# Investigating the Effect of Reducing Agents on the Stability of Arsenate-Bearing Co-Precipitates from Fe(II)/Fe(III)/Al(III) Solutions

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# Abstract

In this thesis the effects of reducing agents on arsenate-bearing Fe(III)/Fe(II)/-Al(III) co-precipitates were investigated. As a first step, co-precipitates with varying molar ratios ([Fe(II)+Fe(III)+Al(III)]/As(V)=4) were produced by lime neutralization in a continuous 2-reactor circuit. Ferrous (Feed: Fe(II)/As(V)=4) was found to remove arsenate by co-precipitation as effectively as ferric to the sub-ppb range. The precipitated molar ratio of ferrous to As(V) (~1.5) indicated possible symplesite-like ($Fe_3(AsO_4)_2 \cdot 8\,H_2O$) formation. Equally effective with minor differences was the removal of arsenate ($M_{tot}$/As(V)=4) by all ferric or mixed Fe(III)/Fe(II) and Fe(III)/Al(III) co-precipitates (≤1mg/L).

The Fe(III)/Fe(II)/As(V) co-precipitates were subjected to stability testing (leachability) over a one year period by exposing them to frequent addition of reducing agents namely sulfite (0.1M, $SO_3^{2-}$) and sulfide (0.1M, $S^{2-}$). No air-excluding measures were taken for these experiments and hence ferrous was found to oxidize even in the presence of reducing agents. By far, the co-precipitates tested without adjustment of pH or $E_h$ proved the most stable, independent of the presence of ferrous, releasing less than 1mg/L As. Frequent chemical adjustment of pH (to pH=8 with lime) and $E_h$ with sulfite (250mV target) or sulfide (0mV target) resulted in higher arsenate release ranging from 1-5mg/L. Hence the co-precipitates were reasonably stable towards reducing agent dosing, proving that they are quite robust arsenate sinks.

To further probe their stability in a completely anoxic environment, Fe(III)/-

As(V)=4 and Fe(III)/Al(III)/As(V)=2/2/1 co-precipitates were exposed to excess sulfide ($S^{2-}$/Fe(III)=1) under inert gas (pH=9.5-10.5 and $E_h$ ~-200mV). The Fe(III)/As(V)=4 series was found to stabilize at ~30mg/L while the aluminum-substituted series released ~15mg/L As after a 4 week equilibration, revealing a significant stabilizing effect for Al(III) in strongly reducing environments. There was only 45% of ferric reduced in both series although enough reduction equivalent was present to reduce all Fe(III) present. Further, there was no significant reduction of arsenate by sulfide, nor evidence of arsenic sulfide formation.

## Résumé

Dans cette thèse, les effets d'agents de réduction sur les co-précipités Fe(III)/-Fe(II)/Al(III) supportant de l'arséniate ont été investigués. Premièrement, des co-précipités avec des ratios molaires variés ([Fe(II)+Fe(III)+Al(III)]/As(V)=4) ont été produites par la neutralisation de lime dans un circuit continue à deux réacteurs. Ferreux (Feed: Fe(II)/As(V)=4) était aussi éfficace pour enlever l'arséniate par co-précipitation que ferrique dans l'intervalle du sub-ppb. Le ratio molaire précipité du ferreux au As(V) (~1.5) a indiqué une formation possible ressemblant le symplesite ($Fe_3(AsO_4)_2 \cdot 8\,H_2O$). Ce qui était égualement efficace avec quelques petites différences était l'enlèvement du arséniate ($M_{tot}$/As(V)=4) par tous co-précipités (≤1mg/L) ferriques ou mélangés Fe(III)/-Fe(II) et Fe(III)/Al(III).

Les co-précipités Fe(III)/Fe(II)/As(V) on été sujets à des tests de stabilité (lixiviats) pour une période d'au-dessus d'un ans en les exposant à des additions d'agents de réduction fréquents, surtout sulfite (0.1M, $SO_3^{2-}$) et sulfide (0.1M, $S^{2-}$). Des mesures sans airs n'ont pas été prises pour ces expériences alors ce

fut trouvé que le ferreux a oxidé même dans la présence d'agents de réduction. De loin, les co-précipité testés sans adjustement de pH ou $E_h$ ont démontré être les plus stables. Ceci était indépendant de la présence du ferreux et laissait passer moins que 1mg/L As. Des ajustements chimiques fréquents de pH (à pH=8 avec lime) et $E_h$ avec sulfite (but de 250mV) ou sulfide (but de 0mV) avaient comme résultat de hautes libérations d'arséniate dans l'interval de 1-5mg/L. Donc, les co-précipités étaient plus ou moins stables envers la réduction d'agents dôpants et ceci démontrait qu'ils étaient des éviers d'arséniate plutôt robustes.

