reactors and post treatment of a sand filtration. The influent of artificial water was pumped in reactor 1 (R1) using an

adjustable flow pump, then into Reactor 2 (R2) after treated through R1. The effluent from R2 then run through the sand filtration.

The effective volume of the reactors are both 10 liters. The combined hydraulic retention time (HTR) for the system is approximately 12 hours for 6 hours each. An overhead mixer is used to provide mixing power in the reaction zone of each reactor.

The artificial water for the system is prepared in the lab once per day. With 20 liters of tap water and 10mg/L of SeCN^- . NaNO_3 was added to the water in the first 5 days with a concentration of 40mg/L $\text{NaNO}_3\text{-N}$.

3.3 Sampling

3.3.1 Batch test

0.5g of ZVI powder (all using HC200 plus except the testing for removal efficiency for different ZVI particles.) was placed in a serum bottle effective volume of 10mL; the bottles with ZVI were transferred to anaerobic chamber if anaerobic condition is needed. The bottles were then fortified with 5ml of 10mg/L SeCN^- with other compounds needed for different tests and sealed in the anaerobic chamber. Finally, the sealed bottles were placed in a rotary arm shaker at room temperature. If anaerobic condition is not needed, the bottles with ZVI powder will be directly fortified with same compounds then put in the rotary arm shaker together. And taking out every hour unseal and reseal for imitate in open atmosphere condition.

Two bottles were withdrawn simultaneously at designated testing times and the solutions were filtered through a $0.45\mu\text{m}$ membrane for analysis.

To evaluate the effect of initial pH, The pH for all other tests was adjusted to 6.0 before mixing.

Testing for pH : 1.0M HCl and 1.0M NaOH was used to adjust pH of the solution at 6.0, 7.0 and 8.0 before mixing. Samples were prepared in atmosphere.

Testing for electrolyte: pH was adjust to 6.0 at beginning. NaCl, CaSO₄ and NaNO₃ were added separately to keep the same conductivity with tap water solutions (0.63ms/cm²). Together with a group of samples prepared with tap water. All samples were prepared in atmosphere.

Testing for ZVI particle size: pH was adjusted to 6.0 at beginning. HC15, H200 plus and 20mesh ZVI were added separately to the samples. All samples were prepared in atmosphere.

Testing for DO: pH was adjusted to 6.0 at beginning. One group of samples was prepared in atmosphere with the other group prepared and sealed in anaerobic chamber.

Testing for ZVI corrosion and Fe(II): pH was adjusted to 6.0 at beginning. 5mmol FeCl₂ was added to one group of samples. All samples were prepared in atmosphere.

3.3.2 hZVI System

Samples were collected every day from influent, effluent of reactor 1 (R1) and reactor 2 (R2) using syringes and filtered through a 0.45µm membrane for analysis.

3.4 Analysis

Different selenium species in filtrate was measured using a Dionex DX 500 model ion chromatographer (IC) equipped with an autosampler and a conductivity detector. Separation of SeCN^- was achieved using a Dionex Ionpac AS-16 column, selenite with AS-22 and selenite with AS-18. The detection limit of the IC was $20 \mu\text{g/L}$ as Se. Total dissolved Se in filtrate was measured using atomic absorption spectrophotometer (AAS). pH measurements were made using an ORION pH meter.

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Effect of ZVI Corrosion and Iron Oxide

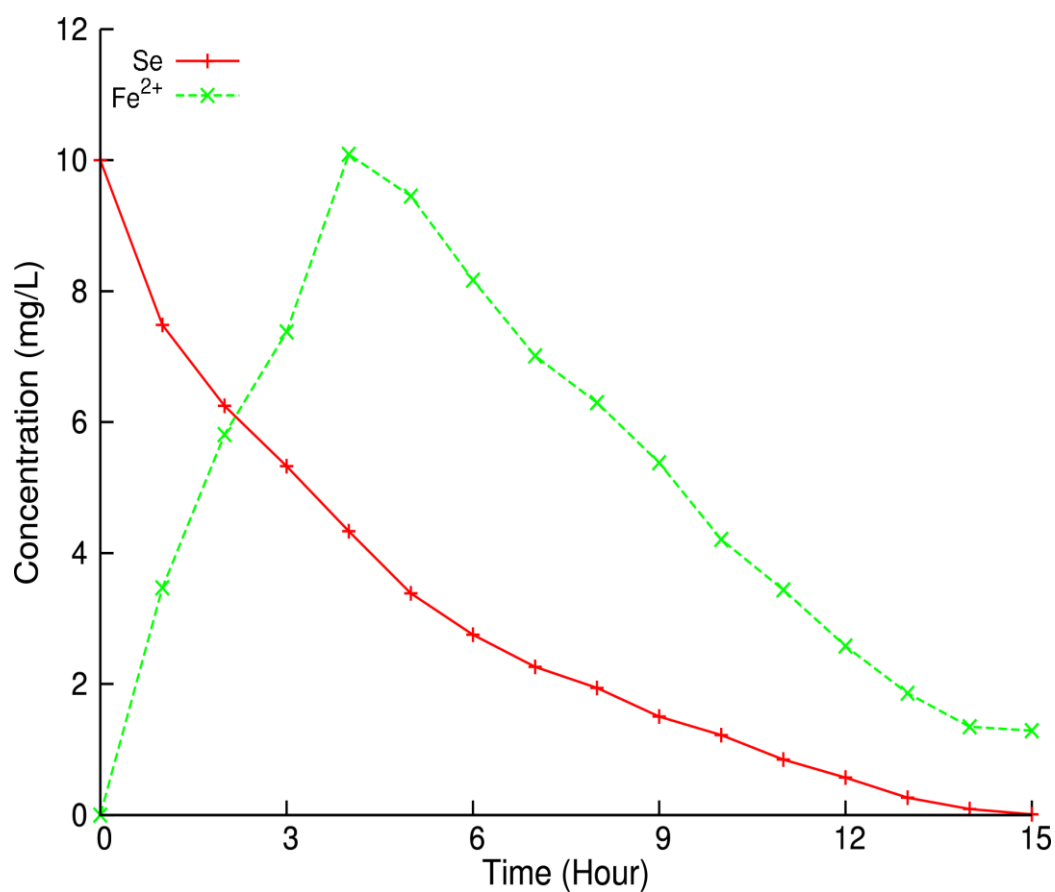


Fig. 3 Concentration of SeCN⁻ and Fe(II) Formation

Oxidation of ZVI occurred during the treatment process. The corrosion and oxidation of ZVI are presents as the following equations:

