Simultaneous Oxidation and Removal of As(III) and As(V) by Electrocoagulation-Filtration
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Simultaneous Oxidation and Removal of As(III) and As(V) by Electrocoagulation-Filtration

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FOREWORD

The Water Research Foundation (Foundation) is a nonprofit corporation that is dedicated to the implementation of a research effort to help utilities respond to regulatory requirements and traditional high-priority concerns of the industry. The research agenda is developed through a process of consultation with subscribers and drinking water professionals. Under the umbrella of a Strategic Research Plan, the Research Advisory Council prioritizes the suggested projects based upon current and future needs, applicability, and past work; the recommendations are forwarded to the Board of Trustees for final selection. The Foundation also sponsors research projects through the unsolicited proposal process; the Collaborative Research, Research Applications, and Tailored Collaboration programs; and various joint research efforts with organizations such as the U.S. Environmental Protection Agency, the U.S. Bureau of Reclamation, and the Association of California Water Agencies.

This publication is a result of one of these sponsored studies, and it is hoped that its findings will be applied in communities throughout the world. The following report serves not only as a means of communicating the results of the water industry's centralized research program but also as a tool to enlist the further support of the nonmember utilities and individuals.

Projects are managed closely from their inception to the final report by the Foundation's staff and large cadre of volunteers who willingly contribute their time and expertise. The Foundation serves a planning and management function and awards contracts to other institutions such as water utilities, universities, and engineering firms. The funding for this research effort comes primarily from the Subscription Program, through which water utilities subscribe to the research program and make an annual payment proportionate to the volume of water they deliver and consultants and manufacturers subscribe based on their annual billings. The program offers a cost-effective and fair method for funding research in the public interest.

A broad spectrum of water supply issues is addressed by the Foundation's research agenda: resources, treatment and operations, distribution and storage, water quality and analysis, toxicology, economics, and management. The ultimate purpose of the coordinated effort is to assist water suppliers to provide the highest possible quality of water economically and reliably. The true benefits are realized when the results are implemented at the utility level. The Foundation's trustees are pleased to offer this publication as a contribution toward that end.

Roy L. Wolfe, Ph.D.
Chair, Board of Trustees
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EXECUTIVE SUMMARY

OBJECTIVES

The objective of the proposed work was to determine the feasibility of using electrocoagulation (EC) for arsenic removal in comparison to conventional chemical coagulation (CC). To attain the objective, the following specific tasks were carried out:

1. Establish the basic features of electrolytic oxidation of iron and formation of hydroxides during and after electrolysis,
2. Verify the reported ability of EC to oxidize As(III) to As(V) and remove As(V) by adsorption onto Fe(OH)_3,
3. Compare EC–filtration (EC–F) to CC–F for As(V) and As(III) removal, and
4. Study the effect of competing ions on arsenic removal during EC and CC

BACKGROUND

CC–F with Fe salts is an effective and widely used technology for treating drinking water to remove arsenic. For small systems, adsorption onto granular ferric hydroxide (GFH) or granular ferric oxide (GFO) is currently the processes of choice. In a comparison of these two processes, CC–F vs. GFH/GFO, a surprising result is obtained. Although the granular media (FeOOH(s)) are exhausted so as to be in equilibrium with the raw water influent arsenic concentration, typically 20–40 μg As/L, and the coagulant Fe(OH)_3(s) is in equilibrium with the effluent arsenic concentration, typically 2–10 μg As/L, the arsenic loading, mg of As/g Fe, on the coagulant is higher than on the solid media. Furthermore, recent experiments have shown that Fe(OH)_3(s) formed-in-place from FeCl_3 hydrolysis is far more effective than preformed Fe(OH)_3(s) and GFH/GFO for adsorption of arsenic in CC–F processes. The disadvantages of using ferric iron as a coagulant are based on the fact that arsenic removal efficiency depends on pH, As(III)/(V) oxidation state, and the effect of competing anions including silicate, phosphate, vanadate and others.

EC–F, which has been applied to treat drinking water and wastewater, can be used for removal of arsenic from drinking water. During EC, ferric ions are generated from zero-valent iron at the anode. These ferric ions rapidly hydrolyze to produce ferric hydroxide (Fe(OH)_3(s)), which strongly adsorbs As(V). According to literature reports, the oxidation state of arsenic will not affect the removal efficiency because As(III) will be oxidized to As(V) during electrolysis. Furthermore, during EC, the hydrolysis of ferric iron does not lower the pH because the hydrogen ions produced from hydrolysis are consumed by the hydroxide ions produced at the cathode from the electrolysis of water. Moreover, EC is simpler because the amount of ferric ion added is controlled by adjusting the electrical current rather than by storing, diluting, and pumping corrosive ferric salts. Therefore, it appears that EC–F has some advantages over CC and would be a better choice for arsenic removal from drinking water for small community.
APPROACH

The project objectives with respect to arsenic removal were attained with a three-cell EC unit and FeCl₃ CC. During the course of the study, it was found that, in contrast to what was reported in the literature, ferrous (Fe(II)) not ferric (Fe(III)) iron was produced at the anode during EC. Ferrous iron production is problematic because, compared with ferric iron, Fe(II) is soluble and must be oxidized to Fe(III) to produce the desired Fe(OH)₃ floc needed for contaminant removal. Thus, further studies were performed to understand the electrolytic oxidation of iron in a single-cell EC unit and its possible implications on contaminant removal.

Although not originally within the scope of work for this project, the study of chlorine generation during EC was undertaken with the objective of oxidizing As(III) to As(V) for better removal and oxidizing Fe(II) to Fe(III) to eliminate residual soluble iron and improve arsenic removal. This study was performed in the three-cell EC unit.

Finally, based on previous research (Lakshmanan et al. 2008) and the current study results with CC, it was found that mixing time had an effect on arsenic removal. Thus, limited experiments were performed.

RESULTS/CONCLUSIONS

The studies on the oxidation of iron during and after electrolysis performed in the single cell EC unit led to the following conclusions:

1. Fe(II), not Fe(III) was produced during EC. The iron generation experimentally was the same as theoretical iron generation capacity (Faraday’s law) based on Fe²⁺ production at the anode for applied currents of 0.05–0.8A and at pH 6.5–8.5. The current efficiency with respect to iron generation was 100%, provided the iron rod was cleaned prior to each iron-generation experiment.
2. During electrolysis, a significant increase from the initial pH was observed due to the continuous production of hydroxide ions. However the pH decreased as the Fe hydroxides were formed and the final pH was the same as initial for pH 7.5, while their was a slight increase and decrease in final pH for initial pHs of 6.5 and 8.5, respectively.
3. Although Fe(II) was generated during the electrochemical oxidation of the iron anode, it was completely oxidized during 2 min mixing/iron generation at pH 8.5, which resulted in formation of the desired ferric hydroxides. However, at pH 6.5 and 7.5, Fe(II) was not completely oxidized, which resulted in a mixture of soluble Fe(II) and precipitated Fe(OH)₃ at the end of 2 min generation/mixing.
4. The greater oxidation of Fe²⁺ during EC compared to FC (FAS as coagulant) at the end of 2 minutes of mixing was due to significant increase in pH during the initial stage of electrolysis, which was not the case during CC experiments, which were carefully pH controlled.
5. At the end of 2 minutes of iron generation and mixing, the % Fe²⁺ remaining decreased with increasing current, and increased with increasing pH.
6. The industrial-grade (98.5% pure) and the reagent-grade (99.995% pure) iron rods behaved in a similar way with respect to total iron generation efficiency and so the purity of the industrial-grade iron rod was not of major concern with respect to the iron generation.
7. Under N₂-purged conditions (DO very low) with an industrial-grade and reagent-grade iron rods, 80–90% of iron was present as Fe²⁺ which confirms that Fe²⁺ is the species that is formed during electrolysis and natural oxidation by DO was the only reason for oxidation of Fe²⁺ to Fe³⁺. The studies on As(III) oxidation during EC and the comparison of arsenic removal during CC and EC in the three-cell EC unit led to the following conclusions:

8. As observed with the single cell EC unit, the iron generation experimentally approached the theoretical iron generation capacity based on Fe²⁺ production at the anodes both in batch and continuous mode operation in the three-cell EC unit, provided the iron rods were cleaned prior to each iron-generation experiment.

9. As(V) removal during EC was very erratic at pH 6.5 with all compositions of challenge water tested: NSFI challenge water, challenge water without silica, challenge water without phosphate, and challenge water without silica and phosphate.

10. The erratic As(V) removal behavior at pH 6.5 was due to (a) the >70% un-oxidized iron (Fe(II)) present in the treated water (b) low amount of ferric hydroxides (15–30%) produced, and (c) variable amount of adsorption of As(V) onto the iron oxide/hydroxide surfaces of the iron rods in the EC unit.

11. As(V) removal was efficient at pH 7.5 and 8.5 during EC with all compositions of challenge water tested, however, a significant and highly variable amount of un-oxidized Fe(II) (10–45%) was present in the treated water at pH 7.5.

12. As(V) removal was highly pH dependent in CC and EC, and the efficiency increased with decreasing pH.

13. The As(V) adsorption capacity was almost the same with CC and EC at pH 7.5 and 8.5. EC was not efficient at pH 6.5.

14. Compared with As(V) removal, the removal of As(III) was poor for both CC and EC. As(III) removal was slightly greater during EC which was pH dependent, compared to CC, which was pH independent.

15. In contrast to what had been reported in the literature, there was no obvious oxidation of As(III) and simultaneous removal of As(V) during EC.

16. As(V) removal using EC is not advisable at pH 6.5 unless there is a very long (>2 hr) oxidation time or higher concentration of dissolved oxygen for nearly complete oxidation of Fe(II) produced.

17. As(V) removal by EC at pH 7.5 should be employed with caution due to potential presence of high concentrations of soluble Fe(II) in the effluent. Oxidation post treatment or longer retention times are a possibility to oxidize Fe(II), but the additional complexity could be undesirable for small community treatment.

18. As(V) removal by EC at pH 8.5 is likely an acceptable small community treatment process because of the rapid oxidation of Fe(II) to Fe(III) at this higher pH.

The studies on factors affecting As(V) adsorption during EC and CC led to the following conclusions:
19. In the NSFI challenge water with phosphate, silica at 20 mg/L significantly reduced the adsorption of As(V) by competing for adsorption sites both in CC and EC and the interference increased with increasing pH.

20. In the NSFI Challenge water with silica, phosphate at 40 μg P/L was found to reduce the adsorption of As(V) significantly at pH 6.5, whereas it had a lesser effect at pH 7.5 and 8.5 during CC. The effect of phosphate at 40 μg P/L was found to reduce the adsorption of As(V) significantly at pH 7.5, whereas it had a lesser effect at pH 8.5 during EC.

21. In the absence of phosphate, silica exhibited a significant effect on the adsorption of As(V), and the effect increased with increasing pH during CC. In the absence of silica, phosphate exhibited a significant effect on the adsorption of As(V) at all pHs during CC with FeCl₃, and the effect increased with decreasing pH.

22. In the absence of phosphate, silica exhibited a significant effect on the adsorption of As(V) and the effect increased with increasing pH during EC. In the absence of silica, phosphate also exhibited a significant effect on the adsorption of As(V) at pH 7.5 and 8.5 during EC.

23. Mixing time was found to have an effect on As(V) adsorption capacity during CC with FeCl₃. However the significance of the effect was dependent on the Fe(III) dose, the removals associated with the Fe(III) dose and the presence/absence of competing ions.

The results of the additional research on electrolytic chlorine generation for oxidizing As(III) to As(V) and Fe(II) to Fe(III) to improve arsenic removal led to the following conclusions:

24. With iron rod as anodes, chlorine was not generated in the EC unit, and, in fact, the reduced oxides/hydroxides on the iron anodes produced a very significant source of chlorine demand in the EC unit.

25. With a graphite rod anode and stainless steel cathode, chlorine was generated at the anode when chloride ions were present in the solution, and complete oxidation of As(III) was possible providing that sufficient current and mixing time were provided.

26. A combination of graphite and iron rods in the same EC unit housing had no significant advantage for As(III) removal compared with the iron rods alone. When Cl₂ was generated at the graphite anodes, it was immediately consumed by the chlorine demand of the reduced iron oxide/hydroxide anode surfaces and by the Fe(II) produced during electrolysis.

27. A two-stage EC process with graphite anodes in a separate stage 1 housing and iron anodes in the stage 2 housing, although more complicated and costly, was effective for As(III) oxidation and removal without any need for dosing of coagulant or oxidant chemicals.

APPLICATIONS/RECOMMENDATIONS

The main purpose of this project was to determine the applicability of EC–F for arsenic removal in small community water supplies. It was discovered during this research that ferrous not ferric iron is generated during iron anode EC with typical ground water in the pH 6.5 to 8.5 range. This makes the EC process unsuitable for application to small community treatment systems under typical ground water conditions. The non-occurrence of simultaneous oxidation
and removal of As(III) as reported in the literature eliminates the major advantage expected of EC process. Furthermore, the possibility of forming secondary contaminant in the form of ferrous iron makes the process even more problematic. Taking the detailed conclusions above into consideration, the following recommendations are made for application of EC for arsenic removal in small systems:

1. The EC process is applicable at high pH (~8 or higher) due to the rapid oxidation of ferrous iron to ferric at high pH.
2. The EC process is not advisable at pH ≤ 7.5 under un-optimized conditions due to the possibility of forming soluble ferrous iron as a secondary contaminant.
3. The EC process at pH ≤ 7.5 could be made more efficient by completely oxidizing the ferrous produced at the anode. The optimization could be made by the combination of the following:
   a. providing a larger retention time,
   b. aerating the water thereby increasing the DO content,
   c. pre-oxidation step such as introduction of oxidant, and
   d. increasing the pH.
4. Caution must be exercised before application of the EC process. The efficiency of the EC process is significantly dependent on the characteristics of the water (pH, DO, etc.) and so pilot-scale studies are necessary before application of the process.
CHAPTER 1
INTRODUCTION

ARSENIC OCCURRENCE, HEALTH EFFECTS AND REGULATIONS

Arsenic (As) is a naturally occurring element present in food, water, and air. Known for centuries to be an effective poison, some animal studies suggest that arsenic may be an essential nutrient at low concentrations. Arsenic occurs in groundwater with no taste, color or odor, but its presence in drinking water can cause serious health effects. In addition to naturally occurring arsenic, which is by far the largest source, arsenic contamination of water also occur due to pesticides, mining, and computer chip manufacturing.

Inorganic arsenic is considered to be a human carcinogen with multiple sites of attack. Epidemiological studies have demonstrated the higher risks of skin, bladder, lung, liver and kidney cancer along with other non-cancerous health effects that result from continued consumption of elevated levels of arsenic in drinking water (Guha Mazumder et al. 1998, Chen et al. 1988, Ferreccio et al. 2000). Non-malignant skin alterations, such as keratosis and hypo- and hyper-pigmentation, have been linked to arsenic ingestion, and skin cancers have developed in some patients. Additional studies indicate that arsenic ingestion may result in internal malignancies, including cancers of the kidney, bladder, liver, lung, and other organs. Vascular system effects have also been observed, including peripheral vascular disease, which in its most severe form, results in gangrene or Blackfoot Disease. Other potential effects include neurologic impairment (Lomaquahu and Smith 1998). The primary route of exposure to arsenic for humans is ingestion. Exposure via inhalation is considered minimal, though there are regions where elevated levels of airborne arsenic occur periodically (Wilkie and Hering 1998). Organic arsenic compounds can cause neither cancer, nor DNA damage. But exposure to high doses may cause certain effects to human health, such as nerve injury and stomach aches. Exposure to inorganic arsenic can cause various health effects, such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes and lung irritation. Arsenite is much more toxic to humans than the oxidized arsenate species.

Many countries around the world are exposed to elevated levels of arsenic in their drinking water. The International Agency for Research on Cancer as well as the United States Environmental Protection Agency (USEPA) has designated arsenic as a Group A "known" human carcinogen. There are numerous reports in the literature, based on past and ongoing experience in various countries in Asia and South America concerning the elevated levels of arsenic in drinking water. Indeed, arsenic is the only major demonstrated human carcinogen where the principle route of human exposure is through drinking water. But, the most devastating incidence of arsenic poisoning has been reported in Bangladesh, and West Bengal-India (Chowdhury et al., 2000; Chowdhury et al., 2000a; Das et al., 1995). Reportedly, more than 6 million people in West Bengal, India, and more than 70 million people in Bangladesh are drinking ground water containing elevated levels (50 µg/L and above) of arsenic (Chakraborti et al. 2002). In Bangladesh out of an estimated 6–11 million shallow tube wells, approximately 27% are contaminated with arsenic above 50 ppb (Kinniburgh and Kosmus 2002). Here in USA, according to the US Geological Survey (USGS) and the USEPA, high concentrations of arsenic in water are widespread in Western, Midwestern and Northwestern United States (http://co.water.usgs.gov/trace/arsenic). The EPA has reported that more than 5.5% of the total...
water supply systems in USA contain arsenic at a level greater than 10 µg/L (http://webserver.cr.usgs.gov/trace/arsenic). Higher levels of arsenic tend to be found more often in ground water than in surface water sources. About 4,100 of the nation’s 54,000 Community Water Supplies and 1,100 of the 20,000 Non-Transient Non-Community water Supplies exceed the current 10 µg/L limit. According to the Natural Resources Defense Council (NRDC 2000), over 34 million Americans drink water that increases their arsenic-related cancer. Due to the elevated health risk, based on the analysis of the United States Environmental Protection Agency (USEPA) and two independent reports by the National Research Council (NRC 1999), USEPA has reduced the maximum contamination level (MCL) of arsenic in drinking water from 50 to 10 µg/L (USEPA 2001).

STATE-OF-THE-ART ARSENIC REMOVAL TECHNOLOGIES

The best available arsenic removal technologies for drinking water include:

1. Precipitative processes, including coagulation–filtration (C–F), coagulation assisted microfiltration (C–MF), enhanced coagulation, lime softening (LS), and enhanced lime softening;
2. Adsorption processes, including activated alumina (AA), and granular ferric hydroxide;
3. Ion exchange (IX) processes, specifically anion exchange;
4. Membrane filtration, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and electrodialysis reversal (EDR); and
5. Alternative treatment processes, including biological processes, sulfur-modified iron and iron filings, and greensand filtration;

In addition to their use for central treatment of drinking water supplies, adsorption, ion exchange and membrane technologies are used for point-of-entry (POE) and point-of-use (POU) devices.

IRON C–F AND ADSORPTION PROCESSES

The most frequently used technology for removing arsenic from drinking water is precipitation/coprecipitation followed by some form of settling and/or filtration. The process is commonly referred to as C–F. This technology is capable of treating a wide range of influent concentrations to the revised MCL for arsenic. According to USEPA more than 52% of the identified applications of arsenic treatment technologies for water are based on coagulation. Many studies have been done to examine the efficiency of arsenic removal using coagulation with ferric and aluminum salts (Gulledge and O’Connor 1973, Edwards 1994, Hering et al. 1996, Ghurye et al. 2004). Coagulant type and dosage, pH, composition of the water, and contaminant type have significant effects on removal efficiency. It is well accepted that removal of arsenate [As(V)] is much better than arsenite [As(III)] (Clifford 1990) and that silica interferes with arsenic removal at higher pH (Tong 1997). For better removal efficiency, pre-oxidation is necessary for As(III) removal.

Small-scale systems and point-of-entry (POE) systems often use adsorption or ion-exchange (IX) in packed-bed processes for arsenic removal, especially when arsenic is the only contaminant to be removed. As with iron and aluminum coagulation, numerous factors including
arsenic oxidation state (III or V), pH, competing anions, media particle size, and empty bed contact time (EBCT) significantly affect arsenic removal by adsorption and IX. However, the major factors limiting the use of adsorption and IX processes include the relatively high cost of the media, the complexity of regeneration, the need for backwash, spent-regenerant, and spent media disposal. Due to high arsenic concentrations in the backwash waters and spent regenerant, direct discharge to a sanitary sewer is usually not acceptable. Therefore, the spent regenerant may need to be further treated by precipitation/coagulation process to produce a sludge that can be thickened and dried prior to disposal. On the other hand, the arsenic-laden sludge produced by coagulation processes does not require an additional precipitation step, and can be directly dried and land filled in hazardous or non-hazardous landfills depending on arsenic concentration.

BACKGROUND OF THE STUDY

Electrocoagulation


EC involves dissolution and hydrolysis of metal from the anode with simultaneous formation of hydroxyl ions and hydrogen gas occurring at the cathode. EC treatment of water has been employed since before the turn of the century with Vik et al. (1984) describing a treatment plant in London built in 1889. In 1909, in the United States, J.T. Harries (Vik et al. 1984) received a patent for wastewater treatment by electrolysis with sacrificial aluminium and iron anodes. An “Electronic Coagulator”, which electrochemically dissolved aluminium ions (Al$^{3+}$) formed at the anode into solution and reacted them with the hydroxyl ions formed at the cathode to form aluminium hydroxides was used in the 1940’s (Matteson et al. 1995). The aluminum hydroxide coagulant particles were flocculated and removed the suspended solids from the water. A similar process was used in Britain in 1956 (Matteson et al. 1995) for which iron electrodes were used to treat river water. Presently EC is marketed by a small number of companies around the world. Often the EC units are used simply as a replacement for chemical dosing systems and do not take advantage of the electrolytic gases produced in the EC process. It is clear that EC has the capability to remove a large range of pollutants varying from suspended solids to viruses to trace inorganic contaminants.

Significance of In-situ Formed Hydroxides

Previous studies conducted by researchers at the University of Houston (Clifford et al. 1997, Ghurye et al. 2004) reported that C–MF with FeCl$_3$ was effective and economical compared with adsorption and ion exchange. It was observed that pH and ferric dose were the most important variables controlling arsenic removal. Experiments were also performed that compared hydrolyzed in-situ Fe(OH)$_3$ with preformed Fe(OH)$_3$. Based on arsenic uptake by the iron oxide/hydroxide surfaces, preformed Fe(OH)$_3$ was not as effective as Fe(OH)$_3$ formed-in-
place (hydrolyzed in situ) by adding FeCl₃ to water and mixing it well. Recently, our research on “A Systematic Comparison of Arsenic Removal by C–F with Zirconium (Zr) and Titanium (Ti) Salts in Comparison with Ferric Salts” (Lakshmanan et al. 2008) found that (a) the in-situ-formed hydroxides of Fe, Ti, and Zr exhibited much greater adsorption capacities than the granular oxide-hydroxide media of Fe, Ti, and Zr and (b) that iron was the most effective and lowest-cost coagulant among the coagulants tested. The reason for the higher arsenic capacity on the formed-in-place coagulant is that the arsenate anions are sorbed by surface complexation onto the short-chain polymers (oligomers) of Feₓ(OH)ᵧ²⁺ as they are forming into Fe(OH)₃ floc particles that can be filtered. Preformed Fe(OH)₃ and granular ferric oxide/hydroxide (GFO/GFH) media simply do not have the available surface area in comparison to the oligomers and polymers of Fe(OH)₃(s) that are formed during Fe³⁺ hydrolysis in coagulation processes.