Pour pousser encore plus la stabilité dans un environement complètement anoxique, des co-précipités de Fe(III)/As(V)=4 et Fe(III)/Al(III)/As(V)=2/2/1 ont été exposés à des excès de sulfide ($S^{2-}$/Fe(III)=1) sous un gaz inerte (pH=9.5-10.5 et $E_h$ ~-200mV). La série Fe(III) / As(V)=4 a démontré une stabilization à ~30mg/L pendant que celui substitué avec de l'aluminium dégageait de l'As ~15mg/L après 4 semaines d'équilibration et révélait un effet de stabilization signifiant pour l'Al(III) dans des environements réduisants. Il y avait seulement 45% de ferrique réduit dans les deux séries. Par ailleurs, une quantité suffisante de réduction équivalente était présente pour réduire tout Fe(III) présent. De plus, il n'y avait pas de réduction signifiante d'arséniate par sulfide, ni de preuve de formation de sulfide arsénique.

# Contributions of Authors

As an alternative to the traditional thesis format, McGill University offers the option to M.Eng. candidates to use a manuscript-based thesis format. The two results chapters of this thesis are intended for publication in Waste Management and Journal of Hazardous Materials respectively (2013).

Christoph Doerfelt and George P. Demopoulos, ”Long-term stability of continuously co-precipitated Fe(II)/Fe(III)/As(V) solids under periodic exposure to reducing agents”.

Christoph Doerfelt, Ranjan Roy and George P. Demopoulos, ”Stability of arsenate-bearing Fe(III)/Al(III) co-precipitates in the presence of sulfide as reducing agent under anoxic conditions”.

In all works presented, the first author produced all materials and conducted all necessary characterization. Ranjan Roy provided his expertise to develop the HPLC-ICP-OES system to analyze for different arsenic species in the second publication. Prof. Demopoulos provided funding and equipment for all materials and characterization and also filled the comprehensive supervisory role on both publications.

The accuracy of the above statements is attested by the student’s supervisor and the co-author.

George P. Demopoulos ___________________________
Ranjan Roy ___________________________

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# 1. Introduction

The abundance of arsenic in the earth's crust is estimated to be 1.5–2.1ppm [1]. Locally the arsenic concentration can be orders of magnitude higher. For example, many high-grade uranium ores of the Athabasca basin yield up to 10 % by weight arsenic [2]. Therefore many mining/metallurgical operations have to cope with high arsenic concentrations in their tailings. The increasing ecological awareness of toxins and pollutants is resulting in stricter regulations regarding the disposal of arsenic-containing waste rock and/or process solution effluents like uranium solvent extraction raffinates. The reduction of the arsenic threshold in drinking water in 2006 by Canada Health down to 0.01 mg/L reflects this well [3]. The Metal Mining Effluent Regulations by the Canadian Department of Justice prescribe the maximum authorized arsenic concentration in a grab sample to be less than 1 mg/L [4]. This requires the arsenic removal from effluent solutions to be complete and the generated tailings solids, which are usually disposed in tailings management facilities (TMF) in a slurry form, to be environmentally stable for thousands of years.

Arsenic in acidic waste effluents gets treated in continuous co-precipitation (CCPTN) process circuits by lime neutralization. The effluents are neutralized step-wise with $Ca(OH)_2$. This involves several reactors in series with increasing pH. In the process the molar Fe(III)/As(V) ratio is adjusted to $>3$ to ensure better arsenic removal and retention [5]. The co-precipitated tailings may contain a big variety of other ions for example ferrous and aluminum. It is therefore of great interest to investigate if these co-ions can increase arsenic stability in the subaqueous disposal environment.

Using a bench-scale two-reactor circuit as opposed to the typical batch laboratory studies, the McGill Hydrometallurgy group has thoroughly investigated the continuous co-precipitation (CCPTN) process for the standard case of Fe(III)/As(V)=4 both in terms of the process itself and the stability of the co-precipitated solids under oxic conditions. De Klerk determined process parameters for optimal arsenic removal and long-term stability of the precipitates under oxic conditions [6]. Various sources [e.g. 1] reported high ferrous concentrations in the tailings. Another investigation by Daenzer examined the effect of ferrous on arsenic retention [7]. CCPTN experiments with increasing partitions of ferrous (Fe(tot)/As(V) = 4) were conducted and the obtained solids exposed to long-term stability testing under oxic conditions [7]. However within the tailings management facilities reducing conditions may develop over the long-term and this needs to be considered. The increasing depth of the sub-aqueous deposited and buried tailings may result in oxygen starvation. Furthermore microbial and bacterial activity can result in reducing conditions on the solid surface. Concerns have been raised that such reductive reactions can result into arsenic release [8, 9]. Therefore the scope of this work was to produce a variety of Fe(II)/Fe(III)/Al(III)/As(V) co-precipitates in the above-mentioned CCPTN circuit and to evaluate their stability not only under oxic but also under anoxic conditions in long-term equilibration tests. The anoxic conditions were generated by the addition of reducing agents like sulfites and sulfides either via frequent dosing without excluding air - the results of this study are presented in Chapter 3 - or under inert gas ensuring complete air exclusion - the results of the latter study are presented in Chapter 4. The two chapters are structured in the form of manuscripts as per McGill's option, explained in the preface of the thesis.