The first one is ZVI producing Fe^{2+} ions with dissolved oxygen.(4). The Fe^{2+} produced then can be further oxidized by the contaminant ions and DO into Fe^{3+} , which may presented in different forms such as iron hydroxide mineral lepidocrocite(5) and the iron oxide mineral magnetite(6). Lepidocrocite will be subsequently tranformed to magnetite by Fe^{2+} . (7) The batch test can also approve this reaction. A brown color was observed after 5 hours of mixing which proved the lepidocrocite is produced. After this time, the brown color became darker, ultimately changing to black, which is the sign of producing magnetite.

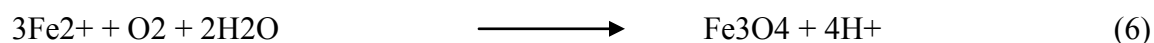
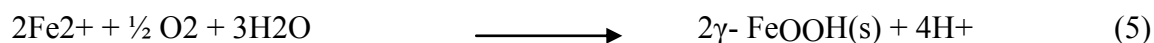
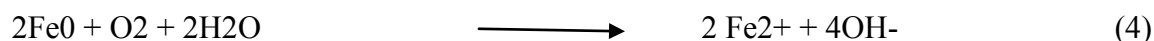


Fig 3. shows the Fe^{2+} concentration during the removal of SeCN^- by ZVI. During the reaction, concentration of Fe^{2+} simultaneously increased up. Fe^{2+} slowly dropped after 5 hours. But the release of Fe^{2+} is continued till the end of the reaction after lepidocrocite transformed to magnetite.

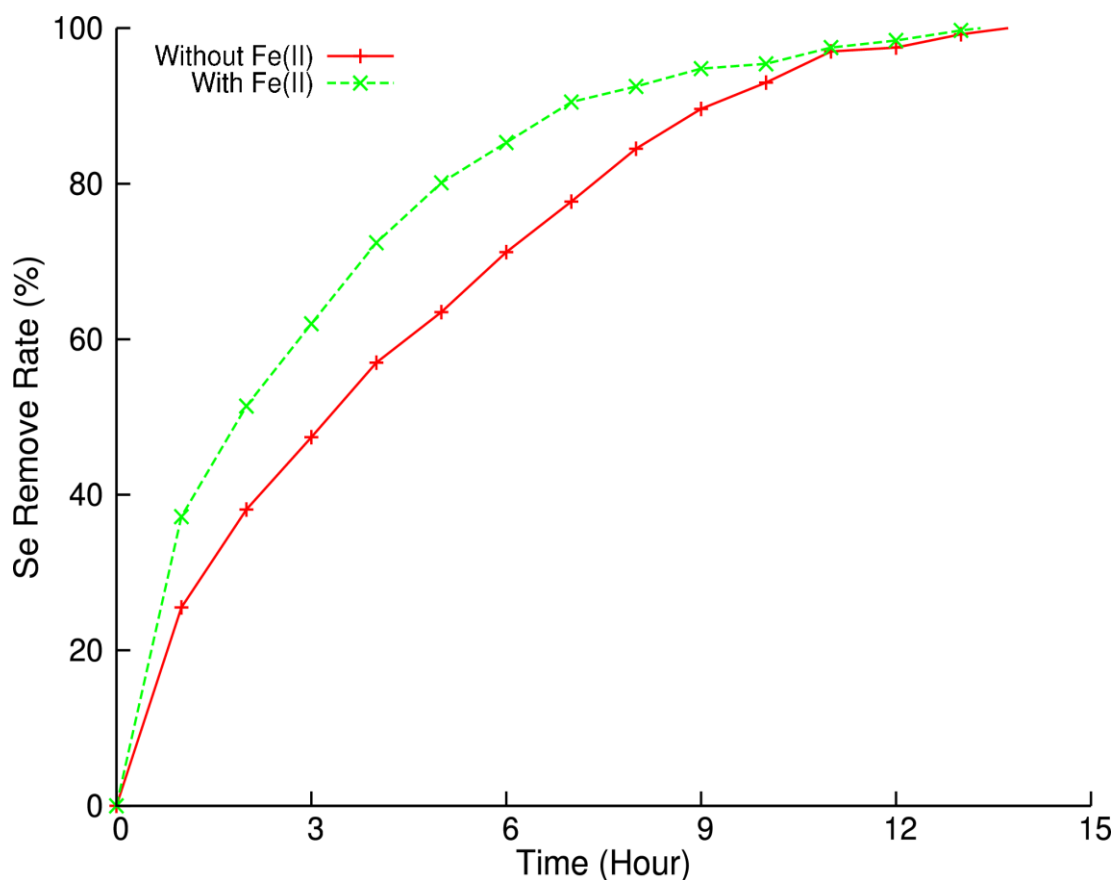


Fig. 4 Effect of Fe(II) on SeCN⁻ Removal

Our previous study shows that during the reaction and corrosion of ZVI, Fe²⁺ are further oxidized into magnetite and get deposited on the ZVI surface. Which will form a layer of black coating over the time onto the ZVI particle surface. When there is SeCN⁻ in the system, lepidocrocite will continue to form and SeCN⁻ absorbed onto the lepidocrocite surface. When SeCN⁻ in the system has been completely reduced. Lepidocrocite will transform to magnetite with the presence of Fe²⁺. Fig.4 shows that when Fe(II) was pre-added to the reaction system, the removal of SeCN⁻ is highly effective during the first a few hours. The removal rate can reach 60% at the first 3 hours

while only 40% of SeCN^- is removed without Fe(II) in the system at the beginning. When Fe(II) was added to the reaction system, the formation of lepidocrocite is accelerated (In-Hu et al., 2011). Therefore the adsorption of SeCN^- onto lepidocrocite is also increased. Pre-added Fe(II) can increase the corrosion and aging of ZVI to form a stable system of ZVI and iron oxide.