During comparison of the processes, the granular iron oxyhydroxide media including GFH (FeOOH(s)) and GFO (Fe₂O₃(s)) were exhausted so as to be in equilibrium with the raw water influent arsenic concentration, typically 10–50 μg As/L, while the coagulant Fe(OH)₃(s) was in equilibrium with the much lower effluent arsenic concentration, typically 2–10 μg As/L. Experimental results showed that the arsenic loading, mg of As/g Fe, on the coagulant was higher than on the solid media. Figure 1.1 compares the variation in adsorption capacities between in-situ formed hydroxides using coagulants and preformed hydroxide media in NSFI 53 challenge water. It can be seen that the in-situ-formed metal hydroxide coagulants had 2–5 times the adsorption capacity of similar granular media. Even though the in-situ formed hydroxides were expected to perform better, the magnitude of the difference was not expected. Thus, the results from the project showed that the in-situ-formed coagulants can provide significant advantages over granular media adsorbents. Usually, chemical coagulation (CC) with iron or aluminum salt is used, however EC is another possibility where in-situ formed hydroxides could be formed in a small space without dosing coagulant chemicals and without pH adjustment.

Figure 1.1 Comparison of As(V) adsorption capacities of coagulant and granular Fe(III) oxyhydroxide media
Arsenic Removal by EC

EC has been applied successfully to treat various wastewaters. Recent studies have shown that arsenic can be used for treatment of natural water and industrial effluents by EC (Balasubramanium and Madhavan 2001, Kim et al. 2002, Kumar et al. 2004, Parga et al. 2005, Hansen et al. 2006). The volume of the reactor had no influence on arsenic removal when the electrode surface area was increased proportionally with the reactor volume. The most important parameter for EC is the current density. Arienzo et al. (2002) investigated the retention of arsenic on hydrous ferric oxides generated by electrochemical using two steel electrodes. They reported more than 99% removal of As(III) using EC process. Kumar et al. (2004) reported that EC had a better As(III) removal efficiency and attributed the reason to the removal mechanism of simultaneous oxidation of As(III) to As(V) and removal by adsorption/complexation with metal hydroxides generated in the process. The literature on electrochemically oxidation of As(III) indicates that traces of free chlorine generated by the oxidation of chloride at the anode rapidly oxidize As(III) (Kim et al. 2002). If this is correct, even a trace amount of free chlorine, which is reported to be formed during electrolysis, will be an advantage for simultaneous oxidation and removal of As(III).

Previous studies conducted by researchers at the University of Houston showed that showed that regardless of pH, the Fe(III) dosage required to achieve a given MS2 virus log reduction value was always significantly less for EC compared with CC pretreatment at different pHs and iron dosages (Zhu 2004). EC not only outperformed CC for virus removal, but also removed natural organic matter (NOM) more efficiently than CC. The studies also showed that the iron coagulation process played the important role in removing virus and NOM, not the filtration process, i.e., sedimentation following coagulation–flocculation was as effective as microfiltration in removing the viruses. Based on our virus removal study, it was expected that for As removal, EC would outperform CC.

Basis of the Project

A comparison of commonly used processes, coagulation and adsorptive media shows that each process has its advantages and disadvantages. A summary of the two processes is given in Table 1.1. From Table 1.1, it is clear that even though coagulation has advantages of better adsorption capacities for arsenic and the sludge disposal not being a problem, it is not the process of choice for small systems because of process complexity, the requirement for continuous supply and dosing of chemicals, and the relatively large land area requirement. Adsorptive processes are currently preferred for arsenic treatment because of simple design and operation and a relatively small space requirement in spite of the fact that the process has disposal issues, less adsorptive capacity, and high media replacement costs. EC is an innovative process reported to oxidize As(III) to As(V) thus eliminating oxidative pretreatment. EC solves the pH adjustment and dosing problems associated with CC, but it still requires settling and/or filtration to remove the coagulated arsenic. All the processes require disposal of arsenic contaminated waste, but CC and EC potentially have less waste to dispose of due to higher loading of arsenic onto the iron oxyhydroxides.
Table 1.1
Adsorptive media and coagulation processes

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ Design and operation are simple and require little space.</td>
<td>× Regeneration cost or media replacement cost</td>
</tr>
<tr>
<td>✓ Common in POU/POE (small) systems and more preferred</td>
<td>× Adsorption capacities much less than with hydroxides formed during coagulation</td>
</tr>
<tr>
<td></td>
<td>× Disposal of spent media involves disposal issues</td>
</tr>
<tr>
<td>Advantages</td>
<td>Disadvantages</td>
</tr>
<tr>
<td>✓ Adsorption capacities are very high than the media</td>
<td>× Preferred in large scale systems only</td>
</tr>
<tr>
<td>✓ No need for media replacement</td>
<td>× Installation costs and space requirements are high</td>
</tr>
<tr>
<td>✓ The arsenic-laden sludge can be disposed directly (less than 0.5% dry</td>
<td>× Chemical storage and addition of coagulant and pH adjustment necessary</td>
</tr>
<tr>
<td>solids and pass the TCLP and WET tests)</td>
<td></td>
</tr>
</tbody>
</table>

OBJECTIVES

The overall objective of the proposed work was to determine the technical and economic feasibility of using the EC–F process for arsenic removal in comparison with CC–F. The specific objectives were to (1) establish the basic features of electrolytic oxidation of iron and formation of hydroxides during and after electrolysis, (2) verify the reported ability of EC to oxidize As(III) to As(V) and remove As(V) by adsorption onto Fe(OH)₃, (3) compare EC–F to CC–F for As(V) and As(III) removal, and (4) study the effect of competing ions on arsenic removal during EC and CC.

To attain the objectives, the following specific tasks were carried out:

1. Study the oxidation of iron rods during electrolysis and examine the ferrous and ferric ions formed during electrolysis.
2. Study the effect of pH on the in-situ formed iron hydroxides during and after electrolysis.
3. Study the removal efficiency of As(V) and As(III) in NSFI-53 challenge water by the iron EC–F and by CC–F process using ferric chloride as coagulant at pH 6.5, 7.5, and 8.5.
4. Study the oxidation of As(III) to As(V) during EC process.
5. Compare the EC–F with the CC–F results for arsenic removal.
6. Study the effect of competing ions such as silicate, and phosphate on As(V) removal in NSFI challenge water during EC and CC.
7. Study the individual effect of competing ions such as silicate, and phosphate on As(V) removal during EC and CC.
8. Study the effect of mixing time on adsorption of arsenic during CC with ferric chloride.
ANTICIPATED PRACTICAL BENEFITS OF THE PROJECT

The water supply community will benefit from the results of this innovative EC research by having access to lower-cost, more effective Fe electrode for arsenic removal. It is expected that EC will have the following advantages over CC using ferric coagulants:

1. No need to adjust pH to compensate for Fe(III) hydrolysis during EC. In the CC process using FeCl₃ adjustment of pH is required because FeCl₃ produces HCl but in the EC process, the change of pH was not expected to be significant.
2. Potentially simpler process design due to elimination of the As(III) oxidation steps in the EC process assuming that As(III) oxidation occurs during electrolysis. The EC process can remove As(III) as efficiently as As(V) if rapid oxidation of As(III) to As(V) occurs.
3. Higher arsenic capacity on iron flocs generated in EC compared with CC because of lower pH in the region of the iron anodes in the EC cell.
4. No need to dose a coagulant or pH-adjusting chemicals during EC.
5. Potentially lower treatment costs for EC due to the above advantages over CC.
CHAPTER 2
MATERIALS AND METHODS

REAGENTS AND STOCKS

All reagents used were of analytical reagent grade. Primary standards of 100 mg As/L of each species were prepared from Arsenic trioxide (As$_2$O$_3$) for As(III) and Sodium arsenate for As(V) (Na$_2$HAsO$_4$) both from Sigma Chemical Co, Mo. The As(V) and As(III) stock solutions (100 mg/L) were prepared and stored in polyethylene (glass) bottles. The stock solutions were then used for spiking the arsenic into the NSF International (NSFI) challenge water. Working standard solutions were prepared daily with proper dilution.

The following salts were used to prepare the challenge water: NaNO$_3$, NaHCO$_3$, Na$_2$HPO$_4$·H$_2$O, NaF, Na$_2$SiO$_3$·9H$_2$O, MgSO$_4$·7H$_2$O, and CaCl$_2$·2H$_2$O. All the chemicals were purchased from Sigma Chemical Co, or EM Science. Concentrated stocks were prepared from these salts and used for the preparation of fresh challenge water on the day of the experiment. The coagulant salts—ferric chloride (FeCl$_3$), ferrous ammonium sulphate (FAS), and ferrous sulphate (FeSO$_4$)—used in the studies were purchased from Sigma Chemical Co, and fresh coagulants were also prepared on the day of the experiment.

Commercially available (Earle M. Jorgensen Co., Houston, TX) inexpensive, industrial-grade (98.5% Fe) iron rods (3/16 in. dia) were used for most of the EC experiments. However, in the final experiments, reagent grade (99.995%) iron rods (0.2 in. dia) purchased from Alfa Aesar were used to compare the efficiency of industrial grade iron rods and reagent grade rods to verify that the performance was similar.

Citric/citrate buffer solution for arsenic analysis was prepared using 2 M citric acid and pH was adjusted to 5.0 using NaOH. A 4-mg/mL solution of L-cysteine (Sigma Chemical Co, Mo.) in HCl solution was used to reduce As(V) to As(III). Sodium tetrahydroborate (EM Science, Germany) solutions, also for arsenic analysis, were prepared fresh daily, and were supplemented with sodium hydroxide.

PREPARATION OF NSFI-53 CHALLENGE WATER

For all chemical and EC studies, arsenic-spiked NSFI-53 Challenge Water, or simply the “challenge water”, was used. Its composition is given in Table 2.1. However, the challenge water was used without spiking of arsenic for studies on electrolytic oxidation of iron. The challenge water contains realistic concentrations of background contaminants including silica, sulfate, phosphate, fluoride, and hardness, which are known to affect the arsenic capacity of adsorbents. Stability was not an issue with the NSFI water because it was made and used on the day of experiment and prior research at UH (Tripp 2001, Swaminathan 2005) had shown that the water was stable with respect to arsenic speciation and CaCO$_3$(s) precipitation for up to 48 hours. The pH of the synthetic groundwater was adjusted by using dilute HCl (2.5 M) or NaOH (0.25 N) solution. The required amount (0.05 mg/L) of As(III) or As(V) was spiked to the challenge water for the arsenic removal studies.
### Table 2.1
Composition of NSF1 53 challenge water

<table>
<thead>
<tr>
<th>Cation</th>
<th>MW (mg/L)</th>
<th>meq/L</th>
<th>Anion</th>
<th>MW (mg/L)</th>
<th>meq/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(^{2+})</td>
<td>40.1</td>
<td>2.00</td>
<td>HCO(_3)</td>
<td>61.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>24.3</td>
<td>1.04</td>
<td>SO(_4^{2-})</td>
<td>96.1</td>
<td>1.04</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>23.0</td>
<td>3.864</td>
<td>Cl(^-)</td>
<td>35.5</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NO(_3^-)</td>
<td>14.0</td>
<td>0.143</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>F(^-)</td>
<td>19.0</td>
<td>0.053</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PO(_4^{-})</td>
<td>31.0</td>
<td>0.0013</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SiO(_3^{-})</td>
<td>60.1</td>
<td>0.666</td>
</tr>
<tr>
<td>As(III)/(V)</td>
<td>74.9</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Σ =</td>
<td>141.57</td>
<td>6.904</td>
<td>Σ =</td>
<td>327.09</td>
<td>6.904</td>
</tr>
</tbody>
</table>

The experimental setup used for studies on deliberate rusting and iron generation efficiency operated under open atmospheric conditions is shown in Figure 2.1. The single electrode cell (cell 1) consists of an electrode chamber made of acrylic tubing (1000 mL capacity), with a porous cylindrical stainless steel cathode surrounding the iron-rod anode, both inserted from the top. The electrolytic cell was constructed to achieve a narrow gap between the central anode and surrounding cathode and this arrangement was ideal for 100% utilization of the surface of the anode and inner surface of the cathode during electrolysis. The electrolytic cell was well mixed with a help of magnetic stirrer. The anode and cathode used were industrial grade iron rod (Earle M. Jorgensen Co., Houston, TX.) and type 304 stainless steel tubing available commercially, the composition given in Table 2.2. The diameter and active surface area of the iron anode was 5 mm and 37.7 cm\(^2\) respectively. A constant direct current from a DC power supply (Hewlett hp Packard 6214A Power supply, 12 V, 1.2 Amp) was applied to the electrodes.

**Effect of Deliberate Rusting on the Iron Anode**

Preliminary studies showed a decrease in iron generation with time due to rusting of the iron electrodes with time. Thus, we tested repeatability of iron generation efficiency in the electrolytic cell (Cell 1) on successive days without cleaning the iron electrodes to determine the importance of cleanliness of the iron rods. The electrolytic cell was operated at current value of 0.2A by varying the electrolysis time (0–60 sec) at pH 6.5–8.5. The challenge water was mixed for a total of 2 min, which included the electrolysis time. After operation of the cell for 1–2 hr in a batch mode every day, the electrodes were taken out of the system and left open to the atmosphere before reuse without cleaning on the next day. The experiments were repeated daily...
over a period of 15 days without cleaning the iron rod. Water samples were collected in 0.1% HNO3 for total iron analysis (Fe(Total)) and in 0.1% HCl for analysis of ferrous (Fe(II)).

Table 2.2
Chemical composition of EC Anode and Cathode

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Anode (Industrial grade)</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (wt %)</td>
<td>98.52(*)</td>
<td>61.08 – 69.00</td>
</tr>
<tr>
<td>Carbon (wt %)</td>
<td>0.17</td>
<td>&lt; 0.08</td>
</tr>
<tr>
<td>Manganese (wt %)</td>
<td>0.78</td>
<td>1.5 – 2.0</td>
</tr>
<tr>
<td>Phosphorous (wt %)</td>
<td>0.019</td>
<td>&lt; 0.04</td>
</tr>
<tr>
<td>Sulphur (wt %)</td>
<td>0.025</td>
<td>&lt; 0.30</td>
</tr>
<tr>
<td>Silicon (wt %)</td>
<td>0.16</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Nickel (wt %)</td>
<td>0.07</td>
<td>12 – 14</td>
</tr>
<tr>
<td>Chromium (wt %)</td>
<td>0.05</td>
<td>17 – 18</td>
</tr>
<tr>
<td>Copper (wt %)</td>
<td>0.21</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>

* Calculated from difference

Source: Data from Earle M. Jorgensen Co., Houston, TX.

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The electrolytic cell with a single electrode (Cell 1) shown in Figure 2.1 was used for the studies on iron generation efficiency. NSFI challenge water with preset pH (6.5 or 7.5), was prepared and transferred into the cell. The iron electrode used in these studies was the industrial grade iron rod of composition given in Table 2.2. The results of the deliberate anode rusting/deterioration experiments showed that the performance of iron generation depended on the cleanliness of the iron-rod anodes. Furthermore, the performance of iron generation was repeatable only by pre-cleaning the iron rods on the day of the experiment. So on the day of experiments, the iron rods were thoroughly scrubbed with sand paper (Waterproof Silicon Paper Sanding Sheet 100 Grit, C-Weight) to remove all of the rust and the hydroxides that were coated on the iron rods. A pH probe was inserted from the top inside the electrolytic cell in order to observe the change in pH during the course of the electrolysis. The electrolytic cell was placed on a magnetic stirrer in order to provide uniform mixing of iron generated in the system. Low voltage direct current (DC) was supplied to the electrodes from a constant-current power supply. The electrolytic cell was operated at current values of 0.05, 0.2, 0.4, and 0.8A by varying the electrolytic generation time in the range of 0 to 60 seconds at both pH 6.5 and 7.5. The challenge water was mixed for a total of 2 min, which included the electrolytic generation time. After 2 min of mixing, samples were collected in 0.1% HNO₃ for total iron analysis (Fe(Total)) and in 0.1% HCl for analysis of ferrous (Fe(II)).
EXPERIMENTAL STUDY OF IRON GENERATION UNDER N₂ SPARGED-LOW DO CONDITION IN SINGLE ELECTRODE CELL 2

To study the effect of dissolved oxygen on the electrolytic generation of iron and for a comparison of an industrial grade iron anode with a reagent grade iron anode, experiments were conducted using an electrolytic cell with a single electrode (Cell 2) under N₂ sparged conditions. The photograph of the experimental setup is shown in Figure 2.2 and a flow diagram is shown in Figure 2.3. The electrolytic cell consists of an electrode chamber made of acrylic tube with a capacity of 450 mL, with a porous cylindrical stainless steel cathode and an iron-rod anode inserted from the top. Two different electrodes were used in these studies: the industrial grade (98.5% Fe) iron rod (Table 2.2) and reagent grade (99.995% Fe) iron rod (Alfa Aesar, MA). The diameter and active surface area of the iron anodes were 5 mm and 18 cm², respectively. The iron rods were thoroughly scrubbed with sand paper (Waterproof Silicon Paper Sanding Sheet 100 Grit, C-Weight) to remove all of the rust and the hydroxides that were coated on the iron rods if needed. NSFI challenge water with pH adjusted to 6.5 or 7.5 was prepared and transferred into the cell. Initially a stopper was inserted in the place of iron electrode in order to prevent the oxidation of iron electrode while the unit was being purged with N₂. The challenge water was uniformly mixed by N₂ sparging and magnetic stirring for 45 minutes, and then the stopper was taken out. The iron electrode was then inserted and sparged for another 15 minutes. After sparging for total of 1 hour, the electrode cell was operated at different current values of 0.05, 0.2, and 0.8 A by varying the generation time (0–60 seconds). During the iron-generation and mixing phase, the challenge water was mixed for a total of 2 minutes, which included the electrolytic generation time. After mixing, samples for analysis were collected from the sample collection outlet into 0.1% HCl for analysis of ferrous (Fe(II)), and in 0.1% HNO₃ for analysis of total iron (Fe(Total)). The experiments were repeated for both reagent grade and industrial grade iron rods under similar conditions.
Figure 2.2 Photograph of Cell 2, a single electrode cell operated under \( N_2 \) purged condition with either an industrial grade (98.5\% Fe) or reagent grade (99.995\% Fe) iron-rod anode. Current values in the range of 0.05 to 0.8 A were used.

Figure 2.3 Schematic diagram of cell 2, a single electrode cell operated under \( N_2 \) purged condition with either an industrial grade (98.5\% Fe) or reagent grade (99.995\% Fe) iron-rod anode. Current values in the range of 0.05 to 0.8 A were used.
STUDY OF THE OXIDATION OF Fe(II) TO Fe(III) DURING COAGULATION EXPERIMENTS USING FERROUS AMMONIUM SULPHATE

Coagulation studies with ferrous ammonium sulphate were performed to determine the extent of oxidation of ferrous iron by dissolved oxygen and the influence of pH on ferrous oxidation. NSFI Challenge water was prepared, and the pH of the challenge water was adjusted to the desired pH (6.5 or 7.5) with dilute HCl and/or NaOH. The coagulant stock, 1.0 g/L Fe$^{2+}$ was prepared using ferrous ammonium sulphate (FAS). The coagulation study was conducted using conventional jar tests. A Phipps and Bird six-position, flat-blade stirring apparatus with 2-L square glass jars was used. Before each experiment, 1-L of challenge water adjusted to a specific pH was added to each jar. The coagulant doses used in these studies were 2.5, 7.5, and 15 mg/L Fe$^{2+}$ in the case of pH 6.5, while at pH 7.5 doses of 2.5, and 7.5 mg/L were used. With the stirring apparatus preset at the rapid-mix speed of 100 rpm, the stirring apparatus was started and a predetermined amount of coagulant was added to each jar. After addition of the Fe$^{2+}$ dose, samples were collected at regular intervals in 0.1% HCl for analysis of Fe$^{2+}$ over a period of time. The experiments to 95% Fe$^{2+}$ oxidation ran for about one hour at pH 7.5 and for more than 24 hours in the case of pH 6.5. During mixing, the pH of challenge water was checked periodically and adjusted to the initial pH by adding dilute HCl or NaOH, as necessary.

THREE-CELL EC UNIT

A photograph of the three-cell EC unit being used for most of the research is shown in Figure 2.4 and a schematic diagram of the EC unit with three anode-cathode pairs is shown in Figure 2.5. This unit is of the same design as the unit used in previous research at UH (Zhu et al. 2005). The EC unit consisted of a flow-through electrode chamber with three iron-rod anodes and three flow-through cylindrical stainless steel cathodes made from SS tubing with holes drilled in it. The fluid volume of the EC unit was 490 mL including the recirculation loop. By adjusting the operating current and the time for current generation the desired iron concentration was obtained. The chemical compositions of the anode and cathode metals are same as given in Table 2.2.

As can be seen in Figure 2.5, the recycle pump discharged into the annular area between the cathode and anode of each of the three cathode-anode pairs in order to flush the anode where iron coagulant was continuously generated. Challenge water spiked with arsenic entered into the center of the unit from the top, and was recirculated through the fluid volume EC chamber by the recirculating pump. Constant DC current was provided by a low-voltage power supply.

Operational Efficiency of the Three-cell EC Unit

The three-cell EC unit was tested for electrode passivation (rusting) effects and the iron generation efficiencies. NSFI challenge water without arsenic spiking was used for these studies. The experiments were carried out both on batch and as well in a continuous mode. On a batch mode study, the EC unit was operated at current of 0.2 A with a generation time of 0 to 3 minutes on consecutive days without cleaning the iron rods to study effect of rusting and anode surface deterioration (passivation). After the generation time, the water was circulated for additional minute in order to provide uniform mixing. Samples for analysis of total iron generated by EC unit were taken and acidified with 0.1% HNO₃. During studies of electrode
deterioration in continuous mode, the EC unit was operated at current values of 0.1 and 0.2 A with an inlet flow of 300 ± 20 mL/min. Samples for analysis of total iron generated by EC unit were taken at regular intervals from the outlet of the EC unit and acidified with 0.1% HNO₃.

Figure 2.4 Photograph of three-cell EC unit with recirculation loop

Figure 2.5 Schematic diagram of batch bench-scale EC system
After deliberate rusting/deterioration of the iron anodes, the three-cell EC unit was tested for its ability to generate iron in proportion to the applied current. The EC unit with precleaned iron rods was operated at different current values of 0.05 and 0.2 A in a batch mode. Samples for analysis of total iron generated by EC unit were taken and acidified with 0.1% HNO₃. Similarly the iron generation was carried out in a continuous mode with applied currents of 0.1 and 0.2A and with an inlet flow rate of 300 ± 20 mL/min. Samples for analysis of total iron generated by EC unit were taken at regular intervals from the outlet of the EC unit and acidified with 0.1% HNO₃.