# 2. Literature Review

The first section of this literature review will be a short introduction of various arsenic immobilization techniques. Afterwards the literature for the co-precipitation of arsenic with ferric as well as the long-term stability of the solids obtained in such processes will be covered especially with regards to reducing conditions (in the following anoxic [$E_h \simeq 0mV$] and sub-oxic [$E_h \simeq 250mV$] conditions). The last part of this literature review will comprise of the precipitation behavior of ferrous and arsenate and the stability behavior of the co-precipitates in anoxic and sub-oxic environments. The stabilizing role of supporting ions such as aluminum will be included.

## 2.1. Arsenic Disposal Practices

Historically there were different methods for the disposal of arsenic. Processes that involved roasting usually captured arsenic as arsenic trioxide fluedust. However arsenic trioxide has, from a disposal point of view, a very high solubility in water (20g/L at 20℃). Therefore the disposal of $As_2O_3$ needs to be in places that are completely surrounded by impermeable rock/mineral. As an example 265.000 tons of $As_2O_3$ were stored in the Giant Mine in Yellowknife as leftover by-product of the gold mine roasting operation [10]. These were stored dry in underground chambers. However concerns of ground water entering the disposal sites arose as a result of permafrost melting. Hence a multi-million dollar project was launched to deep freeze the entire disposal site by liquid $CO_2$ injection [11]. Speaking from an ecological and economical point of view, this is a worst-case scenario. Because of incidents like these arsenic trioxide is not used as an arsenic captor any more.

More recently Ecometales Limited in Chile started treating their arsenic containing flue dusts to recover copper and fix arsenic as scorodite hence solving the problem imposed by arsenic trioixde. After acid leaching the arsenic is precipitated with ferric iron [12]. The crystallization of scorodite is achieved step-wise in a continuous reactor set up to pH=1.5 according to the atmospheric scorodite process developed by the McGill Hydrometallurgy group [13, 14]. For iron deficient arsenic-rich wastes, scorodite represents an excellent arsenic sink due to its high weight percentage of arsenic in the solids (32.5 %). In Japan, Dowa Metals and Mining Ltd. is using their own atmospheric scorodite precipitation to fix arsenic. Because scorodite is stable only under oxic conditions at $pH \leq 7$ [15, 16] Dowa is proposing to wrap scorodite in plastic and bury the bags in concrete tanks [17].

Another approach to arsenic disposal was taken by the Newmont Minahasa Raya gold mine in Indonesia. After gold cyanidation at pH 9-10, ferrous sulfate was added to the effluents to form ferrous arsenate and arsenical ferrihydrite [18]. The tailings were dumped into the sea at 82 m depth and 900 m away from the shore [19]. Concerns have been raised because of the dispersion of the solids into shallower waters [20]. However an environmental monitoring study for the PT Newmont Minahasa Raya by the Centre for Advanced Analytical Chemistry, Energy Technology (CSIRO) did not show any arsenic dissolution in various seawater samples around the disposal site [21].

For process plants with acidic, sulfate containing effluents, the co-precipitation of arsenic (as arsenate) with ferric ion by lime neutralization is by far the best established and accepted arsenic disposal practice [2]. Several uranium mills in Canada are using this process with adaptations to their ore compositions and other elements of concern. [2, 22]. After extraction/precipitation of uranium, arsenic is precipitated with excess ferric. For example, Cameco is using a final pH of 10.5 in their Rabbit Lake Mine [22], while AREVA is coprecipitating arsenic at a final pH of 7-8 at their McCLean Lake Mine [23].

## 2.2. The Fe-As-$H_2O$ system

### 2.2.1. Iron and the Fe-$H_2O$ system

Iron is the second most abundant metal on earth. It occupies 4.7% by weight of the geosphere and has - together with nickel and cobalt - the most stable atom nucleus of all elements. Its favoured oxidation states are +2,+3 and +6. Metallic iron forms a thin oxide layer on the surface, which is not protective (unless alloyed, e.g. in steel). $CO_2$ and the humidity in the earth's atmosphere cause rusting of iron to iron(III)-oxyhydroxides. In aqueous solutions ferric ions hydrolyze into hydrous $Fe_2O_3 \cdot xH_2O$. Pure $Fe(OH)_3$ is not observed [24]. Before precipitation soluble cationic hydroxide complexes (e.g. $Fe(OH)_2^+$) form controlled by ionic strength/pH of the solution [25]. Many Pourbaix diagrams have been published for the system Fe-$H_2O$ at 298.15K. In the pH range of 6 to 11 and an $E_h$ between -500 mV and +500 mV crystalline $Fe_2O_3$ and crystalline $Fe_3O_4$ (magnetite) are the thermodynamically stable phases [26, 27]. A more recent publication however shows a stable region for the ferrous ion up to pH 10 and at progressively decreasing Eh down to -600 mV (see Fig. 2.1).