4.2 Effect of Initial pH

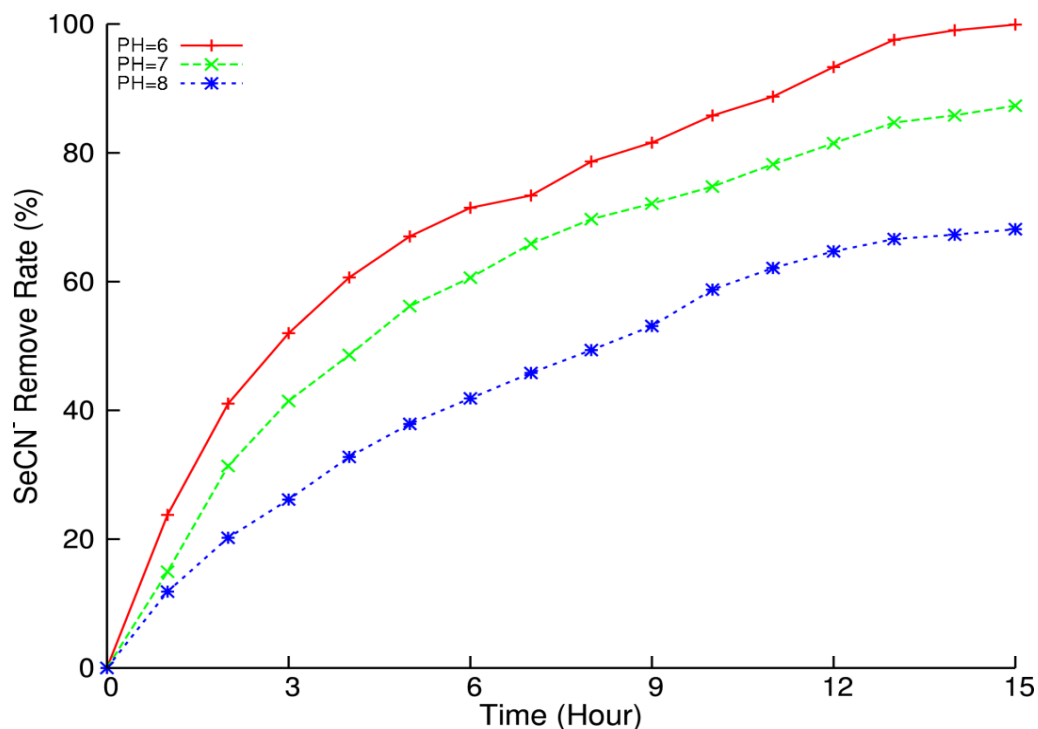


Fig. 5 Effect of Initial pH on SeCN- Removal

The effects of initial pH were investigated (Figure 5). With the increase of pH, the removal efficiency of SeCN^- is decreasing. After 15 hours of reaction, removal rates were 100% and 87% for pH=6 and pH=7. For pH=8 the removal rate was only 69%. The

effects of initial pH on the SeCN^- were from the corrosion rate, corrosion products and the capacity. When pH=6, the generation of surface corrosion rate of ZVI apparently higher than pH=7 and 8. That means the corrosion products are producing faster under lower pH conditions. Meanwhile, ZVI corrosion products are producing different types from ferrihydrite, lepidocrocite, goethite and hematite with increasing of pH and decreasing capacity of adsorption (Mohan et al., 2007; Su et al., 2001; Su et al., 2005, Xie et al., 2007).

