Arsenic Removal at the Household Level

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Zusammenfassung


Das Ziel dieser Arbeit war die Entwicklung einer Methode, die es erlaubt, mit geringem technischem Aufwand Arsen aus dem Wasser zu entfernen.

Das Verhalten von Arsen in der Umwelt ist stark von dessen Redoxzustand abhängig. As(III) ist sehr mobil, wohingegen As(V) aufgrund seiner negative Ladung stark an Oberflächen von Mineralen adsorbiert. Wenn im Wasser zusätzlich Silikat und Phosphat vorkommt, wird hinsichtlich der Entfernung von Arsen, die Oxidation von As(III) zu As(V) umso wichtiger, denn bis zu einem pH von etwa 8 konkurrieren Silikat und Phosphat die Adsorption von As(III) stark.

Im ersten Teil wurde die Oxidation von As(III) nach der Zugabe von Fe(II) in einer As(III) haltigen Lösung untersucht. Es zeigte sich, dass die Oxidation von Fe(II) zu einer partiellen Oxidation von As(III) zu As(V) führt. Nachdem die Oxidation von Fe(II) abgelaufen ist, wurde keine weitere Oxidation von Arsen beobachtet. Die Oxidationsrate von Fe(II) ist stark pH abhängig und nimmt zu bei steigendem pH dadurch wird auch die As(III) Oxidation beschleunigt. As(III) wird durch reaktive intermediäre Oxidationsprodukte wie *OH oder Fe(IV), die während der Oxidation von Fe(II) in belüftetem Wasser entstehen, oxidiert. Da Fe(II) selbst durch diese intermediären Reaktionsprodukte oxidiert wird, ist die Oxidation von As(III) durch die einmalige Zugabe von Fe(II) limitiert.

Im zweiten Teil wird die Arsenentfernung mittels einer 24 cm langen Glassäule durch welche belüftetes Grundwasser fliesst, und die mit 1.5 g Eisenspänen

Im dritten Teil konnte in Bangladesh mit einer mehrstufigen Filteranordnung über 90 L mit Arsen kontaminierten Wassers behandelt werden und den Richtwert von maximal 50 μg/L As erreichen. Die Filter in der Anlage enthielten neben Sand 10 g Eisenspäne, verteilt in 3 bis 5 PET-Flaschen, welche kopfüber und übereinander angeordnet waren. Das Wasser floss durch ein 2 mm breites Loch, welches zuerst in den Schraubverschluss gebohrt wurde. Damit das Filtermaterial, das sich im Flaschenhals befand, nicht weggeschwemmt wurde, wurde dieses Loch im Innendurchmesser des Schraubverschlusses mit einem Papiertuch zugedeckt.

Vergleichbar mit den Laborexperimenten führte die Korrosion der Eisenspäne zur Bildung von Fe(II), welches durch die mehrstufige Filteranordnung langsam und wiederholt oxidierte und so zu einer vollständigen Oxidation des Arsens führte. Weil das so gebildete As(V) vollständig an den frisch gebildeten Eisenhydroxide adsorbierte erreichte das Wasser Trinkwasserqualität.
Summary

Arsenic contamination of groundwater has been documented in many parts of the world. The sources of arsenic can be anthropogenic (e.g. pesticides), volcanic (e.g. hot springs) or come from natural weathering of arsenic bearing minerals (e.g. arsenopyrite). High arsenic concentrations in groundwater were discovered in South - Asia and South - America where arsenic has been mobilized due to strongly reducing conditions or arid environments with high pH. The daily ingestion of arsenic - contaminated water leads to a multitude of severe diseases which may be fatal to the patient. In Bangladesh up to 50 million people drink arsenic contaminated water.

The goal of this work was to develop a method for arsenic removal from drinking water. The fate of arsenic in the environment is mainly controlled by its redox chemistry. Arsenite is highly mobile whereas the negatively charged arsenate strongly adsorbs on mineral surfaces. In the presence of phosphate and silicate, oxidation of As(III) to As(V) is particularly important, as As(III) cannot compete with phosphate adsorption on HFO up to a pH of 8.

In a first step we investigated the effect of Fe(II) oxidation on the redox state of arsenic by adding Fe(II) to As(III) containing water. The oxidation of Fe(II) in air-saturated As(III) solutions lead to partial oxidation of As(III) to As(V). After the oxidation of Fe(II) is complete, As(III) is not further oxidized. Additional experiments with O2, H2O2 and isopropanol allowed to understand in detail the oxidation mechanism of As(III) in the presence of Fe(II) and to develop a kinetic model explaining the results quantitatively. The higher As oxidation rates obtained at increased pH are explained by the pH-dependent rate of Fe(II) oxidation. As(III) was found to be oxidized by reactive intermediates such as *OH and Fe(IV), formed during the reduction of dissolved O2 by Fe(II). Since Fe(II) also consumes the reactive intermediates, As(III) oxidation after a single Fe(II) addition is limited.

In the second part of this thesis a series of experiments were conducted to investigate the arsenic removal capacity of zero valent iron under different conditions. Aerated groundwater flowing through a glass column of 24 cm containing a mixture of 1.5 g iron filings and 3-4 g sand lead to the corrosion of zero-valent iron and release of dissolved Fe(II), up to a concentra-
tion of 8 mg/L. In agreement with previous experiments, the oxidation of Fe(II) by dissolved oxygen in the recipient container caused partial oxidation of As(III). The so-formed As(V) strongly sorbed onto the forming HFO. To complete the oxidation and removal of arsenic, the water was aerated and filtered four times through the zero valent iron-sand filter. In each filtration step, the HFO with adsorbed As(V) was retained by the sand grains and was removed by backwashing. Due to outgassing of dissolved CO2 the pH of the water increased from 7 to 8 during the treatment, leading to accelerated Fe(II) oxidation and increasing fractions of HFO forming directly in the column. Oxidation of Fe(II) in the column and high pH caused formation of scaling on the iron filing which could not be removed completely by backwashing. Natural groundwater constituents such as phosphate and silicate might limit the arsenic removal efficiency of zero valent iron. To improve the method, the influence of phosphate, silicate, calcium, and magnesium were investigated and discussed in the text.

In the third part, arsenic removal experiments were conducted in the laboratory and in Bangladesh with different multiple filtration units. Over 90 L of contaminated groundwater could be treated with a filtration unit containing five filters containing a total of 10 g iron.

The filter columns were build with 3 - 5 vertically aligned PET bottles partially filled with sand and locally produced iron filings. The filter media was placed in the bottleneck. The water flowed through a hole in the screw cap which had first been covered with a tissue in order to retain the sand and iron mix. Similar to previous experiments Fe(II) is continuously formed on the corroding iron surface and partly released into solution. The oxidation of dissolved and adsorbed Fe(II) leads to As(III) oxidation, which explain the observed generally good performance of filters using Fe(0) in terms of arsenic removal. As observed in former experiments DOC, phosphate, silicate, calcium, and magnesium play an important role on the arsenic removal efficiency by zero valent iron. The water constituents listed above were therefore closely monitored during the water treatment and considered in the design of the multiple filtration units to minimize their negative impact.
Chapter 1

Introduction

1.1 Arsenic

Arsenic is a semi-metallic element (no. 33; atomic-weight 74.92) of group number Vb. The discovery of elemental arsenic is generally attributed to Albertus Magnus (1193-1280) who isolated arsenic by heating auripigment (As$_2$S$_3$) and soap. The efficacy of arsenic sulfide for medical purposes and as a poison has been known and documented since the 5th century B.C. (1). The name arsenic, in Latin arsenum and in greek ἀρσενικός, probably derives from the old Persian word az-zarnikh for auripigment (zar = gold) (2, 3).

Arsenic trioxide became famous as an effective, tasteless and odorless poison. In France this notorious white powder was called “poudre de succession” given its tendency to accelerate the inheritance processes. In 1836 James Marsh developed a method to detect arsenic in low concentrations and organic tissues, which decreased the popularity of this poison (Hydride generation with Zink and sulfuric acid and detection of arsine (AsH$_3$) condensation on a cold mirror).

In the past arsenic has mainly been used in medicine but also for poison, as an alloy, and as coloring agent. Today arsenic is used in agriculture (pesticides, insecticides, wood preservatives), in livestock (feed additives, disease prevention), in medicine, in electronics (semiconductor), industry, and metallurgy (2).

1.2 Geochemistry of arsenic

The average concentration of arsenic in the continental crust is documented to be between 1.5 and 2 mg/kg (4). Magmatic rocks and sediments containing iron ores show higher arsenic concentrations (1 to 2900 mg/kg with an average of 400 mg/kg). High arsenic concentrations are also found in coal with an average of 13 mg/kg. Arsenic in soil mainly depends on the bed rock, the
nature of the soil, and the human impact. Typically arsenic concentrations in soils range from 0.1-40 mg/kg with an average of 5-6 mg/kg. Arsenic has been found in over 240 different minerals of which arsenopyrite (FeAs$_{0.9}$S$_{1.1}$ - FeAs$_{1.1}$S$_{0.9}$) is the most frequent. The other minerals are: 27 arsenides, 13 sulfides, 65 sulfosalts, and their oxidation products (2 oxides, 11 arsenites, 116 arsenates and 7 silicates) (4).

The mobility of arsenic in groundwater is mainly controlled by its speciation and adsorption on solids present in aquifers. Like other (semi-)metals (e.g. chromium, selenium, antimony, vanadium) arsenic forms weak acids in aquatic environments. These deprotonate with increasing pH forming negatively charged oxyanions. The Eh-pH stability of the different arsenic species reveals that arsenite forms H$_3$AsO$_3$ in slightly reducing conditions (0.2-0.6 V) and over a wide pH range. The deprotonation of H$_3$AsO$_3$ to H$_2$AsO$_4^-$ occurs at a pH 9.2; thus explaining the mobility of arsenite in anoxic and circumneutral groundwater. Arsenate on the other hand forms better adsorbing oxyanions already at lower pH: the first deprotonation occurs at pH 2.2 (H$_2$AsO$_4^-$), the second at pH 6.9 (HAsO$_4^{2-}$) and the third at pH 11.5 (AsO$_4^{3-}$) (see Fig. 1.1).

Due to the formation of inner sphere complexes with oxide minerals (iron oxide, iron hydroxide, manganese oxides and aluminum oxides) by ligand exchange with surface functional groups (OH$^-$ and OH$^+$), the adsorption capacity of arsenite increases with increasing pH, while it decreases for arsenate. At higher pH the predominant arsenite species (H$_3$AsO$_3^2$) is more readily able to donate a proton to a surface OH group (e.g. on iron hydroxide) than the negatively charged As(V) (5).

Thus the adsorption of arsenic on minerals commonly present in the aquifer (e.g. hydrous iron oxides, aluminum and manganese and clay minerals) depends to a large extent on the water chemistry: pH, Eh, the nature of the solid, and the concentrations of phosphate, silicate, bi-carbonate and natural organic material (NOM) competing for the same adsorption sites on solids.

1.3 Arsenic crisis in Bangladesh

In the mid 1970s a quarter of a million Bangladeshi children died every year due to surface water born diseases. The installation of 8 to 12 million tube wells producing pure drinking water was an effective program and the rate of infant mortality rate was halved. Today 97% of the rural community consumes water from shallow tube wells in depths between 15-30 m. Health problems due to chronic arsenic ingestion in the Bengali basin were first diagnosed in West Bengal (1980) and in Bangladesh (1993) by the dermatologist K.C. Saha, Calcutta (6).

The contamination of groundwater with arsenic was first officially docu-
1.3 Arsenic crisis in Bangladesh

Figure 1.1: Eh-pH diagram showing the different fields of stability for the arsenic species occurring in natural environments. As(III) forms non-ionic species up to pH 9 whereas the better adsorbing As(V) deprotonates at pH 2.2.

mented by the Department of Public Health Engineering (DPHE) in the north of Dhaka in 1993 (region of Chapai Nawabganj). The arsenic contamination of the groundwater in West Bengal was internationally recognized in 1995 after an international conference had been held in Calcutta. During the mid 1990s the School of Environmental Studies at Jadavpur University (SOES), Calcutta and Dhaka Community Hospital (DHC) conducted field investigations in Bangladesh analyzing water and tissue samples. In 1998, SOES and DHC held a conference on arsenic in Dhaka. As a result of the World Bank Fact Finding Mission of 1997 and the screening program of DPHE conducted with the assistance of UNICEF, the Government of Bangladesh was offered a 44 $ million World Bank loan in order to set up an arsenic mitigation program. The Bangladeshi Arsenic Mitigation Water Supply Project (BAMSWP) was created to lead this program. In 1998 the Rapid Investigation project of the British geological Survey (BGS) and DPHE, which was founded by the English Department for International Development (DFID), started. The first results of this rapid investigation were reported in 1999. The second phase was concluded in 2000 with the publication of the final report.

In the final report on the arsenic contamination of groundwater in Bangladesh (published in 2000), the BGS calculated that 28-35 million people are exposed
to arsenic concentrations of 50 μg/L and 46-57 million to 10 μg/L (estimated on the basis of the population of 1999) (6) (see Fig. 1.2). Due to population growth and well drilling these numbers continue to increase. Some estimate that 80 million people consume drinking water with arsenic concentrations above 10 μg/L. So far, water sampled from 1.4 million tube wells in 67 upazilas has been analyzed and 17 million people have been examined for visible symptoms of arsenic poisoning (national arsenic mitigation policy, 2004)
1.4 Source and mobilization of arsenic

1.4.1 Arsenic in the aquifer — worldwide

Numerous aquifers in the world are contaminated with arsenic concentration above 50 µg/L. Apart from Bangladesh, aquifers in Vietnam, Nepal, West Bengal, China, Taiwan, Cambodia, Argentina, Chile, Mexico, the United States, Hungary, and Romania have been shown to be contaminated. High arsenic concentrations have been reported in hot springs and geothermal waters in Argentina, France, Japan, Iceland, New Zealand, Chile, Kamchatka, Dominica and in the USA. Documented arsenic contaminations related to mining activities were found in Thailand, Greece, the USA (Fairbanks, Coeur d’Alene, and Lake Oahe), and in Canada (Moira lake) (7).

The revision of the WHO guideline values (0.2 mg/L in 1958, 0.05 mg/L in 1963 and 0.01 mg/L in 1993) prompted many countries (e.g. USA) to reassess their arsenic situation. Because arsenic had not traditionally been on the list of elements routinely analyzed, an increasing number of locations with groundwater contamination by arsenic have been reported (see Fig. 1.3).

1.4.2 Arsenic mobilization

Contamination of groundwater with arsenic may be caused by natural processes or by industrial activities such as mining. The mining activity leads to localized high arsenic concentrations in the range of mg/L at very low pH (pH < 2). In the mining effluent the arsenic bearing minerals are likely to dissolve through oxidation and release the arsenic. However the arsenic contaminations are of short spatial ranges (8). Large scale aquifer contaminations with arsenic are generally found in two different types of settings: arid and semi-arid closed basins with high evaporation rates, and high pH (>8.5) and highly reducing aquifers at circumneutral pH. Both environments are characterized by young sediments, flat slopes, aquifer material of a normal arsenic content (1-20 mg/L) and slow water recharge.

The high pH in semi arid environments (a result of both high evaporation rate and mineral weathering) leads to desorption of arsenic (especially As(V)) and other oxyanions forming elements (Cr, Se, U, V, and B) from mineral oxides (Fe-oxides) or it prevents from being adsorbed (9-11).

In highly reduced sediments, Fe and Mn (hydr)oxides are totally dissolved and most of the arsenic is released and reduced to As(III). High concentrations of phosphate, silicate, bicarbonate and DOC are commonly measured in these waters. The high spatial variability in arsenic concentration (horizontally as well as vertically) is also a typical feature of these aquifers (7, 12).

The reducing environment is believed to result from microbial reduction of
1. Introduction

DOCUMENTED ARSENIC PROBLEMS IN GROUNDWATER AND THE ENVIRONMENT

![Map showing documented cases of groundwater contamination with arsenic](image)

**LEGEND**
- Arsenic-related aquifers
- Arsenic related to mining operations
- Groundwater wells

Figure 1.3: Documented cases of groundwater contamination with arsenic. The cases include natural, geothermal, and mining activity related problems. Based upon (7) by permission of the British Geological Survey.

organic matter. As a matter of fact peat layers were found within the aquifer sands and in the overlying confining units which are thought to drive of microbial reduction of iron(hydr)oxides in the sediments (13-15). Point sources from human organic waste in latrines seem not to lead to the reduction of iron (hydr)oxides. In other models it has been suggested that superficial organic matter from ponds, river beds, and soils may be brought down into the aquifer by irrigation drawdown. This hypothesis was supported by carbon methane dating suggesting that the organic matter found in the aquifer may be very young (16). Other mechanisms which were proposed explain the mechanism of arsenic release through pyrite oxidation or competitive anion exchange of sorbed arsenic with inorganic phosphate (PO$_4^{3-}$) from fertilizer (17).

1.4.3 Health effects

Ingestion of arsenic is recognized to be noxious, causing cancers and non carcinogenic diseases. Long term ingestions of arsenic may cause skin cancer and
several internal cancers such as bladder, kidney, liver, and lung cancers. Reported non carcinogenic diseases are skin lesions such as hyper-pigmentation on the upper chest, arms and legs (see Fig. 1.4.3), keratosis on palms and soles, gastrointestinal disturbances ranging from abdominal cramping and diarrhea to severe life threatening hemorrhagic gastroenteritis associated with shock. Mild to moderate hepatocellular necrosis might occur. Furthermore the ingestion of arsenic may cause hypotension, congestive heart failure and arrhythmias, hematological, pulmonary, immunological, neurological, and endocrinological effects. Arsenic in water and air has been reported to cause an increase of spontaneous abortions, pregnancy complications, perinatal deaths and congenital malformations (18).

Based on studies in Taiwan and Chile Smith (19) calculated that lifetime consumption of arsenic at a concentration of 500 μg/L would be the cause of 10% of all deaths. A linear extrapolation to the current drinking water standard of Bangladesh at 50 μg/L means that arsenic would be fatal to at least 1% of the population. Yu et al. (20) calculated the health effects of groundwater arsenic in Bangladesh using the epidemiological data from West Bengal and Taiwan combined with the regional exposure distribution. They concluded that on the long term approximately 120'000 cases of hyper-pigmentation, 600'000 cases of keratosis, 125'000 cases of skin cancer, and 3000 fatalities per year from internal cancers will be caused by arsenic containing groundwater. Smith (19) estimated that 200'000 patients would suffer from arsenicosis in West-Bengal. To date, 5000 patients have been identified to have arsenic-related health problems in West Bengal (7).

1.5 Arsenic removal in Bangladesh

1.5.1 General

In the recently published National Policy for arsenic mitigation in Bangladesh (2004), the Bangladeshi government promotes the following options for safe water supplies: improved dug wells, rain water harvesting, surface water treatment (by means of pond sand filter or larger scale surface water treatment), arsenic removal technology, deep hand tube wells and / or the development of a piped water supply system. Furthermore it is stated: “Arsenic mitigation programmes for safe water supply shall promote a range of options but shall give priority to surface water over ground water source. ... It shall endeavour to promote piped water system wherever feasible. ...”. Arsenic free and unpolluted surface water would undoubtedly be easier to treat and should be promoted in this sense. However, the vulnerability of surface water regarding potential natural and anthropogenic organic and inorganic as
1. Introduction

Figure 1.4: Hyper-pigmentation of the palms and soles are typical early stage symptoms of chronic arsenic ingestion. The temporal progression of chronic arsenic poisoning begins with hyperpigmentation which turn into a palmar-plantar hyperkeratoses with time and might end in skin cancers (18). The arsenic related hyperpigmentation is called arsenicosis.

Well as microbial contamination requires an elaborate treatment process prior consumption. The costs related to such treatment plants as well as for piped water systems are high and result in expensive water.

Except for the water treatment technology options, the options for water supply promoted by the Bangladeshi government have serious drawbacks. Dug wells are a simple and traditional method and produce arsenic free water: due to the oxygenation of the anoxic groundwater, arsenic co-precipitates with the natural occurring iron within the well. However dug wells cannot be build in areas with loose sandy soil, in areas with more than 15 meters consolidated clay layer, in the tidal zones of the coastal areas and in areas of stony hills. Rain water is a reasonable alternative water source but is mainly limited to the rainy season and the water stored may not last for a whole year. The ongoing discussion on deep hand tube wells makes clear that this method may imply great risks: by pumping water from the deeper, generally arsenic free aquifer it cannot be excluded that water from the upper potentially arsenic contaminated aquifer would be drawn-down. Piped water supply in Bangladesh is a long term goal and is not a realistic arsenic mitigation strategy for the near future.
1.5.2 Water treatment technologies

A simple water treatment technology should work without addition of chemicals and without complicated manipulations. To develop such a technology an in-depth understanding of the most relevant chemical and physical processes is required. The development of an efficient and adapted technique is made difficult by the high As(III), phosphate (1.5-3 mg/L) and silicate concentrations in the groundwater.

Arsenic removal technologies can be divided into two larger groups: technologies applying to the household and those applying to the community level. The differences are in the flow rate and the cost of the treated water. Hundreds of different arsenic removal techniques have been described in scientific journals: membrane technology, ion exchange, lime softening, passive removal with natural iron, co-precipitation with added iron- or alumsalts, adsorption on mineral surfaces (zeolites, clay etc.), electrochemical oxidation, zero valent iron, phytoremediation or bacterial induced oxidation.