**EC–F PROCEDURE FOR ARSENIC REMOVAL**

The results of the deliberate anode rusting/deterioration experiments showed that the performance of iron generation depended on the cleanliness of the iron-rod anodes. Furthermore, the performance of iron generation was repeatable only by pre-cleaning the iron rods on the day of the experiment. So on the day of experiments, the iron rods were thoroughly scrubbed with sand paper (Waterproof Silicon Paper Sanding Sheet 100 Grit, C-Weight) to remove all of the rust and the hydroxides that were coated on the iron rods. (Note: During typical EC in an actual pilot- or full-scale EC process, it is not necessary to clean the electrodes daily.)

NSFI Challenge water spiked with 50 µg/L of As(III) or As(V) was prepared, and the pH of the challenge water was adjusted to the desired pH in the 6.5 to 8.5 range by using dilute HCl or NaOH solutions. The challenge water was then poured into the EC unit from the top. All experimental arsenic coagulation data from the EC unit was collected while operating in the batch mode, i.e., the EC unit was filled with NSFI water spiked with arsenic and turned on for a specific generation time depending on the dose of iron to be generated, which was in the range of 0 to 5 mg/L Fe in the case of As(V) removal and 0 to 10 mg/L Fe in the case of As(III) removal. The EC unit was then operated until the desired target amount of iron (mg/L) was generated by varying the current and generation time. During current generation, the water was recirculated at about 500 mL/min to ensure that the electrodes remained free of surface deposits and that the Fe generated was quickly released from the surface and hydrolyzed. The challenge water was recirculated for a total of 2 min, which included the iron generation time. After EC, the water was drained into a beaker. There was no settling in this process. A portion of the water sample was immediately collected using a polyethylene syringe, and filtered through a 0.2-μm pore size filter into 0.1% concentrated nitric acid for measurement of total arsenic. For arsenic(III) measurement, 10-mL filtered sample was collected in a 15-mL centrifuge tube containing 0.432 mL of 2 M Acetic acid and 0.134 mL of 0.1 M EDTA as required by the recently developed field speciation method for inorganic arsenic speciation (Clifford et al. 2004). Another set of samples (unfiltered) were acidified with 0.1% nitric acid or 0.1% HCl, respectively for analysis of total iron or ferrous iron generated in the EC unit. Figure 2.6 shows the steps involved in the EC–F process except that the jar tester is replaced with the EC unit.
C–F PROCEDURE

NSFI Challenge water spiked with 50 µg/L of As(III) or As(V) was prepared, and the pH of the challenge water was adjusted to the desired pH in the 6.5 to 8.5 range by using dilute HCl or NaOH solutions. Since the coagulant ferric chloride used were highly acidic, they reduced the pH of the challenge water after dosing, thus it was necessary to bring the challenge water to the initial pH after addition of coagulant. Pre-titrations of the challenge water dosed with varying amounts of coagulant were performed to determine the amount of sodium hydroxide (NaOH) solution required to achieve the desired equilibrium pHs at the different dosages.

The coagulation study was conducted using batch-scale jar tests. A six-position flat-blade stirring apparatus manufactured by Phipps and Bird, USA was used. 2-L square glass jars were used for each experiment. Before each experiment, 1-L of challenge water adjusted to a specific pH (6.5, 7.5, or 8.5) was added to each jar. The coagulant doses used were in the range of 0 to 5 mg/L Fe$^{3+}$ and 0 to 10 mg/L Fe$^{3+}$, respectively for As(V) and As(III) removal. With the stirring apparatus preset at the rapid mix speed of 100 rpm, the stirring apparatus was started and a predetermined amount of coagulant was added to each jar. Immediately after addition of coagulant, the predetermined amount of NaOH solution (0.25 N) was added to restore the challenge water to the initial pH. The jars were mixed at 100 rpm for 2 min. During mixing, the pH of challenge water was checked and adjusted to the initial pH by adding more NaOH, if needed. Figure 2.6 shows the steps involved in the C–F process for arsenic removal.

After mixing, water samples were then collected immediately using a 30-mL polyethylene syringe, and then filtered through a 0.2-µm pore size filter. There was no settling in this process. Samples (30-mL) were collected in 50-mL centrifuge tubes and acidified with 30 µL of concentrated nitric acid to measure total arsenic, As(Tot). For arsenic(III) measurement, 10-mL of filtered sample was collected in a 15-mL centrifuge tube containing 0.432 mL of 2 M Acetic acid and 0.134 mL of 0.1 M EDTA as required by speciation method for inorganic arsenic speciation (Clifford et al. 2004).
Figure 2.6 C–F procedure for arsenic removal with NSFI challenge water

EFFECT OF COMPETING IONS ON ARSENIC REMOVAL

Chemical and EC experiments discussed above were repeated for following compositions of challenge water at pH 6.5, 7.5, and 8.5 to determine the effect of competing ions on arsenic adsorption.

- NSFI-53 without silica (i.e., Si = 0 mg/L, PO₄-P = 40 μg/L)
- NSFI-53 without phosphate (i.e., P = 0 μg/L, Si = 20 mg/L)
- NSFI-53 without silica and phosphate (i.e., Si = 0 mg/L and PO₄-P = 0 μg/L)

INSTRUMENTATION

The arsenic analyses were carried out by flow injection hydride-generation atomic absorption spectroscopy (FI–HG–AAS) using a Perkin–Elmer (Model Zeeman 5000) atomic absorption spectrometer (AAS) equipped with an electrodeless discharge lamp (EDL) operated at 8W from an external power supply. The AAS was coupled with a Perkin–Elmer Flow Injection (FIAS-100) unit for hydride generation for the determinations of As(III) and As(Tot). Detail descriptions of the instrumental conditions are given in Table 2.3. The samples for As(Tot) and speciated As(III) were analyzed by FI–HG–AAS. However, during the course of the study, As(Tot) was analyzed by both FI–HG–AAS and Inductively coupled plasma mass spectroscopy (ICP–MS) (Sciex Elan 6000, Perkin Elmer, Norwalk, CT) equipped with a Gem-Tip cross-flow
nebulizer, a four-channel peristaltic pump (Gibson, Model Minipuls III) and an Autosampler (As-90, Perkin Elmer, Norwalk, CT). Details of the instrumental set up are given in Table 2.4.

Table 2.3
Experimental conditions for the determination of As(III) and As(Tot) by flow injection hydride-generation atomic absorption spectroscopy

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Perkin–Elmer (Zeeman 5000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lamp</td>
<td>8 W EDL</td>
</tr>
<tr>
<td>Wavelength</td>
<td>193.7 nm</td>
</tr>
<tr>
<td>Slit</td>
<td>0.7 nm(low)</td>
</tr>
<tr>
<td>Sample volume</td>
<td>500 µL</td>
</tr>
<tr>
<td>HCl concentration</td>
<td>0.02 M</td>
</tr>
<tr>
<td>Citric/citrate buffer (pH 5.0)</td>
<td>2.0 M</td>
</tr>
<tr>
<td>HCl/citrate buffer flow rate</td>
<td>8 ml/min</td>
</tr>
<tr>
<td>NaBH₄ concentration (for As(Tot))</td>
<td>0.4% in 0.2% NaOH</td>
</tr>
<tr>
<td>NaBH₄ concentration [for As(III)]</td>
<td>0.2% in 0.05% NaOH</td>
</tr>
<tr>
<td>NaBH₄ flow rate</td>
<td>5 ml/min</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Argon</td>
</tr>
<tr>
<td>Carrier gas flow rate</td>
<td>60–70 ml/min</td>
</tr>
<tr>
<td>Quartz cell temp</td>
<td>~900°C, Electrically heated</td>
</tr>
</tbody>
</table>

Table 2.4
Parameters for ICP–MS operation

<table>
<thead>
<tr>
<th>ICP system</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power</td>
<td>1300 W</td>
</tr>
<tr>
<td>Sampler and skimmer</td>
<td>Nickel</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>Cross-flow</td>
</tr>
<tr>
<td>Spray chamber</td>
<td>Double-pass</td>
</tr>
<tr>
<td>Ar-plasma</td>
<td>15.0 (L/min)</td>
</tr>
<tr>
<td>Nebulizer-Ar</td>
<td>0.95–1.0 (L/min)</td>
</tr>
<tr>
<td>Analyte</td>
<td>75As</td>
</tr>
<tr>
<td>For Correction</td>
<td>77Se and 78Se</td>
</tr>
<tr>
<td>Internal standard</td>
<td>127Te</td>
</tr>
</tbody>
</table>

The exact concentrations of the total iron in the coagulant stock and in the EC samples were determined using a Perkin Elmer AAnalyst 300 Atomic Absorption Spectrometer. The AAnalyst 300 is a double-beam atomic absorption system capable of performing flame, furnace, and mercury/hydride single or multi-element analyses. The ferrous concentrations were analyzed by UV spectrophotometry using the 1,10 phenanthroline method.
TOTAL IRON AND FERROUS ANALYSIS

The iron concentrations in the coagulant stock solutions and samples collected from the EC unit were analyzed for total iron (Fe(Tot)) using flame atomic absorption spectroscopy (Flame AA–Analyst 300, Perkin–Elmer Corporation, CT, USA) according to Standard Methods (Clesceri et al. 1998). Five standards were prepared in the range of 0 to 10 mg/L iron, and the standards were periodically checked during analysis. Samples were diluted to the range if needed, and analyses were done in triplicate. The iron concentration of the sample was then obtained from the calibration curve, which was all automated by the software associated with the instrument.

The ferrous iron concentrations were determined using a UV Spectrophotometer with a measurement range of 0–3 mg/L Fe^{2+} using the 1,10 phenanthroline method (Vogel 1978). The required amount of sample preserved in 0.1% HCl was mixed with the required amount of sodium acetate buffer (predetermined by simulation of the experiment) to bring the pH in the range of 3.5 ± 1.0. The required amount of 0.1% 1,10-phenanthroline was then added, which produced a reddish orange color with an absorbance proportional to the Fe^{2+} concentration in the sample. Based on the color intensity, the Fe^{2+} concentration was determined by the spectrophotometer. Standards prepared in the range were periodically checked during analysis.

TOTAL ARSENIC AND ARSENIC(III) ANALYSIS USING FI–HG–AAS

Flow Injection Hydride–Generation Atomic Absorption Spectroscopy (FI–HG–AAS)

To determine total arsenic, samples were treated with L-cysteine in 2 HCl. The samples were kept for 15 minutes at room temperature for the reduction of As(V) to As(III) and then diluted to such a volume as to maintain the concentrations of L-cysteine, and acid to 4 mg/mL, and 0.02 M, respectively. The arsenic concentration was measured by FI–HG–AAS against arsenic standards prepared as samples. Five standards were prepared in the range of 0 to 6 μg/L arsenic, and the standards were periodically checked during analysis. Samples were diluted to the range of 1 to 6 μg/L arsenic. The arsenic concentration of the sample was then obtained from the calibration curve, derived by analysis of the absorbance of the five different arsenic standards. NIST (National Institute of Standards and Technology) 1640 sample was analyzed during the course of analysis as a reference. Reduced arsenic sample was injected by means of a rotary valve fitted with a 500 μL sample loop into the stream of 0.02 M HCl solution which was flowing at 8 mL/min. The injected sample together with carrier solution, met subsequently with a continuous stream of 0.4% sodium tetrahydroborate in 0.2% NaOH flowing at 5 mL/min. After mixing with sodium tetrahydroborate, the generated hydride (AsH3) subsequently entered into the gas-liquid separator. Inside this apparatus a continuous flow of argon carrier gas (70–80 mL/min) carried the hydride to the quartz tube fitted on an electrically heated heater at 900 ºC.

Arsenic adsorption was measured at 193.7 nm. At least triplicate measurements were made for each sample and standard. For the determination of As(III) in the presence of As(V), the samples were not treated with L-cysteine and the carrier HCl solution was replaced by 2 M citric/citrate buffer of pH 5.0. Arsine was generated using 0.2% sodium tetrahydroborate in 0.05% NaOH. Under this condition only As(III) generates AsH3 and As(V) concentration is not measured. The As(V) was then calculated from the difference of As(Total) and As(III).
Inductively Coupled Plasma Mass Spectroscopy (ICP–MS)

Due to instrumentation problems with FI–HG–AAS for a short period of time, ICP–MS was used to measure the arsenic concentration. The Perkin Elmer Sciex Elan 6000 ICP–MS was operated at 1300 W RF power using cross-flow nebulizer and 1 L/min nebulizer argon gas flow rate. All analyses were made in triplicate. Standards were prepared in the range of 0 to 50 μg/L arsenic. In ICP–MS, chloride interferes in the determination of arsenic due to formation of isobaric $^{40}$Ar$^{37}$Cl$^+$ molecular ions, which overlap at m/z with monoisotopic $^{75}$As. The chloride interference was corrected using a standard mathematical correction equation built in the program. NIST (National Institute of Standards and Technology) 1640 sample was analyzed during the course of analysis in order to check the accuracy of the instrument.

EQUILIBRIUM ADSORPTION ISOTHERMS FOR COMPARING COAGULATION EFFECTIVENESS

Equilibrium isotherms are constant temperature plots of the mass of contaminant adsorbed per unit mass of adsorbent (e.g., μg As(V)/mg Fe(III)) versus the concentration of the contaminant in the liquid phase (e.g., μg As(V)/L). In order to use isotherms to estimate the mass adsorbed, equilibrium must be reached between the sorbent and the sorbate. Although the Freundlich isotherm for a particular adsorbate–adsorbent interaction has a theoretical basis which assumes a Boltzmann distribution of site energies and multi-layer adsorption, we generally fit the experimental data to the Freundlich equation and determine the best fit values for K and 1/n by curve fitting techniques:

$$q_e = KC_e^{1/n}$$  \hspace{1cm} (2.1)

where  
$q_e$ = Mass of arsenic adsorbed per mass of the adsorbent, μg/mg  
K = Freundlich constant indicative of adsorption capacity of adsorbent, L/mg  
$C_e$ = Equilibrium concentration of arsenic in the liquid phase, μg/L  
1/n = Freundlich exponent, a constant

Plotting the Freundlich isotherms for various pH and competing ion conditions allows a quick comparison of the effectiveness of arsenic removal under the various pH and competing ion conditions. The isotherms also allow us to compare the effectiveness of Fe(II) vs Fe(III) coagulation for arsenic removal.
CHAPTER 3
ELECTROLYTIC OXIDATION OF IRON

INTRODUCTION

An electrolytic cell is an electrochemical cell in which the energy from an applied voltage is used to drive an otherwise non-spontaneous reaction. Electrolytic cells are composed of an electrolysis chamber, electrolyte, cathode, and anode. The electrolytes and the electrodes in the cell are inert unless driven by external voltage into a redox reaction. Pure water is a very poor conductor of electricity, and one has to have ions in solution to have a significant current flow. In general, two kinds of electrode reactions are possible across the electrode. Ions in the solution actively react across the electrode and become discharged, which is common with inert electrodes. The second type is the self destructive electrode, e. g, an iron rod, which is of interest in this research which studies the electrolytic oxidation of an iron anode to produce iron in solution for coagulation.

Inert electrodes are electrodes, which do not undergo any change during electrolysis. Platinum and carbon are frequently used when inert electrodes are required. Self destructive electrodes are electrodes which undergo chemical change during electrolysis. Iron rod and aluminium rods are examples of self destructive electrodes. At the anode, electrons are produced during oxidation reaction, which migrate to the cathode. This reaction can be reversed to produce electricity in fuel cells. Electrolysis is an important industrial process that is used for the:

1. extraction of metals, notably aluminium, magnesium, and sodium,
2. preparation of halogens, notably chlorine, and
3. refining of metals, such as copper and zinc.

English chemist and physicist Michael Faraday developed the first scientific understanding of fundamental relations in electrochemical processes. He discovered that the amount of a substance produced or consumed in an electrochemical process depends quantitatively on the amount of electricity that flows as the reaction takes place. The amount of electricity (coulombs or ampere-seconds) that passes through is equal to the electrical current (amperes) multiplied by the time (typically seconds). Faraday discovered several relationships that apply to the quantitative measure of electricity. His laws can be summarized using the modern term for quantities of electricity named after him, the faraday. One faraday (1 F) of electricity is equal to one mole of electrons, which is equal to 96,485 coulombs of electricity. If one faraday of electricity flows through an external circuit, \(6.022 \times 10^{23}\) electrons have passed through. Faraday's laws may be condensed into one statement: during an electrochemical process, the passage of one faraday through a circuit results in the transfer of one mole of electrons at the cathode and the transfer of one mole of electrons at the anode. Because the relationship between numbers of moles and the mass of chemical substances involved in a chemical reaction is known, determination of the mass of a material which is oxidized at the anode or reduced at the cathode in an electrochemical cell can be determined provided the number of electrons transferred for each atom of the substance that undergoes the chemical reaction is known. Faraday's laws allow us to determine the amount of electricity (the number of coulombs) required to obtain the electrochemical conversion of a known quantity of a substance.
Given a particular current flow in amperes or coulombs per second, determination of the time required to produce a certain amount of a substance electrochemically can be calculated if the molecular weights of the substances and numbers of electrons required to oxidize or reduce each molecule of the substances are known.

**EFFECT OF ELECTRODE PASSIVATION ON GENERATION CAPACITY**

The iron generation experiments carried out for a period of 15 days without cleaning the iron rod in the electrolytic cell (Cell 1) with single electrode showed that the performance of iron generation decreased with increase in time (day). The corrosion of the iron rod is clearly visible from the photographs (Figure 3.1) of the iron rods over a period of 13 days. The iron rod cleaned on the first day was free of rust and had a shiny silvery color. But as can be seen, with increase in time and usage of the iron rod during electrolysis, the iron rod began to oxidize. The increase in corrosion and the change in brownish red color was due to the formation of iron hydroxides at the surface. After 13 days, the iron rust at the surface was so brittle that upon touching the rod, the rust flaked off easily.

The performance of rusted rods is compared with a clean rod in Figure 3.2. It can be seen that with an uncleaned rod that had been used previously to generate iron, the mass of total iron (Fe(Total)) generated was much lower compared with the performance of a cleaned rod on the day it was cleaned, i.e., on the first day. The performance of iron generation continuously decreased with increase in time (day) when the rod was used without cleaning. The decrease in iron generation efficiency resulting from the formation of iron hydroxides is called “electrode passivation”. By cleaning the iron rods on the day of the experiment, the performance of iron generation was repeatable and electrode passivation avoided. So, on the day of experiments, the iron rods were thoroughly scrubbed with sand paper to remove all of the rust and the hydroxides coating the surfaces. The process of cleaning the iron rods was carried out in all the iron generation efficiency and EC experiments, and the effects of electrode passivation were avoided.

Avoiding electrode passivation is a major operational issue during EC. Passivation of aluminium electrodes has been widely reported in the literature (Nikolaev et al., 1982; Novikova et al., 1982; Osipenko and Pogorelyi 1977). The latter also observed that during EC with iron electrodes, deposits of calcium carbonate and magnesium hydroxide were formed at the cathode and an oxide layer was formed at the anode. Nikolaev et al. (1982) investigated various methods of preventing and/or controlling electrode passivation including:

1. Changing polarity of the electrode,
2. Hydromechanical cleaning,
3. Introducing inhibiting agents, and
4. Mechanical cleaning of the electrodes

According to these researchers, the most efficient and reliable method of electrode maintenance was to mechanically clean the electrodes periodically.
Figure 3.1 Increase in corrosion and hydroxide formation on the surface of the iron rod with increase in time

Figure 3.2 Effect of electrode passivation on iron generation capacity in the electrolytic cell with single electrode
THEORETICAL IRON GENERATION BASED ON FARADAY’S LAW

Faraday’s law of electrolysis consists of 2 separate laws stated by Michael Faraday in 1834. Faraday’s 1st Law of Electrolysis states “The mass of a substance produced at an electrode during electrolysis is proportional to the number of moles of electrons (the quantity of electricity) transferred at that electrode”. Faraday’s 2nd Law of Electrolysis states “The number of Faradays of electric charge required to discharge one mole of substance at an electrode is equal to the number of "excess" elementary charges on that ion”. The amount of any substance dissolved or deposited in electrolysis is proportional to the total electric charge passed. The amounts of different substances dissolved or deposited by the passage of the same electric charge are proportional to their equivalent weights. The amount of electric charge carried by one mole of electrons (6.02 x 10²³ electrons) is called the faraday and is equal to 96,485 coulombs. In equation form, the theoretical amount of species (e.g., iron) that will be generated as a function of current and generation time can be calculated using Faraday’s Law as expressed by Equation 3.1.

\[ m = \frac{Q \times M}{Z \times q \times N_A} = \frac{Q \times M}{Z \times F} = \frac{I \times t \times M}{Z \times F} \]  

where  
- \( m \) is the mass in grams of the species formed at a specific current,  
- \( Q \) is the total electric charge that passes through the solution in coulombs \((Q=I*t)\),  
- \( I \) is the current applied in Amperes,  
- \( t \) is total amount of time of the electrolysis in seconds,  
- \( M \) is the molar mass of the substance in grams per mole \((55.85 \text{ g/mol for Fe})\),  
- \( Z \) is the number of electrons transferred per atom,  
- \( F \) is Faraday’s constant \((96,485 \text{ Coul/eq})\) \((F = q*NA)\),  
- \( q \) is the electron charge \(1.602 \times 10^{-19} \text{ Coul per electron}\),  
- \( N_A \) is Avogadro's number \(= 6.022 \times 10^{23} \text{ ions per mole}\).

The experiments were performed with a current \( I \) in the range of 50–800 mA, and the electrolytic generation time \( t \) in the range of 0 to 60 seconds in an electrolytic cell (single electrode) with industrial-grade iron rod. The electrolytic oxidation of iron \((\text{Fe}_0)\) would result in the generation of ferrous ion \((\text{Fe}^{2+})\) or ferric ion \((\text{Fe}^{3+})\) theoretically. The possible electrolytic oxidation reactions of iron and the standard electrode potentials vs Standard Hydrogen Electrode (SHE) are given in Equations 3.2 to 3.4. When the potential of electrode is moved from its current value towards more positive potentials, the substance that will be oxidized first is the reductant in the couple of least \( E^0 \). So theoretically the electrolytic oxidation of iron rod would result in ferrous ion generation. However these predictions are based on thermodynamic considerations (i.e., reaction energetics) and slow kinetics might prevent a reaction from occurring at a significant rate in a potential region where the \( E^0 \) would suggest the reaction was possible and vice versa.

\[ \text{Fe}^0 \Leftrightarrow \text{Fe}^{2+} + 2e^-; \ E^0 = 0.440 \text{ V} \]  
\[ \text{Fe}^{2+} \Leftrightarrow \text{Fe}^{3+} + e^-; \ E^0 = -0.771 \text{ V} \]
So the electrolytic generation of ferrous ion would result in $Z = 2$, while ferric ion generation would result in $Z = 3$ in Faraday’s law. The theoretical operating curves or the iron generation capacity of the electrolytic cell for a applied current of 0.05, 0.2, 0.4, and 0.8 A based on Faraday’s law when $Z$ is equal to 2 and 3 are shown in Figure 3.3. The theoretical mass of iron that will be generated has been normalized to 1 L of water in Figure 3.3. It can be observed from figure that the total iron generation would be 1.5 times higher if ferrous ($\text{Fe}^{2+}$) is generated at the anode in comparison to ferric ($\text{Fe}^{3+}$) for any particular generation time and current.