4.3 Effect of Different Electrolyte

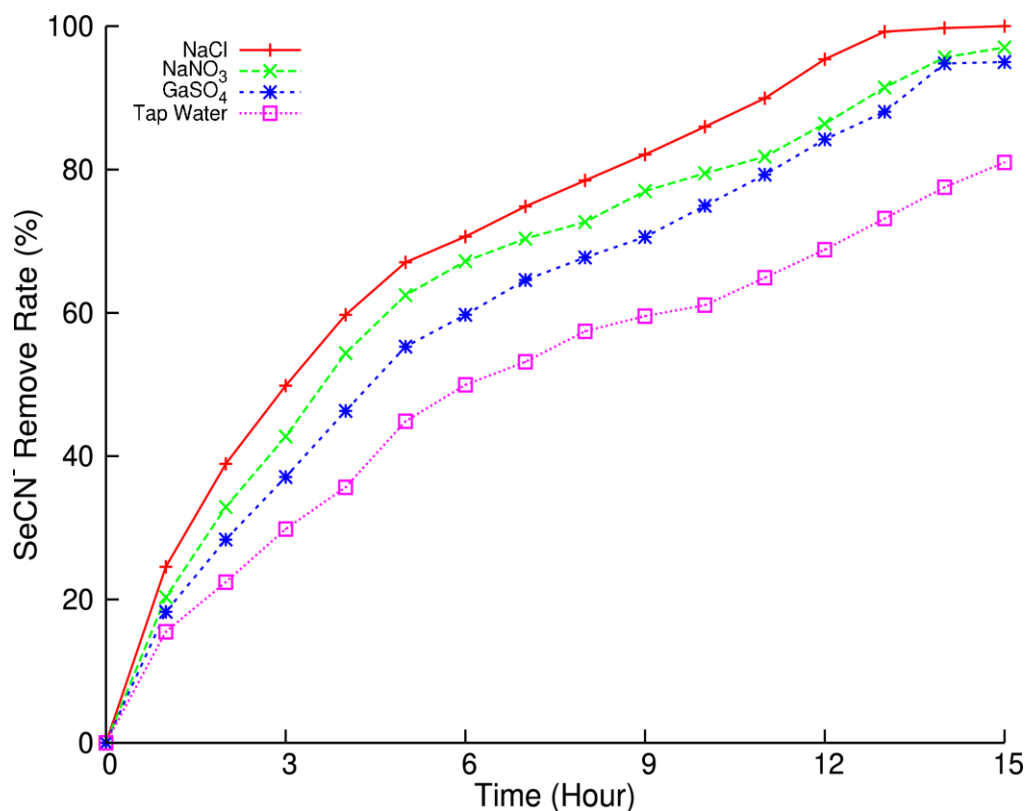


Fig. 6 Effect of Different Electrolyte on SeCN- Removal

Figure 6 depicts the effects in different Electrolyte on SeCN⁻ removal. The results showed that the removal rate of NaCl system approached 100% after 13 hours reaction, which is slightly higher than NaNO₃ and CaSO₄ of 90% and 86%, respectively, after 15 hours. The three system above were higher than the one operated with tap water. Cl⁻ can diffuse to the cracks of Fe⁰ surface oxidation film easily due to its small ionic radius which is about 0.2 nm. After getting into the film, it can neutralize the positive charges of Fe²⁺/Fe³⁺ after Fe⁰ is corroded and corrosion hole forms and Fe⁰ oxidation is enhanced (Caceres et al., 2009). At the same time, Fe⁰ corrosion is intensified when the acidity of aqueous solution increases as a result of Fe²⁺/Fe³⁺ hydrolyzation. Especially when Cl⁻ concentration is high, this process will accelerate because the corrosion surface does not absorb Cl⁻. Su et al reported that anions increase the Fe⁰ corrosion rate and the formation of iron oxides with high absorptive ability improves the removal rate of pollutants. Furthermore, the anions can balance the inhibiting effect of competing absorption happening on the iron oxides surface.

NO₃⁻ can increase the consuming rate of Fe⁰ because it can be reduced by Fe⁰ or the its oxidation products such as Fe²⁺. However, as a result of the fact that NO₃⁻ cannot be absorbed on the surface of oxidation products and its reduction rate will become stable as concentration increases, the concentrations is balanced.

In SO₄²⁻ system, removal rate of SeCN⁻ by Fe⁰ is slightly lower in faintly acid environment. In alkaline solution, the removal rate is same as NaCl⁻ system.

As discussed above, NaCl has the best removal rate of SeCN⁻ followed by NaNO₃ and CaSO₄ at same conductivity level. Tape water has the lowest removal rate.

4.4 Effect of ZVI Particle Size

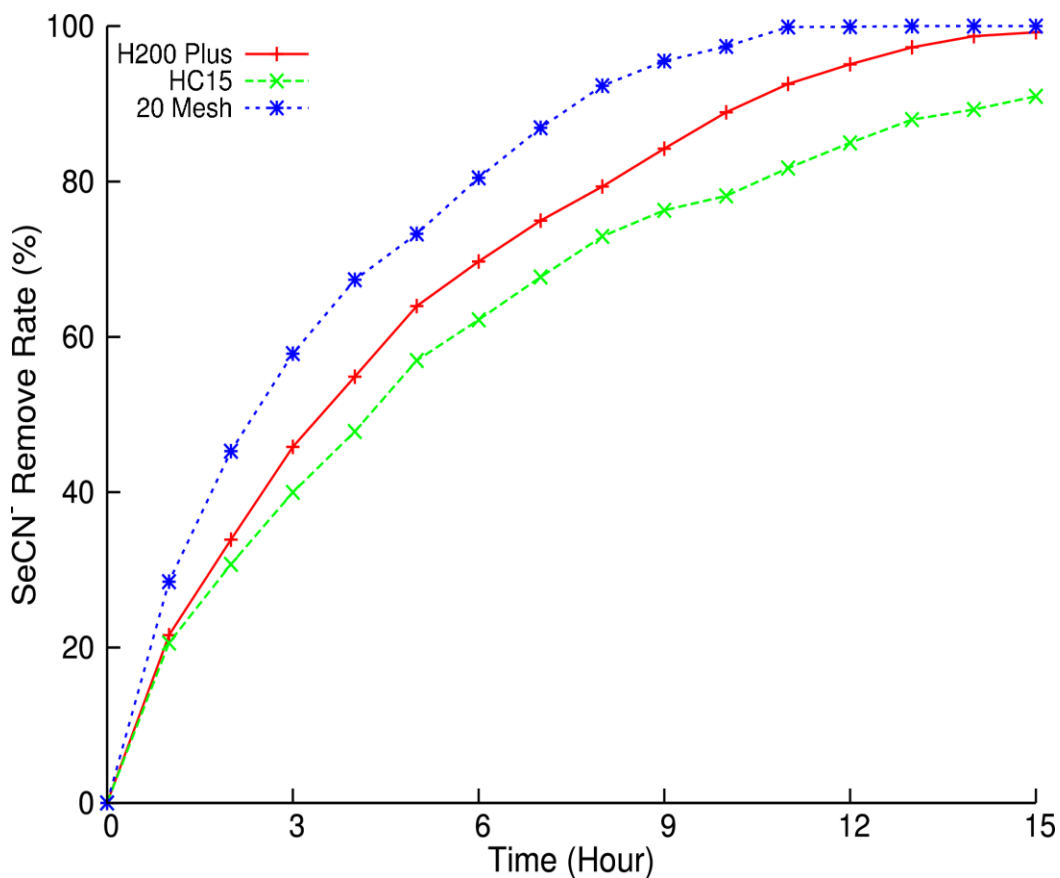


Fig. 7 Effect of ZVI Particle Size on SeCN- Removal

Effect of different ZVI particle size on SeCN- removal is represented in Fig7.