These methods can be effective in arsenic removal but not all are suitable for use in Bangladesh. Membranes are able to remove arsenic to below 10 µg/L but are far too expensive. The high concentration of electrolytes (e.g. phosphate and silicate) severely affects the efficiency of ion exchange. Techniques using lime softening might be suited for large water treatment facilities but not at the household level. Passive removal experiments of arsenic with Fe(II) showed that this method can remove phosphate but the iron content is too low for efficient arsenic removal in Bangladesh (21). Good results have been achieved by the use of oxidants (e.g. KMnO₄, O₃, ClO, Cl₂) to oxidize As(III) to the better adsorbing As(V), and of iron- or aluminium salts to precipitate the As(V) (along with the phosphate) by sorption on Al- or Fe(III)(hydr)oxides.

Despite the good water quality obtained by treating the water with zeolites and other minerals, the material would have to be distributed to the consumer, which is difficult in Bangladesh. The electrochemical oxidation of arsenite prior to its co-precipitation with iron or alumsalts showed good results. However, electrical current is expensive and not available everywhere.

No chemicals and the minimal amount of man-made material is needed when metallic iron is used for the formation of arsenic-sorbing Fe(III)(hydr)oxides (HFO).

1.5.3 Arsenic removal using iron

Co-precipitation of arsenic with naturally present Fe(II) (passive removal) is the simplest conceivable arsenic removal technique (21). To achieve passive removal, the pumped groundwater is usually stored open to the air, for peri-
ods ranging from a few hours to several days, allowing the Fe(II) to oxidize and the forming HFO with adsorbed arsenic to precipitate. However, high concentrations of As(III), phosphate, and silicate or low natural iron concentration exercise a negative impact on the passive arsenic removal.

Phosphate, often present at concentrations up to 3 mg/L, strongly interferes with arsenic removal. As only As(V) can effectively compete with phosphate for the adsorption to HFO, oxidation of As(III) becomes even more important in the presence of phosphate. One way to oxidize As(III) without added chemicals is the use of solar light. A recently developed method (SORAS) enhances photochemical oxidation of As(III) with a few drops of lemon juice per liter of water and achieves average removal efficiencies of about 66%, 2-3 times higher than passive removal with naturally present iron. However, natural iron concentrations are often too low to reach the limit of 50 µg/L with SORAS. The efficiency of SORAS is greatly enhanced by additional iron, e.g. by letting lemon juice react with iron filings prior to use (22).

Various methods using metallic iron have shown good results, and iron is available anywhere where there are tube wells. Among these methods, the 3-Kolshi system which is built with locally available materials such as bricks, sand, charcoal, and iron turnings (23-26) has shown excellent results for the treatment of contaminated water. To further optimize the use of zero-valent iron, the chemical processes (oxidative and reductive pathways) should be better understood.

The possible oxidation of As(III) in contact with corroding iron and the sorption of As(V), As(III), phosphate and silicate on the forming HFO is of particular relevance. In many systems, only a small part of the iron can be used efficiently due to formation of dense scales on the metal surfaces, which limit the contact of the contaminated water with the corroding iron surfaces.

Su (27) has investigated the adsorption of As(III) and As(V) by zero valent iron. Strong evidence for As(III) oxidation to occur in solution was found. In a following study Su and Puls (28) have shown the influence of silicate and phosphate on arsenic removal by zero valent iron for groundwater remediation.

Karschunke and Jekel (29, 30) also conducted experiments with zero valent iron. With 46 g of iron wool it was possible to treat up to 1.2 m³ of Berlin tap water spiked with 500 µg/L As(V). In another study of the same authors the iron corrosion was enhanced by a galvanic contact of iron wool with a copper nail. The good results were however overshadowed by the risk of dissolving copper in the water.

A study conducted by Melitas (31) investigated the mechanisms of soluble arsenate removal from a solution with a 3 mM CaSO₄ background electrolyte and an initial As(V) concentration of 100 µg/L. The results suggest that arsenic removal is dependent on the available adsorption sites produced by the
1.6 The AGS project

The AGS project involves the use of zero valent iron to remove arsenic from water. However, the groundwater chemistry in Bangladesh differs from the conditions chosen by Melitas, so the results may be of limited use.

Removal of arsenic by electrically induced corrosion of zero valent iron has been studied by Arienzo (34). He investigated the electrochemical removal of arsenic. He applied a direct current of 0.25 mA to a solution containing As(III) for 3 min and achieved a removal of about 79.2% of the initial arsenic concentration by co-precipitation with HFO formed at the steel anode.

1.6 The AGS project

The Alliance of Global Sustainability (AGS) is an international partnership of four leading science and technology universities (Massachusetts Institute of Technology (MIT), University of Tokyo (UT), Swiss Federal Institute of Technology (ETHZ), and Chalmers University). This partnership allows dealing with the complex issues that lie at the intersection of environmental, economic and social sciences.

The overall goal of the present project was: "...to establish scientifically reliable and socioeconomically and culturally feasible guidelines for sustainable water use systems in arsenic polluted areas in Asia, focusing on Bangladesh..." To achieve this goal, AGS has founded a collaborative project between three AGS-Universities UT, MIT, ETHZ and the Bangladesh University of Engineering and Technology (BUET).

The partners of this project worked in different institutes on three interrelated key issues.

1.6.1 Health and sociocultural aspects of water use

The primary purpose of the work of the UT group was to describe the human toxicological and the public health aspects at community level. Information about the prevalence of arsenic related health effects and the possible risk population was to be incorporated in designing and planning mitigation or counteracting measures.
1. Introduction

1.6.2 Water treatment options for safe drinking water at the household level

A primary short term goal was the reduction of arsenic intake. To achieve this goal, we worked on the development of a simple, socio-economically acceptable arsenic removal procedure that is adapted to the situation in rural villages.

1.6.3 Long term solutions for community level water supply systems

To predict the level of arsenic contamination in groundwater subject to different long-term management strategies the group at MIT worked on the development of hydrologic models.

1.7 Objectives and outline of this thesis

Arsenic has been recognized to be one of the most problematic inorganic drinking water contaminants worldwide. In Bangladesh arsenic contamination of the aquifers has been found in many parts of the country. As a part of an AGS project involving four universities, EAWAG has been in charge to develop an arsenic removal method for the use at household level in emerging countries with the focus on Bangladesh. The method was required to function without addition of chemicals or complicated manipulation and be applicable to any groundwater type. It needed to be socioeconomically and culturally feasible, and adapted to the rural village situation. To reach this goal, the chemical and physical processes had to be understood in depth.

The publications in chapters 2-5 reflect the development of the research done during 2000-2004.

Chapter 2 consists of the study on arsenic oxidation kinetics by dissolved oxygen and hydrogen peroxide in the presence of Fe(II) and Fe(III). The understanding of the oxidation kinetics and mechanics of As(III) with natural and technical oxidants are important in respect to the behavior of arsenic in the environment and in arsenic removal procedures. As a water contaminant, As(III) forms non-ionic forms to pH up to 9, which are more mobile and therefore more problematic than As(V), which adsorbs strongly to mineral surfaces. As(III) is thus more mobile in groundwater and is also more difficult to remove in arsenic removal treatments. It could be shown that, As(III) was partially or completely oxidized in parallel to the oxidation of 20-90 μM Fe(II) by oxygen and by 20 μM H₂O₂ in aerated solutions.
1.7 Objectives and outline of this thesis

The Chapter 3 includes a study on laboratory experiments with a filter for arsenic removal using zero valent iron and sand. Synthetic groundwater containing As(III), P, Si, HCO$_3^-$, Ca$^{2+}$, and Mg$^{2+}$, was passed four times through a mixture of iron filings and quartz sand in a vertical glass column. We could show that the repetitive oxidation of Fe(II) formed through the corrosion of iron filings by dissolved oxygen, lead to the partial oxidation of As(III). The so originated As(V) sorbed on the forming hydrous ferric oxides which were retained in the next filtration and removed by shaking of the sand-iron mixture with water. Four filtrations lead to complete As(III) oxidation and removal of As(tot) to below 50 $\mu$g/L, without an added oxidant.

In Chapter 4 experiments in Bangladesh and in laboratory with a filter column using zero valent iron and sand for arsenic removal are presented. The three to five vertically arranged 1.5 L filters (made of used PET bottles) were filled with 2.5 g locally produced iron filings and 100-150 g sand. The repetitive oxidation of Fe(II) formed from the corrosion of the iron filings lead to the complete As(III) oxidation without and added oxidant and to over 90% removal of phosphate and arsenic. At a flow rate of 1 L/h, columns in Bangladesh could treat 76 L of tubewell water with three filters and 90 L with four filters to below 50 $\mu$g/L As(tot) without an added oxidant.

The results and the practical implication of this thesis are presented in chapter 6.
Table 1.1: List of the publications developed in the course of this PhD-thesis.

Publications included in this thesis:


Chapter 3  Leupin O.X. and Hug S. J. Oxidation and removal of arsenic (III) from aerated groundwater by filtration through sand and zero-valent iron Submitted to Water Research

Chapter 4  Leupin O. X. and Hug S. J. Oxidative Arsenic Removal with Zero Valent Iron from Tubewell Water in Filter Columns with Iron Filings and Sand Submitted to Environmental Science and Technology

Additional publications not included in this thesis:


Hauke Harms, Julien Rime, Olivier Leupin, Stephan J. Hug, and Jan Roelof van der Meer; (2004) "Influence of the Groundwater Composition on Arsenic Detection by Bacterial Biosensors" (Submitted to Microchimica Acta)


1.7 Objectives and outline of this thesis

Literature


Iron Catalyzed Oxidation of Arsenic(III) by Oxygen and by Hydrogen Peroxide: pH-dependent Formation of Oxidants in the Fenton Reaction

STEPHAN J. HUG AND OLIVIER X. LEUPIN
published in: Environmental Science and Technology (2003), 37, 2734-2742

Abstract: The oxidation kinetics of As(III) with natural and technical oxidants is still not well understood, despite its importance in understanding the behavior of arsenic in the environment and in arsenic removal procedures. We have studied the oxidation of 6.6 µM As(III) by dissolved oxygen and hydrogen peroxide in the presence of Fe(II,III) at pH 3.5-7.5, on a time scale of hours. As(III) was not measurably oxidized by O₂, 20-100 µM H₂O₂, dissolved Fe(III) or by Fe(III)(hydr)oxides as single oxidants, respectively. In contrast, As(III) was partially or completely oxidized in parallel to the oxidation of 20-90 µM Fe(II) by oxygen and by 20 µM H₂O₂ in aerated solutions. Addition of 2-propanol as an *OH-radical scavenger quenched the As(III) oxidation at low pH, but had little effect at neutral pH. High bicarbonate concentrations (100 mM) lead to increased oxidation of As(III). Based on these results, a reaction scheme is proposed in which H₂O₂ and Fe(II) form *OH radicals at low pH, but a different oxidant, possibly an Fe(IV) species, at higher pH. With bicarbonate present, carbonate radicals might also be produced. The oxidant formed at neutral pH oxidizes As(III) and Fe(II), but does not react competitively with 2-propanol. Kinetic modeling of all data simultaneously explains the results quantitatively and provides estimates for reaction rate constants. The observation that As(III) is oxidized in parallel to
the oxidation of Fe(II) by O$_2$ and by H$_2$O$_2$, and that the As(III) oxidation is not inhibited by *OH-radical scavengers at neutral pH, is significant for the understanding of arsenic redox reactions in the environment and in arsenic removal processes, as well as for the understanding of Fenton reactions in general.

2.1 Introduction

With arsenic contaminated ground water affecting 30-50 million people in Bangladesh (1) and around 10 million in Vietnam (2), and the debate around lower limits in the United States (3), arsenic has been recognized as one of the most widespread and problematic water contaminants.

The behavior of arsenic in the environment and in water treatment processes is mainly determined by its redox chemistry. As a water contaminant, As(III) is more problematic than As(V). Unlike the arsenate anions H$_2$AsO$_4^-$ and HAsO$_3^{2-}$, the dominant As(III) species up to pH 8 is the non-ionic H$_3$AsO$_3$, which does not adsorb as strongly to mineral surfaces (1) as As(V) (4). As(III) is thus more mobile in groundwaters and is also more difficult to remove in arsenic removal treatments (5,6). Typically, pre-oxidation to As(V) is necessary in arsenic removal procedures (7). Although As(V) is thermodynamically favored under oxic conditions, As(III) is only slowly oxidized by dissolved O$_2$, e.g. with a half-life of around 9 days in air-saturated water with low iron contents and pH 7.6-8.5 (8). The As(III) oxidation by H$_2$O$_2$ is also slow at neutral and acidic pH, as only H$_2$AsO$_3^-$ and HAsO$_3^{2-}$, but not H$_3$AsO$_3$ react with H$_2$O$_2$ (9). The half-life of As(III) in 1 mM H$_2$O$_2$ at pH 7.5 is 2.1 days. The influence of transition metals on the oxidation of As(III) with H$_2$O$_2$ has recently been studied (10) and it was found that Fe(II) and Fe(III) both increased the oxidation rates to a similar extent, but the effects of Fenton chemistry were not addressed.

The iron catalyzed oxidation of As(III) with O$_2$ and H$_2$O$_2$ is important in both natural and technical systems. The connection between iron and arsenic redox reactions is one of the key factors in understanding the fate of arsenic in the environment. For example, arsenic in the iron crusts of recent sediments from Lake Baikal was found to be enriched by a factor of 58 above background levels (11). In water treatment, oxidation followed by coprecipitation with iron(hydr)oxides is one of the most economic and efficient arsenic removal options (12). The oxidation of As(III) by Fe(II) and H$_2$O$_2$ (Fenton reaction) at pH 1-3 has been studied as early as 1963 (13) and has been tested for the treatment of groundwater with high arsenic concentrations at pH 2.5-3.0 (14). Treatment of As(III)-spiked groundwater by a combination of Fenton chemistry and filtration through scrap iron at neutral pH has recently been
reported (15), but kinetic and mechanistic issues were not discussed.

In a recent study of iron-catalyzed photochemical oxidation and removal of arsenic at neutral pH (16), we found that arsenic was partly oxidized in parallel to the dark oxidation of Fe(II) by dissolved O2. We have attempted to explain these observations with the formation of HO2-/O2−, H2O2, and *OH radicals in the generally stated sequence of Fe(II,III) oxidation/reduction reactions and Fenton chemistry (17-21). However, the involvement of free *OH radicals was not consistent with quenching experiments, in which *OH scavengers such as 2-propanol and 3-butanol had almost no effect on the oxidation of As(III) at neutral pH (16). An important role of

A number of newer studies have suggested that oxidizing species different from free *OH radicals, e.g. Fe(IV)-species, are formed in the Fenton reaction (22-25) and in the oxidation of Fe(II) with O2 (26). Fe(IV) intermediates in iron-porphyrins have been isolated and studied by low-temperature spectroscopy (27). Spectroscopic evidence for a ferryl species and a Fe(III)-dimer formed from ferryl and Fe(II) was also found in the reaction of uncomplexed Fe(II) with O3 at pH below 2 (28, 29), and rate constants for the reaction of ferryl with various compounds at low pH were reported (30). Furthermore, Fe(IV) species were suggested in the reaction of Fe(II)NTA and Fe(II)EDDA (31) and of Fe(II)DTPA (32) with H2O2 at neutral pH. The relative contribution of reaction pathways leading to Fe(IV) and *OH, respectively, seem to depend on various parameters, such as pH and the concentrations of organic and inorganic ligands (33-35).

In the degradation of pollutants, it is generally observed that the efficiency of dark- and photo-Fenton systems decreases with increasing pH (36). For example, atrazine degradation in dark- and photo Fenton systems (37, 38) decreased sharply from pH 4-7 and it was suggested that *OH is formed only at low pH. In contrast, the oxidation of As(III) in Fenton and photo-Fenton reactions appears to be possible at neutral pH. To better understand the reaction pathways and kinetics, we have investigated the dark reaction of Fe(II) with O2 and with H2O2 as a function of pH and bicarbonate concentrations.

2.2 Experimental section

2.2.1 Chemicals

All chemicals were reagent grade from Aldrich or Fluka and were used as received.
2. Fe(II) catalyzed Oxidation of As(III) by O₂ and by H₂O₂

Table 2.1: Experimental Parameters (initial concentrations after mixing)

<table>
<thead>
<tr>
<th>Species (concentration)</th>
<th>Oxidation with O₂ (μM)</th>
<th>Oxidation with H₂O₂ at &gt; pH 6 (μM)</th>
<th>Oxidation with H₂O₂ at &lt; pH 6 (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III) (μM)</td>
<td>6.6</td>
<td>6.6</td>
<td>6.6</td>
</tr>
<tr>
<td>Fe(II) (μM)</td>
<td>90</td>
<td>0.1-20</td>
<td>20</td>
</tr>
<tr>
<td>H₂O₂ (μM)</td>
<td>0</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Initial pH</td>
<td>7.0 and 7.5</td>
<td>7.0 and 7.5</td>
<td>3.5, 4.4 and 5.0</td>
</tr>
<tr>
<td>HCO₃⁻ (mM)</td>
<td>8.30</td>
<td>0*, 2.0, 100†</td>
<td>0</td>
</tr>
<tr>
<td>Ca mg/L (mM)</td>
<td>2.50</td>
<td>0.63</td>
<td>0.63</td>
</tr>
<tr>
<td>Mg mg/L (mM)</td>
<td>1.65</td>
<td>0.41</td>
<td>0.41</td>
</tr>
<tr>
<td>SO₄²⁻ (μM)</td>
<td>90</td>
<td>0.1-20</td>
<td>1110</td>
</tr>
<tr>
<td>2-propanol (mM)</td>
<td>0, 14</td>
<td>0, 14</td>
<td>0, 14</td>
</tr>
</tbody>
</table>

* with H₂PO₄⁻ / HPO₄²⁻ (pH 7.4) = 1 mM.
† in two experiments with 100 mM NaHCO₃ (with and without 2-propanol and formate). The temperature was 22-25°C.

2.2.2 Kinetic experiments

Synthetic groundwater was prepared by dissolution of CaCO₃ and MgCO₃ with an excess of CO₂ in high purity 18 MΩ water (Millipore). The initial pH for the experiments at pH 7.0-7.5 was reached by outgassing of CO₂ by vigorous stirring in open beakers. H₂SO₄ was used to adjust pH values below 6. The initial pH, measured with a combined glass electrode, was ±0.1 units within the indicated value and typically increased by 0.1-0.2 pH units during the kinetic runs due to loss of CO₂.

90 mM (5.0 g/L) Fe(II) stock solutions were always freshly prepared by dissolving FeSO₄·7H₂O in 1 mM HCl. 100 mM H₂O₂ stock solutions were prepared from 30% H₂O₂ (determined by titration with permanganate). For the oxidation experiments with dissolved O₂, acidic Fe(II) stock solution was quickly mixed into 100-200 ml of the pH-adjusted air-saturated synthetic groundwater solutions which already contained the As(III). Aliquots were sampled at specific time intervals. In the experiments with H₂O₂, two equal volumes with the separated reactants at twice the targeted initial concentrations were prepared separately. For example, a pH-adjusted solution containing H₂O₂, As(III) and the *OH-radical scavenger (e.g. 2-propanol) was quickly mixed with the same volume of Fe(II) solution. This approach ensured that the concentrations during the mixing never exceeded the intended initial concentrations. The parameters for all kinetic experiments are listed in Tab. 2.2.
2.2 Experimental section

2.2.3 As(V) analysis

In the experiments where iron was oxidized by dissolved O₂, the sum of dissolved and adsorbed As(V) was measured spectrophotometrically with the molybdenum-blue method (39). Under the acidic and reducing conditions of the reagents, colloidal Fe(III)(hydr)oxides were dissolved. To check for interference with traces of phosphate impurities, absorbance spectra were recorded from 500-900 nm and fitted with the distinct spectra of molybdenum blue formed from phosphate and arsenate (40). The As(V)-specific molybdenum-blue method was more exact than forming differences from As(III)-specific measurements (see below) in experiments where only small fractions of As(III) were oxidized.

2.2.4 As(III) analysis

As(III) was measured with an Atomic Fluorescence Spectrometer (AFS) - Millenium Excalibur (PS Analytical Ltd, Kent, UK). The instrument works with Hydride Generation by continuous flow mixing of the acidified (normally 1 M HCl) sample with 0.7% NaBH₄ in a teflon valve and a liquid-gas separator. To selectively detect As(III), we used a pH 5 citrate buffer (0.5 M di-sodium hydrogen citrate) instead of HCl. Only As(III) (and no As(V)) is converted to AsH₃ under these conditions (41). Aliquots (100 or 200 µl) from the reaction mixtures were diluted 1:50 into 0.5 M citrate buffer. The dilution and lowering of pH stopped the reaction between Fe(II), oxygen and H₂O₂. Both dissolved and adsorbed As(III) were measured, as the pH 5 citrate buffer led to the desorption of As(III) and to dissolution of the amorphous ironhydroxide colloids. We verified that the reactions did not proceed after the sampling and dilution by performing the AFS analysis at several times 5 - 120 min after mixing of the sample aliquot with the buffer.