There is no common and concrete conclusion on the electrolytic oxidation of iron and the hydroxides formed from past studies. The literature does not give enough evidence and information on whether the electrolytic oxidation of iron results in the formation of $\text{Fe}^{2+}$ or $\text{Fe}^{3+}$. A wide variety of opinions exist in the literature for the key mechanisms at the anode and there is a lack of understanding of the system and hence the ability to accurately predict performance. Past studies have reported the electrolytic oxidation of iron anode to produce ferric ions (Balasubramanian and Madhavan 2001, Parga et al. 2005, Kobya et al. 2006) and some have reported the production of ferrous ions (Osipenko and Pogorelyi 1977, Mollah et al. 2001, Hansen et al. 2006).

Although their have been several studies on the electrolytic oxidation of iron anode and removal of contaminants, there is very little literature which explicity compares the experimental iron generated to theoretical capacity (Faraday’s law) based on ferrous/ferric generation and states the current efficiency with respect to ferrous/ferric generation. So there is also a lack of understanding on the mechanism of oxidation of iron during and after electrolysis and the factors that affect the oxidation.
COMPARISON OF EXPERIMENTAL IRON GENERATION TO THEORETICAL IRON GENERATION CAPACITY BASED ON FARADAY’S LAW IN THE ELECTROLYTIC CELL WITH SINGLE ELECTRODE

The electrolytic cell with a single electrode (industrial grade iron anode) was operated at different currents (0.05, 0.2, 0.4, and 0.8 A) and for a different electrolytic generation times (0 to 60 sec) with NSFI challenge water at pHs 6.5 and 7.5.

Comparison of Experimental and Theoretical Iron Generation at pH 6.5

The total iron generated experimentally at pH 6.5 is compared to that the theoretical iron generation capacity (based on $Z = 2$ and $Z = 3$) in Figures 3.4 and 3.5. Figure 3.4 compares the iron generated experimentally with that of theoretical iron generation based on $Z = 2$ and 3 for an applied current of 0.05 and 0.2 A at pH 6.5. It can be observed that the iron generation experimentally perfectly correlated with theoretical iron generation capacity for number of electrons transferred per atom equal to two ($Z = 2$). Similarly the comparison of iron generated experimentally with that of theoretical iron generation for an applied current of 0.4 and 0.8 A shown in Figure 3.5, illustrates that the experimental observation is similar to that of the theoretical iron generation capacity calculated from Faraday’s law for number of electrons transferred is equal to two ($Z = 2$).

![Figure 3.4 Comparison of iron generated in the electrolytic cell with industrial grade iron rod at pH 6.5 to that of theoretical iron generation ($Z = 2$ and $Z = 3$) for applied current of 0.05 and 0.2 A](image-url)
Comparison of Experimental and Theoretical Iron Generation at pH 7.5

Similarly, the iron generated experimentally at pH 7.5 is compared with theoretical iron generation (based on $Z = 2$ and $Z = 3$) in Figures 3.6 and 3.7 for current values of 0.05/0.2 A and 0.4/0.8 A, respectively. It can be observed from the figures that the iron generation experimentally was the same as the theoretical iron generation capacity calculated from Faraday’s law for $Z = 2$. Although Fe$^{2+}$ was the species formed at the anode; oxidation of Fe$^{2+}$ to Fe$^{3+}$ by dissolved oxygen (DO) caused a significant reduction in Fe$^{2+}$ concentration at the end of 2 min of mixing, which is discussed in detail later in this chapter.
Figure 3.7 Comparison of iron generated in the electrolytic cell with industrial grade iron rod at pH 7.5 to that of theoretical iron generation (Z=2 and Z=3) for applied current of 0.4 and 0.8A

*Experimental values are averages of experimental values at pH 6.5 and pH 7.5

Figure 3.8 Comparison of iron generated in the electrolytic cell with industrial grade iron rod to that of theoretical iron generation (Z=2) for applied current in the range of 0.05 to 0.8A

In summary, the total iron generated experimentally was the same as theoretical iron generation based on Faraday’s law when the number of electrons transferred per atom (Z) was equal to two. Figure 3.8 compares the experimental iron generation (average of iron generation data at pH 6.5 and 7.5) with the theoretical iron generation capacity based on Faraday’s law with...
number of electrons transferred to be equal to two \((Z = 2)\). As can be seen the experimental observations perfectly correlated with the theoretical iron generation regardless of pH. Therefore it is clear that Fe(II) is generated at the anode and that the iron generation efficiency is 100\% as a function of applied current when number of electrons transferred is two \((Z=2)\).

**BASIC REACTIONS DURING ELECTROLYSIS**

So, based on the theoretical and experimental observations of total iron production in the EC unit, it is clear that Fe\(^{2+}\) is the species that is formed at the anode. However, the reactions that occur during and after electrolytic generation of Fe\(^{2+}\) are very complex and are very much influenced by pH and DO level of the challenge water. The basic electrochemical reactions occurring in the electrolytic cell are shown in Figure 3.9. The electrolytic oxidation of iron rod (Fe\(^0\)) at the anode results in the generation of ferrous ions (Fe\(^{2+}\)), while the electrolytic reduction of water results in the production of hydrogen gas at the cathode. The electrolytic reduction of water also results in the formation of hydroxides which would indeed result in an increase in pH which was observed during the course of electrolysis. However there was no drastic pH change at the end of 2 minute of mixing because the protons resulting from hydrolysis of Fe\(^{2+}\) and Fe\(^{3+}\) ions (produced by subsequent oxidation of Fe\(^{2+}\) by DO depending on pH) were consumed by the hydroxide ions produced at the cathode during reduction of water to form Fe hydroxide complexes. The variation in pH from the initial pH depended on the rate of the reaction between hydroxides and the iron species. In general the final pH at the end of 2 min of mixing nearly remained unchanged in the case of pH 7.5, while there was an slight increase \((\text{up to +0.25 units})\) from the initial pH of 6.5. The final pH in the case of initial pH being 8.5 was generally lower within 0.2 units of 8.5.

The solubility products, \(K_{sp}\), values, for the Fe (II) and Fe(III) hydroxides and the metal hydrolysis reactions are summarized in Table 3.1 along with the estimated solubility of the metal (Fe\(^{2+}\) or Fe\(^{3+}\)) at pH 6.5, 7.5, and 8.5. Metal solubility = \(K_{sp}/[OH^-]^Z\) where “Z” is the number of hydroxide molecules produced in the hydrolysis reaction. It can be observed from the table that Fe(II) is relatively highly soluble while its oxidant species Fe(III) is virtually insoluble. So the Fe(II) hydroxides formed easily passes through a 0.2 \(\mu\)m filter and would not adsorb the inorganic contaminants in the adsorption process. However the Fe(III) hydroxides are relatively stable and would adsorb the inorganic contaminants and retain them on the filter.
Figure 3.9 Basic Electrolysis Reactions in the Electrolysis cell

Table 3.1 Relevant Hydrolysis and Solubility Reactions of Fe(II) and Fe(III)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Hydrolysis and Solubility Reactions</th>
<th>-log $K_{sp}$</th>
<th>~Metal Solubility, mol/L @ pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.5</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>Fe(OH)$_3$($s$) $\leftrightarrow$ Fe$^{3+}$ + 3OH$^-$</td>
<td>37.4</td>
<td>$10^{-14.9}$</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>Fe(OH)$_2$($s$) $\leftrightarrow$ Fe$^{2+}$ + 2OH$^-$</td>
<td>14.3</td>
<td>5</td>
</tr>
</tbody>
</table>

Even though the metallic iron ($Fe^0$) was oxidized to ferrous state ($Fe^{2+}$) at the anode, an interesting observation was made with regards to the $Fe^{2+}$ that was remaining depended on pH at the end of 2 minutes of mixing. The ferrous ions/hydroxides ($Fe^{2+}$) remaining were 70–90, 10–45, and $\approx$0% at pH 6.5, 7.5, and 8.5, respectively. So it was clear that the ferrous ions/hydroxides formed were oxidized by the DO in the challenge water and the oxidation rate increased with increase in pH. This is consistent with the studies on oxidation of Fe(II) by oxygen, which have found that the oxidation rate ($d[Fe^{II}]/dt$) increases 100-fold for each unit increase in pH (Stumm and Lee 1961, Singer and Stumm 1970, Stumm and Morgan, 1981). A more detailed discussion on the oxidation of Fe(II) by DO in the EC cell with variation in current is given later in this chapter.

The Fe(II) produced in the EC unit undergoes complete oxidation to form Fe(III) hydroxides at pH 8.5. At pH 7.5, the oxidation rate is slower and a mixture of soluble Fe(II) and insoluble Fe(III) hydroxides was present at the end of 2 minutes of mixing. Due to negligible oxidation of $Fe^{2+}$ by DO at pH 6.5, most of the iron present at the end of 2 min mixing was soluble Fe(II).

**CHANGE IN PH DURING ELECTROLYSIS**

During the electrolytic generation time, a significant increase in pH was observed in electrolytic cell 1. The pH increased from an initial pH of 6.5 to 7.0 ± 0.1 in NSFI challenge
water during the electrolytic generation time. After electrolysis and during the period of mixing, the pH slowly decreased and was within +0.25 unit of the initial pH value (pH 6.5). However in all cases, the final pH was about 0.1 to 0.2 units greater than 6.5 after 2 minutes of mixing. This trend is clearly visible in Figure 3.10, which shows the rapid increase in pH during electrolysis and then slow decrease of pH during final mixing.

Similar observations were made for pH 7.5. However, in contrast to what happened at pH 6.5, there was no significant change in the final pH value for initial pH 7.5. Figure 3.11 illustrates the pH increase during electrolysis and subsequent decrease in pH in NSFI challenge water with an initial pH of 7.5 under three electrolytic generation time periods. As can be seen in the figure, there was a sharp increase from the initial pH value of 7.5 to around 8.2 ± 0.2 during the electrolytic generation time. However during high electrolytic generation time (e.g. 40sec and 60sec in figure), the pH started to decrease from its peak value even during the electrolysis period itself. However after electrolys is the pH decreased very rapidly and restored the original pH value at the end of 2 minutes of mixing.

In the case of initial pH being 8.5, detailed experiments were not performed for the variation in pH. However in general the final pH value was within 0.2 units lower than the initial pH value at the end of 2 min of mixing.

![Figure 3.10](image-url) Variation in pH during and after electrolysis in NSFI challenge water with initial pH of 6.5 and applied current of 0.2A
EC REACTIONS THAT INFLUENCE PH

As explained earlier, electrolysis with an iron anode gives the following electrode reactions:

Anode: \( \text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2e^- \)  \hspace{1cm} (3.5)
Cathode: \( 2 \text{HOH} + 2 e^- \rightarrow 2\text{OH}^- + \text{H}_2 \)  \hspace{1cm} (3.6)

When ferrous iron produced at the anode is oxidized to ferric iron by dissolved oxygen, the following overall reaction describes the process. This overall reaction includes Fe(II) oxidation and Fe(III) hydrolysis:

\[ 2 \text{Fe}^{2+} + \frac{1}{2} \text{O}_2 + \text{HOH} + 4 \text{OH}^- \rightarrow 2 \text{Fe(OH)}_3(s) \]  \hspace{1cm} (3.7)

In addition to being oxidized to Fe\(^{3+}\), the Fe\(^{2+}\) produced at the EC anode readily forms ferrous hydroxide complexes (Fe(OH)\(^+\) and Fe(OH)\(_2\)^0) that are reported to increase the rate of oxidation of Fe(II) (Wherli 1990). When taking the above reactions into consideration it is suggested that the pH varies during and after batch EC in the EC cell. The reason for this behavior with variation in pH is due to the combination of the following reactions:

1. The formation of hydroxide ions at the cathode during electrolysis results in an immediate increase in pH near the cathode, which spreads to the solution by the strong mixing that is occurring in the EC cell.
2. The Fe\(^{2+}\) produced at the anode is oxidized by DO and OH\(^-\) to insoluble Fe(OH)\(_3\)(s) at a rate that increases dramatically as pH (OH\(^-\) concentration) increases.
3. The pH of the cell fluid decreases slowly as hydroxide ions are consumed by oxidation of Fe\(^{2+}\) and by formation of soluble Fe(II) complexes with hydroxide (Figure 3.12 and Table 3.2).

Figure 3.11 Variation in pH during and after electrolysis in NSFI challenge water with initial pH of 7.5 and applied current of 0.2A
As mentioned earlier, the concentration of ferrous (Fe$^{2+}$) that was remaining at the end of 2 minutes of mixing was less than the total iron and the difference in magnitude varied as function of pH. Although the metallic iron was oxidized to soluble Fe$^{2+}$ at the anode, the Fe$^{2+}$ remaining was negligible at pH 8.5, 10–50% at pH 7.5, and 65–85 % at pH 6.5 at the end of 2 minutes of mixing in the electrolytic cell. Figure 3.13 shows the % Fe$^{2+}$ remaining at the end of 2 minute of mixing for applied currents (0.05, 0.2, 0.4, and 0.8A) and electrolytic generation times.
(0 to 60 seconds) at pH 6.5. It can be observed from Figure 3.13 that, with increasing current, there was a small decrease in the percentage Fe\(^{2+}\) remaining. When these results are compared with Figure 3.14a which describes similar experiments conducted under N\(_2\) purged conditions (low DO), the Fe\(^{2+}\) remaining were consistently in the range of 80–95\% regardless of current. Thus, it appears that in DO saturated water at pH 6.5 (Figure 3.13) there was some Fe\(^{2+}\) oxidation. By comparison, experiments conducted on oxidation of Fe\(^{2+}\) during coagulation with ferrous ammonium sulfate (FAS) in NSFI challenge showed almost no oxidation of Fe(II) at the end of 2 min of mixing at pH 6.5. More than 95\% of iron was in Fe\(^{3+}\) form at the end of 2 min of mixing during coagulation with FAS. The reason for greater oxidation of Fe\(^{2+}\) by EC at pH 6.5 is the temporarily elevated pH due to hydroxide production at the anode (See Figure 3.10). This pH elevation did not occur in the experiments with FAS.

Similar observations regarding the effect of current were made in the case of initial pH of 7.5. The percentage Fe\(^{2+}\) remaining decreased significantly with increase in current. Figure 3.15 shows the Fe\(^{2+}\) remaining for applied currents of 0.05, 0.2, 0.4, and 0.8 A and electrolytic generation times of 0 to 60 seconds at the end of 2 minute of mixing at pH 7.5. It can be observed that the concentrations of Fe\(^{2+}\) remaining were 40–45\%, 35–45\%, 20–30\%, and 10–20\% for applied currents of 0.05, 0.2, 0.4, and 0.8 A respectively. However, from the experiments conducted under N\(_2\) purged conditions (Figure 3.14b) using an industrial-grade iron rod, the concentrations of Fe\(^{2+}\) remaining were in the range of 80–95\% regardless of current. It was even more apparent in these pH 7.5 experiments that the Fe\(^{2+}\) ions produced at the anode were oxidized by the DO in the oxygen saturated challenge water and that the oxidation rate increased with increasing current, which produced increasingly higher pH in the EC cell. However, the percentages of Fe\(^{2+}\) remaining in the EC cell were far less than the percentages Fe\(^{2+}\) remaining during coagulation with FAS at the end of 2 min of mixing, again, because there was no pH increase due to current during the FAS experiments.

![Figure 3.13 Percentage of ferrous ions remaining during electrolytic oxidation of iron as a function of current after 2 min of mixing with industrial-grade iron rod at pH 6.5](image-url)
Figure 3.14 Comparison of ferrous ions remaining as a percentage of total iron during electrolytic oxidation of iron as a function of current after 2 min of mixing with industrial-grade iron rod under N₂ purged condition at pH (a) 6.5 and (b) pH 7.5

Figure 3.15 Percentage of ferrous ions remaining during electrolytic oxidation of iron as a function of current after 2 min of mixing with industrial-grade iron rod at pH 7.5
Oxidation of Ferrous by Dissolved Oxygen During Fe(II) CC Experiments with NSFI Challenge Water at pH 6.5 and 7.5

CC experiments conducted with ferrous ammonium sulfate (FAS) to determine the oxidation of Fe^{2+} by DO showed that the oxidation of ferrous iron (Fe^{2+}) by DO was much faster at pH 7.5 compared to pH 6.5. Figures 3.16 and Figure 3.17 show the percentage Fe(II) remaining at different time intervals at pH 6.5 and pH 7.5, respectively. As can be seen from these figures, approximately 95% of Fe^{2+} was oxidized within 30 minutes at pH 7.5, while at pH 6.5 it took about a day for the same oxidation to occur. At the end of 2 minutes of mixing, more than 95% Fe^{2+} was present un-oxidized at pH 6.5, while at pH 7.5, 65–80% Fe^{2+} was present unoxidized. So it was clear that with increase in pH, there was significant oxidation regardless of initial dose of Fe^{2+}.

The oxidation of ferrous iron by DO (Eq 3.8) and the kinetic relationship (Eq 3.9) are well explained in literature (Stumm and Lee 1961, Singer and Stumm 1970):

$$Fe^{2+} + H^+ + \frac{1}{4}O_2 \rightarrow Fe^{3+} + \frac{1}{2}H_2O$$

$$\frac{d(Fe^{2+})}{dt} = -k(Fe^{2+})(P_{O_2})(OH^-)^2$$

where $k$ is the rate constant,

$[OH^-]$ is the concentration of hydroxyl ions, and

$[Fe(II)]$ is the concentration of total ferrous iron.

When pH and $P_{O_2}$ are kept constant, Equation 3.9 reduces to a first order equation. The reaction of ferrous oxidation is said to be first order with respect to iron and oxygen concentrations and second order with respect to the hydroxyl ion concentration. The reaction is found to be temperature and acid dependent (Stumm and Lee 1961, Singer and Stumm 1970, Sung and Morgan 1980, Klein 2005).
Figure 3.16 Percent of ferrous iron remaining un-oxidized with increasing time during coagulation with ferrous ammonium sulfate (FAS) in NSFI Challenge water at pH 6.5

**Figure 3.17 Percent of ferrous iron remaining un-oxidized with increasing during coagulation with FAS in NSFI Challenge water at pH 7.5**

**COMPARISON OF TOTAL IRON AND FE$^{2+}$ GENERATION WITH INDUSTRIAL-GRADE AND REAGENT-GRADE PURE IRON ROD UNDER LOW DISSOLVED OXYGEN (DO) CONDITION (N$_2$ PURGED CONDITION)**

In order to ensure that Fe$^{2+}$ is generated during the electrolytic oxidation of iron regardless of the purity of iron, experiments were conducted with reagent-grade (99.995% Fe) pure iron electrode (Sigma Aldrich Co.,) and industrial-grade (98.5% Fe) rod which was used in the course of the project under similar conditions in the smaller electrolytic cell (Cell 2). The
experiments were conducted with NSFI challenge water with initial pH of 6.5 and 7.5 with an applied current of 50 to 800 mA. In order to suppress the natural oxidation of ferrous, the DO in the challenge water was stripped off by N₂ purging. Simulation of these experiments gave DO values of 228 ± 76 mg/L in the samples collected at the outlet after 1 hr of N₂ purging. Under N₂ purged conditions, CO₂ was also depleted out of the system along with DO which resulted in drastic increase in pH and the final pH was in the range of 9.0 ± 0.5. Even though the pH was uncontrollable and initial pH not maintained, efforts were not made to maintain the initial pH because the main purpose of these experiments were attained even with the increase in pH. Firstly, the pH increase occurred under both the conditions tested (industrial-grade and reagent-grade rod) and so the conditions were the same. Secondly, even with the increase in pH, the system was almost stripped of DO and so the natural oxidation was impossible under those conditions as will be observed in the results.

Comparison of Theoretical Iron Generation with Experimental Fe²⁺ Generation with Reagent- and Industrial-Grade Iron rod

The iron generated experimentally with the reagent-grade pure iron rod and industrial-grade iron rod under N₂ purged condition are compared to the theoretical iron generation capacity (based on Z = 2) in Figures 3.18 and 3.19 respectively. It can be observed from Figure 3.18 that the iron generation experimentally with reagent-grade pure iron rod perfectly correlated with theoretical iron generation considering ferrous is produced during electrolysis for an applied current range of 0.05 to 0.8A. Similar observation was also made in the case of industrial-grade iron rod as shown in Figure 3.19, where the experimental and theoretical iron generation capacities were similar for an applied current range of 0.05 to 0.8A. Thus, the industrial-grade iron rod and the reagent-grade pure iron rod behaved in a similar way with respect to the of total iron generation efficiency. So it was clear that the purity of the industrial-grade iron rod was not of major concern with respect to the iron generation.
Figure 3.18 Comparison of iron generation with theoretical iron generation (based on Fe\(^{2+}\)) during electrolytic oxidation of reagent-grade pure iron rod as a function of current under N\(_2\) purged condition.

Figure 3.19 Comparison of experimental and theoretical iron generation (based on Fe\(^{2+}\)) during electrolytic oxidation of industrial-grade iron rod as a function of current under N\(_2\) purged condition.
Ferrous Remaining During Electrolytic Oxidation of Iron Under N₂ Purged Condition

The other main objective with respect to the study under N₂ purged condition was to inhibit the natural oxidation of Fe²⁺ by DO and test for the possibility of direct electrolytic oxidation of iron (Fe⁰) or subsequent electrolytic oxidation of ferrous (Fe²⁺) to ferric state (Fe³⁺). So the Fe²⁺ produced during electrolysis should be un-oxidized at the end of 2 minutes of mixing if there was no electrolytic oxidation in the electrolytic cell. Figure 3.20 shows the percentage of ferrous ions (Fe²⁺) remaining at the end of 2 minutes of mixing during electrolytic oxidation of iron with reagent-grade pure iron rod with an applied current of 0.05, 0.2, and 0.8 A. It can be seen that at all applied currents, 80–90% of iron was present as Fe²⁺, which confirms that Fe²⁺ is the species that is formed during electrolysis. Similar observation was made with an industrial-grade iron rod with an applied current of 0.05, 0.2, and 0.8 A during N₂ purged conditions. Figure 3.21 shows the percentage of ferrous ions (Fe²⁺) remaining at the end of 2 minutes of mixing during electrolytic oxidation of iron with industrial-grade iron rod and it can be seen that 80–95% of iron was present as ferrous (Fe²⁺) at the end of mixing for all applied currents: 0.05, 0.2, and 0.8 A. So it is clear that it was the natural oxidation of Fe³⁺ by DO which caused a significant decrease in ferrous concentration depending upon pH as was observed in Figures 3.13 and 3.15, which were operated under open atmospheric conditions.

The important point is that the final pH was not the initial pH and instead was in the range of 9.0 were oxidation by DO is expected to be faster. Even at that pH natural oxidation was impossible in the cell due to continuous N₂ purging and so the only possibility was at the time of sample collection. So the remaining 10–20% which was not accounted for Fe²⁺ during analysis could be the oxidation during sample collection and also due to the oxidized species present in the rod even after cleaning which is not visually seen.