With the decrease of particle size, SeCN- removal rate is increasing. When using H200 plus ZVI, removal rate of SeCN- is significantly higher than the 20 mesh due to the smallest size of ZVI particles. After 15 hours, the H200 plus removal rate reached 99% and the HC15 is 90%. We know that from table 1 and table 2, the size of H200 plus is a larger than HC15 but contained less other metal and compounds than HC15. The results

of the test shows that the removal efficiency of SeCN⁻ is not only related to the particle size of ZVI, but also to the purity of it.

4.5 Effect of Dissolve Oxygen

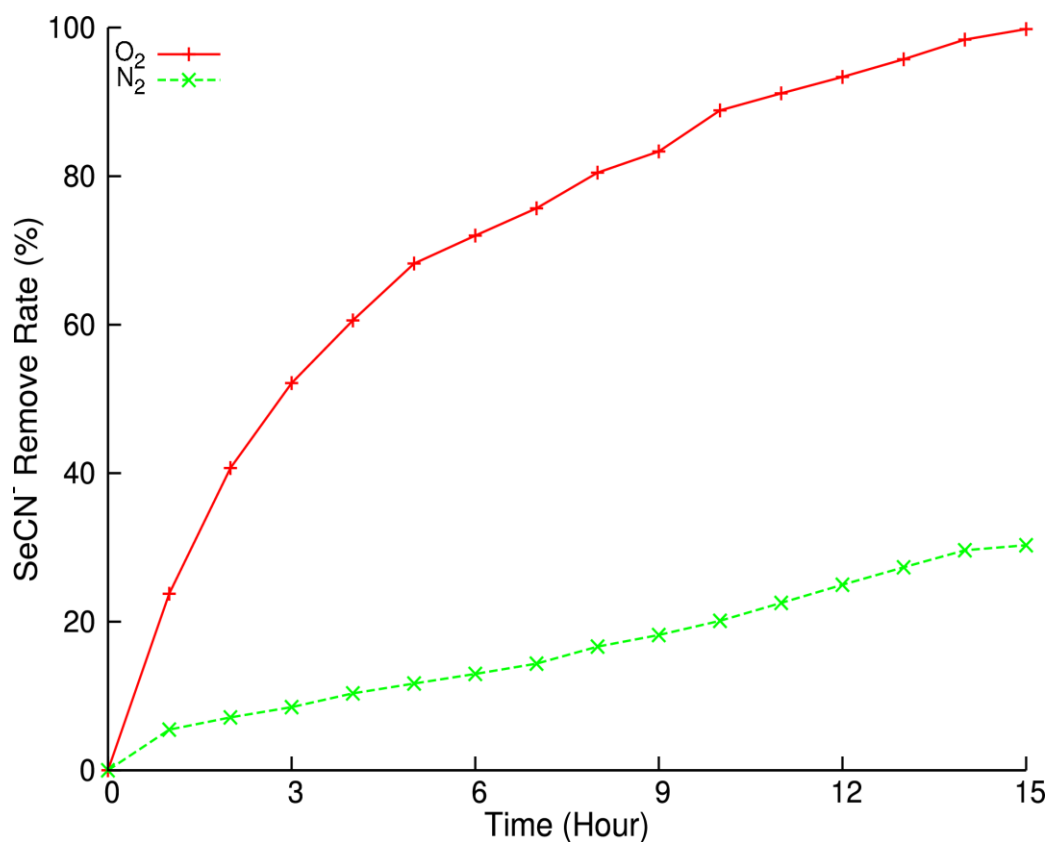


Fig. 8 Effect of Dissolved Oxygen on SeCN⁻ Removal

Fig. 8 shows the removal efficiency of SeCN⁻ under the two different conditions. After 15 hours of reaction, the removal rate under open air is 99% while only 30% of SeCN⁻ is removed under anaerobic conditions. The difference in removal efficiency comes from the following reasons:

1) The corrosion speed of ZVI in atmosphere is much higher than in anaerobic conditions. Thus the coprecipitation reaction in atmosphere will also be faster than in anaerobic condition.

2) Study shows that the corrosion products of ZVI are different under different ambient atmosphere. Farrel et al. showed that under hypoxic conditions FeOOH forms into magnetite and maghemite, which is denser. In the atmosphere, the iron oxide products are mainly ferrihyrite, lepidocrocite and gerthite, which has a loose surface(Huang et al., 2005; Farrell et al., 2001; Furukawa et al., 2002). Thus the adsorption capacity in the atmosphere is much higher than in anaerobic condition.

4.6 Removal of SeCN⁻ Using hZVI System

4.6.1 Operation and Maintenance

The system was set up on Jan 15th, 2011. NaNO₃ and Fe(II) was added to the system in the first 5 days to accelerated the corrosion of ZVI in order to get a stabilized ZVI and iron oxide system. 5ppm of SeCN⁻ was started to add to artificial water on Jan 18th, 2011.

The problem in the first few days is the poor settling property of the reactive solid. A quite amount of the reactive solid loss was observed at the beginning. The reactor was stopped twice on Jan 17th and Jan 20th for approximately 10 hours each time in order to settle the solid. After that, both reactors works good from observation. The system formed a dark brown to black color due to the lepidocrocite and magnetite formation. The system was stopped on May 8th .