2.2.5 Reproducibility

Each experiment was repeated two to three times. The analysis of As(III) and As(V) showed standard deviations of ± 7%. The standard deviations of the Fe(II) measurements (phenanthroline method) was ± 5%. The reproducibility between different experiments was mostly limited by the pH increases due to loss of CO₂ from the solutions during the sampling, and due to lack of buffering below pH 6. The deviations between repeated experiments were approximately ±10%.
22 2. Fe(II) catalyzed Oxidation of As(III) by O₂ and by H₂O₂

2.2.6 FTIR-Spectra of colloids

Colloids were collected on 0.25 μm Teflon filters and measured on a Biorad FTS 575C FT-IR instrument equipped with a Harrick Meridian Diamond Split Pea ATR unit.

2.2.7 Formation of acetone from 2-propanol

The formation of acetone during the reaction of 20 μM H₂O₂, 20 μM Fe(II) and 0.5 mM 2-propanol as a function of pH was measured in two experiments with direct-injection GC-MS (GC8000 and MD800, Fisons, Manchester) (42).

2.2.8 Kinetic modeling

Kinetic modeling was performed with ACUCHEM (43) and with improved global fitting routines written in Matlab (The MathWorks Inc.), but otherwise similar as in previous studies of illuminated Fe(III) systems (38,44-46). The list of reactions in Table Tab. 2.2 was used as the input for ACUCHEM. Equilibrium reactions were written as separate forward and back reactions, with fast, non-rate determining forward/back rate constants and the pH was kept constant for each experiment by formulating all equilibrium reactions as H⁺-preserving reactions. The concentration of dissolved O₂ was kept constant by equilibrium with a large reservoir of air. The input file for ACUCHEM is provided as supplementary material. The adjustable rate constants were changed by the Matlab routine until the total sum of normalized squared differences between data and model for all experiments was minimized with the Nelder-Mead simplex routine.

2.3 Results and discussion

2.3.1 Oxidation of Fe(II) and As(III) in aerated solutions with O₂

The concentration change of As(V) and Fe(II) after addition of 90 μM Fe(II) to air-saturated 6.6 μM As(III) solutions are shown in Fig. 2.1. The solid lines in these and in all following figures represent the output from the model calculation (Tab. 2.2 and Tab. 2.3, Model 2b ). In the following discussion, we refer to the reactions in Tab. 2.2, but the reaction model will be discussed in more detail in the following section.

It can be seen that parallel to the disappearance of Fe(II) due to oxidation by dissolved O₂, As(III) is partly oxidized to As(V). After the oxidation of
2.3 Results and discussion

Fe(II) is complete, As(III) is not oxidized further, with the fraction of oxidized As(III) remaining between 25 and 30%. The higher oxidation rates at pH 7.5 compared to pH 7.0 are explained by the pH-dependent conditional rate constants for Fe(II) oxidation taken from the literature (47). The oxidation of As(III) must occur by reactive oxygen species (O$_{2}^{*-}$, H$_{2}$O$_{2}$, O$_{2}^{*OH}$, or other oxidizing intermediates) which are formed as intermediates during the reduction of O$_{2}$ with Fe(II). The small effect of 2-propanol shows that O$_{2}^{*OH}$ cannot be the oxidant for As(III). At the added concentration of 14 mM, 2-propanol would completely inhibit the oxidation of As(III) by quantitatively scavenging the O$_{2}^{*OH}$ radicals. Also, H$_{2}$O$_{2}$ did not oxidize As(III) on a time scale of hours, in agreement with other studies (9). The role of O$_{2}^{*-}$ as an oxidant was discounted in our previous work (16). To better understand this system, we have conducted experiments in which As(III) was oxidized with H$_{2}$O$_{2}$ and with Fe(II) at various pH values.

2.3.2 Oxidation of Fe(II) and As(III) with added H$_{2}$O$_{2}$

Fig. 2.2A-D show the oxidation of 6.6 µM As(III) with 20 µM Fe(II) and 20 µM H$_{2}$O$_{2}$ in aerated solutions, without and with 14 mM 2-propanol, at different pH values. At pH 7, the oxidation of As(III) is rapid but incomplete. The fraction of As(III) oxidized decreased only slightly in the presence of 2-propanol. At pH 5.0, As(III) was completely oxidized, but slightly slower in the presence of 2-propanol. At pH 4.4, the effect of 2-propanol was clearly evident, both in the smaller oxidation rate and in the reduced fraction of oxidized As(III). At pH 3.5, 2-propanol almost completely inhibited the oxidation of As(III). These experiments clearly demonstrate that the reaction mechanism undergoes significant changes between pH 3.5 and pH 7.5. The most important conclusion is that O$_{2}^{*OH}$ might be the oxidant for As(III) at low pH, where the oxidation of As(III) is almost completely quenched by the reaction of O$_{2}^{*OH}$ with 2-propanol. However, with increasing pH, an additional oxidant, which does not react competitively with 2-propanol, must be formed. HO$_{2}^{*}$ and O$_{2}^{*-}$ as significant oxidants can be discounted for the following reasons: At low pH, O$_{2}^{*OH}$ reacts with 2-propanol mainly to acetone and HO$_{2}^{*}$ (48). Since the As(III) oxidation is almost completely quenched by 2-propanol at pH 3.5, HO$_{2}^{*}$ cannot be a significant oxidant for As(III) in this system. At higher pH, O$_{2}^{*-}$ is formed. Since O$_{2}^{*-}$ is a weaker oxidant than HO$_{2}^{*}$ and H$_{3}$AsO$_{3}$ remains the dominant As(III) species over the entire pH-range used, O$_{2}^{*-}$ can also not be a significant oxidant for As(III). This is consistent with our former photochemical study (16). In the pulse-radiolysis study of Klaning et al. (49), oxidation of As(III) by O$_{2}^{*-}$ was also not reported. Thus, an additional oxidant must be formed in the Fenton reaction at higher pH. To account for these observations, we added the reactions (F1-F3) in which Fe(II) and H$_{2}$O$_{2}$
### 2. Fe(II) catalyzed Oxidation of As(III) by O$_2$ and by H$_2$O$_2$

**Table 2.2: Kinetic Model.** List of reactions used for modeling. Species in italics are written to keep equations balanced, but were not included in the model. Rate constants typed in bold were optimized by simultaneous fitting, those marked with * are non-rate determining and were estimated, all others were taken from the literature. The conditional, pH-dependent $k_{c}$ and $k_{0}$ were calculated from Millero et al (47): $14$ M$^{-1}$s$^{-1}$ at pH $7.42$, $3.0$ M$^{-1}$s$^{-1}$ at pH $7.10$ and $1.3\times10^{-4}$ M$^{-1}$s$^{-1}$ at pH $5.0$ ($I = 0.01$ M. In some optimizations, $k_{9}$–$k_{12}$ were kept at fixed values and left adjustable in others (see Tab. 2.3).

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Uni- and bimolecular rate constants in s$^{-1}$ and M$^{-1}$s$^{-1}$</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Arsenic oxidations</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>As(III) + *OH $\rightarrow$ As(IV)</td>
<td>$8\times10^{10}$</td>
</tr>
<tr>
<td>A2</td>
<td>As(III) + CO$<em>{3}^{2-}$ $\rightarrow$ As(IV) + HCO$</em>{3}^{-}$</td>
<td>$1.3\times10^{10}$</td>
</tr>
<tr>
<td>A3</td>
<td>As(IV) + O$<em>2$ $\rightarrow$ As(V) + O$</em>{2}^{2-}$</td>
<td>$1.1\times10^{9}$</td>
</tr>
<tr>
<td><strong>Fe(II) – Oxidations</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>Fe$^{2+}$ + O$<em>2$ $\rightarrow$ O$</em>{2}^{2-}$ + Fe$^{3+}$</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>Fe$^{2+}$ + O$_{2}^{2-}$ + 2H$^+$ $\rightarrow$ Fe$^{3+}$ + H$_2$O$_2$</td>
<td>$10^{5}$</td>
</tr>
<tr>
<td>B3</td>
<td>Fe$^{2+}$ + H$_2$O$_2$ + H$^+$ $\rightarrow$ Fe$^{3+}$ + H$_2$O$_2$</td>
<td>$1.2\times10^{5}$</td>
</tr>
<tr>
<td>B4</td>
<td>Fe$^{2+}$ + *OH $\rightarrow$ Fe$^{3+}$ + OH$^-$</td>
<td>$3.2\times10^{8}$</td>
</tr>
<tr>
<td>B5</td>
<td>Fe$^{2+}$ + CO$_3^{2-}$ $\rightarrow$ Fe$^{3+}$ + HCO$_3^{-}$</td>
<td>$3.6\times10^{5}$</td>
</tr>
<tr>
<td><strong>Fenton reactions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F1</td>
<td>Fe$^{2+}$ + H$_2$O$_2$ $\rightarrow$ Fe$^{3+}$ + *OH</td>
<td></td>
</tr>
<tr>
<td>F2</td>
<td>Fe$^{2+}$ + H$_2$O$_2$ $\rightarrow$ INT + OH$^-$</td>
<td></td>
</tr>
<tr>
<td>F3</td>
<td>Fe$^{2+}$ + H$_2$O$_2$ $\rightarrow$ INT + CO$_3^{2-}$</td>
<td></td>
</tr>
<tr>
<td>F4</td>
<td>INT + *OH + H$^+$ $\rightarrow$ Fe$^{3+}$ + e$^-$</td>
<td>(10)$^*$</td>
</tr>
<tr>
<td>F5</td>
<td>INT + CO$_3^{2-}$ $\rightarrow$ Fe$^{3+}$ + INT$^-$ + CO$_3^{2-}$</td>
<td>(10)$^*$</td>
</tr>
<tr>
<td><strong>Fenton(III) reactions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J1</td>
<td>Fe$^{3+}$ + Fe$^{2+}$ $\rightarrow$ Fe$^{3+}$ + Fe$^{3+}$</td>
<td></td>
</tr>
<tr>
<td>J2</td>
<td>Fe$^{3+}$ + Fe$^{2+}$ + H$^+$ $\rightarrow$ Fe$^{3+}$ + Fe$^{3+}$ + H$^+$</td>
<td></td>
</tr>
<tr>
<td>J3</td>
<td>Fe$^{3+}$ + H$_2$O$_2$ $\rightarrow$ Fe$^{3+}$ + H$_2$O$_2$</td>
<td></td>
</tr>
<tr>
<td>J4</td>
<td>As(III) + Fe$^{3+}$ $\rightarrow$ As(IV) + Fe$^{3+}$</td>
<td>$1.5\times10^{5}$</td>
</tr>
<tr>
<td><strong>Fe(CVII) reactions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J1</td>
<td>Fe$^{2+}$ + Fe$^{3+}$ $\rightarrow$ Fe$^{3+}$ + Fe$^{3+}$</td>
<td>$1.5\times10^{5}$</td>
</tr>
<tr>
<td>J2</td>
<td>Fe$^{2+}$ + Fe$^{3+}$ + H$^+$ $\rightarrow$ Fe$^{3+}$ + Fe$^{3+}$ + H$^+$</td>
<td>$1.5\times10^{5}$</td>
</tr>
<tr>
<td><strong>Fe(III) reductions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J3</td>
<td>Fe$^{2+}$ + O$_{2}^{2-}$ $\rightarrow$ Fe$^{3+}$ + O$_2$</td>
<td>$1.5\times10^{5}$</td>
</tr>
<tr>
<td>J4</td>
<td>Fe$^{2+}$(OH$^-$)$^2$ + O$_2$ $\rightarrow$ Fe$^{3+}$ + O$_2$ + OH$^-$</td>
<td>$1.5\times10^{5}$</td>
</tr>
<tr>
<td>J5</td>
<td>Fe$^{2+}$ + *OH + H$^+$ $\rightarrow$ Fe$^{3+}$ + *OH + H$^+$</td>
<td>$1.5\times10^{5}$</td>
</tr>
<tr>
<td><strong>Reactive oxygen radical reactions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q1</td>
<td>HO$<em>2$ + O$</em>{2}^{2-}$ + H$^+$ $\rightarrow$ H$_2$O$_2$ + O$_2$</td>
<td></td>
</tr>
<tr>
<td>Q2</td>
<td>HO$_2$ + O$_2$ $\rightarrow$ H$_2$O$_2$ + O$_2$</td>
<td>$8.3\times10^{5}$</td>
</tr>
<tr>
<td>Q3</td>
<td>H$_2$O$_2$ + *OH $\rightarrow$ HO$_2$ + H$_2$O</td>
<td>$3.0\times10^{5}$</td>
</tr>
<tr>
<td>Q4</td>
<td>HCO$_3^{-}$ + *OH $\rightarrow$ CO$_2$ + *OH$^-$ + H$_2$O</td>
<td>$8.5\times10^{7}$</td>
</tr>
<tr>
<td>Q5</td>
<td>H$_2$O$_2$ + CO$_3^{2-}$ $\rightarrow$ HO$_2$ + HCO$_3^{-}$</td>
<td>$4.5\times10^{5}$</td>
</tr>
<tr>
<td>Q6</td>
<td>*OH + 2H$^+$ $\rightarrow$ CO$_3^{2-}$ + OH$^-$ + 2H$_2$O</td>
<td>$1.9\times10^{8}$</td>
</tr>
<tr>
<td>Q7</td>
<td>CO$_3^{2-}$ + 2H$^+$ $\rightarrow$ 2CO$_2$ + 2H$_2$O</td>
<td>$5\times10^{8}$</td>
</tr>
<tr>
<td><strong>Fe(III)–equilibrium</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E1</td>
<td>Fe$^{3+}$ + Fe$^{2+}$ + CO$_2$ + H$^+$ $\rightarrow$ 2Fe$^{2+}$ + CO$_2$ + H$^+$</td>
<td>$4.57\times10^{5}$ / $10^{12}$ (pK$K_{6}$2.3)</td>
</tr>
<tr>
<td>E2</td>
<td>Fe$^{3+}$ + Fe$^{2+}$ + CO$_2$ + H$^+$ $\rightarrow$ 2Fe$^{2+}$ + CO$_2$ + H$^+$</td>
<td>$2.51\times10^{9}$ / $10^{12}$ (pK$K_{6}$3.4)</td>
</tr>
<tr>
<td>E3</td>
<td>Fe$^{3+}$ + (OH$^-$)$^2$ $\rightarrow$ Fe$^{2+}$ + (OH$^-$)$^2$ + H$^+$</td>
<td>$1.17\times10^{10}$ / $10^{14}$ (pK$K_{9}$7.3)</td>
</tr>
<tr>
<td><strong>Fe(II)–precipitation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>Fe$^{2+}$ + Fe$^{2+}$ + Fe$^{2+}$ (OH$^-$)$^2$ $\rightarrow$ Precip</td>
<td>$k_{p}$</td>
</tr>
<tr>
<td>P2</td>
<td>Fe$^{2+}$ + Fe$^{2+}$ + Precip</td>
<td>$k_{p}$</td>
</tr>
<tr>
<td><strong>Fe(II)–equilibrium</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E5</td>
<td>Fe$^{2+}$ + Fe$^{2+}$ + CO$_2$ $\rightarrow$ 2Fe$^{2+}$ + CO$_2$</td>
<td>$3.09\times10^{3}$ / $10^{12}$ (pK$K_{6}$9.51)</td>
</tr>
<tr>
<td>E6</td>
<td>Fe$^{2+}$ + CO$_3^{2-}$ $\rightarrow$ Fe$^{2+}$ + CO$_2$</td>
<td>$4.89\times10^{12}$ / $10^{7}$ (logK = 5.69)</td>
</tr>
<tr>
<td><strong>Superoxide equilibria</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E7</td>
<td>O$_2$ + H$^+$ $\rightarrow$ HO$_2$</td>
<td></td>
</tr>
<tr>
<td>E8</td>
<td>HO$_2$ + O$_2$ $\rightarrow$ 2HO$_2$</td>
<td>$10^{12}$ / $1.3\times10^{12}$ (pK$K_{6}$4.8)</td>
</tr>
<tr>
<td><strong>Carbonate equilibria</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E9</td>
<td>HCO$_3^{-}$ + CO$_2$ $\rightarrow$ CO$_2$ + H$^+$</td>
<td>$4.66\times10^{7}$ / $10^{12}$ (pK$K_{6}$10.33)</td>
</tr>
<tr>
<td>E10</td>
<td>CO$_2$ + CO$_3^{2-}$ $\rightarrow$ HCO$_3^{-}$ + H$^+$</td>
<td>$4.66\times10^{7}$ / $10^{12}$ (pK$K_{6}$6.35)</td>
</tr>
</tbody>
</table>
Figure 2.1: Oxidation of 6.6 μM As(III) after the addition of 90 μM Fe(II) in aerated solutions. The formation of As(V) (A) and the disappearance of Fe(II) (B) in the same experiments is indicated by symbols. Error bars (±10%) in these and the following figures are not shown for clarity. The lines represent the output of the model 2c (Tab. 2.2), which simultaneously fits all the data in these and the following figures. Adding 14 mM 2-propanol as an OH-radical scavenger did not significantly lower the oxidation of As(III).
Table 2.3: Effect of Model Variations Fitted rate constants and Sum of Squared Differences (SSD) for different model variations. Numbers printed in italics indicate that rate constants were kept at fixed values, while the rate constants in bold print were optimized by simultaneous fitting. The last column lists \( \log(k) \)'s reported in other studies under similar conditions: \(^a\) Millero et al. (47,60); \(^b\) Sedlak and Hoigne (44); \(^c\) King and Farlow (55); \(^d\) \( \log(k) \) for the reaction of Fe\(^{III}\)CO\(_3\) and Fe\(^{II}\)(CO\(_3\))\(^2-\) with H\(_2\)O\(_2\), respectively (55). (All Fe(II)-carbonate species in our model were represented by Fe\(^{II}\)CO\(_3\)).

<table>
<thead>
<tr>
<th>Rate constant</th>
<th>Model 1 ((P1))</th>
<th>Model 2a ((P1 + P2))</th>
<th>Model 2b ((P1 + P2))</th>
<th>Model 2c ((P1 + P2))</th>
<th>Reported ( \log(k) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 ) Fe(^{II})CO(_3) + H(_2)O(_2)</td>
<td>6.11</td>
<td>5.99</td>
<td>5.94</td>
<td>5.95</td>
<td>4.34(^d), 7.52(^d)</td>
</tr>
<tr>
<td>( pK_2 ) INT ↔ INT - OH + H(^+)</td>
<td>5.16</td>
<td>5.14</td>
<td>5.24</td>
<td>5.34</td>
<td></td>
</tr>
<tr>
<td>( k_3 ) CO(_3) partitioning</td>
<td>6.66</td>
<td>6.61</td>
<td>6.63</td>
<td>6.63</td>
<td>6.59</td>
</tr>
<tr>
<td>( k_4 ) Fe(^{II}) + Fe(IV)</td>
<td>3.92</td>
<td>3.09</td>
<td>3.28</td>
<td>3.59</td>
<td></td>
</tr>
<tr>
<td>( k_5 ) Fe(^{II})OH(^+) + Fe(IV)</td>
<td>8.51</td>
<td>7.93</td>
<td>8.13</td>
<td>8.10</td>
<td></td>
</tr>
<tr>
<td>( k_6 ) Fe(^{II})CO(_3) + Fe(IV)</td>
<td>7.22</td>
<td>6.63</td>
<td>6.56</td>
<td>6.55</td>
<td></td>
</tr>
<tr>
<td>( k_7 ) As(III) + Fe(IV)</td>
<td>6.28</td>
<td>5.65</td>
<td>5.62</td>
<td>5.58</td>
<td></td>
</tr>
<tr>
<td>( k_8 ) Fe(OH)(_3) Precip.</td>
<td>9.52</td>
<td>8.30</td>
<td>8.29</td>
<td>8.36</td>
<td></td>
</tr>
<tr>
<td>( k_9 ) Fe(II) + O(_2) (pH 7.5)</td>
<td>1.15</td>
<td>1.15</td>
<td>1.17</td>
<td>1.15(^a)</td>
<td></td>
</tr>
<tr>
<td>( k_{10} ) Fe(II) + O(_2) (pH 7.2)</td>
<td>0.48</td>
<td>0.48</td>
<td>0.47</td>
<td>0.48(^a)</td>
<td></td>
</tr>
<tr>
<td>( k_{11} ) Fe(^{III}) + H(_2)O(_2)</td>
<td>1.60</td>
<td>1.60</td>
<td>1.43</td>
<td>2.11(^a)</td>
<td>1.80(^b), 1.92(^c)</td>
</tr>
<tr>
<td>( k_{12} ) Fe(^{II})OH(^+) + H(_2)O(_2)</td>
<td>7.21</td>
<td>7.21</td>
<td>7.12</td>
<td>7.21(^a)</td>
<td>6.77(^b), 5.58(^c)</td>
</tr>
</tbody>
</table>

SSD | 1.46 | 1.32 | 1.26 | 1.66 | |

form an intermediate that leads to formation of Fe(IV) at neutral pH and to \(^*\)OH at low pH (II-15). Fe(IV) oxidizes Fe(II) (J1-J3) and As(III) (J4), but not 2-propanol. The mechanistic reasoning for this model will be discussed in more detail in a separate paragraph below.