![Graph showing ferrous ions remaining at the end of 2 minutes mixing](image)

Figure 3.20 Comparison of ferrous ions remaining as a percentage of total iron during electrolytic oxidation of iron as a function of current after 2 min of mixing with reagent-grade iron rod under N₂ purged condition
CONCLUSIONS

The total iron generated experimentally was the same as theoretical iron generation based on Faraday’s law when the number of electrons transferred per atom (Z) was equal to two. The current efficiency with respect to iron generation was 100%, providing the iron rod was cleaned prior to each iron-generation experiment. The electrolytic oxidation of iron rod (Fe$^0$) at the anode resulted in the generation of ferrous ions (Fe$^{2+}$), while the electrolytic reduction of water resulted in the production of hydrogen gas at the cathode. The electrolytic reduction of water at the cathode also resulted in the formation of hydroxides, which were consumed by the protons resulting from hydrolysis of Fe$^{2+}$ and Fe$^{3+}$ ions (produced by subsequent oxidation of Fe$^{2+}$ by DO depending on pH) to form Fe hydroxide complexes. Even though Fe$^{2+}$ was produced at the anode, the Fe$^{2+}$ that was remaining was less than the total iron generated and depended on pH at the end of 2 minutes of mixing. The ferrous ions/hydroxides (Fe$^{2+}$) remaining decreased with increasing pH, which was consistent with the studies on oxidation of Fe$^{2+}$ during coagulation with ferrous ammonium sulfate. The coagulation studies showed that the oxidation of Fe$^{2+}$ by DO was extremely pH dependent as predicted by the literature and found to be much faster at high pH compared with low pH. During electrolysis, a significant increase in pH from the initial pH was observed which was due to the continuous production of hydroxide ions and the slow formation of Fe hydroxide complexes. During electrolysis under open atmospheric conditions, the percentage Fe$^{2+}$ remaining decreased with increase in current and the significance increased with increase in pH. The variation in Fe$^{2+}$ remaining at the end of 2 minutes of mixing in the case of electrolytic cell compared to coagulation experiments was due to significant increase in pH during electrolysis which was not the case during coagulation experiments. The industrial-grade iron rod and the reagent-grade pure iron rod behaved in a similar way with respect to the of total iron generation efficiency and so the purity of the industrial-grade iron rod was not of major
concern with respect to the iron generation. Under N₂ purged conditions (DO very low) with an industrial-grade and reagent-grade iron rod, 80–90% of iron was present as Fe²⁺ which confirms that Fe²⁺ is the species that is formed during electrolysis and natural oxidation by DO was the only reason for oxidation of Fe²⁺ to Fe³⁺.
CHARTER 4
ARSENIC (III) OXIDATION AND REMOVAL

It has been found in several studies of arsenic occurrence that only, inorganic arsenite (As(III)), and arsenate (As(V)) are important in ground water supplies (Irgolic 1982). As(V) is the thermodynamically stable species and As(III) is the metastable species. In the natural pH range of 6 to 9, As(III) is mostly present as H₃AsO₃, while As(V) exists either as H₂AsO₄⁻ or HAsO₄²⁻. Table 4.1 presents the dissociation constants (pKₐ’s) of arsenic and arsenous acids. As(V), the oxidized form of arsenic is more easily removed from water by ion exchange, adsorption, and membrane processes compared with As(III), which, in general, requires pre-oxidation. Arsenous acid exists as uncharged species to a large extent at pH< pKₐ1 = 9.23 which, is the primary reason for lesser adsorption of As(III) compared to As(V).

In coagulation treatment, trace inorganic contaminants, are removed by the sorption onto the surfaces of freshly formed metal hydroxides/oxyhydroxides (Mₓ(OH)ᵧ⁺), which are formed upon metal coagulant addition and hydrolysis reaction. Stumm (1992) reported anion removal by metal oxyhydroxide surfaces by the process of ligand exchange (Figure 4.1). During ligand exchange, the ligand H₂AsO₄⁻ replaces two hydroxides and forms a bidendate surface complex on the metal oxyhydroxide surface. This reaction is facilitated by low pH and excess hydrogen ions, which consume the hydroxides released. Silicate, phosphate, and vanadate, three common competing anions that could compete for adsorption sites are shown in the figure. The surface complex formed between the metal and the arsenate anion is very strong and not easily reversed except at high pH when the reaction is reversed due to the presence of hydroxide ions, which are ligands highly preferred by the central-atom metals.

In addition to producing competing hydroxide ions, an increase in pH decreases the fraction of positively charged adsorption sites on the metal hydroxide surface resulting in lesser adsorption of negatively charged As(V) species. With decrease in pH, the concentration of monovalent As(V) (H₂AsO₄⁻) increases significantly from 0.02 to 0.5 μM from pH 8.5 to 6.5 (Table 4.1) which would result in greater removals of As(V) due to the process of ligand exchange at low pH. Also, as can be seen in Table 4.1, with increasing pH, the concentration of monovalent As(III) (H₂AsO₃⁻) increases which would result in greater removals of As(III) due to the process of ligand exchange at high pH. This trend of increasing As(III) removal with increasing pH is offset by the increasing competition from hydroxide ions at the higher pH.

EC has been effectively applied to remove arsenic from water and waste water (Balasubramanium and Madhaven 2001, Arienzo et al et al. 2002, Kumar et al. 2004, Parga et al. 2005, Hansen et al. 2006). Arienzo et al. (2002) investigated the retention of arsenic on hydrous ferric oxides generated electrochemically using two steel electrodes. This EC process removed more than 99% of As(III). Kumar et al. (2004) reported that EC had a good removal efficiency for As(III) and attributed the reason to the removal mechanism, which was simultaneous oxidation of As(III) to As(V) and subsequent removal by adsorption/complexation with metal hydroxides generated in the process. The literature on electrochemical oxidation of As(III) also indicate that traces of free chlorine generated by the oxidation of chloride at the anode rapidly oxidize As(III) (Kim et al. 2002). So even the trace amounts of free chlorine which are reported to be formed during electrolysis should oxidize As(III) to As(V) during electrolysis, and will be an advantage for simultaneous oxidation and removal of As(III).
Table 4.1
Composition of Species present in pH 6.5–8.5

<table>
<thead>
<tr>
<th>Species</th>
<th>pKₐ values</th>
<th>Concentration of species</th>
<th>pH 6.5</th>
<th>pH 7.5</th>
<th>pH 8.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic acid, Cₜ = 0.67 μM (50 μg/L)</td>
<td>pKₐ₁ = 2.26</td>
<td>H₂AsO₄⁻</td>
<td>0.5</td>
<td>0.15</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>pKₐ₂ = 6.79</td>
<td>HAsO₄²⁻</td>
<td>0.17</td>
<td>0.52</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>pKₐ₃ = 11.29</td>
<td></td>
<td>0.17</td>
<td>0.52</td>
<td>0.65</td>
</tr>
<tr>
<td>Arsenous acid, Cₜ = 0.67 μM (50 μg/L)</td>
<td>pKₐ₁ = 9.23</td>
<td>H₃AsO₃</td>
<td>0.67</td>
<td>0.66</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>pKₐ₂ = 12.1</td>
<td>H₂AsO₃⁻</td>
<td>0.001</td>
<td>0.01</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Source: Data from Schecker 1998.

Figure 4.1: Mechanism of arsenate ligand exchange on the surface of metal oxyhydroxides

Thus, EC–F was expected to be a better choice for oxidation of As(III) and simultaneous removal of arsenic from drinking water. The electrolytic oxidation of iron rod (Fe⁰) at the anode was expected to result in the generation of ferric ions, while the electrolytic reduction of water results in the production of hydrogen gas at the cathode. The electrolytic reduction of water also results in the formation of hydroxides. In contrast to CC using ferric salts, there was a expectation of no pH change during EC because the protons resulting from hydrolysis of ferric ions were expected to consume the hydroxide ions produced at the cathode during reduction of water to form Fe hydroxide complexes. This would eliminate the consumption of alkalinity by iron hydrolysis, which occurs during CC with ferric salts.

Iron coagulation followed by flocculation and filtration (Cheng et al. 1994) or iron C–F without flocculation (Ghurye et al. 2004) have been shown to be effective technologies for removing As(V) from drinking water. The arsenic removal efficiency depends on the pH,
As(III/V) speciation, and coagulant dose. Among the coagulants, ferric chloride is the one most commonly used due to widespread use, availability, low cost, and high capacity for arsenic.

**OPERATIONAL EFFICIENCY OF EC UNIT**

**Electrode Passivation in the EC Unit**

After designing and building the three-cell EC unit, it was tested for its ability to generate iron in proportion to the current in NSFI challenge water at pH 7.5. The EC unit was operated at current value 0.2 A on consecutive days with and without cleaning the iron rods. Samples for analysis of total iron generated by EC unit were taken from the EC unit and the studies showed that the performance of iron generation decreased on successive days which were observed with the electrolytic cell. The comparison of iron generation with a rod that was not cleaned, cleaned rod on day 1 and on day 2 are shown in Figure 4.2. It can be seen that with an uncleaned rod that had been used previously to generate iron, the mass of iron generated was much lower compared with the performance of a cleaned rod on the day it was cleaned, i.e., the first day. The performance of iron generation decreased on the second day when the rod was used without cleaning. So it was noted that the performance of iron generation depended on the cleanliness of the iron-rod anodes. By cleaning the iron rods on the day of the experiment, the performance of iron generation was repeatable. So on the day of experiments, the iron rods were thoroughly scrubbed with sand paper to remove all of the rust and the hydroxides that were coated on the iron rods.

![Figure 4.2 Effect of electrode passivation on iron generation in the EC unit operated on batch mode at applied current of 0.2A with NSFI challenge water at pH 7.5](image)

The three-cell EC unit was operated for three days without cleaning the iron-rod anodes. Then, the rod was thoroughly cleaned and tested for iron generation. Figures 4.3 and Figure 4.4
compare iron generation with a rod that was not cleaned for the first three days with that of cleaned rod on day three and four at applied current values of 0.1 and 0.2A, respectively. It can be seen from both the figures that with an uncleaned rod, the mass of iron generated decreased gradually for the first three days. But, after the rod was cleaned, the iron generation increased significantly as can be seen from the performance of clean rod on day 3. By cleaning the iron rods on the fourth day, the performance of iron generation was repeatable as that of the third day in both applied currents tested.

Figure 4.3 Effect of electrode passivation on iron generation in the EC unit operated on continuous mode at applied current of 0.1A with NSFI challenge water at pH 7.5

Flow rate= 300mL/min
Comparison of Actual and Theoretical Iron Generation in the EC Unit in Batch Mode

The three-cell EC unit with pre-cleaned anodes was operated in batch mode at current values of 0.05, and 0.2 A and generation times in the range of 0 to 60 seconds. NSFI challenge water at pH 6.5, 7.5, and 8.5 was used in these studies. Samples for analysis of total iron generated were taken from the EC unit. The results are shown in Figure 4.5, the total iron production as a function of time. The experimental data shown is a combination of the experimental values obtained at all three pH values. So by adjusting the operating current and generation time, the desired iron concentration could be obtained. The operating curve of EC and the theoretical value of iron based on Fe$^{2+}$ and Fe$^{3+}$ are compared in Figure 4.5 which shows that the iron generation experimentally was closer to the theoretical iron generation capacity based on Fe$^{2+}$ production at the anode, although the experimental data did not fit the theoretical curve as well as was observed with the electrolytic cell.

As was observed during iron generation in the single-cell EC unit, the concentration of Fe$^{2+}$ remaining at the end of 2 minutes of mixing was dependent on pH and the electrolysis/oxidation time. The percentages of ferrous remaining at the end of two minutes of iron generation/mixing were 70–85, 10–45, and ≈0% at pH 6.5, 7.5, and 8.5, respectively.
Figure 4.5 Comparison of iron generation in three-cell EC unit with theoretical iron generation capacity in batch mode operation at applied current of 0.2A with NSFI challenge water

Comparison of Actual and Theoretical Iron Generation in the EC Unit in Continuous Mode

Comparisons of experimental vs. theoretical iron generation were also made while operating the three-cell EC unit in the continuous mode at current values of 0.1, and 0.2 A and a flow rate of 300 ± 20 mL/min. NSFI challenge water at pH 7.5 was used in these studies. Source water was pumped into the top of the EC at a flow rate of 300 mL/min. The EC unit was operated at different current values. Samples for analysis of total iron generated by EC unit were taken from the overflow of the EC unit. The results are shown in Figure 4.6, the Fe production as a function of time for applied currents of 0.1 and 0.2A.

In continuous operation, it took about six EC-unit volumes (3L) before steady state iron concentration was observed in the effluent. After the steady-state iron concentration was attained it did not change and was proportional to the applied current. By adjusting the operating current and flow rate of source water to be treated, the desired iron concentration was obtained. For example, when the feed flow rate was 300 mL/min and the operating current was 0.1 A, the steady-state iron concentration was about 5.4 mg/L. Also, the comparison of experimental Fe concentration with theoretical value of Fe(II) and Fe(III) concentration was conducted. Theoretical value of Fe concentration was calculated using Faraday’s law (Equation 3.1) modified into Equation 4.1

\[
C_{Fe} = \frac{m}{q_f \times t} = \frac{I \times M}{q_f \times Z \times F} \tag{4.1}
\]

where \(C_{Fe}\) is the concentration of total iron generated in EC unit for \(Z = 2\) and \(3\) for \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) generation respectively, and \(q_f\) is the flow rate (L/s) of water passing through the EC unit.
The continuous EC operating curves for 0.1 and 0.2 A are compared with the steady-state theoretical iron production (horizontal curves) for Fe\(^{2+}\) and Fe\(^{3+}\) generation in Figure 4.6. For both current values, the iron generation experimentally approached the theoretical iron generation capacity based on Fe\(^{2+}\) production at the anodes.

![Figure 4.6 Comparison of iron generation in EC unit with theoretical iron generation capacity in continuous mode operation at current with NSFI challenge water at pH 7.5](image)

**ARSENIC REMOVAL STUDY PROCEDURE**

NSFI challenge water spiked with 50 µg/L of As(III) or As(V) was used in the CC and EC experiments, which were performed at pH 6.5, 7.5, and 8.5 to establish arsenic removal efficiency as a function of pH and coagulant dose.

**As(V) Removal During CC with Fe(III) Using Ferric Chloride**

The removal efficiencies of As(V) in NSFI Challenge water during CC with ferric(III) chloride as a function of coagulant dose and pH are shown in Figure 4.7, which indicates that removal efficiency of As(V) was pH dependent. With increase in pH, the removal efficiency of As(V) decreased. The percentage removals of As(V) with 1 mg/L Fe(III) dosage at pHs 6.5, 7.5, and 8.5 were 89, 73, and 33%, respectively.

**As(V) Removal During CC with Fe(II) Using Ferrous Sulfate at pH 6.5**

Coagulation experiments were conducted with ferrous sulfate as coagulant in NSFI challenge water at pH 6.5 under similar conditions to those used for CC with FeCl\(_3\) (rapid mix at 100 rpm for 2 min). The objective was to study the removal efficiencies of Fe\(^{2+}\) vs. Fe\(^{3+}\) coagulants. Figure 4.8 compares the As(V) removal efficiencies with ferric chloride and ferrous
sulphate on a metal basis at pH 6.5. The percentage removal of As(V) with 1 mg/L Fe(III) dosage at pH 6.5 was 89%, while the removal was only 6% with Fe(II) for the same dose. So it was clear that with FeSO₄ as coagulant, there was no significant removal in comparison to FeCl₃. The analysis of filtrate showed > 95% Fe²⁺ remaining in the treated challenge water for all doses. These results were expected from the oxidation studies on Fe²⁺ with FAS coagulant discussed in Chapter 2. The oxidation results showed insignificant oxidation (< 5%) at the end of 2 min of mixing at pH 6.5, and so significant Fe³⁺ was expected in the filtrate as observed.

![Figure 4.7](image1.png)  
**Figure 4.7** Removal efficiency of As(V) during CC in NSFI Challenge water as a function of ferric chloride dose and pH

![Figure 4.8](image2.png)  
**Figure 4.8** Comparison of removal efficiency of As(V) during CC in NSFI challenge water with ferric chloride and ferrous sulfate as coagulant at pH 6.5
As(V) Removal During EC with Fe Ions

The As(V) removal efficiencies in NSFI challenge water during Fe generation in the three-cell EC unit as a function of total iron dose and pH are shown in Figure 4.9. It can be seen that removal efficiency of As(V) vs. iron dose was very erratic at pH 6.5, while at pH 7.5 the removal efficiencies were more consistent. Generally, the As(V) removal efficiencies at pH 6.5 and 7.5 were similar. However comparison of removal efficiencies at pH 7.5 and 8.5 showed that with increasing pH, the removal increased as was the case with CC. The removal percentages of As(V) with 1.0 mg/L of total iron generated in EC unit at pHs 7.5, and 8.5 were 70–80, and 36%, respectively. The As(V) removal efficiency at pH 7.5 was good, significant soluble iron concentrations were observed in the filtrate at pH 7.5 depending on the conditions of the experiment. This is a cause for concern because of the potential for subsequent oxidation of ferrous iron and precipitation of Fe(OH)₃ in a distribution system.. A comparison of As(V) removals at pH 6.5 in Figures 4.8 (CC) and 4.9 (EC) shows that >50% removal was possible in the EC unit, while <10% was possible with Fe²⁺ coagulant. Although only 15–30% of the Fe²⁺ generated was oxidized in the EC unit compared with 5% oxidation during coagulation at pH 6.5, the arsenic removals in the EC unit were found to be higher than expected. The higher adsorption in EC was possibly due to the iron oxide/hydroxide surfaces of the iron rods in the EC unit, which have the capability of adsorbing As(V).

![Figure 4.9 Removal efficiency of As(V) during EC in NSFI challenge water as a function of iron dose and pH](image)

The ferrous ions present in the EC unit at the end of 2 minutes of iron generation and mixing would be soluble and would pass through the 0.2 μm filter. To study this, the total iron concentration in the filtrate (sample used for arsenic analysis) was analyzed and compared with the filtered samples to give the concentration of Fe(III) hydroxides present at the end of 2 minutes of mixing. These Fe(III) hydroxides would adsorb arsenic in the EC unit. Figures 4.10 show the percent Fe(II) and Fe(III) remaining in the EC unit at the end of 2 minute of mixing at pH 6.5 and 7.5.
At pH 6.5, (Fig. 4.10a) most of the iron present after 2 minutes is soluble Fe$^{2+}$, which would not adsorb As(V). However, in spite of the fact that the system was pre-equilibrated with the challenge water, significant As(V) was removed by the iron rods in the system at pH 6.5, even without applying current. So the percentage removals shown in Figure 4.9 at pH 6.5 are a combination of removals caused by the Fe(III) hydroxides formed and the iron oxide/hydroxide coated anodes in the EC unit.

At pH 7.5 (Fig. 4.10b) about 70–80% of the iron present in the EC unit after 2 min was in the form of insoluble Fe(III) hydroxides capable of adsorbing As(V). Thus, the overall As(V) removal was good — 80–95% — as seen in Figure 4.9. Nevertheless, the 20-30% Fe$^{2+}$ remaining in the effluent is a concern. In summary, good As(V) removal by EC at pH 7.5 is possible, but attention should be given to optimizing the EC system. For example, increasing the residence time could result in complete oxidation of Fe$^{2+}$ and full usage of iron generated in the system.

As(III) Removal During CC Using Ferric (III) Chloride

The As(III) removal efficiencies in NSFI challenge water during CC with ferric chloride as a function of coagulant dose and pH are shown in Figure 4.11, which indicates that removal efficiency of As(III) was not significantly pH dependent. The percentage removals of As(III) with 2 mg/L Fe(III) dosage at pHs 6.5, 7.5, and 8.5 were 18.2, 18.7, and 19.2%, respectively. So the removal efficiencies were approximately the same at all three pH conditions tested.
The percent change or percent removal efficiency of As(III) species was found to be approximately the same as that of the removal efficiency of As(Tot), which is shown in Figure 4.12. With 2.0 mg/L Fe, the arsenic removal efficiencies calculated as total arsenic were 18.2, 18.7, and 19.2% at pH 6.5, 7.5, and 8.5, respectively, while the removals of As(III) (as determined by speciation) were 18.5, 18, and 21% at pH 6.5, 7.5, and 8.5, respectively. Therefore, based on speciation of samples after coagulation, it can be concluded that there was no oxidation of As(III) during coagulation with ferric chloride.
As(III) Removal During EC with Fe ions

The As(III) removal efficiencies in NSFI Challenge water using EC with Fe ions as a function of coagulant dose and pH are shown in Figure 4.13, which indicates that removal efficiency of As(III) was slightly dependent on pH and the efficiency increased with increasing pH. The percentage removals of As(III) with 2.0 mg/L Fe dosage at pHs 6.5, 7.5, and 8.5 were approximately 40, 48, and 50% respectively. The EC-F removal efficiencies for As(III) were about double the efficiencies during CC for 2.0 mg/L Fe dose. But at higher doses, the difference in removal efficiency between EC and CC decreased.

Figure 4.13 Removal efficiency of As(III) during EC in NSFI challenge water as a function of iron dose and pH
A comparison of removal efficiencies of As(III) speciated with that of As(Tot) measured as As(Tot) is shown in Figure 4.14. It was observed that the percent change/removal efficiency of As(III) was found to be approximately the same as that of the removal efficiency of As(Tot) at pH 6.5, while at pH 7.5 and 8.5, percent change/removal efficiency of As(III) was found to be greater than that of the removal efficiency of As(Tot). With 2.0 mg/L Fe dose, the As(Tot) removal were 40, 48, and 50% at pH 6.5, 7.5, and 8.5, respectively, whereas the As(III) removal efficiencies were approximately 41, 56, and 66% at pH 6.5, 7.5, and 8.5, respectively. So there was a small change in total arsenic removal compared with As(III) removal at pH 7.5 and 8.5 where there was a significant difference between As(III) speciated to that of total arsenic at all doses (Figures 4.14). One reason for funding this research, based on literature reports, was that the EC–F process could simultaneously oxidize and remove As(III). However, the oxidation of As(III) observed in the EC unit was not very significant. Because the As(III) oxidation was not significant and because As(III) removals were not nearly as good as As(V) removals the oxidation of As(III) was not further studied.

The removal efficiencies of As(V) and As(III) in EC–F are compared in Figure 4.15, which indicates that the removal efficiency of As(V) was very high compared to As(III). The removal percentages of As(V) were 94, 89, and 58% at pHs 6.5, 7.5, and 8.5, respectively for 2 mg/L Fe dosage during EC whereas the As(III) removal efficiencies were approximately 40, 48, and 50% at pH 6.5, 7.5, and 8.5, respectively. As there was no significant oxidation of As(III) during EC, the removal of As(III) was significantly less than the removals observed with As(V).
ARSENIC ADSORPTION ISOTHERMS

Graphs showing percent arsenic removal as a function of coagulant dose and pH are of practical importance, but the equilibrium adsorption isotherm provides a more fundamental comparison of the effectiveness of coagulants. The adsorption isotherms of As(V) on the in-situ formed hydroxides of Fe(III) with CC and EC experiments at pH 6.5, 7.5, and 8.5 are shown in Figures 4.16 and 4.17. The most favorable As(V) adsorption isotherm in the case of CC was observed at pH 6.5 as can be observed in Figure 4.16. In the case of EC, the most favorable As(V) adsorption isotherm was observed at pH 7.5, while at pH 6.5, the adsorption isotherm is kind of a misleading one and less reproducible as discussed earlier.