4.6.2 Performance and Results

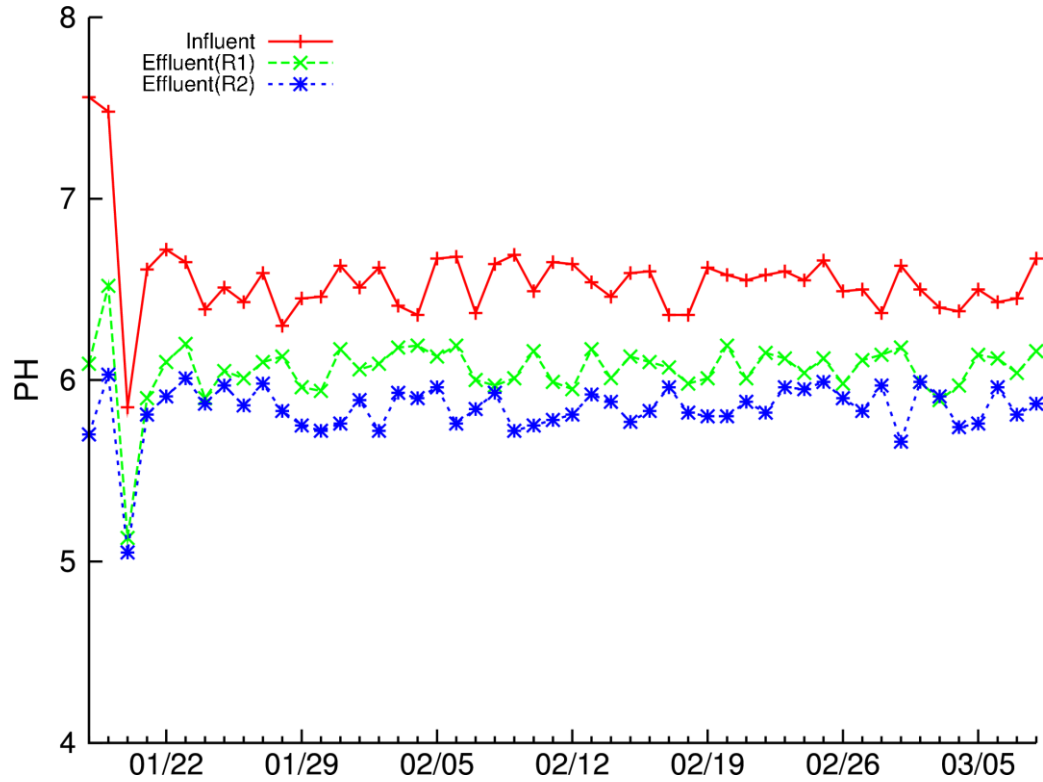


Fig. 9 Influent and Effluent pH of the hZVI System

After the first three days, pH of the influent holds between 6.4 to 6.7 till the end of the test. The pH of effluent of R1 and R2 remains 5.9-6.2 and 5.7-5.9 as shown in fig. 9. This result indicates that the pH is dropping slowly during the reaction. Also after ZVI and iron oxide form a stable system, the pH in the reactor is highly stable, which is beneficial for a stable and reliable removal efficiency.

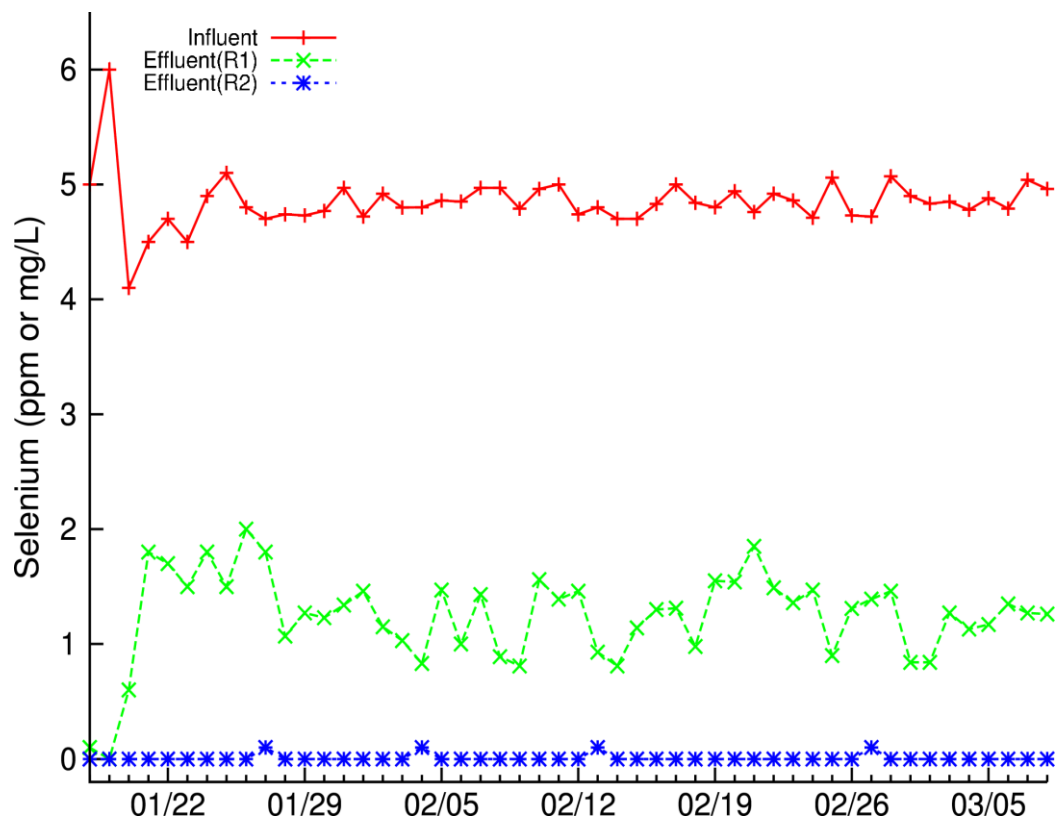


Fig. 10 Influent and Effluent CSeCN- of the hZVI System

The results of concentration of SeCN⁻ in influent and effluent are shown in fig. 10. The feeding concentration of SeCN⁻ is 5mg/L approximately. Around 70% of SeCN⁻ was removed in R1 and other 30% in R2. The removal efficiency of the system is above 99.9% and very stable as expected.