The relative reaction rates of the proposed oxidant with the competitive reductants Fe(II) and As(III) at close to neutral pH were studied by varying the amount of added Fe(II) to the otherwise constant concentrations of 20 \( \mu \)M H\(_2\)O\(_2\) and 6.6 \( \mu \)M As(III) at pH 7.2-7.5. The results are shown in Fig. 2.3. At low concentrations of added Fe(II), several times more As(III) is oxidized than Fe(II) added. \( R_{\text{As}/\text{Fe}} \), the ratio of As(III) oxidized over Fe(II) added, is about 3 for 0.5 \( \mu \)M added Fe(II). At higher concentrations of added Fe(II), \( R_{\text{As}/\text{Fe}} \) drops to below 1 (e.g. below 0.33 for 20 \( \mu \)M Fe(II)). Overall, the model accounts well for the observed trends. The addition of very low concentrations of Fe(II) starts a chain reaction. The first step is the reaction of Fe(II) with H\(_2\)O\(_2\) and the formation of Fe(IV). The reaction of Fe(IV) with As(III) forms Fe(III) and As(IV) (J4). As(IV) reacts almost diffusion controlled mainly with dissolved O\(_2\) (A3) (which is an order of magnitude more
2.3 Results and discussion

Figure 2.2: Effect of pH on the oxidation of 6.6 μM As(III) with 20 μM Fe(II) and 20 μM H2O2. The addition of 14 mM 2-propanol had only a small effect above pH 5 (A and B), but lowered the rate and the fraction of As(III) oxidation at pH 4.4 (C) and almost completely inhibited the As(III) oxidation at pH 3.5 (D).

concentrated than H2O2) to As(V) and O2-. The chain is propagated by the reduction of Fe(III) with O2- to re-form Fe(II) (R1-R3). With increasing concentrations of Fe(II), Fe(IV) reacts with Fe(II) to two Fe(III) in a chain terminating reaction (J1-J3). With increasing pH, the increasing fraction of Fe(II) (E5) reacts more quickly with Fe(IV). This explains the incomplete oxidation of As(III) at pH 7 (Fig. 2.2A) compared to the complete oxidation at pH 5 (Fig. 2.2B) in the presence of H2O2, as well as the only 20-30% oxidation at the higher Fe(II) concentrations with O2 (Fig. 2.1A).

2.3.3 Influence of bicarbonate

The possible role of Fe(II)-carbonate species and of carbonate radicals was investigated in experiments with 20 μM H2O2, 6 μM Fe(II) and different bicarbonate concentrations. The results in Fig. 2.4A show that about twice as much As(III) is oxidized in the presence of 100 mM HCO3- than with only 2 mM
Figure 2.3: Oxidation of 6.6 μM As(III) in 20 μM H₂O₂ after the addition of 0.1-20 μM Fe(II) at pH 7.2-7.5. The ratio of As(III) oxidized over Fe(II) added decreases with increasing concentrations of added Fe(II).
HCO\textsuperscript{3−}. In solutions buffered with phosphate, even less As(III) is oxidized. The same experiments with 14 mM added formate are shown in Fig. 2.4B (another experiment with 14 mM 2-propanol is not shown). Within the scatter of the data, there is no clear difference between the results with and without formate or 2-propanol. Bicarbonate increases the fraction of oxidized As(III), possibly by formation of carbonate radicals or by changing the speciation of Fe(II). The small or absent influence of formate and 2-propanol again confirms that at pH 7.5, *OH radicals are not the main oxidant of As(III).

2.3.4 Formation of acetone from 2-propanol as a function of pH

The final concentration of acetone formed 2 h after mixing of equal volumes of Fe(II) and H\textsubscript{2}O\textsubscript{2} solutions to initial concentrations of 20 μM H\textsubscript{2}O\textsubscript{2}, 20 μM Fe(II) and 0.5 mM 2-propanol are shown in Fig. 2.5. The large error bars in the pH-values represent the pH-changes during the reactions in the unbuffered solutions. Despite the detection limit of 2 μM for acetone and the uncertainty in the pH values, it is clearly apparent that the formation of acetone decreased steeply with increasing pH. Assuming a 65% yield of acetone in the reaction of *OH with 2-propanol and subsequent oxidation of the organic radical by O\textsubscript{2} (summarized in reaction Q1 in Tab. 2.2), the model correctly predicts the acetone formation as a function of pH. (The reported maximum yield of acetone formation from 2-propanol and OH in aerated solutions is 87% (48)). These measurements confirm that at higher pH, 2-propanol is not oxidized and thus does not quench the oxidation of As(III) at neutral pH.

2.3.5 Characterization of colloids

The colloids formed from the oxidation of 90 μM Fe(II) by dissolved O\textsubscript{2} in aerated solutions were investigated by ATR-FTIR spectroscopy (Fig. 2.6) and compared to spectra of known Fe(III) phases (50). Spectrum 1 is of the colloids formed from oxidation of Fe(II) in synthetic groundwater at pH 7.0-7.3. The only clear spectral features are the two rather small peaks characteristic of lepidocrocite at 743 cm\textsuperscript{−1} and 1017 cm\textsuperscript{−1} and two peaks of adsorbed carbonate at 1375 cm\textsuperscript{−1} and 1492 cm\textsuperscript{−1}. The rather uncharacteristic increasing absorbance toward lower wavenumbers indicates amorphous ferric hydroxides. Geothite, akaganeite and δ-FeOOH can be excluded, as none of their spectral characteristics are observed (50). The lepidocrocite fraction is estimated at 5-10% by comparison with spectrum 2, where 10% of crystalline lepidocrocite was added. Spectra 3-5 are of precipitates formed at pH 7.0-7.2, without and with As(III) and with As(V) (6.6 μM), respectively. In the presence of As(III) and
2. Fe(II) catalyzed Oxidation of As(III) by O₂ and by H₂O₂

Figure 2.4: Oxidation of 6.6 μM As(III) in 20 μM H₂O₂ after the addition of 6 μM Fe(II) at pH 7.2-7.5 with different concentrations of bicarbonate (A). Figure 4B shows the same experiments with 14 mM formate added. Addition of 2-propanol (not shown) had a similarly small effect as formate.
2.3 Results and discussion

Figure 2.5: Formation of acetone after mixing of 40 μM H₂O₂ and 500 μM 2-propanol with an equal volume of 40 μM Fe(II) at various pH-values. Measured data points are indicated with error bars. The lines are the predicted acetone concentrations by the model (Tab. 2.2), assuming a yield for acetone of 86% (upper line) and 65% (lower line).

As(V), less lepidocrocite and more adsorbed carbonate is observed. This indicates a lower crystallinity, consistent with the inhibition of crystal growth by strongly adsorbing anions such as arsenate. Adsorbed arsenate is visible between 800 cm⁻¹ and 900 cm⁻¹ (Spectrum 5) and also in the precipitates formed in the presence of only As(III) (Spectrum 4).

2.3.6 Hypothetical reaction model and possible reaction mechanism

The model in Tab. 2.2 was constructed by collecting all the pertinent reactions for which rate constants have been reported in the literature and in the on-line data base of the Notre Dame Radiation Laboratory (51). Since this list was insufficient to explain the observed pH dependence, we replaced the Fenton reactions as usually formulated (f1-f3) by the more detailed equations (F1-F3,
2. Fe(II) catalyzed Oxidation of As(III) by O$_2$ and by H$_2$O$_2$

Figure 2.6: ATR-FTIR spectra of the colloids formed from the oxidation of 90 μM Fe(II) by dissolved O$_2$ at pH 7.0-7.3. Spectrum 1: in synthetic groundwater with As(III). Spectrum 2: same as 1, but with the addition of 9 μM crystalline lepidocrocite. Spectrum 3: without As(III) at pH 7.0-7.2. Spectrum 4: same as 3, with As(III). Spectrum 5: same as 3, with As(V). Spectral assignments: preformed crystalline lepidocrocite, 1024 cm$^{-1}$ and 751 cm$^{-1}$. Lepidocrocite formed from Fe(II) oxidation, 1017 cm$^{-1}$ and 743 cm$^{-1}$. Adsorbed As(V), 804 cm$^{-1}$ and 841 cm$^{-1}$, adsorbed (bi)carbonate, 1375 cm$^{-1}$ and 1492 cm$^{-1}$.
2.3 Results and discussion

The resulting reaction model is also shown as a pictorial reaction scheme in Fig. 2.7. Rectangular boxes mark the added reactions and intermediates.

For simplicity, we have treated all experiments as homogenous systems and considered only the reactions between dissolved species. Other than as a sink for dissolved Fe(III), we have ignored the role of solids and of surface reactions. This approximation can be justified by the following considerations: 1) In all experiments with H₂O₂, only 20 µM Fe(III)-hydroxides (ca. 2 mg Fe(OH)₃/L) are formed at the end of the reaction and most of the Fe(II) and H₂O₂ is consumed before all colloids have formed. 2) Even at the larger Fe(III) concentration (90 µM) used in the oxidation experiments with O₂, only small fractions of the reactants (O₂, As(III) and Fe(II)) and the intermediates (H₂O₂) are adsorbed on the iron(hydr)oxide colloids at circumneutral and lower pH-values. In the course of the formation of colloids, As(V) adsorption does become important, but the fate of As(V) as a final product does not influence the reaction kinetics. However, the role of forming colloids (P₁ and P₂) as a sink for dissolved Fe(III) is important and was included in the model, in order not to overestimate the reduction of dissolved Fe(III) by O₂⁻ (R₁-R₃).

The key reaction is the Fenton reaction between Fe(II) and H₂O₂. As discussed above, several oxidants have been suggested to be formed, depending on the reaction conditions. The direct formation of free *OH-radicals and Fe(III) in the common formulation of the Fenton reaction (f₁-f₃) would imply an outer-sphere electron transfer reaction between H₂O₂ and Fe(II). However, it is widely accepted that the reaction between Fe(II) and H₂O₂ occurs via an inner-sphere mechanism (23,34,52), wherein a first step, one water ligand is exchanged by H₂O₂:

\[
\text{[Fe}^{II/(H₂O)₆}^{2+} + \text{H}_₂\text{O} \rightarrow \text{[(H}_₂\text{O)}₅\text{Fe}^{II} - \text{O}_₂\text{H}_₂]^{2+} + \text{H}_₂\text{O} \quad 1a
\]

\[
\text{[(H}_₂\text{O)}₅\text{Fe}^{II}(\text{OH})]^{+} + \text{H}_₂\text{O} \rightarrow \text{[(H}_₂\text{O)}₄(\text{HO})\text{Fe}^{II} - \text{O}_₂\text{H}_₂]^{+} + \text{H}_₂\text{O} \quad 1b
\]

Since the ligand exchange is faster than the following reactions, but slower than the protonation equilibrium of the water ligands with the surrounding solution, we would expect that \([(H₂O)₅Fe^{II} - O₂H₂]^{2+}\) and \([(H₂O)₄(HO)Fe^{II} - O₂H₂]^+\) are at equilibrium before the next steps occur.

In the rate determining electron-transfer and internal rearrangement reactions, two intermediates (INT and INT-OH) are formed:
2. Fe(II) catalyzed Oxidation of As(III) by O₂ and by H₂O₂

\[
[(H_2O)_5Fe^{II} - O_2H_2]^{2+} \rightarrow \text{INT} \quad 2a
\]

\[
[(H_2O)_4(HO)Fe^{II} - O_2H_2]^{+} \rightarrow \text{INT-OH} \quad 2b
\]

The formulation of the Fe(II) oxidation as parallel reactions of differently protonated Fe(II) species retains consistency with the generally accepted formulation of the Fe(II) oxidation (47,53). For the rate determining formation of INT and INT-OH, we have used values close to the reported rate constants for the oxidation of Fe²⁺ and Fe(II)(OH)⁺ by H₂O₂ (Tab. 2.3). Since the two ligand-exchange reactions 1a and 1b are not rate determining, we have summarized the reactions 1a and 2a, as well as 1b and 2b, each as a single combined, rate determining reaction (F1 and F2) in our model (Tab. 2.2). We then assume that once INT and INT-OH are formed, they are in a fast, not rate determining protonation equilibrium with the surrounding water:

\[
\text{INT-OH} + H^+ \rightarrow \text{INT} \quad 3(11)
\]

The final products are formed in reactions that are faster than 2a and 2b and are thus also not rate determining.

\[
\text{INT} \rightarrow \text{Fe}^{III}(OH)^{2+} \text{and} \text{*OH} \quad 4a(12)
\]

\[
\text{INT-OH} \rightarrow \text{Fe(IV)} \quad 4b(13)
\]

The protonation equilibrium between INT and INT-OH leads to a pH-dependent partitioning of the reactions into *OH-radicals at low pH, and more weakly oxidizing Fe(IV) species at higher pH.

The nature of INT and INT-OH and of the final products cannot be stated with certainty and depends on how the reactions proceed in detail. We propose two possible sequences:

1. INT is formed by an one-electron transfer (followed by dissociation of HO-OH and loss of an H₂O ligand) and could be formulated as \([(H_2O)_4Fe^{III}(OH)(*OH)]^{2+}\). A free *OH-radical could then be formed, more likely by hydrogen abstraction from a surrounding water molecule than by ligand exchange. In INT-OH, formulated as \([(H_2O)_5Fe^{III}(OH)_2(*OH)]^{+}\), a second electron transfer, favored by the electron-donating hydroxyl groups, leads to the formation of an Fe(IV) species, e.g. \([(H_2O)_3Fe^{IV}(OH)_3]^+\).
2. INT and INT-OH could be both Fe(IV) species. A recent theoretical study using density functional theory (DFT) (52) found that 

\[
[(H_2O)_4Fe^{IV}(OH)_2]^{2+}
\]

is formed by Fe-facilitated OH-OH bond breaking, loss of an H2O ligand and hydrogen abstractions from Fe-bound H2O ligands while formation of a free \( \cdot \)OH radical was not favored. In a second DFT study including surrounding water molecules (54), it was again concluded that an Fe(IV) species is favored over the formation of a free \( \cdot \)OH radical, but it was suggested that the two forms 

\[
[(H_2O)_4Fe^{IV}(OH)_2]^{2+}\text{ and }[(H_2O)_3Fe^{IV}(OH)_3]^+
\]

(possibly equivalent to INT and INT-OH in our model) are in a protonation equilibrium with the solution. Again, 

\[
[(H_2O)_4Fe^{IV}(OH)_2]^{2+}
\]

could form a free or bound \( \cdot \)OH-radical, while 

\[
[(H_2O)_3Fe^{IV}(OH)_3]^+
\]

could itself be the final Fe(IV) product with less oxidizing power (expected to be the consequence of an additional OH\(^-\) group) or it could form a ferryl ( \( [O = Fe^{IV}(H_2O)]^{2+}\text{ ) species (23,52,54). It was suggested that ferryl exists in the hydrolytic forms }[(H_2O)_4Fe^{IV}(OH)_2]^{2+}\text{ and }[(H_2O)_3Fe^{IV}(OH)_3]^+\text{ above }pH\text{ 3 (30) and we would expect }[(H_2O)_3Fe^{IV}(OH)_3]^+\text{ and possibly }[(H_2O)_3Fe^{IV}(OH)_4]\text{ to dominate at neutral }pH\text{. The following rate constants for ferryl with other compounds were measured at }pH\text{ 1-3 (30): }k_{HCOOH} = 160\text{ M}^{-1}\text{s}^{-1}, k_{HCOO}^- = 3 \cdot 10^5\text{ M}^{-1}\text{s}^{-1}, k_{ethanol} = 400\text{ M}^{-1}\text{s}^{-1}\text{. Since these rate constants are small in comparison with the expected rate constants for the reactions of Fe(IV) with As(III) and Fe(II) (and are expected to still be lower at higher }pH\text{ we have not included the reaction of ferryl with 2-propanol or with HCOO}^-\text{ in our model.}

The suggested partitioning of the reaction pathways does not change the accepted overall kinetics of the reaction of Fe(II) with H\( _2\)O\( _2\). Both products, \( \cdot \)OH and Fe(IV), react with Fe(II) in fast and non-rate determining reactions to Fe(III). However, the partitioning of the Fenton reaction into \( \cdot \)OH- or \( \cdot \)OH-like radicals at low pH and a less reactive Fe(IV) species at higher pH explains our quenching experiments and is also consistent with many other studies and suggestions. Gallard et al. studied the degradation of atrazine by the Fenton reaction between pH 1 and 8 and also suggested an intermediate which forms \( \cdot \)OH at low pH, and a different intermediate, which does not react with atrazine, at higher pH (37). While the intermediate suggested by Gallard et al. was not able to oxidize atrazine, it might well be able to oxidize As(III).
2.3.7 Role of carbonate and carbonate radicals

In groundwater with high bicarbonate concentrations, additional pathways are possible. King et al. (55) have found that Fe(II)-carbonate complexes contribute significantly to the oxidation of Fe(II) by H₂O₂ in the presence of 2 mM NaHCO₃. The importance of Fe(II) species decreases in the order: Fe²⁺CO₃ > Fe²⁺OH⁻ > Fe²⁺(CO₃)²⁻ at pH 5.5–7.3 and Fe²⁺CO₃ > Fe²⁺(CO₃)²⁻ > Fe²⁺OH⁻ at pH > 7.3.

In our model, we have included only the Fe²⁺CO₃, as each additional species in the model also requires the addition of the corresponding reactions with Fe(IV) and with O₂⁻. The fitted log(k) for the reaction of H₂O₂ with Fe²⁺CO₃ was between the values reported for Fe²⁺CO₃ and for Fe²⁺(CO₃)²⁻ (Tab. 2.3).

For the reaction of Fe²⁺CO₃ with H₂O₂, we propose the formation of an intermediate INT-CO₃, which can form either carbonate radicals, Fe(IV), or both. (As the pKₐ of the bicarbonate/carbonate radical is reported as < 0 (56), we have considered only CO₃⁻. The partitioning into a Fe(IV) and CO₃⁻ pathways was left open by leaving one of the fast and non-rate determining rate constants (14, 15) adjustable and the fitting suggests that 4.5 times more Fe(IV) than CO₃⁻ (14 and 15) is formed. The simplified model for carbonate reproduces the trends observed in Fig. 2.4, but is not able to fully account for the experimental results. The role of Fe(II)-carbonate species and of carbon-
ate radicals will need further attention, however, we do not currently have sufficient data to add more reactions into the proposed model.

2.3.8 Uncertainties of the model

Fig. 2.8 shows the variation of the adjustable rate constants and the resulting Sum of Squared Differences (SSD) for model 2b. For the fitting, all data were normalized such that the highest concentration was 1.0 in each kinetic run, to give all experiments the same weight. The minimum total SSD of 1.26 (205 data points in 27 experiments) translates to an average standard deviation of 8.3%, which agrees with the estimated 10% error between the different experiments. The steep parabolic shapes (except for k4) indicate that the fits are well constrained and that the resulting rate constants are reliable to within 0.5 log units in the constraint of this model and data set. The value for k4 cannot be determined better in these experiments, as the reaction of Fe(IV) with Fe2+ does not contribute significantly under the employed experimental conditions.

The effect of changes in the reaction scheme on the optimized rate constants and the SSD is shown in Tab. 2.3. In model 1, Fe(III) precipitation was described simply as a dimerization (P1), in model 2a-2c as a polymerization (P1 and P2). For P1 and P2, the same adjustable rate constants were used to avoid the introduction of more parameters. Model 2a lead to a lower SSD and to better fits of the data in Fig. 2.1A, as well as to more plausible rate constants for Fe(III) polymerization than model 1. The rate constant for dimerization of Fe(OH)3 has been estimated at > 107 M^{-1}s^{-1} (57). The description of Fe(III) removal by precipitation is important, as it affects the reduction of dissolved Fe(III) species by O2~ (R1-R3) and with it the fits in Fig. 2.3 and Fig. 2.4. Following the suggestion by Sedlak and Hoigne (44), we have used the same rate constants for the reaction of Fe^{III}(OH)^{2+} and Fe^{III}(OH)^{2+} with O2~. Assuming that only Fe^{III}(OH)^{2+} reacts with O2~ still leads to good fits in Fig. 2.1 and Fig. 2.2, but to unsatisfactory fits of the data in Fig. 2.3 and Fig. 2.4. The role of Fe(III) speciation and precipitation in Fenton systems at neutral pH is still difficult to describe and will require further attention.

The reaction scheme in models 2a-2c is identical, but the rate constants for Fe(II) oxidation are different. In model 2b, all rate constants for the Fe(II) oxidation were left adjustable. This increased flexibility slightly improved the fits, but the output of model 2a (not shown) is almost indistinguishable from the output of model 2b (shown in the Figures). Model 2c, with the rate constants for Fe(II) oxidation fixed to the values according to Millero et al., results in a somewhat faster oxidation of As(III) than observed in Fig. 2.2B-D, but the fits for all other figures were the same as those of model 2b. Various studies have found slightly different rate constants for the oxidation of
2. Fe(II) catalyzed Oxidation of As(III) by O₂ and by H₂O₂

Fe²⁺ and Fe²⁺OH⁺ with H₂O₂ (see last column in Tab. 2.3). Given the experimental uncertainties (e.g. 0.1-0.2 pH unit increase during the reactions and ~10% relative errors in the As(III) determinations) and the simplification in the model (e.g. only one carbonate species), the log(k)'s for the oxidation of Fe(II) species are in good agreement with the values reported by others. The most important part of the model, the pH-dependent partitioning of the Fenton reaction into *OH and another oxidizing species (suggested to be Fe(IV)) was rather invariant to differences in the other rate constants or to the exact description of Fe(III) precipitation.