Figure 4.15 Comparison of As(V) & As(III) removal efficiency in NSFI Challenge water during EC as a function of Fe dose and pH (a) 6.5, (b) 7.5, and (c) 8.5
The adsorption isotherms of As(III) on the in-situ formed hydroxides of Fe(III) with CC and EC experiments at pH 6.5, 7.5, and 8.5 are shown in Figures 4.18 and 4.19. From the figures, it can be seen that CC was found to be pH independent, while EC appeared to be slightly pH dependent and much less reproducible at the three pHs tested. Notably, CC produced favorable (convex upward) isotherms, whereas, in the case of EC, linear or slightly unfavorable (convex downward) isotherms were obtained. As discussed previously, the scatter in the EC data results from the production of Fe$^{2+}$ in the EC unit and its variable oxidation to Fe$^{3+}$ depending on mixing time and dissolved oxygen content of the water.
Figure 4.18 As(III) adsorption isotherms onto in-situ formed Fe(III) hydroxide during CC with FeCl₃ at pH 6.5, 7.5, and 8.5

Figure 4.19 As(III) adsorption isotherms onto in-situ formed Fe hydroxide during EC with Fe at pH 6.5, 7.5, and 8.5

COMPARISON OF ARSENIC ADSORPTION ISOTHERMS AND ADSORPTION CAPACITIES

Comparison of As(V) Adsorption for CC–F and EC–F

The adsorption isotherms of As(V) on the in-situ formed Fe hydroxides during C-F and EC-F at pH 6.5, 7.5, and 8.5 are compared in Figure 4.20. The removal of As(V) for both EC–F and C–F was pH dependent, and the removal efficiency increased with decreasing pH at pH 7.5
and 8.5. It is noted, however, that in the case of EC, the pH change during electrical generation was less significant compared with CC, where it was necessary to add NaOH to adjust pH after ferric chloride addition. The EC–F and C–F adsorption isotherms were almost exactly the same at pH 7.5 and 8.5, whereas, at pH 6.5, EC showed a much poorer and less reproducible adsorption isotherm compared to CC with FeCl₃.

The As(V) arsenic adsorption capacities of Fe hydroxide during CC and EC are compared in Figure 4.21 for an equilibrium concentration of 10 μg/L As(V). As observed earlier, the adsorption capacity was almost the same at pH 7.5 and 8.5. However at pH 6.5, CC had a better adsorption capacity than pH 7.5 and 8.5, which was not the case with EC. Based on the known generation of Fe²⁺ EC showed a higher-than-expected adsorption capacity at pH 6.5, which was likely due to the adsorption of arsenic by iron oxides/hydroxides on the iron rods in the system, and the As(V) remaining did not correlate well with the Fe²⁺ remaining at the EC outlet.

![Figure 4.20 Comparison of As(V) adsorption onto Fe hydroxide during chemical and EC at pH (a) 6.5, (b) 7.5, and (c) 8.5](image)
Figure 4.21 Comparison of As(V) adsorption capacities for an equilibrium concentration of 10 μg/L As(V) as a function of pH during chemical and EC with Fe

<table>
<thead>
<tr>
<th>pH</th>
<th>CF (μg As(V)/mg Fe)</th>
<th>ECF (μg As(V)/mg Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>48.8</td>
<td>21.6</td>
</tr>
<tr>
<td>7.5</td>
<td>30.6</td>
<td>30.5</td>
</tr>
<tr>
<td>8.5</td>
<td>10.2</td>
<td>9.8</td>
</tr>
</tbody>
</table>

Figure 4.22 Comparison of As(III) adsorption onto Fe hydroxide during CC and EC at (a) pH 6.5, (b) 7.5, and (c) 8.5

Comparison of As(III) Adsorption for CC–F and EC–F

The adsorption isotherms of As(III) on the in-situ formed hydroxides of Fe during C–F and EC–F at pH 6.5, 7.5, and 8.5 are compared in Figure 4.22. Though the adsorption isotherms
of EC–F showed relatively poor As(III) adsorption compared with As(V), EC–F showed higher adsorption capacities than CF at higher equilibrium concentrations.

The As(III) adsorption capacities of Fe hydroxides produced during CC and EC are compared in Figure 4.23 for an equilibrium concentration of 10 μg/L As(III). EC showed a higher adsorption capacity for As(III) at all three pHs tested compared to coagulation with FeCl₃. As previously discussed, the apparently higher As(III) capacity of iron hydroxide produced by EC was thought to be due to partial oxidation of As(III) to As(V) by EC. It is noteworthy that this partial oxidation of As(III) to As(V) seems to increase with increasing pH, as the advantage of EC–F over C–F improves with increasing pH.

![Figure 4.23 Comparison of As(III) adsorption capacities for an equilibrium concentration of 10 μg/L as a function of pH during chemical and EC with Fe](image)

![Figure 4.24 Comparison of As(III) and As(V) adsorption capacities for an equilibrium concentration of 10 μg/L as a function of pH during chemical and EC with Fe](image)
Figure 4.24 compares the As(III) and As(V) adsorption capacities for EC–F and C–F for an equilibrium concentration of 10 μg/L as a function of pH. Clearly, the As(V) adsorption capacities are much higher than the As(III) adsorption capacities for both processes, which reinforces idea that As(III) must be oxidized to As(V) prior to treatment using iron oxides/hydroxides for sorption regardless of the source of these iron oxides hydroxides.

CHLORINE GENERATION AND UTILIZATION IN THE EC UNIT

From the experimental results on As(III) removal, it was concluded that there was no significant oxidation of As(III) in the EC unit during iron generation. The literature on electrochemical oxidation of As(III) indicates that traces of free chlorine generated by the oxidation of chloride at the anode rapidly oxidized As(III) (Kim et al. 2002). So, experiments were conducted with NSFI challenge water (without arsenic) to clarify whether Cl₂ was produced at the anode. The experimental procedure was the same as described above except that arsenic was not spiked in the challenge water. Experiments in the EC unit were conducted using industrial grade iron rods by varying the current in the range of 50 to 800 mA and the samples were analyzed for chlorine. The measurement of total chlorine was performed by DPD Photometric method using powder pillows (Hach Company 1992), which had a detection range of 0 to 2 mg/L total Cl₂. The experimental results showed no measurable chlorine generation in the EC unit with the industrial grade iron rods.

Experiments were also conducted to study whether Cl₂ was being consumed in the EC unit. Chlorinated water (1.5 mg/L Cl₂) was prepared by adding sodium hypochlorite solution (10–13% available Cl₂ solution) to DIW. The chlorinated water was then passed through the EC unit for a total time of 2 minutes, and iron in the range of 0 to 3 mg/L was generated. The samples were collected and analyzed for chlorine and iron. The results are given in Table 4.2, which shows that the chlorine in the water decreased with increasing iron concentration. Also, there was a significant decrease (~65%) in chlorine concentration even when iron was not generated in the EC unit, which could be due to the chlorine being consumed by contact with the iron rods where Fe⁰ was being oxidized to Fe²⁺. With increasing iron generation, the chlorine content in the water decreased and no chlorine was detected in the outlet sample when iron concentration was 2.7 mg/L. The decrease in chlorine concentration with increasing iron concentration was assumed to be due to chlorine oxidation of the Fe²⁺ produced at the anode to Fe³⁺.

Thus, from the above experiments, it was concluded that chlorine was not being produced in the EC unit, and even if it was being produced, it was used up in the EC unit by the iron rods and the Fe²⁺ that was generated.
Table 4.2
Utilization of chlorine in the EC unit

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th>Fe in the sample (mg/L)</th>
<th>Initial Cl₂ concentration (mg/L)</th>
<th>Final Cl₂ concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No iron generation but chlorinated water passed through the iron rods</td>
<td>0.13</td>
<td>1.55</td>
<td>1.02</td>
</tr>
<tr>
<td>50 mA, 25 s (1.25 Coul)</td>
<td>0.61</td>
<td>1.58</td>
<td>0.48</td>
</tr>
<tr>
<td>50 mA, 50 s (2.5 Coul)</td>
<td>1.12</td>
<td>1.58</td>
<td>0.31</td>
</tr>
<tr>
<td>100 mA, 60 s (6 Coul)</td>
<td>2.67</td>
<td>1.56</td>
<td>0.01</td>
</tr>
</tbody>
</table>

AS(III) OXIDATION USING GRAPHITE RODS

Because no significant oxidation of As(III) nor chlorine generation was observed when using iron anodes, it was decided to study the possible generation of chlorine using graphite rods instead of iron rods. So experiments were conducted with NSF1 challenge water at pH 7.5 to determine whether Cl₂ was produced at a graphite-rod as anode. The experimental procedure was the same as described above except that arsenic was not spiked into the challenge water, and a single graphite-rod anode was used in place of the three standard iron-rod anodes. Experiments in the EC unit were conducted by varying the current in the range of 200 to 600 mA, and the samples were analyzed for chlorine. The experimental results showed that chlorine, as reported in Table 4.3, was being produced at the anode. However, the amount of Cl₂ produced (0.015–0.037 mg/L Coul) was far below the maximum expected amount (0.775 mg/L Coul) based on coulombs of charge provided to the electrochemical cell containing 475 mL active volume. Possible reasons for the low Cl₂ residual are (a) side reactions that produce oxygen and other water electrolysis products, and (b) residual Fe⁰ and Fe²⁺ being oxidized by the Cl₂ produced.

The EC reactions at the anode and cathode (Skoog et al. 2004) which resulted in production of chlorine are given below:

Anode: \(2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-\) \hspace{1cm} (4.1)

Cathode: \(2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2\) \hspace{1cm} (4.2)
Table 4.3
Chlorine produced in challenge water without As(III) when using one graphite rod anode and stainless steel cathode

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th>Coulombs</th>
<th>Theoretical Max Cl₂ (mg/L)</th>
<th>Cl₂ residual (mg/L)</th>
<th>mg Cl₂ L/Coul</th>
<th>Cl₂ residual % of Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 mA, 30 s</td>
<td>6.0</td>
<td>4.65</td>
<td>0.22</td>
<td>0.037</td>
<td>4.7</td>
</tr>
<tr>
<td>200 mA, 1 min</td>
<td>12.0</td>
<td>9.30</td>
<td>0.4</td>
<td>0.033</td>
<td>4.3</td>
</tr>
<tr>
<td>200 mA, 1 min</td>
<td>12.0</td>
<td>9.30</td>
<td>0.37</td>
<td>0.031</td>
<td>4.0</td>
</tr>
<tr>
<td>300 mA, 30 s</td>
<td>9.0</td>
<td>6.97</td>
<td>0.28</td>
<td>0.031</td>
<td>4.0</td>
</tr>
<tr>
<td>300 mA, 1 min</td>
<td>18.0</td>
<td>13.9</td>
<td>0.52</td>
<td>0.029</td>
<td>3.7</td>
</tr>
<tr>
<td>390 mA, 30 s</td>
<td>11.7</td>
<td>9.06</td>
<td>0.35</td>
<td>0.030</td>
<td>3.9</td>
</tr>
<tr>
<td>390 mA, 1 min</td>
<td>23.4</td>
<td>18.1</td>
<td>0.51</td>
<td>0.022</td>
<td>2.8</td>
</tr>
<tr>
<td>600 mA, 1 min</td>
<td>36.0</td>
<td>27.9</td>
<td>0.55</td>
<td>0.015</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Factors Affecting As(III) Oxidation Using Graphite Rods

Since the production of chlorine was possible with graphite rods, chlorine generation experiments were conducted as above, but in the presence of As(III) in the challenge water. The current was varied in the range of 50 to 600 mA for 60s, and the resulting samples were analyzed for chlorine and As(III) by speciation. The amount of chlorine in the challenge water in the presence of As(III) is given in Table 4.4, which indicates that the resulting chlorine concentration was lower when 50 μg/L As(III) was present.

Although the current efficiency was quite low, based on the determination of As(III) by speciation, it was found that As(III) oxidation increased with increase in current both at pH 7.5 or 8.5 as shown in Figure 4.25. It was clear that As(III) oxidation was possible by using the graphite rods. However it was not clear whether the oxidation of As(III) occurred at the anode surface due to redox reaction or due to the oxidation by chlorine produced. Thus, experiments were carried out in the absence of chloride ions. The results showed no significant oxidation of As(III) at even higher currents regardless of pH 7.5 or 8.5 as can be seen from Figure 4.25. Therefore, it was confirmed that As(III) oxidation occurred by the chlorine produced form the chloride ions at the anode.

Table 4.4
Chlorine remaining in the challenge water spiked with 50 μg/L As(III) when using one graphite rod anode and stainless steel cathode

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th>Coul</th>
<th>Theoretical Max Cl₂ (mg/L)</th>
<th>Cl₂ Residual (mg/L)</th>
<th>Cl₂ Demand of 50 μg/L As(III) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mA, 60 s</td>
<td>3.0</td>
<td>2.32</td>
<td>0.01</td>
<td>0.047</td>
</tr>
<tr>
<td>100 mA, 60 s</td>
<td>6.0</td>
<td>4.65</td>
<td>0.12</td>
<td>0.047</td>
</tr>
<tr>
<td>200 mA, 60 s</td>
<td>12.0</td>
<td>9.30</td>
<td>0.21</td>
<td>0.047</td>
</tr>
<tr>
<td>390 mA, 60 s</td>
<td>23.4</td>
<td>18.1</td>
<td>0.35</td>
<td>0.047</td>
</tr>
<tr>
<td>600 mA, 60 s</td>
<td>36.0</td>
<td>27.9</td>
<td>0.33</td>
<td>0.047</td>
</tr>
</tbody>
</table>
Experiments were conducted at pH 7.5 with NSFI-53 Challenge Water spiked with As(III) at two different initial arsenic concentrations (50 and 100 μg/L) to determine the effect of initial arsenic concentration on the oxidation of As(III). The experimental procedure was the same as described above wherein a single graphite rod anode was used in place of the three standard iron-rod anodes. The experiments were conducted by varying the current in the range of 25 to 150 mA for 1 min (1.5–9.0 Coul generated) and recirculated for another minute. The samples were speciated to determine the As(III) that was oxidized. The experimental results shown in Figure 4.26 showed that the oxidation of As(III) was slightly faster at low As(III)
concentrations due to the higher ratio of Cl₂ to As(III). Again, it is noted that these differences in rates for such low As(III) concentrations are only observable because of the extremely poor efficiency of Cl₂ generation (2–5% based on the residuals observed), which makes the Cl₂ demand of As(III) significant in comparison with the actual amount of Cl₂ generated.

STUDY ON SIMULTANEOUS OXIDATION AND REMOVAL OF AS(III) USING A COMBINATION OF GRAPHITE AND IRON RODS

Based on the results obtained with graphite rods on oxidation of As(III), experiments were conducted to study simultaneous oxidation and removal of As(III) using a combination of graphite and iron rods in the same EC-unit housing. Experiments with one graphite and one iron rod, one graphite and two iron rods, two graphite and one iron rod were performed with NSFI challenge water spiked with 50 μg/L As(III) in the EC unit at pH 7.5. The samples were analyzed for As(III), As(Tot), and residual chlorine.

The As(III) removal efficiencies in NSFI Challenge water using EC with the combination of graphite and iron rods is shown in Figure 4.27, which indicates that removal efficiency of As(III) was approximately the same in all cases. Even though the removal efficiencies seemed to increase with the use of graphite rods due to the oxidation of As(III) with generated Cl₂, the increase was not significant.

The percent change or removal efficiency of As(III) was found to be approximately the same as that of the removal efficiency of As(Tot) which is shown in Figure 4.28 and so there was no significant oxidation of As(III) with the use of one or two graphite rods in the same EC-unit housing. No chlorine was detected in the EC effluent samples, which suggested that the chlorine produced at the graphite rods was immediately consumed by the chlorine demand of the iron rods and ferrous iron generated by the iron rods. Thus, in order for As(III) to be oxidized by electrically generated Cl₂, the Cl₂ would have to be generated in a separate housing ahead of the housing containing the iron rods.

Figure 4.27 As(III) removal efficiency in NSFI Challenge water during EC with graphite and iron rods as a function of Fe dose at pH 7.5

The percent change or removal efficiency of As(III) was found to be approximately the same as that of the removal efficiency of As(Tot) which is shown in Figure 4.28 and so there was no significant oxidation of As(III) with the use of one or two graphite rods in the same EC-unit housing. No chlorine was detected in the EC effluent samples, which suggested that the chlorine produced at the graphite rods was immediately consumed by the chlorine demand of the iron rods and ferrous iron generated by the iron rods. Thus, in order for As(III) to be oxidized by electrically generated Cl₂, the Cl₂ would have to be generated in a separate housing ahead of the housing containing the iron rods.

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Figure 4.28 Comparison of removal efficiencies of As(Tot) & As(III)(speciated) during EC with graphite and iron rods in the same EC-unit housing as a function of Fe dose at pH 7.5

Figure 4.29 As(III) adsorption isotherms onto in-situ formed Fe(III) hydroxide during EC with graphite and iron rods at pH 7.5

The adsorption isotherms of As(III) on the in-situ-formed hydroxides of Fe for the combination of graphite and iron rods are shown in Figure 4.29. The isotherms indicate that there was possibly a slight increase in As(III) adsorption capacity of the iron generated when chlorine was simultaneously generated. However, the advantage of graphite and iron rods in the same housing was not apparent.
TWO-STAGE PROCESS FOR AS(III) OXIDATION AND REMOVAL

As shown above, the advantage of oxidizing As(III) by Cl₂ generated from a graphite rod was hindered by (a) the reduced surfaces of the iron rods and (b) the ferrous iron generated in the EC unit. So a two-stage process of As(III) oxidation using graphite rods followed by removal of As(V) (oxidized As(III)) using iron rods was designed and implemented (Figure 4.30). Although more complicated, the two stage process was expected to be effective for As(III) oxidation and subsequent As(V) removal without any need for chemical addition for oxidation of As(III). Experiments were conducted in NSFI challenge water spiked with 50 μg/L As(III) at pH 7.5 and 8.5 to study oxidation followed by removal of As(III) using a two-stage oxidation–coagulation process (Figure 4.30). The samples were analyzed for As(III) and As(Total) at the outlet of the first and second stages. As expected, the test results showed that As(III) was completely oxidized in the first stage where Cl₂ was generated at a graphite anode in the absence of iron anodes. The As(III) removal efficiencies in NSFI Challenge water using the two-stage electro-oxidation–coagulation process were equal to or greater than the As(V) removal efficiencies of EC at pH 7.5 and 8.5. This improved performance for As(III) removal was a result of oxidation of As(III) to As(V) in the first stage and subsequent As(V) removal in the second stage.

The adsorption isotherms of As(III) on the in-situ formed hydroxides of Fe in the two-stage EC process at pH 7.5 and 8.5 are shown in Figures 4.31. The highest arsenic adsorption capacity was observed at the lower pH which is consistent with As(V) adsorption isotherms.
As mentioned above, the As(V) adsorption in the two-stage EC process with As(III) feed was even greater than the As(V) adsorption in the single stage EC process. This is shown graphically in Figure 4.32 for pH 7.5 and 8.5 for an equilibrium As(V) concentration of 10 μg/L. The improved performance of the two-stage process probably resulted from some oxidation of Fe^{2+} by the Cl₂ generated in stage 1 of the two stage process. The improved ferrous iron oxidation by chlorine produced more ferric hydroxide for As(V) adsorption.

Figure 4.32 Comparison of As(III) (two-stage process) and As(V) adsorption capacities during EC for an equilibrium concentration of 10 μg/L. (Note: As(III) was oxidized to As(V) in the two-stage process.)
SUMMARY AND CONCLUSIONS

The overall objective of the research was to determine the technical and economic feasibility of using EC–F for arsenic removal from drinking water. The research described in this chapter included (a) optimization of the EC design for oxidation of As(III) to As(V) and removal of As(V), (b) comparison of CC with EC, (c) determination of the effect of pH on As(III) and (V) removal, and (d) determination of the suitability of the EC–F process for treating small community ground waters contaminated with arsenic. The results of the research led to the following conclusions:

1. In contrast to literature reports, ferrous (Fe(II)) not ferric (Fe(III)) iron was produced at the anode during EC. Ferrous iron production is problematic because, compared with ferric iron, Fe(II) is much more soluble and must be oxidized to Fe(III) to produce the desired Fe(OH)₃ floc needed for arsenic removal.
2. The iron generation experimentally approached the theoretical iron generation capacity based on Fe²⁺ production at the anodes both in batch and continuous mode operation, provided the iron rods were cleaned prior to each iron-generation experiment.
3. Although Fe(II) was generated during the electrochemical oxidation of the iron anode, it was completely oxidized during 2 min mixing/iron generation at pH 8.5, which resulted in the desired ferric hydroxides. However, at pH 6.5 and 7.5, Fe(II) was not completely oxidized, which resulted in a mixture of soluble Fe(II) and Fe(OH)₃ at the end of 2 min generation/mixing.
4. For the EC process, 70–85% Fe(II) was present at pH 6.5, while 10–45% Fe(II) was present at pH 7.5 at the end of 2 minutes of iron generation and mixing.
5. As(V) removal during EC was very erratic at pH 6.5 due to (a) the >70% un-oxidized iron (Fe(II)) present in the treated water (b) low amount of ferric hydroxides (15–30%) produced, and (c) variable amount of adsorption of As(V) onto the iron oxide/hydroxide surfaces of the iron rods in the EC unit.
6. As(V) removal using EC is not advisable at pH 6.5 unless there is a very long (>2 hr) oxidation time or higher concentration of dissolved oxygen or oxidants available for nearly complete oxidation of Fe(II) produced.
7. As(V) removal was efficient at pH 7.5 and 8.5 during EC, however, a significant and highly variable amount of un-oxidized Fe(II) (10–45%) was present in the treated water at pH 7.5.
8. As(V) removal by EC at pH 7.5 is not advisable because of potentially high concentrations of soluble Fe(II) present in the effluent. Oxidation post treatment is a possibility to oxidize Fe(II), but the additional complexity is undesirable for small community treatment.
9. As(V) removal by EC at pH 8.5 is likely an acceptable small community treatment process because of the rapid oxidation of Fe(II) to Fe(III) at this higher pH.
10. As(V) removal was highly pH dependent in CC, and the efficiency increased with decreasing pH.
11. The As(V) adsorption capacity was almost the same with CC and EC at pH 7.5 and 8.5. EC was not efficient at pH 6.5
12. Compared with As(V) removal, the removal of As(III) was poor for both EC and CC.
13. As(III) removal was slightly greater during EC which was pH dependent, compared to CC, which was pH independent.