Results of this test shows that the two-stage ZVI system can achieve a good removal efficiency of SeCN⁻ under bench scale. Further experiment may be text under larger scale and more complicated conditions.

CHAPTER V

CONCLUSIONS

The reduction of SeCN⁻ by ZVI under various conditions (initial pH, DO, ZVI particle size and electrolyte) was investigated in this study to prove the highest efficiency for SeCN⁻ removal. The removal rate of SeCN⁻ can reach over 99% in the presence of DO and at initial pH of approximately 6.

The removal efficiency also increases with a smaller ZVI particle size, more pure products.

This study also demonstrates how the reduction and adsorption of SeCN⁻ by ZVI occurred and how iron oxide was produced and formed on the ZVI surface.

The removal of SeCN⁻ by hZVI system is also tested under the best reaction conditions indicated through the batch test. When the system was operated with a two-stage configuration with an HRT of 12 hours, the system may reduce over 99% of the SeCN⁻ at bench scale.

Further study may include but not be limited to:

1) Experiments with XRD and SEM analyses to further understand the CORROSION and layer formation of iron oxide on the surface of ZVI and the oxidation of SeCN⁻ and adsorption on ZVI surface.

2) Bench scale test for treating SSW using hZVI system and design of pilot scale and full scale to test and improve the removal efficiency of SeCN⁻.

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APPENDIX

Effect of Fe(II) on SeCN- Removal

Time/h	Without Fe(II)		With Fe(II)	
	Con.(mmol/L)	Removal/%	Con.(mmol/L)	Removal/%
0	10	0	10	0
1	7.49	25.5	6.35	37.2
2	6.23	38.1	4.93	51.4
3	5.3	47.4	3.87	62
4	4.34	57	2.83	72.4
5	3.69	63.5	2.06	80.1
6	2.92	71.2	1.54	85.3
7	2.27	77.7	1.02	90.5
8	1.59	84.5	0.82	92.5
9	1.08	89.6	0.59	94.8
10	0.74	93	0.53	95.4
11	0.34	97	0.32	97.5
12	0.29	97.5	0.23	98.4
13	0.12	99.2	0.1	99.7
14	0.01	100	0	100
15	0.01	100	0	100

Effect of ZVI Corrosion and Fe(II) Formation

Time/h	C _{SecN-}	C _{Fe(II)}
0	10	0
1	7.484	3.47
2	6.25	5.81
3	5.328	7.38
4	4.335	10.09
5	3.387	9.45
6	2.754	8.17
7	2.264	7.01
8	1.942	6.3
9	1.505	5.38
10	1.221	4.21
11	0.846	3.44
12	0.573	2.58
13	0.265	1.86
14	0.093	1.35
15	0.01	1.29

Effect of Initial pH on SeCN- Removal

Time/h	pH=6		pH=7		pH=8	
	Con.(mmol/L)	Removal/%	Con.(mmol/L)	Removal/%	Con.(mmol/L)	Removal/%
0	10	0	10	0	10	0
1	7.622	23.78	8.504	14.96	8.504	14.96
2	5.897	41.03	6.863	31.37	6.863	31.37
3	4.801	51.99	5.855	41.45	5.855	41.45
4	3.936	60.64	5.139	48.61	5.139	48.61
5	3.297	67.03	4.382	56.18	4.382	56.18
6	2.854	71.46	3.938	60.62	3.938	60.62
7	2.664	73.36	3.414	65.86	3.414	65.86
8	2.136	78.64	3.03	69.7	3.03	69.7
9	1.842	81.58	2.789	72.11	2.789	72.11
10	1.421	85.79	2.524	74.76	2.524	74.76
11	1.128	88.72	2.177	78.23	2.177	78.23
12	0.667	93.33	1.85	81.5	1.85	81.5
13	0.244	97.56	1.531	84.69	1.531	84.69
14	0.098	99.02	1.419	85.81	1.419	85.81
15	0.01	99.9	1.269	87.31	1.269	87.31

Effect of Different Electrolyte on SeCN- Removal

Time /h	NaCl		NaNO3		CaSO4		Tap Water	
	Con.(mmo l/L)	Remova l/%	Con.(mmo l/L)	Remova l/%	Con.(mmo l/L)	Remova l/%	Con.(mmo l/L)	Remova l/%
0	10	0	10	0	10	0	10	0
1	7.544	24.56	7.966	20.34	8.172	18.28	8.451	15.49
2	6.108	38.92	6.712	32.88	7.164	28.36	7.757	22.43
3	5.017	49.83	5.726	42.74	6.289	37.11	7.018	29.82
4	4.028	59.72	4.563	54.37	5.369	46.31	6.433	35.67
5	3.296	67.04	3.755	62.45	4.471	55.29	5.514	44.86
6	2.936	70.64	3.281	67.19	4.028	59.72	5.004	49.96
7	2.515	74.85	2.967	70.33	3.542	64.58	4.683	53.17
8	2.154	78.46	2.733	72.67	3.227	67.73	4.257	57.43
9	1.791	82.09	2.302	76.98	2.941	70.59	4.045	59.55
10	1.403	85.97	2.055	79.45	2.507	74.93	3.893	61.07
11	1.006	89.94	1.82	81.8	2.072	79.28	3.509	64.91
12	0.463	95.37	1.363	86.37	1.581	84.19	3.118	68.82
13	0.077	99.23	0.855	91.45	1.194	88.06	2.684	73.16
14	0.026	99.74	0.434	95.66	0.522	94.78	2.249	77.51
15	0.001	99.99	0.297	97.03	0.5	95	1.9	81