Finally, it should be noted that the proposed model does not mean that no *OH radicals are formed at neutral pH. Rather, the model states that the yield of *OH formation drops sharply between pH 5 and 6 and tenfold with each pH unit increase above pH 6. Compounds that only react with *OH can still be oxidized in the Fenton reaction at pH 7, although with low yields, and the addition of 2-propanol or other *OH scavengers inhibits their oxidation.
2.3 Results and discussion

2.3.9 Environmental and technical significance

The finding that As(III) is partly oxidized in parallel to the oxidation of Fe(II) is significant in all situations where oxygen is introduced into circumneutral waters containing As(III) and Fe(II). The co-oxidation of As(III) with Fe(II) by O₂ might be one of the most important abiotic pathways for As(III) oxidation and might help to explain why both As(III) and As(V) are typically found in ground water samples after they have been pumped to the surface.

The oxidation of As(III) with H₂O₂ and Fe(II) is important in natural and technical systems at pH values up to 8, below which As(III) is not oxidized at appreciable rates by H₂O₂ alone. H₂O₂ can occur naturally at micromolar concentrations in rainwater and in soil waters and it is used at millimolar concentrations in water treatment. The observation that the As(III) oxidation at circumneutral pH is not quenched by typical °OH-scavengers such as 2-propanol or formate (in contrast to the almost complete quenching at low pH) is important in natural and technical systems, as it can be expected that naturally present dissolved organic matter would also not significantly affect As(III) the oxidation by scavenging °OH scavengers. Since the rate and extent of the As(III) oxidation strongly depends on pH and As(III), Fe(II), O₂, H₂O₂, HCO₃⁻ in concentrations ranges that are common in natural and technical systems, a good quantitative understanding of these reactions is important. The proposed kinetic model provides a base for the understanding of the important factors in these systems and for the optimization of arsenic removal methods.
40 2. Fe(II) catalyzed Oxidation of As(III) by O₂ and by H₂O₂

Literature


2.3 Results and discussion


2. Fe(II) catalyzed Oxidation of As(III) by \( \text{O}_2 \) and by \( \text{H}_2\text{O}_2 \)


2.3 Results and discussion


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Chapter 3

Oxidation and removal of arsenic (III) from aerated groundwater by filtration through sand and zero-valent iron

OLIVIER X. LEUPIN AND STEPHAN J. HUG
submitted to: Water Research

Abstract: Removing arsenic from contaminated groundwater in Bangladesh is challenging due to high concentrations of As(III), phosphate and silicate. Application of zero-valent iron as a promising removal method was investigated in detail with synthetic groundwater containing 500 μg/L As(III), 2-3 mg/L P, 20 mg/L Si, 8.2 mM HCO₃⁻, 2.5 mM Ca²⁺, 1.6 mM Mg²⁺ and pH 7.0. In a series of experiments, one liter was repeatedly passed through a mixture of 1.5 g iron filings and 3-4 g quartz sand in a vertical glass column (11.5 mm diameter), allowing the water to re-aerate between each filtration. At a flow rate of 1 L/h, up to 8 mg/L dissolved Fe(II) was released. During the subsequent oxidation of Fe(II) by dissolved oxygen, As(III) was partially oxidized and As(V) sorbed on the forming hydrous ferric oxides (HFO). HFO was retained in the next filtration step and was removed by shaking of the sand-iron mixture with water. Rapid phosphate removal provided optimal conditions for the sorption of As(V). Four filtrations lead to almost complete As(III) oxidation and removal of As(tot) to below 50 μg/L. In a prototype treatment with a succession of four filters, each containing 1.5 g iron and 60 g sand, 36 L could be treated to below 50 μg/L in one continuous filtration, without an added oxidant.
3.1 Introduction

Arsenic contaminated groundwater in Bangladesh (1) is difficult to treat due to high concentrations of As(III), phosphate, silicate and DOC. Phosphate, at concentrations of 1.5-3 mg/L P in many regions (1), strongly competes with the sorption of arsenic in filter materials and precipitates and needs to be removed before or together with the arsenic (2). The capacity of pre-made filters using adsorbents such as iron- or aluminum oxides is bound to be exhausted quickly and the necessary maintenance and periodic replacement are not easily achieved in millions of rural households. More effective in terms of minimizing the necessary amount of materials is the use of oxidants (e.g. KMnO₄ (3-5) or bleach (6, 7)) to oxidize As(III) to the better adsorbing As(V), and of iron- or aluminum salts (8, 9) to precipitate the As(V) (and necessarily also the phosphate) by sorption on Al- or hydrous ferric oxides. No chemicals and a minimal amount of man-made material is needed if metallic iron can be used for the formation of arsenic-sorbing Fe(III)(hydr)oxides (HFO). The use of zero-valent iron has been studied under numerous conditions, e.g. arsenic removal from mine tailings (10), groundwater (11), and drinking water (12,13). Karschunke and Jekel (13) showed that with 45.8 g of iron wool it was possible to treat up to 1.19 m³ of Berlin tap water spiked with 500 µg/L As(V). For the treatment of arsenic contaminated water in Bangladesh, the application of locally built filters made with iron turnings and sand (3-Kolshi filter) (14) has shown to be effective under certain conditions. In waters with low phosphate concentrations, 3-Kolshi units with 3 kg of iron turnings have treated up to 6 m³ of contaminated water to less than 10 ppb arsenic in the effluent over a period of 9 months (15). However, the performance of 3-Kolshi filters in Bangladesh has been variable. Filters often clog and pathogens have been detected in some filters over time (16). Moreover, the influence of the water composition on arsenic removal in 3-Kolshi filters has not been investigated systematically. In terms of efficiency, the 3-Kolshi filters are far from optimal. The use of 3 kg of iron for the treatment of 6 m³ of water corresponds to 0.5 g of iron per liter of water. A recent study has found that slow addition of 20-25 mg/L Fe(II) to water containing 500 µg/L As(III), 3 mg/L P and 30 mg/L Si was sufficient to oxidize and remove over 90 % of the arsenic without an added oxidant (17).

The mechanism of arsenic removal in systems with Fe(0) remains unclear due to the number and complexity of possible reactions. Many studies have been conducted under conditions different than those encountered in Bangladesh and results are not easily comparable due to the variability of water parameters (pH, water composition, oxic versus anoxic conditions). Under oxic conditions, iron corrosion leads to the formation of various mixed Fe(II, III)(oxyhydr)oxide phases, which adsorb As(V) and As(III) (18). Un-
nder anoxic conditions, As(III) might be reduced to insoluble As(0) on the iron surface. In the presence of sulfate, formation of arsenic sulfides has been suggested but the pathways for sulfate reduction have not been specified (19, 20).

Most studies agree that As(V) is not reduced by iron metal surfaces or by adsorbed or dissolved Fe(II) on a time scale of several days. No As(V) reduction was observed in an electrochemical study with iron wires, even under anoxic conditions (2, 21) and in batch tests with iron filings and iron powder (22) (although some reduction was observed after 60 days). Melitas showed that As(V) reduction only occurs at potentials below those that are obtainable in freely corroding iron media (21). A recent study also did not find reduction of As(V), but found oxidation of As(III) to As(V) during the corrosion of iron powder and filings under aerobic conditions (18). The As(III) oxidation was attributed to certain maghemite and hematite phases and to elevated pH conditions at the surface of corroding iron. However, only one previous study has found evidence for As(III) oxidation by an Fe(III)(oxyhydr)oxide formed from oxidation of Fe(II) (23), while most studies did not find oxidation of As(III) by Fe(III) e.g. (17, 24, 25). It appears that the oxidation of As(III) is linked to the presence of dissolved, adsorbed, or structural Fe(II) and the presence of dissolved oxygen. Three recent studies found that arsenic is oxidized in parallel to the oxidation of initially dissolved Fe(II) by dissolved oxygen, most likely by reactive intermediates such as Fe(IV), reactive oxygen species and/or carbonate radicals (17, 25, 26). Most studies with metallic iron have focused on the overall removal of arsenic and on the detailed characterization of the solids formed on the surface of iron. To our knowledge, no study has yet addressed the concentration of dissolved Fe(II) released during the corrosion and its role in the oxidation of arsenic in the presence of dissolved oxygen. Since metallic iron is usually mixed with sand, the transport and oxidation of dissolved Fe(II) plays an important role in the formation of Fe(III) coatings and oxidation of As(III) (17, 25, 26). The present study investigates, to our knowledge for the first time, the concentrations and the redox states of dissolved and adsorbed arsenic and iron in a filter containing a mixture of iron filings and sand with synthetic groundwater representative of groundwater in Bangladesh. Although our experiments are designed for later testing in field trials with locally available materials, the aim of this study is to shed light on the relevant chemical processes.
3.2 Experimental section

3.2.1 Materials

All chemicals were reagent grade from Merck (VWR), Aldrich or Fluka and were used as received.

3.2.2 Iron filings

Iron filings (Fig. 3.1) were always freshly produced with a "bastard" hand file (Baiter AG, Switzerland) and St-37 steel (C: 0.17%, Si: 0.3 %, Mn: 1.4 %, P: 0.045 %, S: 0.045 %, N: 0.009 % (27). The steel used was provided from the Swiss Federal Laboratories for Materials Testing and Research (EMPA). St-37 steel is used worldwide and is easily available in Bangladesh.

3.2.3 Quartz sand

Merck lab-ware sand of analytical purity (washed and calcined) with a grain size of 0.2-0.8 mm, was used as received.

3.2.4 Synthetic groundwater

All experiments were performed with synthetic, arsenic spiked groundwater with the main characteristics of Bangladeshi groundwater (see Tab.3.1). CaCO₃ (250 mg/L) and MgCO₃ (138.75 mg/L) were dissolved in high purity 18 MΩ water (Milli-Q®, A10, Millipore) by bubbling excess CO₂ gas into the water under intense stirring, resulting in a clear solution at pH 6.0. Silicate was added from a 2.0 g Si/L, daily prepared stock solution (202.4 mg Na₂SiO₃·9H₂O in 10 ml). To prevent any polymerization of the silicate, 10 mL of the alkaline stock solution were rapidly diluted into slightly acidic groundwater (pH 6.0 - 6.3 with excess dissolved CO₂), before the pH was raised to pH 7.0 ± 0.1 by bubbling compressed air into the solution. Phosphate was added from a 1M KH₂PO₄ stock solution. In a final step As(III) was spiked from a neutral stock solution. The final pH was 7.0 ± 0.1. (combined Metrohm glass electrode).

3.2.5 As(III)

Analysis was performed with an Atomic Fluorescence Spectrometer (AFS) (PS Analytical Ltd., Kent, UK). For the selective detection of As(III), a 0.5 M disodium citrate buffer solution (pH 5.0) was used for the hydride generation
3.2 Experimental section

Figure 3.1: Freshly prepared iron filings. The particles consist mainly of single, strongly folded sheets.

instead of HCl. Only As(III) is converted to AsH₃ at pH 5 (28) and detected in the AFS instrument.

3.2.6 As(tot) analysis

To measure As(tot) (As(V) and As(III)), 100 µl sample, 100 µl 10 M HCl and 20 µl of reducing agent (0.6 M ascorbic acid and 3 M KI) were mixed and left to react for 60 min, prior to 1:50 dilution with the citrate buffer and subsequent analysis with AFS.

3.2.7 SEM/EDS analysis

Scanning Electron Microscopy-investigations (SEM) and Electron Microscopy Dispersive Spectra (EDS) were performed with a Philips XL-30 (25kV, LaB₆ filament) on air-dried filter cakes produced with 0.2 µm pore-diameter hplc-nylon filters.
Table 3.1: Composition of the used synthetic groundwater. Synthetic groundwater composition and corresponding mean values and standard deviations of groundwater parameters in Bangladesh, as obtained from the BGS database (Values of pH and HCO$_3^-$ from the special Study Areas; all other values were taken from National Survey Data, using only wells with As $>$ 50 $\mu$g/L for data analysis). For each solute, the percentage of wells in the BGS database with a concentration [x] greater than that of the synthetic groundwater [xs] is also given.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Synthetic groundwater</th>
<th>Bangladesh groundwater</th>
<th>% of the wells with [x] $&gt;$ [xs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH initial</td>
<td>7.0 ± 0.05</td>
<td>7.0</td>
<td>0.2</td>
</tr>
<tr>
<td>HCO$_3^-$ (mM)</td>
<td>8</td>
<td>7.8 ± 2.7</td>
<td>45</td>
</tr>
<tr>
<td>Ca (mM)</td>
<td>2.5</td>
<td>1.9 ± 1.4</td>
<td>32</td>
</tr>
<tr>
<td>Mg (mM)</td>
<td>1.6</td>
<td>1.3 ± 0.8</td>
<td>24</td>
</tr>
<tr>
<td>Si (mg/L)</td>
<td>20</td>
<td>19.2 ± 4.7</td>
<td>2</td>
</tr>
<tr>
<td>P (mg/L)</td>
<td>2.3</td>
<td>1.47 ± 1.48</td>
<td>8</td>
</tr>
<tr>
<td>As (µg/L)</td>
<td>500</td>
<td>199 ± 166</td>
<td>7</td>
</tr>
</tbody>
</table>

3.2.8 XRD

X-ray Powder Diffractograms were measured with a Phillips Scintag XDS 2000 (Cu-Cathode 45 kV and 40 mA) from 2° - 60° 2θ. Samples were air dried, homogenized and mixed with an internal standard (silicon).

3.2.9 ICP-OES

An Inductively Coupled Plasma Optical Emission Spectrometer (Spectro Ciros CCD) was used to analyze P, Mg, Ca and Si.

3.2.10 Fe(II) measurement

Fe(II) was sampled by directly collecting 5 mL column (effluent) into vials containing 2 mL phenanthroline and 1 mL acetate buffer. The Fe(II) was quantified by UV-vis Spectrophotometry in optical quartz cells (1 or 4 cm) at $\lambda$ = 512 nm.

3.2.11 Oxygen-measurements

Oxygen in the column effluents was measured with a WTW (Wissenschaftlich-Technische Werke) GmbH Co. KG, Weilheim, Germany) Clark Sensor.
(CellOx 325) mounted in a 1ml volume flow-through cell. Reference measurements were performed by switching the flow between the sample column and a reference column filled with only sand fed by air saturated water. The signals were scaled to the tabulated oxygen saturation in the reference column of 262µM at 1038 hPa and 24°C.

3.2.12 Column experiments

The experimental setup is shown in Fig. 3.2. All labware was acid washed prior to the experiments. To prevent clogging due to rusting iron filings, it was important that the iron filings and the sand grains (1.5 g Fe(0) and 4 g quartz sand) be homogeneously mixed. The treatment process consisted of passing the same water through the column four times, in four identical cycles: one liter of synthetic groundwater flowed from the upper tank through the column into the lower tank. When all the water had passed through the filter, it was transferred back into the upper tank. To remove and sample the precipitates, the filter was rinsed after each filtration by filling the column with 30 ml of synthetic groundwater and shaking for 2 minutes.

3.2.13 Flow rate

To keep the flow rate constant, regardless of the decreasing water level in the column, a peristaltic pump (Fig. 3.2) at the outlet of the column was used. To maximize the leaching of Fe(II), it was necessary to achieve an optimal balance between sufficient contact time for the oxidation of Fe(0) to dissolved Fe(II) and the transport of the Fe(II) out of the column. Rapid removal of dissolved Fe(II) minimizes the formation of scales on the iron filings due to the formation of Fe(II)-carbonate and oxidation of Fe(II) on the iron surface. A flow rate of 0.3 mL/s, providing a contact time of 5.3 s has been found to give good results. The contact time was calculated with the measured pore volume of 1.6 cm³ of the sand-iron filter (total volume: 2.9 cm³).

3.2.14 Collection of samples

Three different sampling points: effluent (E), recipient (R) and backwash (B) are shown in Fig. 3.2. Tab. 3.2 gives an overview of the treatments and storage of the different samples. Samples for the determination of dissolved concentrations, [X]d, were passed through 0.2 µm Nylon filters. Samples for the determination of total concentrations (dissolved and adsorbed), [X]tot, from the backwash and recipient were mixed with an equal volume of 1 M oxalic acid and left to react for 2 h to achieve dissolution of solid phases. The unfiltered samples from the effluent and the filtered samples (0.2 µm nylon
Figure 3.2: Experimental setup with the three sampling points: effluent, recipient, and backwash. The filter media in the column consisted of iron filings and quartz-sand. The flow rate was controlled by the peristaltic pump.
HPLC-filters) from the recipient were acidified with HCl (100 μL 2 M HCl to 5 mL sample) to prevent further Fe(II) oxidation and to preserve the oxidation state of the arsenic species. The sampling of the recipient took place at the end of each filtration to ensure that the formation of HFO was completed. Immediately after the pretreatment, samples were frozen at -20°C until analysis. Prior to measuring Fe, Si, Ca, Mg, P by ICP-OES, 1 ml of the thawed samples were diluted with 9 ml high purity water and acidified with 100 μl 14 M HNO₃.

### 3.2.15 Multiple filtration unit

A prototype filter for future field trials was built with five vertically arranged 1.5 L PET-bottles (Fig. 3.11). The bottom of each bottle was cut out and the bottles were used head down, with small holes in the closed screw caps. Pieces of cloth over the holes served as filters. A mixture of 1.5 g iron filings and 60 g sand was poured into the caps and the narrowing necks of the first four bottles, the fifth bottle contained only sand. Water from a large reservoir flowed slowly (0.8 - 1.5 L/h) from the top to the lowest bottle. The sand-iron mixtures were completely immersed, with water levels reaching 5 - 12 cm above the sand in each bottle.

### 3.3 Results and discussion

#### 3.3.1 Removal of arsenic

Fig. 3.3 shows the arsenic concentrations in the recipient after passing 1 L of water one to four times through the column. The x-axis gives total volume of water passed through the column: 1000 ml after the first and 4000 ml after the fourth filtration. Clearly, the overall arsenic removal was very efficient. Even in water with 2 mg/L P and 20 mg/L Si, the initially 500 μg/L As(III) could be lowered to less than 15 μg/L As(tot) in four filtrations. The pH increased from 7.1 to 8.1 due to loss of dissolved CO₂ to the air and to consumption of protons in the corrosion reactions.

The analysis of total and dissolved As(III) and As(tot) in the recipient provided more details on the removal mechanisms. During the first filtration, the in-flowing water did not yet contain iron and suspended HFO and the recipient water still contained 410 μg As(tot) tot. Thus, less than 20% of the initial arsenic was removed during the first filtration. However, the speciation of the arsenic in the recipient, where HFO was now formed from the oxidation of Fe(II) leaving the column, had changed. The dissolved As(tot)_d was 275 μg/L, meaning that 145 μg/L As was adsorbed on the suspended
3. Oxidation and removal of As(III) with Fe(0) and sand

Table 3.2: Sample treatment and analysis. Acidification with HCl prevented any further oxidation of Fe(II) and redox reaction of As(III) and As(V). Oxalic acid was used to non-reductively dissolve HFO. Dissolved Fe(II) in the effluent was measured by collecting 5 ml sample directly into a vial with 2 ml phenantroline and 1 ml acetate buffer.

<table>
<thead>
<tr>
<th>Effluent, dissolved concentrations</th>
<th>Recipient, dissolved concentrations</th>
<th>Recipient, total concentrations</th>
<th>Backwash, total concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 ml sample 100 µl 2M HCl</td>
<td>5 ml sample 0.2 m Nylon filter</td>
<td>5 ml sample 5 ml 100 µl 2 M HCl</td>
<td>5 ml sample 5 ml 100 µl 2 M HCl</td>
</tr>
<tr>
<td>frozen</td>
<td>frozen</td>
<td>frozen</td>
<td>frozen</td>
</tr>
</tbody>
</table>

As(III) and As(tot) analysis

As(III): 1: 50 in citrate buffer (dilution based on initial sample volume)

As(tot): after reduction 1: 50 in citrate buffer (dilution based on initial sample volume)

As(III)\textsubscript{d}, As(III)\textsubscript{t}, As(III)\textsubscript{tot}, As(III)\textsubscript{tot}

As(tot)\textsubscript{d}, As(tot)\textsubscript{t}, As(tot)\textsubscript{tot}, As(tot)\textsubscript{tot}

ICP-OES Analysis of Fe(tot), P, Ca, Mg, Si

Pre-treated samples were diluted 10 fold and acidified with 100 µl 14 M HNO\textsubscript{3}

Fe(tot)\textsubscript{d}, Fe(tot)\textsubscript{t}, Fe(tot)\textsubscript{tot}, P\textsubscript{t}, P\textsubscript{tot}, Ca\textsubscript{t}, Ca\textsubscript{tot}, Mg\textsubscript{t}, Mg\textsubscript{tot}

Fe(tot)\textsubscript{tot}, P\textsubscript{tot}, Si\textsubscript{t}, Si\textsubscript{tot}, Ca\textsubscript{tot}, Mg\textsubscript{tot}
3.3 Results and discussion

HFO. Dissolved As(III)\textsubscript{d} and As\textsubscript{tot}\textsubscript{d} concentrations were almost identical, indicating that only As(V) was adsorbed on the HFO. Importantly, about 25\% of the arsenic in the recipient was oxidized to As(V) (difference between As\textsubscript{tot} and As\textsubscript{tot}\textsubscript{tot}). During the second filtration, a much larger fraction (more than 200 \(\mu\text{g/L}\)) of the arsenic was removed, mainly as a consequence of the removal of the HFO-precipitates with the adsorbed arsenic in the column. More As(III) was oxidized in the recipient and only As(III) remained in solution. As(III) oxidation and removal continued during the third and fourth filtration. The As\textsubscript{tot} in the filtered recipient was reduced to below the Bangladesh standard of 50 \(\mu\text{g/L}\) after the third filtration, and close to the WHO guideline value of 10 \(\mu\text{g/L}\) after the fourth filtration.