Although not originally within the scope of work for this project, the study of chlorine generation during EC was undertaken with the objective of oxidizing As(III) to As(V) for better removal and oxidizing Fe(II) to Fe(III) to eliminate residual soluble iron and improve arsenic removal. The results of the additional research into electrolytic chlorine generation led to the following conclusions.

1. With iron rod as anodes, chlorine was not generated in the EC unit, and, in fact, the reduced oxides/hydroxides on the iron anodes produced a very significant source of chlorine demand in the EC unit.
2. With a graphite rod anode and stainless steel cathode, chlorine was generated at the anode when chloride ions were present in the solution, and complete oxidation of As(III) was possible providing that sufficient current and mixing time were provided. Unfortunately, the efficiency of Cl₂ generation was only 2–5%, possibly due to electrolysis of water and production of mixed oxides.
3. A combination of graphite and iron rods in the same EC unit housing had no significant advantage for As(III) removal compared with the iron rods alone. When Cl₂ was generated at the graphite anodes, it was immediately consumed by the chlorine demand of the reduced iron oxide/hydroxide anode surfaces and by the Fe(II) produced during electrolysis.
4. A two-stage EC process with graphite anodes in a separate stage 1 housing and iron anodes in the stage 2 housing, although more complicated and costly, was effective for As(III) oxidation and removal without any need for chemicals.

The main objective of this project was to determine the suitability of EC–F for arsenic removal from small community water supplies. Taking the detailed conclusions above into consideration, the following is the overall conclusion of the project.

Because it was discovered during this research that ferrous not ferric iron is generated during iron anode EC with typical ground water in the pH 6.5 to 8.5 range, the EC process is generally unsuitable for convenient application to small community water supply treatment to remove arsenic. The process produces erratic results at pH 6.5 due to poor oxidation of Fe(II). EC is nearly as effective as CC for As(V) removal at pH 7.5, but residual Fe(II) is a major problem. The EC process may have some application at high pH (~8.5 or higher) due to the rapid oxidation of ferrous iron to ferric at high pH.
CHAPTER 5
EFFECT OF COMPETING IONS AND MIXING TIME

INTRODUCTION

The adsorption of arsenic occurs by the process of ligand exchange as discussed in Chapter 4 (Figure 4.1). However the adsorption is influenced by the presence of competing anions in source water such as bicarbonate, sulfate, silica, phosphate, and vanadate. These anions are expected to sorb onto the metal hydroxides and competition between these substances for adsorption sites will significantly interfere with As removal. This competition has the potential to reduce the overall effectiveness of arsenic removal from source water. The NSFI challenge water under study contains silica and phosphate, which will compete with arsenates for adsorption sites on the oxyhydroxide surfaces because they form strong surface complexes with iron, aluminum and similar metal oxides (Hingston 1981). Table 5.1 gives the equilibrium constants (pKₐ’s) for arsenic-containing acids, silicic acid, phosphoric acid and the concentrations of the species present at pH 6.5–8.5.

Soluble silica in water exists as silicic acid (H₄SiO₄) which dissociates to H₃SiO₄⁻ (pKₐ₁ = 9.84). So at pH of 6.5–8.0, silica exists almost entirely as uncharged H₄SiO₄, but at pH 8.5–9.0, the fraction of silica existing as anionic silicate, H₃SiO₄⁻ is significant. Both neutral H₄SiO₄ and anionic H₃SiO₄⁻ can act as ligands and form surface complexes, but the anions are stronger ligands. Although the neutral species dominates at pH 6.5–8.5, the concentration of silica is so high (712 μM) that the monovalent silicic acid concentration (H₃SiO₄⁻) is very high in comparison to the arsenic species at pH 7.5 and 8.5 and nearly equal at pH 6.5 (Table 5.1). Because of the high concentration of silica (H₃SiO₄⁻), compared with the concentration of arsenic, silica is expected to compete significantly with arsenic for adsorption sites at pH 6.5–8.5.

Phosphoric acid has similar pKₐ values to that of arsenic acid, and phosphate exists as monovalent and divalent H₂PO₄⁻ and as HPO₄⁻² at pH 6.5–8.5, which are similar in chemical behavior to H₂AsO₄⁻ and HAsO₄²⁻. Both H₂PO₄⁻ and HPO₄⁻² can have ligand exchange reactions with the hydroxides formed and will compete for adsorption sites with the arsenates. Since the concentration of phosphorous (1.29 μM) is higher than that of arsenic (0.67 μM), phosphate is expected to compete strongly with arsenic for adsorption sites.

<p>| Table 5.1 Composition of species of some important acids present at pH 6.5–8.5 (Source: Data from Schecher 1998) |
|-----------------------------------------------|-------------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>pKₐ</th>
<th>pH 6.5</th>
<th>pH 7.5</th>
<th>pH 8.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic acid (0.67 μmol/L)</td>
<td>pK₁=2.22</td>
<td>H₂AsO₄⁻</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>pK₂=6.98</td>
<td>HAsO₄²⁻</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>pK₃=11.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphoric acid (1.29 μmol/L)</td>
<td>pK₁=2.16</td>
<td>H₂PO₄⁻</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>pK₂=7.2</td>
<td>HPO₄⁻²</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>pK₃=12.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicic acid (712 μmol/L)</td>
<td>pK₁=9.84</td>
<td>Si(OH)₄</td>
<td>712</td>
</tr>
<tr>
<td></td>
<td>pK₂=13.2</td>
<td>H₂SiO₄⁻</td>
<td>0.33</td>
</tr>
</tbody>
</table>

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CC and EC experiments were performed using challenge water with silica (SiO$_2$ = 20 mg/L) and without silica (SiO$_2$ = 0 mg/L) in the presence of phosphate. The objective was to study the effect of silica in the challenge water on arsenic removal in the pH range of 6.5 to 8.5. The experiments were also performed using challenge water with phosphate (PO$_4$-P = 40 μg/L) and without phosphate (PO$_4$-P = 0 μg/L) in the presence of silica to study the effect of phosphate in the challenge water on arsenic removal in the pH range of 6.5 to 8.5.

Effect of Silica in NSFI Water with Phosphate Using Ferric (III) Chloride as Coagulant

Based on jar tests in the presence and absence of silica, it was found that silica does have a significant effect on the adsorption of arsenic and the effect increases significantly with increasing pH. The removal percentages of As(V) at 1 mg/L Fe(III) dosage at pHs 6.5, 7.5, and 8.5 were 89, 71, and 33%, respectively, in the presence of silica. In the absence of silica, the removal percentages at the same pHs were 93, 76, and 60%, respectively for the same doses, which shows that removal efficiency was higher in the absence of silica. This can be observed in Figure 5.1 through the more favorable adsorption isotherms in the absence of silica and the effect of silica increasing with increase in pH.
Effect of Silica in NSFI Water with Phosphate Using Fe ions Produced During EC

Based on EC experiments in the presence and absence of silica in NSFI, it was found that silica does have a significant impact on the adsorption of arsenic and the effect increases with increasing pH. As was observed with NSFI challenge water at pH 6.5 and pH 7.5 (Chapter 4), arsenic removal in challenge water without silica was also very erratic at pH 6.5 and significant soluble iron concentrations observed in the filtrate at pH 7.5, eventhough the removals were good. The removal percentages of As(V) at 1 mg/L total iron dosage at pHs 7.5, and 8.5 were ≈75, and 40%, respectively, in the presence of silica. In the absence of silica, the removal percentages at the same pHs were 84, and 64%, respectively for the same doses, which shows that the decrease in removal efficiency was significant in the presence of silica at pHs 7.5 and 8.5. This can be observed in Figure 5.2 through the more favorable adsorption isotherms in the absence of silica at pHs 7.5 and 8.5.

![Figure 5.2](image.png)

Figure 5.2 Effect of silica on As(V) adsorption at different pHs with in-situ formed Fe hydroxide formed during EC in NSFI water with phosphate

Effect of Phosphate in NSFI Water with Silica Using Ferric (III) Chloride as Coagulant

The presence of phosphate in NSFI water with silica had a significant effect at pH 6.5 and the effect decreased with increasing pH during coagulation with FeCl₃. The removals of As(V) in the presence of phosphate at 1 mg/L Fe(III) dosage at pHs 6.5, 7.5, and 8.5 were 89, 71, and 33%, respectively. In the absence of phosphate, the removals at the same pHs were 93, 78, and 38%, respectively for the same dose, which shows that the decrease in removal efficiency was significant in the presence of phosphate at pHs 6.5 and was less significant at pH 7.5 and 8.5. This can be observed in Figure 5.3 through the more favorable adsorption isotherms in the absence of phosphate at pH 6.5 as compared with the influence of phosphate on the adsorption isotherms at pH 7.5 and 8.5.
Effect of Phosphate in NSFI Water with Silica Using Fe ions Produced During EC

Based on EC experiments in the presence and absence of phosphate in NSFI water with silica, it was found that phosphate does have a significant effect on the adsorption of As(V) at pH 7.5 and no significant effect at pH 8.5. It was observed that removal efficiency of As(V) at pH 6.5 in NSFI without phosphate was also erratic. The removals of As(V) in the presence of phosphate at 1 mg/L Fe dosage at pHs 7.5, and 8.5 were ≈75, and 40%, respectively. In the absence of phosphate, the removals at the same pHs were 83, and 41%, respectively for the same
dose, which shows that the decrease in removal efficiency was significant in the presence of phosphate at pH 7.5 as compared to the effect at pH 8.5. This can be best observed in Figure 5.4 through the more favorable adsorption isotherms in the absence of phosphate at pH 7.5 as compared to pH 8.5.

INDIVIDUAL EFFECTS OF SILICA AND PHOSPHATE IN NSFI CHALLENGE WATER DURING CC AND EC

The individual effects of competing ions were evaluated by studying the effect of each competing ion under study (silicate, and phosphate) in the absence of the other competing ion. The previously reported effects of silica, and phosphate were determined in the presence of other competing ions, e.g., the effect of silica (0 and 20 mg/L) was performed using challenge water containing phosphate, and the effect of phosphate (0 and 40 μg P/L) was determined in the NSFI water containing silica.

Therefore, to study the individual effect of silica on arsenic adsorption in the absence of competing ions, experiments were performed using NSFI water with silica (SiO2 = 20 mg/L) and without silica, in the absence of phosphate in the pH range of 6.5 to 8.5 with ferric chloride and in-situ generated iron as coagulants during CC and EC experiments, respectively. Similarly the effect of phosphate on arsenic removal in the absence of silica was studied in the pH range of 6.5 to 8.5 during CC and EC.

Effect of Silica in the Absence of Phosphate in NSFI Challenge Water Using Ferric Chloride as Coagulant

Based on jar tests in the presence and absence of silica, it was found that silica does have a significant impact on the adsorption of As(V) and the effect increases with increasing pH during coagulation with FeCl3. The removals of As(V) in the presence of silica at 1 mg/L Fe(III) dosage at pHs 6.5, 7.5, and 8.5 were 93, 78, and 38%, respectively. In the absence of silica, the removals at the same pHs were ≈96, 88, and 73%, respectively for the same dose, which shows that the decrease in removal efficiency was significant in the presence of silica at pHs 7.5 and 8.5 and a minor decrease at pH 6.5. This can be observed in Figure 5.5 through the more favorable adsorption isotherms in the absence of silica at pHs of 7.5 and 8.5 as compared with the influence of silica on the adsorption isotherms at pH 6.5.

Effect of Silica in the Absence of Phosphate in NSFI Challenge Water Using Fe ions Produced During EC

Based on EC experiments in the presence and absence of silica, it was found that silica does have a significant effect on the adsorption of As(V) and the effect increases with increasing pH. It was observed that As(V) removal efficiencies were erratic at pH 6.5 under both experimental conditions, as observed earlier. The removals of As(V) in the presence of silica at 1 mg/L Fe(III) dosage at pHs 7.5, and 8.5 were 83, and 41%, respectively. In the absence of silica, the removals at the same pHs were 92, and 75%, respectively for the same dose, which shows that the decrease in removal efficiency was significant in the presence of silica at pH 8.5 compared to pH 7.5. This can be observed in Figure 5.6 through the more favorable adsorption isotherms in the absence of silica at pHs 7.5 and 8.5, and the effect of silica increasing with increase in pH.
Figure 5.5 Effect of silica on As(V) adsorption at different pHs with in-situ formed Fe(III) hydroxides during coagulation with FeCl₃ in the absence of phosphate.

Figure 5.6 Effect of silica on As(V) adsorption at different pHs with in-situ formed Fe hydroxides formed during EC in the absence of phosphate.
Effect of Phosphate in the Absence of Silica in NSFI Challenge Water Using Ferric Chloride as Coagulant

In the absence of silica, phosphate does have a significant effect on the adsorption of As(V) during coagulation with FeCl₃ and the effect increases with decreasing pH. The removals of As(V) in the presence of phosphate at 1 mg/L Fe(III) dosage at pHs 6.5, 7.5, and 8.5 were 93, 76, and 60%, respectively. In the absence of phosphate, the removals at the same pHs were ≈96, 88, and 73%, respectively for the same dose, which shows that the decrease in removal efficiency was significant in the presence of phosphate. This can be observed in Figure 5.7 through the more favorable adsorption isotherms in the absence of phosphate at all three pHs tested and the effect increasing with decrease in pH.

![Figure 5.7 Effect of phosphate on As(V) adsorption at different pHs with in-situ formed Fe(III) hydroxides during coagulation with FeCl₃ in the absence of silica](image)

Effect of Phosphate in the Absence of Silica in NSFI Challenge Water Using Fe ions Produced During EC

Based on experiments in the absence of silica, phosphate does have a less significant effect on the adsorption of As(V) during EC compared with CC. As was observed earlier the As(V) removal efficiency with EC was erratic at pH 6.5. The removals of As(V) in the presence of phosphate at 1 mg/L Fe dosage at pHs 7.5, and 8.5 were 84, and 64%, respectively. In the absence of phosphate, the removals at the same pHs were 92, and 75%, respectively for the same dose, which shows that the decrease in removal efficiency was significant in the presence of phosphate at pH 7.5 and less significant at pH 8.5. This can be observed in Figure 5.8 through the more favorable adsorption isotherms in the absence of phosphate at pH 7.5 as compared to pH 8.5.
Ferrous Remaining in the EC Unit at pH 6.5 and 7.5 during Competing Ions Study

The ferrous ions present in the EC unit at the end of 2 minutes of iron generation and mixing would be soluble and would pass through the 0.2 μm filter. To study this, the total iron concentration in the filtrate (sample used for arsenic analysis during competing ions study) was analyzed for all compositions of NSFI challenge water used: challenge water, challenge water without silica, challenge water without phosphate, and challenge water without silica and phosphate. Figures 5.9 shows the percent Fe(II) remaining in the EC unit at the end of 2 minute of mixing at pH 6.5 and 7.5.

At pH 6.5, (Fig. 5.9a) most of the iron present after 2 minutes is soluble Fe$^{2+}$ (~80%), which would not adsorb As(V). In spite of the fact that the system was pre-equilibrated with the challenge water, significant As(V) was removed by the iron rods in the system at pH 6.5, even without applying current. So the removals shown in Figures 5.2, 5.4, 5.6, and 5.8 at pH 6.5 are a combination of removals caused by the very small amount Fe(III) hydroxides formed and by the iron oxide/hydroxide coated anodes in the EC unit.

At pH 7.5 (Fig. 5.9b) about 55–90% of the iron present in the EC unit after 2 min was in the form of insoluble Fe(III) hydroxides capable of adsorbing As(V). Thus, the overall As(V) removal was good due to formation of Fe(III) hydroxides. Nevertheless, the 10–45% Fe$^{2+}$ remaining in the effluent is a concern, and optimizing the EC system is necessary if operated at pH 7.5.
Figure 5.9 Fe$^{2+}$ remaining for iron doses generated during EC with various compositions of NSFI challenge water at the end of 2 min of mixing at (a) pH 6.5 and (b) pH 7.5. The y-axis label “% Fe$^{2+}$ in filtrate” refers to that fraction of the total iron generated that is in the filtrate. It is assumed that all iron in the 0.2 μm membrane filtrate is soluble Fe$^{2+}$.

**AS(V) REMOVAL DURING CC USING FERROUS SULFATE AT PH 6.5 FOR VARIOUS COMPOSITIONS OF NSFI CHALLENGE WATER**

Coagulation experiments were conducted with ferrous sulfate as coagulant for the following compositions of challenge water at pH 6.5: NSFI challenge water without silica, NSFI challenge water without phosphate, and NSFI challenge water without silica and phosphate. The experimental conditions were similar to those of FeCl$_3$ CC (rapid mix at 100 rpm for 2 minutes). Figure 5.10 compares the As(V) removal efficiencies with ferric chloride and ferrous sulphate on total iron basis at pH 6.5. The percentage removal of As(V) with 1.0 mg/L Fe(III) dosage in NSFI without silica and phosphate, NSFI without silica, and NSFI without phosphate were ≈96, 93, and 93%, while for the same dose of Fe(II), the removals were < 20, 9, and 13%, respectively. So it was clear that with FeSO$_4$ as coagulant, the removals were much less in comparison to FeCl$_3$ at pH 6.5. The analysis of filtrate showed >95% Fe$^{2+}$ remaining in all the compositions of challenge water for all doses. The oxidation results discussed in Chapter 3 (where the redox standard ferrous ammonium sulfate was used as a source of Fe$^{2+}$ ions) showed insignificant oxidation of Fe$^{2+}$ (<5%) at the end of 2 min of mixing at pH 6.5, and so significant Fe$^{2+}$ in the filtrate was expected. These results showing little if any As(V) adsorption during Fe$^{2+}$ CC confirm that the higher-than-expected As(V) adsorption during pH 6.5 EC probably resulted from As(V) adsorption onto iron oxide/hydroxide coated anodes in the EC unit.
Figure 5.10 Comparison of As(V) removal efficiencies during CC with ferric chloride and ferrous sulfate as coagulant at pH 6.5 in various compositions of NSFI challenge water

EFFECT OF COMPETING IONS ON THE ARSENIC ADSORPTION CAPACITY IN NSFI CHALLENGE WATER

Figure 5.11 compares the As(V) adsorption capacities of ferric (III) hydroxides formed during coagulation with FeCl₃ for an equilibrium concentration of 10 μg/L As(V) in the pH range 6.5–8.5 in the presence and absence of silica and phosphate in NSFI challenge water. Based on the experiments, the presence of silica significantly reduced the adsorption capacity of As(V) onto Fe(OH)₃ at high pH compared to low pH, and the effect increased with increasing pH. The results are understandable considering that percent silica as ionic H₄SiO₄ are 99.95, 99.54, and 95.63% respectively at pH 6.5, 7.5, and 8.5 respectively and so significant amount of ionic H₄SiO₄ is present at pH 8.5 compared to pH 6.5. Phosphate also significantly lowered the adsorption of As(V) in NSFI challenge water at pH 6.5, but had a lesser effect at pH 7.5 and 8.5. The presence of silica lowered the effect of phosphate at high pH due to its own significant effect at that pH.
Figure 5.11 Effect of competing ions (silica and phosphate) in NSFI challenge water on arsenic adsorption capacities of in-situ formed Fe(III) hydroxides formed during CC with FeCl₃ for an equilibrium concentration of 10 μg/L As(V) in the pH range of 6.5–8.5.

<table>
<thead>
<tr>
<th>Condition</th>
<th>pH 6.5</th>
<th>pH 7.5</th>
<th>pH 8.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC, NSFI-53</td>
<td>48.8</td>
<td>30.6</td>
<td>10.24</td>
</tr>
<tr>
<td>CC, NSFI without silica</td>
<td>55.0</td>
<td>39.4</td>
<td>22.00</td>
</tr>
<tr>
<td>CC, NSFI without phosphate</td>
<td>78.2</td>
<td>37.2</td>
<td>13.80</td>
</tr>
</tbody>
</table>

Figure 5.12 Effect of competing ions (silica and phosphate) in NSFI challenge water on arsenic adsorption capacities of in-situ formed Fe hydroxides formed during EC for an equilibrium concentration of 10 μg/L As(V) at pH 7.5 and 8.5.

<table>
<thead>
<tr>
<th>Condition</th>
<th>pH 7.5</th>
<th>pH 8.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC, NSFI-53</td>
<td>30.49</td>
<td>9.83</td>
</tr>
<tr>
<td>EC, NSFI without silica</td>
<td>46.21</td>
<td>24.54</td>
</tr>
<tr>
<td>EC, NSFI without phosphate</td>
<td>44.94</td>
<td>13.60</td>
</tr>
</tbody>
</table>
Figure 5.12 compares the As(V) adsorption capacities of Fe hydroxides formed during EC for an equilibrium concentration of 10 μg/L As(V) in the pH range 7.5–8.5 in the presence and absence of silica and phosphate in NSFI challenge water. The adsorption capacities were not calculated for pH 6.5 because Fe(II) was not significantly oxidized to Fe(III) at pH 6.5, and it was likely the As(V) that was removed was adsorbed onto the iron oxide/hydroxide surfaces of the iron rods in the EC unit. Based on the experiments, the presence of silica significantly reduced the adsorption capacity of As(V) onto Fe hydroxides at pH 8.5 compared to pH 7.5, and so the effect increased with increasing pH. Phosphate also significantly lowered the adsorption of As(V) at pH of 7.5 but had a lesser effect at pH 8.5. The presence of silica again lowered the effect of phosphate at pH 8.5 due to its own significant effect at that pH.

INDIVIDUAL EFFECT OF COMPETING IONS ON THE ARSENIC ADSORPTION CAPACITY

Figure 5.13 compares the individual effects of silica, and phosphate on the As(V) adsorption capacities of ferric (III) hydroxides formed during coagulation with FeCl₃ for an equilibrium concentration of 10 μg/L As(V) in the pH range 6.5–8.5. In the absence of phosphate, silica significantly reduced the adsorption capacity of As(V) onto Fe(OH)₃ and the effect increased significantly with increasing pH. Phosphate also significantly lowered the adsorption of As(V) at all pHs in the absence of silica and the effect increased with decreasing pH.

Figure 5.14 compares the individual effects of silica and phosphate on As(V) adsorption capacities of Fe hydroxides formed during EC for an equilibrium concentration of 10 μg/L As(V) at pH 7.5 and 8.5. The adsorption capacities were not calculated for pH 6.5 because Fe²⁺ was not oxidized to Fe(III) and the As(V) adsorption that occurred was onto the surfaces of the anodes. Based on the experiments, the presence of silica significantly reduced the adsorption capacity of As(V) onto Fe hydroxides at pH 8.5 compared to pH 7.5. Phosphate also significantly lowered the adsorption of As(V) at pH 7.5 and 8.5 in the absence of silica.
Figure 5.13 Individual effects of competing ions (silica and phosphate) on arsenic adsorption capacities of in-situ formed Fe(III) hydroxides formed during CC with FeCl₃ for an equilibrium concentration of 10 μg/L As(V) in the pH range 6.5–8.5.