Effect of ZVI Particle Size on SeCN- Removal

Time/h	20 Mesh		H200		HC15	
	Con.(mmol/L)	Removal/%	Con.(mmol/L)	Removal/%	Con.(mmol/L)	Removal/%
0	10	0	10	0	10	0
1	7.152	28.48	7.84	21.6	7.94	20.6
2	5.473	45.27	6.61	33.9	6.929	30.71
3	4.216	57.84	5.416	45.84	6.001	39.99
4	3.267	67.33	4.512	54.88	5.218	47.82
5	2.673	73.27	3.605	63.95	4.303	56.97
6	1.954	80.46	3.03	69.7	3.78	62.2
7	1.308	86.92	2.505	74.95	3.231	67.69
8	0.767	92.33	2.065	79.35	2.707	72.93
9	0.45	95.5	1.578	84.22	2.371	76.29
10	0.261	97.39	1.108	88.92	2.185	78.15
11	0.011	99.89	0.743	92.57	1.828	81.72
12	0.009	99.91	0.49	95.1	1.504	84.96
13	0.001	99.99	0.273	97.27	1.203	87.97
14	0.001	99.99	0.129	98.71	1.075	89.25
15	0.001	99.99	0.08	99.2	0.904	90.96

Effect of Dissolved Oxygen on SeCN- Removal

Time/h	O2		N2	
	Con.(mmol/L)	Removal/%	Con.(mmol/L)	Removal/%
0	10	0	10	0
1	7.622	23.78	9.452	5.48
2	5.931	40.69	9.288	7.12
3	4.787	52.13	9.149	8.51
4	3.943	60.57	8.963	10.37
5	3.176	68.24	8.832	11.68
6	2.8	72	8.703	12.97
7	2.434	75.66	8.565	14.35
8	1.954	80.46	8.335	16.65
9	1.669	83.31	8.178	18.22
10	1.116	88.84	7.988	20.12
11	0.886	91.14	7.747	22.53
12	0.665	93.35	7.501	24.99
13	0.427	95.73	7.267	27.33
14	0.162	98.38	7.036	29.64
15	0.022	99.78	6.97	30.3

Influent and Effluent pH of the hZVI System

Date	Influent	Effluent(R1)	Effluent(R2)
18-Jan	7.56	6.09	5.7
19	7.48	6.52	6.03
20	5.85	5.13	7.35
21	6.61	5.9	5.81
22	6.72	6.1	5.91
23	6.65	6.2	6.01
24	6.39	5.9	5.87
25	6.51	6.05	5.97
26	6.43	6.01	5.86
27	6.59	6.1	5.98
28	6.3	6.13	5.83
29	6.45	5.96	5.75
30	6.46	5.94	5.72
31	6.63	6.17	5.76
1-Feb	6.51	6.06	5.89
2	6.62	6.09	5.72
3	6.41	6.18	5.93
4	6.36	6.19	5.9
5	6.67	6.13	5.96

6	6.68	6.19	5.76
7	6.37	6	5.84
8	6.64	5.97	5.93
9	6.69	6.01	5.72
10	6.49	6.16	5.75
11	6.65	5.99	5.78
12	6.64	5.95	5.81
13	6.54	6.17	5.92
14	6.46	6.011	5.88
15	6.59	6.13	5.77
16	6.6	6.1	5.83
17	6.36	6.07	5.96
18	6.36	5.98	5.82
19	6.62	6.01	5.8
20	6.58	6.19	5.8
21	6.55	6.01	5.88
22	6.58	6.15	5.82
23	6.6	6.12	5.96
24	6.55	6.04	5.95
25	6.66	6.12	5.99
26	6.49	5.98	5.9

27	6.5	6.11	5.83
28	6.37	6.14	5.97
1_Mar	6.63	6.18	5.66
2	6.5	5.99	5.99
3	6.4	5.89	5.91
4	6.38	5.97	5.74
5	6.5	6.14	5.76
6	6.43	6.12	5.96
7	6.45	6.04	5.81
8	6.67	6.16	5.87

Influent and Effluent CSeCN- of the hZVI System

Date	Influent	Effluent(R1)	Effluent(R2)
18-Jan	5	0.1	0
19	6	0	0
20	4.1	0.6	0
21	4.5	1.8	0
22	4.7	1.7	0
23	4.5	1.5	0
24	4.9	1.8	0
25	5.1	1.5	0
26	4.8	2	0
27	4.7	1.8	0.1
28	4.74	1.07	0
29	4.73	1.27	0
30	4.77	1.23	0
31	4.97	1.34	0
1-Feb	4.72	1.46	0
2	4.92	1.15	0
3	4.79	1.03	0
4	4.8	0.83	0.1
5	4.86	1.47	0

6	4.85	1	0
7	4.97	1.43	0
8	4.97	0.89	0
9	4.79	0.81	0
10	4.96	1.56	0
11	5	1.39	0
12	4.74	1.46	0
13	4.8	0.93	0.1
14	4.7	0.81	0
15	4.7	1.14	0
16	4.83	1.3	0
17	5	1.31	0
18	4.84	0.97	0
19	4.8	1.55	0
20	4.94	1.54	0
21	4.76	1.85	0
22	4.92	1.49	0
23	4.86	1.36	0
24	4.71	1.47	0
25	5.06	0.9	0
26	4.73	1.31	0

27	4.72	1.39	0.1
28	5.07	1.46	0
1_Mar	4.9	0.84	0
2	4.833	0.84	0
3	4.85	1.27	0
4	4.78	1.13	0
5	4.88	1.17	0
6	4.79	1.35	0
7	5.04	1.27	0
8	4.96	1.26	0