The concentrations of As(III) and As(V) in the effluent at the beginning and at the end of each filtration are shown in Fig. 3.4, together with the corresponding dissolved Fe(II) and oxygen concentrations in Fig. 3.5. The effluent did not contain solids, as the HFO precipitates were efficiently retained in the sand (Fig. 3.6). The dissolved iron in the effluent was predominantly Fe(II) and did not oxidize and form HFO in the less than 10 seconds from exiting the column to sample collection directly into tubes with HCl or acetate buffer. During the first filtration, the effluent contains 8 - 9 mg/L Fe (> 90\% as Fe(II)). Consistent with the recipient concentrations in Fig. 3.2, only about 20\% of the arsenic is retained in the column. During the second filtration, arsenic concentrations in the effluent decreased steeply, as a large fraction of the arsenic was adsorbed on the HFO which had formed in the recipient. The HFO precipitates were retained in the top layers of the sand in the column. In the runs with 3 mg/L P, the larger drop in arsenic concentration occurred only after the second filtration, when most of the phosphate had been removed.

3.3.2 Oxidation of As(III) and Fe(II)

The determination of the redox states of arsenic and iron in the effluent and in the recipient provide information about the oxidation mechanism. In the experiments with 2 mg/L P, arsenic left the column predominantly as As(III) (> 90\%) and all iron (9-4 mg/L) left the column as Fe(II). During the collection time of 1h during each filtration, more than 90\% of the Fe(II) was oxidized to Fe(III) in the recipient and formed suspended HFO. As shown in Fig. 3.3, only around 75\% of the total arsenic (dissolved and adsorbed) in the recipient was As(III) after the first filtration and this fraction dropped to about 50\% in the next filtrations. This means that 25-50\% of the As(III) leaving the column was oxidized in the recipient after each filtration, parallel to the oxidation of Fe(II). This finding is consistent with recent studies and will be discussed in more detail in the next section.

In addition to oxidation in the recipient, Fe(II) was also oxidized in the
3. Oxidation and removal of As(III) with Fe(0) and sand

Figure 3.3: As and P in the recipient after one (1000 ml) to four (4000 ml) filtrations of 1 L synthetic groundwater through sand and iron filings. As(III)\textsubscript{d} and As(tot)\textsubscript{d} are dissolved As(III) and As(tot) (As(III)+As(V)). As(III)\textsubscript{tot} and As(tot)\textsubscript{tot} are the corresponding total (dissolved and adsorbed) concentrations. Essentially all dissolved arsenic was As(III). Almost all As(V) was bound to suspended HFO and was retained in the sand column in each subsequent filtration. After phosphate was removed during the first filtration, arsenic removal improved significantly.

The decrease of dissolved oxygen was around 220 \( \mu \text{M} \) during each filtration and was higher than the corresponding concentration of Fe(II) in the effluent (Fig. 3.5). During the first filtration, the dissolved Fe(II) concentration of 160 \( \mu \text{M} \) (9 mg/L) accounts for 80 \( \mu \text{M} \) \( \text{O}_2 \) consumption (2 Fe(II) per \( \text{O}_2 \)). The remaining 140 \( \mu \text{M} \) \( \text{O}_2 \) must have lead to the formation of 187 \( \mu \text{Mol} \) Fe(III) (\( \frac{3}{2} \) Fe(III) per \( \text{O}_2 \)) in the column. During the last filtration, 70 \( \mu \text{M} \) dissolved Fe(II) and, correspondingly, 250 \( \mu \text{Mol} \) Fe(III) in the column were formed. The increasing formation of Fe(III) in the column is explained by the rising pH and the growing amounts of HFO in the column, both factors which strongly increase the Fe(II) oxidation rate.

There is strong evidence that Fe(II) oxidation in the column also lead to oxidation of As(III). The 20\% of the arsenic retained in the first filtration was most likely oxidized to As(V), as As(III) would not have been adsorbed while the phosphate concentration was still high. Furthermore, in the experiments with 3 mg/L P, around 15\% of the arsenic leaves the column as As(V) during the first two filtrations, due to strong competition between phosphate...
3.3 Results and discussion

Figure 3.4: Dissolved As(III) and As(tot) in the column effluent at the start and end of each filtration. Most of the arsenic leaving the column was As(III). With 2 mg/L P (n=3), arsenic removal is considerably faster than with 3 mg/L P. The least amount of arsenic was removed in the first step, when the in-flowing water does not yet contain HFO precipitates. With 3 mg/L P, the largest arsenic decrease occurred only after the second step when most phosphate was removed.

and arsenate.

3.3.3 Role and removal of phosphate

Fe(II) concentrations in the effluent were generally lower with water containing initially 3 mg/L P than with water containing 2 mg/L P (Fig. 3.7). This is not surprising, as phosphate is known to act as a corrosion inhibitor. With 2 mg/L P (on average 3 experiments), a filter containing 1.5 g Fe(0) released a total of 22.7 mg Fe(II) in fourfiltrations. With 3 mg/L P the total release of Fe(II) was 13.7 mg (Fig. 3.7).

3.3.4 Role and removal of phosphate

As can be seen in Fig. 3.3, in water with initially 2 mg/L P, all dissolved phosphate was removed in the first filtration and was bound in the column and on the precipitates formed in the recipient. The influence of phosphate on Fe(II) release and arsenic removal in the column is significant during all filtrations,
Figure 3.5: Simultaneous measurements of Fe(II) and dissolved O₂ in the effluent. More O₂ was consumed than needed to account for dissolved Fe(II), indicating that a part of the Fe(II) was oxidized within the filter. The increasing pH promotes Fe(II) oxidation in the column. The superscripts a, b, and c designate three different experiments. Reapplication of fresh groundwater with pH 6.7 in the fifth filtration (a) increased the Fe(II) release above the initial value (data point at 4020 ml). Fresh water at pH 7.0 results in a Fe(II) concentration similar to the initial value (b). If the water is not changed (c) Fe(II) concentration continued to decrease.

as illustrated in Fig. 3.4. Arsenic concentrations in the effluent remain higher with initially 3 mg/L P and arsenic leaves the column as As(V) during the first two filtrations. Phosphate is most likely involved in the formation of scales on the surface of iron filings, lowering Fe(II) release and As(V) adsorption in the column.

3.3.5 Removal of precipitates from the column in the backwash

Back-washing after each filtration (by shaking with 30 ml of synthetic groundwater for 2 min and decanting the brown and turbid suspension from the coarser and rapidly settling particles after 30 sec) successfully avoided clogging of the column. Synthetic groundwater was used in view of future applications in the field, where unpolluted water might not be available. The amounts of phosphate and arsenic removed by backwashing are shown in Fig. 3.8 (corrected for the amounts already present in the 30 ml back-wash
3.3 Results and discussion

Figure 3.6: HFO coating on a quartz grain surface after four filtrations and backwash cycles.

... water). Only about 60% or 55% of the arsenic and 30% or 61% of the phosphate could be recovered by back-washing in the experiments with initially 2 mg/L P or 3 mg/L P, respectively. The remaining phosphate and arsenic in the column must have been sorbed on iron scalings and on coarser agglomerates formed from precipitates (Fig. 3.9). With initially 2 mg/L P, most arsenic in the backwash was found after the second filtration, while with 3 mg/L P, most arsenic was found in the third filtration, after most of the phosphate had been removed. This finding is consistent with the development of the arsenic concentrations in the effluent (Fig. 3.4).

3.3.6 Removal of silicate

The silicate concentrations were reduced by less than 25% in four filtrations (data not shown). We did not attempt to investigate silicate removal more precisely, as it is not a health-sensitive water parameter and the slight decrease of its concentration during the treatment does not significantly change...
the adsorption behavior of the more strongly adsorbing arsenic and phosphate. Previous studies have shown that the sorption equilibrium constants for co-precipitation with HFO decrease in the order phosphate > arsenate > arsenite > silicate (2, 17). Silicate concentrations of 15 or 20 mg/L Si lower the adsorption of As(III) to a similar extent.

3.3.7 Calcium

The concentrations of Ca in the unfiltered recipient were reduced by 10-20% with 1.5 g of iron filings with an initial concentration of 100 mg/L (data not shown). Calcium seemed to accumulate in the sand filter: precipitates containing calcium could be identified by SEM/EDX (data not shown). Precipitation of calcium (predominantly as CaCO$_3$ and MgCO$_3$) can be expected during the increase of the pH from 7 to 8 during the four filtrations, and might be initiated by locally higher pH values (up to pH 10) on the surface the corroding iron filings.
3.4 Mechanisms of arsenic removal with Fe(0) in aerated columns

To our knowledge, this is the first study that clearly shows to what extent and how As(III) is oxidized by repeated contact with Fe(0). The overall reactions can be formulated as follows:

1. \[
\text{Fe}(0) + 2 \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow \text{Fe(II)} + \text{H}_2\text{O} + 2 \text{OH}^- 
\]
2. \[
\text{Fe(II)} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe(III)} + \frac{1}{2} \text{H}_2\text{O} + \text{OH}^- 
\]
3. \[
\text{Fe(III)} + 3 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ 
\]
4. \[
\text{As(III)} + \text{reactive intermediates(*OH, Fe(IV))} \rightarrow \text{As(IV)} 
\]
5. \[
\text{As(IV)} + \text{O}_2 \rightarrow \text{As(V)} + \text{O}_2^- 
\]

Fe(II) formed during corrosion is released from the iron surface and partly exits the column as dissolved Fe(II). Some Fe(II) also re-adsorbs on the surface of iron filings and sand, or is never released from the iron surface at all. Both, initially dissolved Fe(II) and adsorbed Fe(II), are oxidized to Fe(III).
3. Oxidation and removal of As(III) with Fe(0) and sand

Figure 3.9: Iron filings after four filtrations. The metal surfaces are covered by amorphous scales and rust. The chemical composition of the scales recorded by EDS show ca. 75-80 wt% Fe, 5-20 wt% As, 1-15 wt% Si and 0-2 wt% P. Generally edges and corners are more affected from the alteration process than the surfaces.
3.4 Mechanisms of arsenic removal with Fe(0) in aerated columns

in aerated water (eq. 2).

Fe(II) oxidation by dissolved O₂ involves the formation of oxidizing intermediates, (O₂⁻, H₂O₂, and *OH or Fe(IV)) some of which are able to oxidize As(III) (eq. 4). The oxidation of As(III) to As(V) after the addition of Fe(II) to aerated water has been measured and explained in two previous studies (25, 26). Importantly, addition of Fe(II) in multiple doses with sufficient time for Fe(II) oxidation leads to higher fractions of oxidized As(III) than one single addition of the same total amount of Fe(II). The reason is that Fe(II) itself consumes oxidizing species and outcompetes As(III) at the usually higher Fe(II) concentrations. The oxidation of As(III) is optimal with prolonged low steady-state concentrations of Fe(II), which is continuously oxidized by dissolved oxygen. Slow and continuous release of Fe(II) in a column of corroding iron thus provides ideal conditions for the oxidation of As(III), as long as the water contains dissolved O₂ and there is sufficient time for the oxidation of Fe(II).

In order to substantiate our findings from the column experiment, we conducted batch experiments (Fig. 3.10) in which either Fe(II) or Fe(III) was continuously added to stirred synthetic groundwater with 500 μg/L As(III), 3 mg/L P and 30 mg/L Si at a rate of 15 mg/L Fe in 4 hours. It can clearly be seen that As(III) was efficiently oxidized during the addition and oxidation of Fe(II), leading to over 90% arsenic and phosphate removal. In contrast, addition of Fe(III) did not lead to As(III) oxidation and to only 20% arsenic removal. Phosphate was still sorbed to over 90% after addition of Fe(III), but As(III), which cannot compete with sorption of phosphate, remains to 80% in solution. Fig. 3.10 also shows that Fe(II) produces HFO with higher adsorption site density for phosphate, in agreement with previous studies (17).

The oxidation rates of dissolved Fe(II) with dissolved O₂ are strongly pH-dependent, with half-lives on the order of 50 min at pH 7.0 and 30 s at pH 8.0 (29). At iron concentrations above 5 mg/L, an autocatalytic acceleration is observed due to Fe(II) adsorption on the forming HFO (30). While we have good evidence of the As(III) oxidation in parallel to the oxidation of initially dissolved Fe(II), the role of adsorbed Fe(II) is more difficult to quantify. In a previous study (17), similar fractions of As(III) were oxidized after each of four additions of 5 mg/L Fe(II). HFO that was present after the first addition apparently did not lower the As(III) oxidation by added Fe(II). In the batch experiments in this study (Fig. 3.10), where HFO is produced continuously and increasing fractions of Fe(II) must be adsorbed, the As(III) oxidation progresses at similar rates. In the column experiments in this study, a part of the As(V) was formed directly in the column, as the experiments with 3 mg/L P show. Thus, from the presently available data, we conclude that the oxidation of both dissolved and adsorbed Fe(II) lead to the oxidation of As(III) with similar efficiency.
3. Oxidation and removal of As(III) with Fe(0) and sand

Figure 3.10: Arsenic and phosphate removal with continuous addition of 15 mg/L Fe(II) (full symbols) or Fe(III) (empty symbols) in the course of 4 h to aerated and stirred water with 500 µg/L As(III), 3 mg/L P and 30 mg/L Si. As(III) is completely oxidized with Fe(II), but not with Fe(III). Phosphate is sorbed more quickly than arsenic. Silicate is only removed to a small extent.

3.5 Practical implications

A question of direct practical relevance is how much iron is needed for the removal of As(III). Meng (6) reported that removal of 90% arsenic in phosphate and silicate rich water (1.9 mg/L P, 18 mg/L Si) required a Fe/As ratio of at least 40, after the As(III) has been oxidized to As(V) with hypochlorite. Similar to these findings, we found that 15-18 mg Fe(III) are needed to remove 90% of 500 µg/L As(V) (with 3 mg/L P and 20 mg/L Si). As(III) removal under the same conditions required over 80 mg/L Fe(III) (17). In contrast, addition of a total of 20 mg/L Fe(II) in eight additions every 30 min (17) or 15 mg/L Fe(II) added continuously (this study) was sufficient to remove 90% of As(III) without an added oxidant. In addition to silicate and phosphate, Bangladesh groundwater contains relatively high concentrations of DOC: 3.35 mg/L (STDEV = 2.8) in average (1). Some additional iron might thus be needed to remove the DOC. According to Aguiar (31), about 2 mg Fe(II)/mg DOC are required to co-precipitate DOC with HFO in the absence of As(V). Thus, for Bangladesh, additional 6-7 mg/L Fe(II) would be needed if all DOC components compete strongly with As(V) adsorption, which is
3.6 Conclusions

unlikely. The sorption competition of As(V) and organic carbon on different iron(hydr)oxides was investigated by several authors. Gräfe (32) showed that humic acids did not displace As(V) from ferrihydrite. Although their experiments were conducted at high concentrations (1 mM As(V) and 1mM C as DOC) which are not representative for Bangladesh, they suggest that DOC does not effectively compete with As(V) adsorption on HFO. In a suspension containing 2.5 g/L goethite and 1 mM As(V), 1mM C as DOC lowered adsorption of As(V) to 27% (33). Redman (34) confirmed a strong competition for sorption sites on hematite between NOM and As(V) at environmentally relevant and higher concentrations. From the available information we estimate that removal of about 30% of the DOC with 2-3 mg/L Fe would be sufficient to remove the fraction that competes with As(V) adsorption. Since we do not have representative DOC samples for laboratory experiments, only field experiments in Bangladesh (which are planned) will be able to clarify this issue.

Experiments with a multiple filtration unit showed that with 6 g iron over 35 L contaminated groundwater could be treated to below 50 μg/L (Fig. 3.9). Compared to similar systems i.e. 3-Kolshi filters, the iron consumption could be reduced by a factor 3.3 per Liter of treated water (14). In experiments conducted with steel wool and Berlin tap water spiked with As(V) (13), the necessary iron to arsenic ratio was 77.5, compared to 349 in our system. However, spiked Berlin water contained As(V) and no phosphate. If the phosphate in our experiments (2 mg/L) is included and added to the arsenic concentration, then the iron to arsenic and phosphate ratio drops to 68.6. Importantly, the As(III) in our experiments was oxidized without an added oxidant.

3.6 Conclusions

To understand the reactive pathways and to optimize arsenic removal with metallic iron, controlled experiments with synthetic groundwater have been conducted. It was found that repeated contact of aerated water with zero-valent iron lead to continued release of Fe(II) and to complete oxidation of As(III) in parallel to the oxidation of Fe(II) with dissolved oxygen and without an added oxidant.

• The repeated oxidation of Fe(II) to Fe(III) in the recipient converted As(III) to As(V), by oxidation with reactive intermediates, as described in our former work (25).

• The HFO formed from the oxidation of Fe(II) in solution was found to be an excellent adsorbent for As(V). HFO loaded with As(V) was
retained by the sand in each filtration step and could be removed by backwashing.

- The consumption of oxygen indicates that Fe(II) is also oxidized in the column and that Fe(III) precipitates are formed within the column. Fe(II) oxidation in the column also lead to partial As(III) oxidation.

- Phosphate was removed more quickly than arsenic, which first had to be oxidized to As(V) to show similar sorption capacities on HFO.

Overall, the slow and continuous release of Fe(II) during four filtrations with zero-valent iron and the quick removal of phosphate provided close to ideal conditions for arsenic removal without added oxidant. In a prototype multistep filter (Fig. 3.11), 6 g iron treated 36 L of contaminated water, which is 12% of the theoretical capacity (assuming 20 mg/L Fe(II) are sufficient to treat water of this type and all Fe(0) can be converted to Fe(II) before it forms Fe(OH)). The reaction that most likely limits the efficiency is the oxidation of Fe(II) on the metal surface, with formation of scales that lower Fe(II) release and access of As(III) to the oxidizing iron species and reactive intermediates. To improve the efficiency, the ratio and size of iron and sand particles and the flow conditions need to be optimized to transport Fe(II) away from the metal surface, so it is mixed with As(III) and is oxidized in solution and on the surrounding sand grains. Since metallic iron is widely available and contains three times more iron per weight than most common iron salts, and an additional oxidant is not needed for As(III) removal, optimized columns with sand and iron filings might the method of choice for arsenic removal in rural households.
Figure 3.11: Two identical experiments showing arsenic removal in a filter column with five 1.5 L PET bottles. With a total of 6 g iron and 300 g sand, 36 L of water containing 500 μg/L As(III), 2 mg/L P and 20 mg/L Si could be treated to below 50 μg/L arsenic. The inset in the graph shows the experimental set-up.
3. Oxidation and removal of As(III) with Fe(0) and sand

Literature


3. Oxidation and removal of As(III) with Fe(0) and sand


Arsenic Removal from Bangladesh Tubewell Water with Filter Columns containing Zero-Valent Iron Filings and Sand

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Abstract: Arsenic removal from tubewell water is often challenging due to high concentrations of As(III), phosphate and silicate and low concentrations of natural iron. The application of zero valent iron is a promising treatment option, as metallic iron is widely available. However, the pathways for arsenic removal remained unclear and the efficiency of currently used units has not been tested systematically, partly due their large size and long operation time. This study investigated smaller filter columns, consisting of three to five vertically arranged 1.5 L filters (made of used PET bottles), each containing 2.5 g locally produced iron filings and 100-150 g sand, with tube well water and synthetic groundwater in the range of 440-500 µg/L As, 1.8-3.0 mg/L P, 18-20 mg/L Si, 5-6 mg/L TOC and 0-4.9 mg/L Fe. At a flow rate of 1 L/h, columns in Bangladesh could treat 76 L of tubewell water with three filters and 90 L with four filters to below the Bangladesh drinking water limit of 50 µg/L As(tot), without an added oxidant. Columns with several open filters allowed repeated aeration and prevented anoxic conditions, which would develop in a closed system. Iron corrosion lead to continuous formation of dissolved and adsorbed Fe(II). During the oxidation of Fe(II) by dissolved oxygen, As(III) was oxidized by reactive oxygen and iron intermediates and As(V) was sorbed on the forming hydrous ferric oxides (HFO). The repeated corrosion and oxidation lead to complete As(III) oxidation and to over 90% removal of phosphate and arsenic. Natural TOC did not appear to interfere
with arsenic removal and both TOC and silicate was reduced by less than 20%. About 100 mg iron per liter of tubewell water was required, which is by a factor of three to five better than in larger units using sand and iron turnings.

4.1 Introduction

In Bangladesh, up to 50 million people consume drinking water with arsenic concentrations exceeding the guide line values of WHO (10 µg/L) and of Bangladesh (50 µg/L) (1). From the 9-11 million tube wells installed, over one fourth produce water contaminated with arsenic (2). The chronic ingestion of arsenic causes skin lesions, hyperkeratosis, melanosis, skin cancer and internal cancer (3). The groundwater is pumped mainly by simple hand-pumps to the surface where it is directly consumed. Recent studies have shown that other Asiatic countries e.g. India (4), Vietnam (5), Nepal (6), China (7), Taiwan (8), Thailand (9), and possibly Cambodia, Pakistan, and Myanmar (1) are affected with arsenic contaminated water. The development of an adapted drinking water treatment is made difficult due the high As(III), phosphate (1.5-3 mg/L) and silicate concentrations.