<table>
<thead>
<tr>
<th>pH</th>
<th>Experiment</th>
<th>qₑ (μg As(V)/mg Fe(III))</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>CC, NSFI without silica and phosphate</td>
<td>91.72</td>
</tr>
<tr>
<td></td>
<td>CC, PO₄=40 ug/L</td>
<td>54.96</td>
</tr>
<tr>
<td></td>
<td>CC, Si=20 mg/L</td>
<td>78.17</td>
</tr>
<tr>
<td>7.5</td>
<td>CC, NSFI without silica and phosphate</td>
<td>55.62</td>
</tr>
<tr>
<td></td>
<td>CC, PO₄=40 ug/L</td>
<td>39.43</td>
</tr>
<tr>
<td></td>
<td>CC, Si=20 mg/L</td>
<td>37.23</td>
</tr>
<tr>
<td>8.5</td>
<td>CC, NSFI without silica and phosphate</td>
<td>29.89</td>
</tr>
<tr>
<td></td>
<td>CC, PO₄=40 ug/L</td>
<td>22.00</td>
</tr>
<tr>
<td></td>
<td>CC, Si=20 mg/L</td>
<td>13.80</td>
</tr>
</tbody>
</table>

Figure 5.14 Individual effect of competing ions (silica and phosphate) on arsenic adsorption capacities of in-situ formed Fe hydroxides formed during EC for an equilibrium concentration of 10 μg/L As(V) at pH 7.5 and 8.5.

<table>
<thead>
<tr>
<th>pH</th>
<th>Experiment</th>
<th>qₑ (μg As(V)/mg Fe(III))</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>EC, NSFI without silica and phosphate</td>
<td>58.87</td>
</tr>
<tr>
<td></td>
<td>EC, PO₄=40 ug/L</td>
<td>46.21</td>
</tr>
<tr>
<td></td>
<td>EC, Si=20 mg/L</td>
<td>44.94</td>
</tr>
<tr>
<td>8.5</td>
<td>EC, NSFI without silica and phosphate</td>
<td>32.27</td>
</tr>
<tr>
<td></td>
<td>EC, PO₄=40 ug/L</td>
<td>24.54</td>
</tr>
<tr>
<td></td>
<td>EC, Si=20 mg/L</td>
<td>13.60</td>
</tr>
</tbody>
</table>
CC experiments with ferric chloride as coagulant in the project were conducted with 2 min of rapid mixing without any flocculation step involved. Comparing the CC results with the previous project, “Arsenic Coagulation With Iron, Aluminum, Titanium, and Zirconium Salts” (Lakshmanan et al. 2008), where 20 min of flocculation step was involved, indicated that the percentage removals obtained with 2 minute of rapid mix were less than the removals obtained during 1 minute of rapid mix followed by 20 minutes of flocculation. The increase in mixing time resulted in higher adsorption capacities during 21 min of mixing (1 min rapid mixing plus 20 min slow mixing) as compared with 2 min of rapid mixing. However the significance of the effect of mixing was dependent on the Fe(III) dose and the presence/absence of competing ions.

Figures 5.15 compares the effect of mixing time on As(V) adsorption isotherms in NSFI challenge water, NSFI challenge water without silica, NSFI challenge water without phosphate, and NSFI challenge water without silica and phosphate. The As(V) adsorptions during 21 min of mixing (1 min rapid mix followed by 20 min of slow mixing) was more favorable compared to 2 min of mixing for all compositions of challenge water and at all pHs tested. However the significance in difference was dependent on the composition of challenge water. The effect of mixing time was most significant in challenge water without silica and phosphate (Figure 5.15d), while the effect was least in standard NSFI challenge water which contained silica and phosphate (Figure 5.15 a). In the challenge water without phosphate, the effect of mixing time on arsenic adsorption isotherms was significant at low pH (6.5) compared to high pH (8.5) due to the influence of silica at high pH (Figure 5.15c). In the challenge water without silica, the effect of mixing time on arsenic adsorption was significant at all pHs (Figure 5.15b). So it was clear that the effect of mixing time was significantly dependent on the presence of competing ions, and with the absence of competing ions the effect increased. The effects of mixing time on As(V) adsorption were confirmed from the differences in adsorption capacities for an equilibrium concentration of 10 μg/L As(V) of ferric (III) hydroxides for 2 and 21 min of mixing in the pH range 6.5–8.5 for all compositions of NSFI challenge water (Figure 5.16). It can be seen that the effect was significant in the absence of competing ions compared to the effect when competing ions were present.
Figure 5.15 Effects of mixing time on As(V) adsorption during CC with FeCl₃ in (a) NSFI challenge water (b) NSFI challenge water without silica (c) NSFI challenge water without phosphate and (d) NSFI challenge water without silica and phosphate
Figure 5.16 Effect of mixing time on As(V) adsorption capacities for an equilibrium concentration of 10 μg/L in (a) NSFI challenge water (b) NSFI challenge water without silica (c) NSFI challenge water without phosphate and (d) NSFI challenge water without silica and phosphate.

Figure 5.17 Effect of mixing time on As(V) removal efficiency during coagulation with ferric chloride.
It is generally perceived that the arsenic adsorption occurs only in the first few minutes of mixing. However, the comparison of results showed that the mixing time did affect arsenic adsorption and the adsorption increased with increase in mixing time. So coagulation experiments were performed with 0.5 mg/L Fe\textsuperscript{3+} dosed in NSFI without silica and phosphate. The mixing speed was kept constant at 100 rpm, while the mixing time was varied (0.25–21 min) to determine the effect of mixing time on removal efficiency. Figure 5.17 shows the increase in As(V) removal with increase in mixing time. It can be seen that the As(V) removal increased from about 67 to 88% with an increase in mixing time of 1 to 21 minutes of mixing. So it was clear that even though significant adsorption occurred during the first few minutes, arsenic was continuously adsorbed onto ferric hydroxides at a slower pace.

Even though mixing time does increase the adsorption, caution is to be exercised in concluding the inference from these results. It is important to note that the effect of mixing time is dependent on the Fe\textsuperscript{3+} dose, the removals associated with the dose, and the presence of competing ions. This is due to the following reasons:

1. With higher doses of Fe\textsuperscript{3+}, e.g. 2–5 mg/L Fe typical for full-scale coagulation processes, As(V) removals of 85–100% would be attained, and so the increase in removals with increase in mixing time would be less evident.
2. But with lower doses of Fe\textsuperscript{3+} and in the absence or low concentrations of competing ions, the increase in As(V) removals with increase in time are significant and are more observable.
3. Silica and phosphate competed strongly with As(V) for adsorption sites with the magnitude of competition depending on the pH. When silica and phosphate were present, the effect of mixing time on As(V) removal was less significant.

CONCLUSIONS

The objectives of this portion of the study were to determine the (a) effects of competing ions (silica and phosphate) on As(V) adsorption during chemical and EC and (b) effect of mixing time on As(V) adsorption. The results led to the following conclusions:

1. As was observed with NSFI challenge water, As(V) removal during EC at pH 6.5 was very erratic with all compositions of challenge water tested due to (a) approximately 80% un-oxidized iron (Fe(II)) present in the treated water, (b) low amount of ferric hydroxides produced, and (c) variable amount of adsorption of As(V) onto the iron oxide/hydroxide surfaces of the iron rods in the EC unit depending upon the conditions. The effect of competing ions at pH 6.5 during EC was not considered for discussion due to the erratic results at this pH.
2. As(V) removal was efficient at pH 7.5 and 8.5 during EC with all compositions of challenge water tested, however, a significant and highly variable amount of un-oxidized Fe(II) (10–45%) was present in the treated water at pH 7.5.
3. In the NSFI challenge water with phosphate, silica at 20 mg/L significantly reduced the adsorption of As(V) by competing for adsorption sites both in CC and EC and the effect increased with increasing pH.
4. In the NSFI Challenge water with silica, phosphate at 40 \( \mu g \) P/L was found to reduce the adsorption of As(V) significantly at pH 6.5, whereas it had a lesser effect at pH 7.5 and
8.5 during CC. The effect of phosphate at 40 μg P/L was found to reduce the adsorption of As(V) significantly at pH 7.5, whereas it had a lesser effect at pH 8.5 during EC. The presence of silica lowered the effect of phosphate at pH 8.5 due to its own significant effect at that pH.

5. In the absence of other competing ions with ferric chloride as coagulant, it was found that silica, and phosphate exhibited significant competitive effects on the adsorption of As(V). In the absence of phosphate, silica exhibited a significant effect on the adsorption of As(V), and the effect increased with increasing pH. In the absence of silica, phosphate exhibited a significant effect on the adsorption of As(V) at all pHs during coagulation with FeCl₃ and the effect increased with decreasing pH.

6. In the absence of other competing ions during EC, silica exhibited a significant effect on the adsorption of As(V) and the effect increased with increasing pH. In the absence of silica, phosphate also exhibited a significant effect on the adsorption of As(V) at pH 7.5 and 8.5 during EC.

7. As expected, the competing ions under study did affect the adsorption of arsenic in most of the cases. However the significance of effect depended on the presence of other competing ion under study. In particular, the effect of phosphate was highly influenced by the co-occurrence of silica.

8. Mixing time was found to have an effect on As(V) adsorption capacity during coagulation with FeCl₃. However the significance of the effect was dependent on the Fe(III) dose, the removals associated with the Fe(III) dose and the presence/absence of competing ions.
CHAPTER 6
SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

SUMMARY

The objective of the proposed work was to determine the feasibility of using EC for arsenic removal in comparison to conventional CC. The project objectives with respect to arsenic removal were attained with a three-cell EC unit and FeCl₃ CC, and the following tasks performed:

1. Study the effect of electrode passivation on iron generation in the EC unit,
2. Estimate the current efficiency as measured by iron generation in the EC unit,
3. Study the ability of EC to simultaneously oxidize and remove As(III),
4. Compare the removal of As(V) and As(III) in NSFI-53 challenge water by EC with CC at pH 6.5–8.5,
5. Study the effect of pH and competing ions (silica and phosphate) on As(V) removal at pH 6.5–8.5, and
6. Recommend the optimum conditions for EC process to be suitable for small community ground waters contaminated with arsenic.

During the course of the study, it was found that, in contrast to what was reported in the literature, ferrous (Fe(II)) not ferric (Fe(III)) iron was produced at the anode during EC. Ferrous iron production is problematic because, compared with ferric iron, Fe(II) is soluble and must be oxidized to Fe(III) to produce the desired Fe(OH)₃ floc needed for contaminant removal. So the following studies were performed to understand the electrolytic oxidation of iron in a single cell EC unit and its possible implications on contaminant removal:

1. Study the effect of electrode passivation on iron generation,
2. Compare the experimental iron generation to theoretical iron generation capacity (Faraday’s law) to determine the type of iron species (Fe²⁺/Fe³⁺) generated at the anode,
3. study the effect of pH and dissolved oxygen (DO) on the in-situ formation of iron hydroxides during and after electrolysis,
4. Study the oxidation of Fe²⁺ by DO during CC with the redox standard ferrous ammonium sulfate (FAS) as coagulant, and compare the results with ferrous ion oxidation during EC.
5. Compare the iron generation efficiencies with industrial-grade (98.5%) and reagent-grade (99.995%) iron rods to determine the importance of iron rod purity, and,
6. Study the oxidation of iron using industrial- and reagent-grade iron anodes, in a N₂ purged EC cell to confirm that the oxidation of Fe²⁺ was a result of the dissolved oxygen present in the open-to-the-atmosphere EC unit.

Although not originally within the scope of work for this project, the study of chlorine generation during EC was undertaken with the objective of oxidizing As(III) to As(V) for better removal and oxidizing Fe(II) to Fe(III) to eliminate residual soluble iron and improve arsenic removal. The following tasks were performed in the three-cell EC unit with the above purpose in mind:
1. Study the chlorine generation and utilization in the EC unit with an industrial-grade iron rod as anode,
2. Study the chlorine generation and As(III) oxidation using graphite rod as anode,
3. Study the simultaneous oxidation and removal of As(III) using a combination of graphite and iron rods in the same EC housing, and
4. Study the two-stage process for As(III) oxidation and removal using graphite and iron rods as anode in stage 1 and 2, respectively.

Based on previous research (Lakshmanan et al. 2008) and the current study results with CC, it was found that mixing time had an effect on arsenic removal. So limited experiments were performed to

1. Study the effect of mixing time on arsenic adsorption during CC with ferric chloride, and
2. Determine the conditions under which mixing time has an effect on arsenic adsorption.

CONCLUSIONS

The studies on the oxidation of iron during and after electrolysis performed in the single-cell EC unit led to the following conclusions:

1. The iron generation experimentally was the same as theoretical iron generation capacity (Faradays’ law) based on Fe²⁺ production at the anode for applied currents of 0.05–0.8A and at pH 6.5–8.5. In addition, the current efficiency with respect to iron generation was 100%, provided the iron rod was cleaned prior to each iron-generation experiment.
2. The electrolytic reduction of water at the cathode resulted in the formation of hydroxides which were consumed by the protons resulting from hydrolysis of Fe²⁺ (produced from the oxidation of iron at the anode) and Fe³⁺ ions (produced by subsequent oxidation of Fe²⁺ by DO) to form Fe hydroxide complexes depending upon pH.
3. During electrolysis, a significant increase from the initial pH was observed due to the continuous production of hydroxide ions. However the pH decreased as the Fe hydroxides were formed and the final pH was the same as initial for pH 7.5, while their was a slight increase and decrease in final pH for initial pHs of 6.5 and 8.5, respectively.
4. Although Fe(II) was generated during the electrochemical oxidation of the iron anode, it was completely oxidized during 2 min mixing/iron generation at pH 8.5, which resulted in formation of the desired ferric hydroxides. However, at pH 6.5 and 7.5, Fe(II) was not completely oxidized, which resulted in a mixture of soluble Fe(II) and precipitated Fe(OH)₃ at the end of 2 min generation/mixing.
5. At the end of 2 minutes of iron generation and mixing in the EC process, 70–90% Fe(II) was present at pH 6.5, while 10–45% Fe(II) was present at pH 7.5 and ≈0% at pH 8.5.
6. The coagulation studies with FAS as coagulant showed that the oxidation of Fe²⁺ by DO was fast at pH 8.5 and extremely slow at pH 6.5, which is consistent with the literature and with observations made during EC.
7. The greater oxidation of Fe²⁺ during EC compared to CC (FAS as coagulant) at the end of 2 minutes of mixing was due to significant increase in pH during the initial stage of
electrolysis, which was not the case during coagulation experiments, which were rather controlled.

8. At the end of 2 minutes of iron generation and mixing, the % Fe\(^{2+}\) remaining decreased with increasing current, and increased with increasing pH. This was likely due to the more sustained increase in pH with increasing current and the greater oxidation time available during electrolysis at high current and low generation time in comparison to low current and high generation time.

9. The industrial-grade (98.5% pure) and the reagent-grade (99.995% pure) iron rods behaved in a similar way with respect to total iron generation efficiency. Thus, the purity of the industrial-grade iron rod was not of major concern with respect to the iron generation.

10. Under N\(_2\) purged conditions (DO very low) with an industrial-grade and reagent-grade iron rod, 80–90% of iron was present as Fe\(^{2+}\) which confirms that Fe\(^{2+}\) is the species that is formed during electrolysis and natural oxidation by DO was the only reason for oxidation of Fe\(^{2+}\) to Fe\(^{3+}\).

The studies on As(III) oxidation during EC and the comparison of arsenic removal during EC (three-cell EC unit) to CC led to the following conclusions:

1. As observed with the single cell EC unit, the iron generation experimentally approached the theoretical iron generation capacity based on Fe\(^{2+}\) production at the anodes both in batch and continuous mode operation in the three-cell EC unit, provided the iron rods were cleaned prior to each iron-generation experiment.

2. At the end of 2 minutes of iron generation and mixing in the three-cell EC unit, 70–85% Fe(II) was present at pH 6.5; 10–45% Fe(II) was present at pH 7.5, and ≈0% Fe(II) was present at pH 8.5.

3. As(V) removal during EC was very erratic at pH 6.5 with all compositions of challenge water tested: NSFI challenge water, challenge water without silica, challenge water without phosphate, and challenge water without silica and phosphate.

4. The erratic As(V) removal behavior at pH 6.5 was due to (a) the >70% un-oxidized iron (Fe(II)) present in the treated water (b) low amount of ferric hydroxides (15–30%) produced, and (c) variable amount of adsorption of As(V) onto the iron oxide/hydroxide surfaces of the iron rods in the EC unit.

5. As(V) removal was efficient at pH 7.5 and 8.5 during EC with all compositions of challenge water tested, however, a significant and highly variable amount of un-oxidized Fe(II) (10–45%) was present in the treated water at pH 7.5.

6. As(V) removal was highly pH dependent in CC and EC, and the efficiency increased with decreasing pH.

7. The As(V) adsorption capacity was almost the same with CC and EC at pH 7.5 and 8.5. EC was not efficient at pH 6.5.

8. Compared with As(V) removal, the removal of As(III) was poor for both CC and EC. As(III) removal was slightly greater during EC which was pH dependent, compared to CC, which was pH independent.

9. In contrast to what had been reported in the literature, there was no obvious oxidation of As(III) and simultaneous removal of As(V) during EC.
10. As(V) removal using EC is not advisable at pH 6.5 unless there is a very long (>2 hr) oxidation time or higher concentration of dissolved oxygen for nearly complete oxidation of Fe(II) produced.

11. As(V) removal by EC at pH 7.5 should be exercised with caution due to potential presence of high concentrations of soluble Fe(II) in the effluent. Oxidation post treatment or longer retention times are a possibility to oxidize Fe(II), but the additional complexity could be undesirable for small community treatment.

12. As(V) removal by EC at pH 8.5 is likely an acceptable small community treatment process because of the rapid oxidation of Fe(II) to Fe(III) at this higher pH.

The studies on factors affecting As(V) adsorption during EC and CC led to the following conclusions:

1. In the NSFI challenge water with phosphate, silica at 20 mg/L significantly reduced the adsorption of As(V) by competing for adsorption sites both in CC and EC and the interference increased with increasing pH.

2. In the NSFI Challenge water with silica, phosphate at 40 μg P/L was found to reduce the adsorption of As(V) significantly at pH 6.5, whereas it had a lesser effect at pH 7.5 and 8.5 during CC. The effect of phosphate at 40 μg P/L was found to reduce the adsorption of As(V) significantly at pH 7.5, whereas it had a lesser effect at pH 8.5 during EC. The presence of silica lowered the effect of phosphate at pH 8.5 due to its own significant effect at that pH.

3. In the absence of phosphate, silica exhibited a significant effect on the adsorption of As(V), and the effect increased with increasing pH during CC. In the absence of silica, phosphate exhibited a significant effect on the adsorption of As(V) at all pHs during coagulation with FeCl₃ and the effect increased with decreasing pH.

4. In the absence of phosphate, silica exhibited a significant effect on the adsorption of As(V) and the effect increased with increasing pH during EC. In the absence of silica, phosphate also exhibited a significant effect on the adsorption of As(V) at pH 7.5 and 8.5 during EC.

5. As expected, the competing ions silica and phosphate did affect the adsorption of arsenic in most of the cases. However the significance of effect depended on the presence of other competing ion under study.

6. The comparison of As(V) adsorption capacities during 2 min and 21 min of mixing showed a higher adsorption capacity during 21 min of mixing and the significance increased with absence of competing ions.

7. As(V) removal was found to increase with increasing mixing time, even though significant removal occurred in the first few minutes of mixing.

8. The significance of the mixing time effect was dependent on the Fe(III) dose, the removals associated with the Fe(III) dose, and the presence/absence of competing ions.

The results of the additional research on electrolytic chlorine generation for oxidizing As(III) to As(V) and Fe(II) to Fe(III) to improve arsenic removal led to the following conclusions.
1. With iron rod as anodes, chlorine was not generated in the EC unit, and, in fact, the reduced oxides/hydroxides on the iron anodes produced a very significant source of chlorine demand in the EC unit.
2. With a graphite rod anode and stainless steel cathode, chlorine was generated at the anode when chloride ions were present in the solution, and complete oxidation of As(III) was possible providing that sufficient current and mixing time were provided. Unfortunately, the efficiency of Cl₂ residual was only 2–5%, possibly due to electrolysis of water and production of mixed oxides.
3. A combination of graphite and iron rods in the same EC unit housing had no significant advantage for As(III) removal compared with the iron rods alone. When Cl₂ was generated at the graphite anodes, it was immediately consumed by the chlorine demand of the reduced iron oxide/hydroxide anode surfaces and by the Fe(II) produced during electrolysis.
4. A two-stage EC process with graphite anodes in a separate stage 1 housing and iron anodes in the stage 2 housing, although more complicated and costly, was effective for As(III) oxidation and removal without any need for dosing of coagulant or oxidant chemicals.

RECOMMENDATIONS

The main purpose of this project was to determine the applicability of EC–F for arsenic removal in small community water supplies. It was discovered during this research that ferrous not ferric iron is generated during iron anode EC with typical ground water in the pH 6.5 to 8.5 range. This makes the EC process unsuitable under normal conditions, which is necessary for easy application to small community treatment systems. The non-occurrence of simultaneous oxidation and removal of As(III) as reported in the literature eliminates the major advantage expected of EC process and the possibility of forming secondary contaminant in the form of ferrous makes the process even more problematic. Taking the detailed conclusions above into consideration, the following recommendations are made for application of EC for arsenic removal in small systems:

1. The EC process is applicable at high pH (~8 or higher) due to the rapid oxidation of ferrous iron to ferric at high pH.
2. The EC process is not advisable at pH < 7.5 under un-optimized conditions due to the possibility of forming soluble ferrous iron as a secondary contaminant.
3. The EC process could be made more efficient by completely oxidizing the ferrous produced at the anode. The optimization could be made by the combination of the following:
   a. providing a larger retention time,
   b. aerating the water thereby increasing the DO content,
   c. pre-oxidation step such as introduction of oxidant, and
   d. increasing the pH.
4. Caution must be exercised before application of the EC process. The efficiency of the EC process is significantly dependent on the characteristics of the water (pH, DO, etc.) and so pilot scale studies are necessary before application of the process.
REFERENCES


**ABBREVIATIONS**

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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>A</td>
<td>Ampere</td>
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<tr>
<td>AAS</td>
<td>Atomic Absorption Spectrometer</td>
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<td>AWWA</td>
<td>American Water Works Association</td>
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<td>°C</td>
<td>degree Celcius</td>
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<td>Ce</td>
<td>Equilibrium concentration</td>
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<td>FI–HG–AAS</td>
<td>flow injection hydride generation atomic absorption spectrometer</td>
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<td>ICP–MS</td>
<td>Inductively Coupled Plasma–Mass Spectrometer</td>
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<td>MCL</td>
<td>Maximum contaminant level</td>
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<td>nm</td>
<td>nanometer</td>
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<tr>
<td>NSFI</td>
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<td>pH</td>
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<td>pKa</td>
<td>Negative of logarithm of an ionization/ equilibrium constant</td>
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<td>POU/POE</td>
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<td>TCLP</td>
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