Several methods have been proposed to remove arsenic from drinking water, e.g. reverse osmosis (10), ion exchange (11), lime softening (12), passive removal with natural iron (13), or chemical oxidation and precipitation with alum or iron salts (14). While these methods can be effective for arsenic removal, they might not be suitable for use in Bangladesh. Reverse osmosis is costly and requires pretreatment of the water to remove constituents that could clog and foul the membrane. The capacity of ion exchange resins for arsenic removal is severely limited by competing phosphate and silicate and the resins need to be regenerated and tend to become covered by precipitating HFO. Techniques using lime softening require larger amounts of Ca(OH)₂ and are more suited for large water treatment facilities than for treatment at the household level. Passive removal by simply allowing naturally present Fe(II) to oxidize and the HFO to precipitate was found to efficiently remove phosphate, but not arsenic. The iron content of typically 2-10 mg/L is too low for efficient arsenic removal (13).

Effective in terms of minimizing the necessary amount of materials is the use of oxidants (e.g. KMnO₄, bleach) to oxidize As(III) to the better adsorbing As(V), and of iron- or aluminum salts to precipitate the As(V) (and necessarily also the phosphate) by sorption on Al- or Fe(III)(hydr)oxides. No chemicals and the minimum mass of man-made material is needed if metallic iron can be used for the formation of arsenic-sorbing HFO. The use of zero-valent iron has been studied under numerous conditions, e.g. arsenic removal
4.1 Introduction

from mine tailings, groundwater, and drinking water. Karschunke and Jekel showed that with 45.8 g of iron wool it was possible to treat up to 1.19 m$^3$ of Berlin tap water spiked with 500 $\mu$g/L As(V) (15). In order to enhance iron corrosion, some experiments were conducted with iron nails embedded in copper wool (16).

In spite of quite numerous arsenic removal studies with Fe(0), the mechanisms remained unclear. One group of studies has proposed reductive pathways in which dissolved arsenic is reduced to As(0), arsenic sulfides or arsenopyrite on the surface of Fe(0) (17-19). Studies in well aerated systems have proposed the formation of HFO and iron oxide scalings on the surface of Fe(0) which sorb of As(III) and As(V). Recently it has been shown that As(III) is partly oxidized in Fe(II) containing water during the oxidation of Fe(II) with dissolved O$_2$ (13,20). Slow addition of 20-25 mg Fe(II) in several smaller portions to aerated water with 500 $\mu$g/L As(III), 3 mg/L P and 30 mg/L Si was sufficient to oxidize and remove over 90% of the arsenic without an added oxidant (13). A very recent study shows that Fe(II), which is released from corroding iron filings in aerated water also leads to As(III) oxidation and to sorption of As(V) on the forming HFO (21).

Munir (22) and Sutherland (23) investigated locally built 3-Kolshi filters consisting of a first container with 3 kg iron turnings and 2 kg sand, a second container with 2 kg sand and 1 kg charcoal, and a third container serving as the recipient for the filtered water. In waters with low phosphate concentrations, 3-Kolshi units have treated up to 6 m$^3$ of contaminated water over a period of 9 months to less than 10 $\mu$g/L arsenic in the effluent. However, to our knowledge, the 3-Kolshi units have never been systematically tested until break-through of the arsenic, thus, their capacity under various conditions remains unknown. The large size and long operation time of several months make systematic studies difficult. Problems with pathogens and bacteria normally develop before the breakthrough of the arsenic. Due to restricted flow in parts of the Kolshi filters, anoxic zones are likely to develop around the iron turnings, such the contribution of oxic and anoxic pathways for arsenic removal is not known. The goal of the present study is smaller, well aerated filters that can be tested until breakthrough within in a few days. In recent work (21), arsenic contaminated water was repeatedly filtered through a glass column containing sand and iron filings. After four filtrations, synthetic groundwater with initially 500 $\mu$g/L As(III) met the guide line value of 50 $\mu$g/L.

The overall reactions leading to Fe(II), HFO and As(V) can be formulated as follows:
According to equation 1, aerated water flowing through sand and iron filings lead to the formation of dissolved Fe(II). During the oxidation of Fe(II) to Fe(III) (eq. 2) in the sand and in the recipient placed below the filter, the forming reaction intermediates (RI) (e.g. OH* and Fe(IV)) partially oxidize As(III) to As(V) (eq. 4) which is efficiently sorbed on the precipitating HFO (eq. 3). The freshly formed HFO was retained by the sand grains when the water was re-filtered through the column. Due to the continuous release of Fe(II) through the corrosion of Fe(0), As(III) could be oxidized and removed without addition of an oxidant. The results showed that phosphate was removed before arsenic, which had to be oxidized first to the better sorbing As(V). The silicate concentration was reduced by around 10%. Due to loss of CO₂ and the ongoing corrosion processes the pH increased from 7-8, accelerating the oxidation of ferric iron.

Based on the overall stoichiometry in eq. 1-4, air saturated water with 9 mg/L O₂ can lead to the release and oxidation of maximally 21 mg Fe(II) before the water becomes anoxic. Since 20-25 mg Fe(II) are needed for sufficient arsenic removal (13,24), and the corrosion process is not 100% efficient, more oxygen needs to be introduced during the filtration. Oxic conditions are conveniently maintained in a filter column with multiple filters that are open to the air.

A first attempt of up scaling in the laboratory lead to the development of a filter column made of five PET-bottles (four bottles containing 2.5 g iron filings and 100-150 g sand, followed by a fifth bottle containing sand only. This simple set up lowered the arsenic concentration to below 50 μg/L for about 36 L of synthetic groundwater containing 500 μg/L As(III), 2-3 mg/L P, 20 mg/L Si, 8 mM HCO₃⁻, 2.5 mM Ca, 1.6 mM Mg, but no Fe(II) and DOC. To study the impact of other water components found in the groundwater of Bangladesh (e.g. DOC, natural ferrous iron, anoxic conditions etc.) field experiments with arsenic contaminated water from tubewells were conducted in Bangladesh.

The aim of this study was to develop arsenic filters for the removal of arsenic with locally available materials and to understand all relevant processes for the future optimization, up-scaling and application of filters using iron filings and sand.
4.2 Materials and Methods

4.2.1 Materials

All chemicals were reagent grade from Merck (VWR), Aldrich or Fluka and were used as received. Iron filings. Iron filings were always freshly produced with a "bastard" hand file (Baiter AG, Switzerland). The iron was provided from BUET and was the same used for the construction of water pipes and wells. For the experiments done in laboratory St-37 steel was used (C: 0.17%, Si: 0.30%, Mn: 1.4%, P: 0.045%, S: 0.045%, N: 0.009%, (25) provided from the Swiss Federal Laboratories for Materials Testing and Research (EMPA).

4.2.2 Sand

Merck lab-quartz sand of analytical purity (washed and calcined) with a grain size of 0.2-0.8 mm, was used as received. For the experiments in Bangladesh, locally available construction sand was used. Prior to the experiments, the sand was washed several times to remove the silt and fine sand fraction, and then boiled for 10 min. The so prepared sand had a bulk density of 1.5 g/cm³ and a porosity of about 40% was measured.

4.2.3 Synthetic Groundwater

All laboratory experiments were performed with synthetic, arsenic spiked groundwater with the main characteristics of Bangladeshi groundwater except for the iron content and DOC (see Tab. 4.1). CaCO₃ (250 mg/L) and MgCO₃ (138.75 mg/L) were dissolved in high purity 18 MΩ water (Milli-Q®, A10, Millipore) by bubbling excess CO₂ gas into the water under intense stirring, resulting in a clear solution at pH 6.0. Silicate was added from a 2.0 g Si/L, daily prepared stock solution (202.4 mg Na₂SiO₃· 9 H₂O in 10 ml). To prevent polymerization of the silicate, 10 mL of the alkaline stock solution were rapidly diluted into slightly acidic groundwater (pH 6.0 - 6.3 with excess dissolved CO₂), before the pH was raised to pH 7.0 ± 0.1 by bubbling compressed air into the solution. Phosphate was added from a 1M KH₂PO₄ stock solution. In a final step As(III) was spiked from a neutral stock solution. The final pH was 7.0 ± 0.1. (Combined Metrohm glass electrode).

4.2.4 Groundwater in Bangladesh

Water was collected from a tube well built in 1996 and 150 ft. depth, (label: well 2) in the village of Srinagar in the district of Munshiganj, 30 km South of Dhaka. Prior to sampling, the tube well was flushed for at least
4. Arsenic Removal from Bangladesh Water with Fe(0)/ Sand Columns

Table 4.1: The different composition of the water in comparison. Synthetic groundwater, well water composition and corresponding mean values and standard deviations of groundwater parameters in Bangladesh, as obtained from the BGS database (Values of pH, DOC and HCO₃⁻ from the special Study Areas; all other values were taken from National Survey Data, using only wells with As > 50 μg/L for data analysis).

<table>
<thead>
<tr>
<th></th>
<th>Bangladesh groundwater</th>
<th>water from well no.2</th>
<th>synthetic groundwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH initial</td>
<td>7.0 ± 0.05</td>
<td>7.1</td>
<td>7.0 ± 0.2</td>
</tr>
<tr>
<td>HCO₃⁻ (mM)</td>
<td>8</td>
<td>7.8 ± 2.7</td>
<td></td>
</tr>
<tr>
<td>Ca (mM)</td>
<td>2.5</td>
<td>1.9 ± 1.4</td>
<td></td>
</tr>
<tr>
<td>Mg (mM)</td>
<td>1.6</td>
<td>1.3 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>Si (mg/L)</td>
<td>20</td>
<td>19.2 ± 4.7</td>
<td></td>
</tr>
<tr>
<td>P (mg/L)</td>
<td>2.3</td>
<td>1.90</td>
<td>1.47 ± 1.48</td>
</tr>
<tr>
<td>As (μg/L)</td>
<td>500</td>
<td>440.94</td>
<td>199 ± 166</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>0</td>
<td>5.63</td>
<td>5.3 ± 4.8</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>0</td>
<td>4.87</td>
<td>3.3 ± 2.8</td>
</tr>
</tbody>
</table>

two minutes to avoid residual water. The water was transported in 5 Gal PE-tanks, headspace free. The water was treated in Dhaka within one day of sampling. For the composition of the groundwater see Tab. 4.1.

4.2.5 Filtration Unit

Used 1.5 L drinking water PET bottles were obtained locally in Zürich or in Dhaka. Before use, the bottles were flushed several times with tap water. To construct filters, the bottom of the bottles was cut off and the bottles were used upside down, with the sand and iron filings filled in the bottle neck (Fig. 4.1 and Fig. 4.2). Three to five bottles were aligned vertically to allow the water to flow from one bottle to the next through perforated caps. The hole in the caps was made with a bodkin and had a diameter of circa 2 mm. To avoid loss of sand grains, a piece of textile was fixed in the screw cap to cover the hole. Experiments were performed with different arrangements of sand and iron (Fig. 4.2). The columns were attached to a bamboo rack and a water tank was placed such that the water in the first bottle and the tank was on the same level. The water flow was regulated by changing the height of the filter columns. Tab. 4.2 gives an overview of the different columns.
Figure 4.1: The filter columns made of PET bottles were fixed to a bamboo rack. A 25 L water tank with contaminated water was connected to the first filter by 3 mm diameter silicon tubing, such that the water levels in the tank and first filter remained equal. The flow rate was regulated by the water level, which was adjusted by lifting or lowering the filter column. The treated water was collected in 5-10 L recipients. (a) filter column consisting of four filters with sand and iron filings and one filter with sand (b) column with 3 filters each with a layer of sand and iron filings and a layer of sand.
Figure 4.2: Two different arrangements of sand and iron filings. The sand and iron filings were either homogeneously mixed in the whole filter (left), or a homogenous mixture of sand and iron filings was followed by a layer of only sand (right).
4.2 Materials and Methods

4.2.6 Column sampling

Samples (5-20 ml) were taken directly at the outflow of each filter and from recipient. The collected 5 ml water was stored in the prepared vials containing 200 μl 2 M HCl.

4.2.7 As(III) and As(tot) analysis

Analysis was performed with an Atomic Fluorescence Spectrometer (AFS) (PS Analytical Ltd., Kent, UK). For the selective detection of As(III), a 0.5 M disodium citrate buffer solution (pH 5.0) was used for the hydride generation instead of HCl. Only As(III) is converted to AsH₃ at pH 5 and detected in the AFS instrument. To measure As(tot) (As(V) and As(III)), 100 μl sample, 100 μL 10 M HCl and 20 μl of reducing agent (0.6 M ascorbic acid and 3 M KI) were mixed and left to react for 60 min, prior to 1:50 dilution with the citrate buffer and subsequent analysis with AFS.

4.2.8 ICP-OES

An Inductively Coupled Plasma Optical Emission Spectrometer (Spectro Ciros CCD) was used to analyze P, Mg, Ca and Si.

4.2.9 Fe(II) measurement

Fe(II) was sampled by directly collecting 5 mL column (effluent) into vials containing 2 mL phenanthroline and 1 mL acetate buffer. The Fe(II) was quantified by UV-vis Spectrophotometry in optical quartz cells (1 or 4 cm) at λ = 512 nm.

4.2.10 XRD

Powder x-ray diffractograms were measured with a Phillips Scintag XDS 2000 (Cu-Cathode 45kV and 40mA) from 2° - 60°2θ. For the qualitative measurements, the samples were air dried, homogenized and mixed with an internal standard (Si). To analyze the coating on the sand and the scaling on the iron filings, the samples were treated for 10 min with ultrasound. Small amounts of the suspended material were dried with a nitrogen stream on a glass disk and placed in the sample holder for XRD analysis.
Table 4.2: List of the different columns investigated for this study. In the text the short form of the labels was used (e.g. instead of Cl-4 x Sa, Cl).

<table>
<thead>
<tr>
<th>design parameters of the filter</th>
<th>sand and iron filing configuration</th>
<th>feed Water</th>
<th>label</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 x 150-200g sand</td>
<td>sand only</td>
<td>Well 2</td>
<td>C1-4 x Sa</td>
</tr>
<tr>
<td>4 x 2.5 g Fe + 1 x 150-200 g sand</td>
<td>homogeneously mixed</td>
<td>Well 2</td>
<td>C2-4 x FeSa+Sa</td>
</tr>
<tr>
<td>4 x 2.5 g Fe / 150-200 g sand</td>
<td>layers</td>
<td>Well 2</td>
<td>C3-4 x FeSa/Sa</td>
</tr>
<tr>
<td>3 x 2.5 g Fe / 150-200 g sand</td>
<td>layers</td>
<td>Well 2</td>
<td>C4-3 x FeSa/Sa</td>
</tr>
<tr>
<td>4 x 2.5 g Fe + 1 x 150-200g sand</td>
<td>homogeneously mixed</td>
<td>Synthetic water</td>
<td>L1-4 x FeSa+Sa</td>
</tr>
</tbody>
</table>

4.2.11 TOC measurements

30 ml of samples were filled in vials containing 200 μl 5M HCl and measured with a Shimadzu 5000 TOC. The samples were stored in the fridge during duration of the field campaign.

4.3 Results and Discussion

Collection, transport, and filtration of well water. After the water was pumped and filled into 25 L plastic tanks, oxidation of the natural Fe(II) started and the water turned slowly brown within several hours. Filling the tanks free of a headspace with air slowed the oxidation, but at least partial aeration took place during pumping. We made no attempts to avoid aeration, as water treatment in villages would involve the same steps. The water was transported to Dhaka for treatment within one hour and each tank was used up within 24 hours. During this time, the water turned brown and some precipitation took place, but most of the HFO remained in suspension in the containers and was retained within the first few millimeters of the first filter. The flow rate of the columns was controlled by the water level in the first filter. The water levels in the next filters adjusted accordingly, until all filters reached an equal steady-state flow rate of 0.5-1.5 L/h, with an average of around 1 L/h. The sand-iron filing layers in each filter remained immersed in water during the entire filtration, with the height of water column above the sand varying between 2 cm and 20 cm.

4.3.1 Four filters containing sand only (Column C1)

The efficiency of simple sand filtration was investigated with a filter column made of four filters containing sand without iron filings (C1). The arsenic removal was insufficient (Fig. 4.3) and did not meet the guide line values of
4.3 Results and Discussion

Figure 4.3: Arsenic concentrations in the filter effluents and in the recipient of C1-4 × Sa (four filters containing sand) as a function of filtered water volume. The arsenic concentrations could not be reduced to below 200 µg/L.

Bangladesh (50 µg/L). The concentration of arsenic was reduced by 37% after the first filter by co-precipitation with natural HFO and by less than 5% in the following filters. In the recipient, an average removal of 43% was achieved. Compared to other studies at the same concentration of 4.7 mg/L Fe(II), this is higher than the value expected from Roberts (13) in passive removal experiments (about 15%) but lower than the arsenic removal achieved in Vietnam with simple sand filters (between 60 - 85%) (Berg, personal communication).

In contrast to arsenic, the phosphate content was strongly reduced (81%) after the first filter (Fig. 4.4) and an average of 90% phosphate removal was achieved in the recipient. Analogous to the arsenic most of the phosphate is removed by coprecipitation of HFO in the first filter, but phosphate outcompetes As(III) and to some extent also As(V) due its much higher initial concentration. The arsenic concentration in the recipient showed a tendency to higher arsenic values with time, which was probably due to competition for sorption sites on HFO with the accumulation of phosphate. Due to the relatively low iron content and high phosphate and silicate concentrations, simple sand filtration is not a sufficient treatment option in Bangladesh.
4. Arsenic Removal from Bangladesh Water with Fe(0) / Sand Columns

Figure 4.4: Phosphate concentrations in the filter effluents and in the recipient of Cl-4 × Sa. The initial phosphate concentration (1.9 mg /L P) was reduced by more than 75% after the first filter, mainly by co-precipitation with natural iron. The small decrease of the phosphate concentration in the following filters is probably due to adsorption on mineral surfaces in the sand.

4.3.2 Four filters with homogenously mixed sand and iron (Column C2)

In C2 four filters contained 2.5 g of iron filings homogenously mixed with the sand. To provide colorless HFO-free water, a fifth filter containing sand was added to remove the HFO formed from corrosion in the last filter with Fe(0). The arsenic concentrations measured after filter 1 (Fig. 4.5) show first a decline and reach a minimum after 30 L, before increasing again. The breakthrough to concentrations above 50 ppb was not reached when the experiment had to be stopped at 75 L. After the first filter 74% of total arsenic was removed. The following filters retained 78%, 68%, and 56% of the arsenic, respectively.

As shown in Fig. 4.6, up to 3 mg/L iron left the first filter at an initial stage and filters 2, 3, and 4 leached 2.5 mg/L, 1.5 mg/L and 0.5 mg/L of iron, respectively. The decreasing iron concentrations in the effluents from filter 1 to 4 are a consequence of the pH increase from 7 to 8 (Fig. 4.11), caused by the corrosion reactions and the loss of dissolved CO₂ in the open system: Less Fe(0) is corroded at higher pH and the formed Fe(II) is oxidized more quickly within each filter. The iron leaching also continuously decreased with time, which
4.3 Results and Discussion

Figure 4.5: Arsenic concentrations in the filter effluents and in the recipient of C2-4 \times \text{SaFe+Sa} (four filters with homogenous mixtures of iron filings and sand and of one filter with sand).

can be explained by the accelerated Fe(II) oxidation on the surface of HFO accumulating in each filter (26). At the beginning of the experiment, most of the Fe(II) formed from the corrosion of Fe(0) left the first filter as Fe(II). Once sufficient HFO accumulated within the first filter, more Fe(II) was oxidized and the arsenic concentration was reduced. The next filters show similar trends, but the arsenic concentrations are generally much lower. C2 produced a nearly phosphate free water with concentration lower than 50 \mu g/L (Fig. 4.12).

4.3.3 Four filters with iron filings-sand and sand layers (Column C3)

In order to simplify the construction of the filter columns, a sand filtration was incorporated in each single filter: C3 consisted of four filters, each containing a layer of sand in the bottle neck topped by a layer of sand mixed with of 2.5 g iron filings. The purpose of the two layers was that the formation of Fe(II), its subsequent oxidation, and the retention of HFO in the sand was completed within each single filter of the column. Thus, an additional filter with only sand would become superfluous.
The scatter in the arsenic concentrations at the outflow (Fig. 4.7) of the first filter reflects changes in the flow rate. In fact, the variations in the arsenic concentrations in the outflow of the first filter and the time of sampling are correlated (not shown). During the night time, when the flow rate was 0.5-1.0 L/h, less arsenic was leached from the first filter than during day time, when the flow was kept at 1.0-1.5 l/h. The observed variations were much smaller after filters 2 to 4. The relative arsenic reductions were 77%, 67%, 33%, and 26% from the first to the fourth filter, respectively. The breakthrough is reached after filtration of about 90 of L water.

As shown in Fig. 4.8, the iron concentrations leached from the single filters could indeed be reduced by a factor of ten, without compromising the removal of arsenic. The phosphate concentrations measured in the recipient of C3 were lower than 50 µg/L.

4.3.4 Three filters with iron filings - sand and sand layers (Column C4)

In C4, the number of filters was reduced to three. Fig. 4.9 shows the arsenic concentrations in the outflow of the three different filters in C4 and in the
4.3 Results and Discussion

Figure 4.7: Arsenic concentrations in the effluents and in the recipient of C3-4 × SaFe/Sa (four filters with the layered iron filings and sand). Around 90 L of contaminated water could be treated.

Figure 4.8: Iron concentrations in the effluents and in the recipient of C3-4 × SaFe/Sa. Compared to C2-SaFe+Sa, the iron concentrations leached out of each filter are much lower.
recipient. The variations again reflect changes in the flow rates. An arsenic breakthrough occurs in the outflow of filter 3 after the filtration of 76 L, which is 14 L less of treated water compared to C3. The arsenic concentration was lowered by the first filter in average by 80%. The second and third filter reduced the arsenic by 71%, and 74%, respectively. The water in the outflow in C4 remained clear and colorless throughout the experiment. As in C3, the amount of iron leached from the single filters was up to ten times lower than in C2, where the iron and sand were homogenously mixed. Phosphate concentrations measured in the recipient show variations that reflect changes in the flow rates, similar as was observed for the iron. The phosphate concentrations in the treated water were higher than in C3, but below 200 μg/L and less than 10% of the initial value.

4.3.5 Iron leaching

Iron concentrations measured at the outflow of the filters generally decreased with running time. Different processes may explain this decline: a) Less Fe(II) was be leached due to the consumption of iron filings by corrosion. b) Analogous to prior experiments (21), high carbonate and phosphate concentrations lead to the formation of scales on the iron filings, which reduces oxygen diffu-
**4.3 Results and Discussion**

Figure 4.10: The pH evolution in several columns at different times of the treatment. There are slight differences, but the pH generally increases from pH 7.0 ± 0.1 to pH 8.0 ± 0.2 from the first to the last filter.

sion to the metal's surface. SEM imaging revealed that the iron fillings were covered by precipitates containing carbonates, phosphate and HFO on the surface. c) With running time, increasing HFO concentrations within the filter accelerated the oxidation rate of leached Fe(II), thus reducing the soluble iron concentration leaving the filters.

### 4.3.6 Increasing pH

In, measured pH values in each filter are plotted for the different columns. A general increase of the pH from raw water 7.1 to 8.1 in the recipient was observed and was not significantly affected by the variation in the construction of the column and during the operation. The pH increased mainly due to the loss of dissolved CO₂. According to Equations 1-4, the overall corrosion reaction including the precipitation of HFO is pH-neutral, but it is known that the pH increases more strongly at the surface of metal, as the proton-consuming Fe(0) oxidation is at least in part spatially separated from the proton-releasing formation of Fe(OH)₃.
Table 4.3: TOC concentration measured in the raw respectively well water and in the recipients of column C3 and C4. The TOC content could not be significantly reduced after filtration.

<table>
<thead>
<tr>
<th>label of sample</th>
<th>sample taken after</th>
<th>TOC [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well2</td>
<td>raw water (average)</td>
<td>6.1 ± 0.5</td>
</tr>
<tr>
<td>C4</td>
<td>32.3 L in C4</td>
<td>5.0 ± 0.5</td>
</tr>
<tr>
<td>C4</td>
<td>76 L in C4</td>
<td>5.9 ± 0.5</td>
</tr>
<tr>
<td>C3</td>
<td>76.2 L in C3</td>
<td>5.8 ± 0.5</td>
</tr>
</tbody>
</table>

Table 4.4: The results of a titration experiment with Fe(II) show that the TOC could not be significantly reduced by co-precipitation with HFO formed from FeII SO4.

<table>
<thead>
<tr>
<th>added Fe(II) [mg/L]</th>
<th>TOC [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.4 ± 0.5</td>
</tr>
<tr>
<td>5</td>
<td>6.0 ± 0.5</td>
</tr>
<tr>
<td>10</td>
<td>6.1 ± 0.5</td>
</tr>
<tr>
<td>15</td>
<td>6.0 ± 0.5</td>
</tr>
<tr>
<td>20</td>
<td>5.4 ± 0.5</td>
</tr>
<tr>
<td>25</td>
<td>5.8 ± 0.5</td>
</tr>
</tbody>
</table>

4.3.7 TOC and silicate concentrations

The TOC in the treated water was lowered by less than 20% (Tab. 4.3). Additional titration experiments adding Fe(II) to well water revealed that the TOC could not be reduced significantly by co-precipitation with HFO. Even after adding 25 mg/L Fe(II) from ferrous sulfate stock solutions and filtration through 0.2 M nylon filters after 4h, more than 80% of the TOC remained in solution (Tab. 4.4). The water treatment lowered the silicate contents in the recipient by less than 25% (data not shown). As silicate is not a health-sensitive water parameter we did not attempt to investigate silicate removal more precisely.

4.3.8 Remaining Fe(0) in the filters

To estimate the amount of Fe(0) consumed during the filtration, the sand and iron mix of C2 was dissolved in 16% hydrochloric acid. Carbonates were dissolved previously in 10% acetic acid. The hydrogen produced through the dissolution of remaining Fe(0) was collected in a measuring cylinder immersed in water. The amount of remaining Fe(0) calculated from the volume of evolved H2 was between 0.7-0.5 g for the filter 2 in C2. Thus, between 1.8-2.0 g of iron was consumed by the filtration of 75L. Between 1.3 g and 1.6 g remained in filter 4 of C2. If all the iron would be used, over 100 L could be
treated. Nevertheless the scales produced through corrosion inhibit the use of all the iron filings.

4.3.9 XRD analysis of precipitates and scalings

The XRD spectra of the precipitates and scalings did not indicate the presence of any crystalline phase. Also in the scalings, which were observed by SEM in previous experiments (21), no crystalline phase could be detected by XRD. If such crystalline phases were present, the amounts were too small to be detected by XRD.

4.3.10 Comparison of columns in Bangladesh with laboratory columns

Fig. 4.11 shows the arsenic concentration in four different columns. The columns labeled L1 and L2 were run at EAWAG with synthetic groundwater; columns C2 and C3 were built and run in Bangladesh with well water. The columns in Bangladesh could filter nearly twice the amount of water compared to the columns at EAWAG. This effect is mainly due to the difference in the water composition and illustrates the effect of Fe(II) in the well water. The coprecipitation of mainly phosphate and arsenic with the naturally present Fe(II) leads to a reduction of phosphate by 80-90% and of arsenic by 30-40% in the first few millimeters of the sand iron-mixture of the first filter (C1), before the water interacted with the iron filings.

4.3.11 Arsenic removal mechanism

Previous studies (20) found that addition of 5 mg/L Fe(II) to aerated water with 500 µg/L As(III) lead to the oxidation of 25-33% of the As(III). During the oxidation of Fe(II), intermediates such as *OH or Fe(IV) oxidize As(III) to As(IV) which rapidly reacts with dissolved oxygen to As(V). Better results in terms of As(III) oxidation were obtained when high initial Fe(II) concentrations were avoided by adding Fe(II) in multiple small portions over several hours (13), as Fe(II) competes with As(III) in the reaction with oxidizing intermediates.

In a more recent study (21), aerated groundwater flowing through a column with a mixture of 1.5 g iron filings and 6 g sand lead to the corrosion of zero-valent iron and release of dissolved Fe(II) up to concentrations of 8 mg/L. The subsequent oxidation of Fe(II) by dissolved oxygen in the recipient caused partial oxidation of As(III) and sorption of As(V) on the forming
HFO. In the present work, contaminated water flowing through the filters oxidized Fe(0) and Fe(II) was continuously released. Analogous to the experiments described above, As(V) was co-precipitated with the forming HFO, either in the same or in the next filter depending on how the sand and iron were mixed.

Additional experiments (not shown) found that the oxidation rate of Fe(II) was accelerated by suspended HFO, as expected from published work (26), and that the same acceleration was observed with HFO adsorbed on quartz grains. The increase in the oxidation rate of Fe(II) resulted in an acceleration of the As(III) oxidation. These additional observations are in agreement with previous studies (13, 20).

Oxidation of As(III) to As(V) on corroding iron was also observed by Manning et al. (27). These authors argue that Fe(II) is formed as an intermediate in the formation of Fe(III)(hydr)oxides and that As(III) is oxidized during the corrosion process and possibly also by forming maghemite and hematite. Oxidation of As(III) was observed at high Fe/As ratios of 3400 by HFO prepared from slow oxidation of Fe(II) at pH 6.5 (29) but not with an Fe/As ratio of 10 with HFO prepared from Fe(III) (30). We never observed oxidation of As(III) by ironhydr(oxides) on the time scale of hours (31) after they had

Figure 4.11: Comparison of two columns treating well water (C2-4×FeSa+Sa and C3-4×FeSa/Sa) and two laboratory columns treating synthetic water (L1-4×FeSa+Sa and L2-4×FeSa+Sa). Twice the amount of well water with 5.6 mg/L natural Fe(II) could be treated compared to synthetic water with no Fe(II).
4.3 Results and Discussion

Figure 4.12: Phosphate concentrations in the recipient of the different columns. With a few exceptions at the beginning of the filtration, more than 90% of the initially 1.9 mg/L P was removed.

been formed by hydrolysis of Fe(III) or after complete oxidation of Fe(II). All considered studies thus give a consistent picture that As(III) is oxidized in parallel to dissolved and adsorbed Fe(II) by dissolved oxygen. Possibly, As(III) is also oxidized in parallel to oxidation of Fe(0) to Fe(II), but there is no direct evidence. Furthermore and congruently to our results, Farrell et al. (28) showed that reduction of As(III) to metallic arsenic during corrosion of zero valent iron under conditions applicable to drinking water treatment, is unlikely.

For the columns with several filters, we propose the following mechanisms for the arsenic removal: Similar to the observation of Su et al. (32) a large fraction of phosphate (80-90%) and a smaller fraction of arsenic (30-40%) is adsorbed on HFO forming from naturally present Fe(II) after pumping the groundwater to the surface, before the water enters the filter column. As(III) adsorption is limited by initially high concentrations of phosphate and silicate (33,34) and only about 30% of the As(III) is oxidized. In the filter column, already precipitated HFO is retained within the first few millimeters of the sand - iron filings mixture. The downwards flowing aerated water corrodes metallic iron and forms Fe(II), which is partly transported down the column in dissolved form and partly remains sorbed on corrosion products on or in the immediate vicinity of the iron surfaces. Dissolved Fe(II) readily mixes with
dissolved As(III) and is oxidized by dissolved oxygen, partly in solution and partly adsorbed on surfaces, leading to partial oxidation of As(III). As this process is repeated many times down the filter column, As(III) is completely oxidized and As(V) is sorbed on the forming HFO. How far the dissolved Fe(II) moves down the column is dependent on the flow rate, the pH, and the amount of active surfaces that accelerate the Fe(II) oxidation. The contact time of the water in the sand and iron filing mixtures with a void volume of ca. 50 cm³ was around 3 min at a flow rate of 1L/h. According to Millero (35) the life time of dissolved Fe(II) is in this type of water is in the order of 50 min at pH 7.5, 1 min at pH 7.5, and 30 sec at pH 8. Thus, in the initial absence of HFO and limited acceleration on the surface of the sand grains, almost all Fe(II) formed from corrosion leaves the first filter at pH 7.0 and almost no Fe(II) leaves the last filter at pH 8.0. With HFO accumulating on the sand grains, the Fe(II) oxidation rate increases and less Fe(II) and As(III) is found in the effluents of all filters with increasing filtration time. With the slowing corrosion due to formation of scales on the iron filings and with the saturation of HFO with phosphate and arsenic, the arsenic concentrations (but not the iron concentrations) increase again. Fig. 4.5, Fig. 4.6, Fig. 4.7, Fig. 4.10, and Fig. 4.11 clearly reflect these trends. Since similar fractions of As(III) are co-oxidized with adsorbed and dissolved Fe(II), it does not matter how far the Fe(II) is transported, as long as mixing with As(III) can occur. However, Fe(II) enclosed in scalings at the surface of the corroding iron (e.g. in magnetite and Fe(II) carbonate phases) might not be as efficient for As(III) oxidation. The scalings limit the access of As(III) and oxygen, lower the corrosion rate, and reduce the overall arsenic removal efficiency.

4.4 Practical Implications

A crucially important aspect of using zerovalent iron is the efficiency of the arsenic removal, e.g. expressed as the necessary amount of iron per liter of treated water. In this study, around 90 L of water could be treated with four filters containing a total of 10 g iron filings, or around 75 L with three filters containing 7.5 g iron. Thus, 100-110 mg of iron per liter was necessary to treat water with initially 440 µg/L As(III). This is a significant improvement over the the 3-Kolshi Filter investigated by Munir (22) which used 500 mg iron per liter by treating 6 m³ (4850 L containing 80-100 µg/L and 1000 L containing 1900 µg/L As(tot)) of nearly phosphate free water with 3 kg of iron turnings. According to Roberts (13), 20-25 mg/L slowly added Fe(II) was sufficient to reduce the arsenic concentration to below 50 µg/L in water of this type. Meng (24) reported that for Bangladeshi water containing phosphate (up to 1.9 mg/L) and silicate (up to 18 mg/L) required a ratio of at least 40 mg Fe
4.4 Practical Implications

To reduce the arsenic concentration to less than 50 μg/L after the As(III) has been oxidized to As(V) with hypochlorite. Thus, both Meng and Roberts conclude that a minimum of 20-25 mg of iron is needed for water with 500 μg/L As(III), but slow addition of Fe(II) to aerated water avoids the necessity for an added chemical oxidant. Compared to addition of dissolved iron, 20-25% of the metallic iron in our columns could be used to remove arsenic.

Larger water volumes per time could be treated by up-scaling of the filter columns. Instead of 1.5 L PET bottles, larger containers could be used to construct each filter and the containers could be stacked on top of each other to simplify the construction of the columns. However, careful consideration has to be given to the filter dimensions. Increasing the diameter would simply increase the water flow proportionally to the area and is the simplest measure for up-scaling. Increasing the length of the filters while maintaining the flow rate per area would increase the reaction time with the iron filings and could lead to anoxic conditions at the end of each filter. Longer columns would require a higher flow velocity in order to maintain oxic conditions.

Other parameters that could be changed are the size of the iron filings and the proportions of sand and iron filings. Larger iron filings decrease the surface to volume ratio and would most likely lead to a less efficient use of Fe(0), as more iron would become covered by corrosion scalings. An increase in the proportion of iron to sand can lead to clogging of the columns. The transformation of Fe(0) to HFO leads to a large volume increase, which has to be accommodated in the void volume of the sand. As a rough estimate, 2.5 g of Fe(0) with a volume of 0.35 cm³ can lead to 4.78 g of Fe(OH)₃ with a volume of 4.78 cm³ assuming a density of 1. With a pore volume of 40% for typical sand, at least 35 cm³ of sand should be used per g of iron to avoid the clogging of more than 20% of the void volume.

The production of iron fillings is time consuming and laborious. For 10 g of iron filings 40 minutes of filing are required. However, an increasing demand in iron fillings could be met by the production of iron filings in local mechanical shops. After 4-5 days of operation, the breakthrough of the arsenic to concentrations above 50 ppb requires the exchange of the filter media. In contrast to the iron filings which have to be replaced the sand can be washed and recycled. To avoid the presence of pathogens in the filters, the relatively small amounts of sand can be sterilized by boiling in water for 10 minutes.

A frequently discussed issue is the stability of the arsenic containing sludge. Sorbed phosphate, arsenate and silicate decrease the rates of HFO transformations, however, on a time scale of months to years, precipitated HFO might undergo transformation leading to thermodynamically more stable forms. Importantly, Ford et al. (36) have shown in a laboratory study that transformation of HFO over four months to the more crystalline hematite and goethite
did not result in a desorption of adsorbed As(V). Similar observations were made by Dixit and Hering (37), although the possibility that increasing crystallinity might lower the uptake of arsenic was also mentioned. To minimize possible risks, sludge be disposed away from children and should not be buried in surface soils where strongly reductive conditions are expected or where food crops are grown. Disposal of large amounts into deeper pits, possibly encased in concrete, is one possibility. Small amounts of sludge from single households could be disposed into moving oxic water bodies, where there is rapid dilution to background levels and the risk of remobilization is small. Ideally, sludge could be disposed into larger rivers where it is carried into the ocean. In the discussion about the possible threats posed by sludge, it should be kept in mind that only a few percent of the tubewell water pumped for households is used for drinking. Water treatment prevents the arsenic from passing through humans, but it does not change the overall arsenic flux. In comparison to household use, the arsenic loads delivered to fields by irrigation pumping from shallow tubewells are by orders of magnitude larger.
4.4 Practical Implications

Literature


4. Arsenic Removal from Bangladesh Water with Fe(0)/Sand Columns


Chapter 5

Conclusion and outlook

The fate of arsenic in the environment and in water treatment processes is mainly determined by its redox chemistry. One of the major challenges encountered in the removal of arsenic from groundwater is to oxidize As(III) with natural oxidants to As(V) which adsorbs strongly to mineral surfaces. We succeeded in oxidizing As(III) in parallel to the oxidation of Fe(II) with oxygen and with H₂O₂ in solution. We could show that the oxidation of As(III) was due to the formation of *OH at lower pH and possibly to Fe(IV) at higher pH. The data obtained were fitted with a model to provide an estimate of the rate constants and a quantitative approximation of the results (Chapter 2).

Experiments revealed that aerated synthetic groundwater repetitively filtered through a zero valent iron-sand filter releases Fe(II). During the subsequent oxidation of Fe(II) by dissolved oxygen, As(III) is partially oxidized. The so-formed As(V) sorbs on the precipitating hydrous ferric oxides (HFO). Multiple filtration lead to optimal conditions for arsenic removal: As(V) sorbs on the HFO which is retained by the sand grains during the next filtration and removed by backwashing (Chapter 3).

Based on these promising results, a treatment option applying zero valent iron, was investigated on well water using small filter columns in Bangladesh and in the laboratory. Filter columns made of three to five vertically mounted 1.5 L containers could treat up to 90 L tube well water to below 50 μg/L As(tot) without using an added oxidant (chapter 4).

The observation that As(III) is oxidized in parallel to the oxidation of Fe(II) is also significant for the understanding of Fenton reactions in general, for arsenic redox reactions in the environment and in arsenic removal processes, as well. No addition of oxidant would be required to oxidize As(III) to As(V) for the treatment processes if naturally present Fe(II) could oxidize to Fe(III) and the forming HFO precipitate. However, due to the high phosphate and low iron content this method has been found to be inappropriate.

The results from chapter 3 and 4 show that zero valent iron efficiently re-
moves arsenic from contaminated water on a oxidative pathway and that the results from our previous study can be confirmed even if Fe(II) was produced through the corrosion of zero valent iron.

The filter column investigated in Bangladesh might be constructed for larger amounts of water. Some constraints with respect to up scaling are discussed in the section on practical implications in chapter 4.

New questions and considerations emerge from this last chapter and should stimulate further investigations from an engineering and implementation point of view:

**Can this filter method be used to mitigate the arsenic crisis?** A number of conditions have to be fulfilled before an arsenic removal technology can be used. In the case of Bangladesh a new technology can only be brought to the population, if it has been tested and validated by the Bangladesh Council for Scientific and Industrial Research (BCSIR). For this technology evaluation the BCSIR has to develop protocols approved by the National Committee of Experts on Arsenic. If the proposed technology has been approved by the BCSIR it can be spread among the affected populations.

The filter described in chapter 4 shows how to efficiently remove arsenic from drinking water by simple means and at low costs. However, people will prefer using an arsenic removal technology with a small effort (and costs)-to-drinking-water-volume ratio and which is suited for women and girls traditionally in charge of the water. Therefore further improvements as described in chapter 4 will be necessary.

Finally, agencies in charge of implementing this process and educating people on how to use it will have a great impact on its potential success.

**What happens with the sludge?** According to the National Policy for Arsenic Mitigation, the supplier of an arsenic removal technology should give a detailed procedure or method on how the sludge can be collected centrally. The disposal should take place under the supervision of an agency designated by the government. Furthermore the sludge should be encapsulated in a 2.5 m concrete lined PVC container and buried in a place away from populated areas in a depth of 2 to 2.6 m.

However, to date arsenic is spread in great quantities through agricultural irrigation all over the rice fields. The existing arsenic removal methods are conceived to treat drinking water which is a small fraction of the arsenic pumped to the surface. If the sludge originating from these arsenic removal methods is disposed in a way that it cannot be reduced (e.g. open water bodies), it will not affect the population negatively. Arsenic mitigation especially in Bangladesh should not be further delayed by non-appropriated legislations. Further investigation on this issue would be of great help to formulate adequate guidelines for sludge disposal.

**How can the arsenic concentration in drinking water be estimated?** The
arsenic concentration in the filtered water unlike the HFO is invisible and therefore a general rule has to be formulated to decide if the water might be drunk or not. A statistical evaluation of the water quality produced with the arsenic removal method described in this thesis has to be carried out. The results should enable to give a range of filtered water volume produced with a well defined amount of filter material. Another possibility is to test the water quality with arsenic field tests or even biosensors which would imply a comprehensive training of the users.

In south Asia millions of people are affected with high arsenic concentrations in drinking water. The problems generated by this mass poisoning are not limited to the people’s health. Social as well as economical consequences are emerging and are delaying the country’s development.

In the past five years numerous scientific papers on the arsenic issue have been published and a lot more is known about arsenic in the environment today. In the future the mitigation of the arsenic crisis will require strong and effective policies based on scientific understanding.
Curriculum Vitae

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March 1, 1975  Born in Bern, Switzerland

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