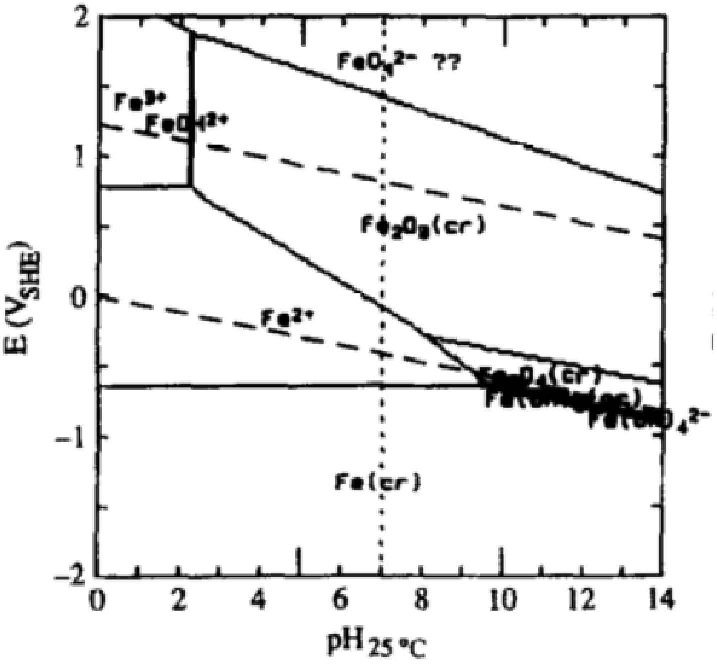

Figure 2.1.: The Fe-$H_2O$ system at 298K [28]

These $E_h$-pH diagrams however do not reflect the kinetics, and the input data to model these systems at steady-state equilibrium have to be carefully chosen to not limit their validity. At lower temperatures the kinetic product is more likely. For example a rapid neutralization of ferric nitrate with alkali to pH 7 at ambient temperatures produces 2-line ferrihydrite, which is a poorly crystalline iron oxyhydroxide (FeOOH) [29]. This homogeneous crystallization results in small particle sizes and therefore high specific surfaces. BET surfaces as high as 350 $m^2/g$ have been reported [30]. Over time ferrihydrite transforms into goethite ($\alpha$-FeOOH) or hematite ($\alpha$-$Fe_2O_3$) depending on temperature and pH [31]. Onto ferrihydrite adsorbed silicates, phosphates and arsenates have been shown to retard the transformation significantly [32–34].

### 2.2.2. Arsenic and the As-$H_2O$ system

Arsenic is an abundant element in the geosphere with the atomic number 33. Its favored oxidation states are -3, +3, +5 [24]. Its toxicity decreases with increasing oxidation state, although metallic arsenic is relatively non-toxic compared to As(III) and As(V). One reason for this being that metallic arsenic is not dissolved in the human stomach or generally speaking by non-oxidizing acids like hydrochloric acid [24]. Arsenite on the other hand has an oral 'Lethal Dose' $LD_{50}$ (mouse) of 26 mg As/kg. Apart from the acute toxic effects it was shown that arsenic is carcinogenic even in small doses. Frequent oral uptake of arsenic is especially carcinogenic for skin, bladder, liver and kidney [35, 36]. According to its position in the electrochemical series, As is dissolved by oxidizing acids (depending on the acid concentration) to form arsenious or arsenic acid [24]. The dominant aqueous species are As(III) and As(V) as arsenite and arsenate respectively.

The oxidation kinetics of As(III) are slow at ambient temperature due to the necessary two electron transfer. For example in air saturated water (with low dissolved iron) As(III) has a half life of nine days, meaning only half of the As(III) is being oxidized to As(V) by dissolved oxygen in nine days [37]. Therefore the behavior of As(III) in the presence of catalysts and various oxidizing agents is especially of interest. Hug et. al used a ~0.5 ppm As(III) solution to measure the oxidation in the presence of $O_2$, $H_2O_2$, Fe(II,III) and ferric (hydr-)oxides. They found that none of these substances alone could oxidize As(III). However the combinations $H_2O_2/O_2$ and Fe(II)/$O_2$ were able to at least partially oxidize As(III) [38]. Leupin and coworkers used zerovalent iron to oxidize 0.5mg/L

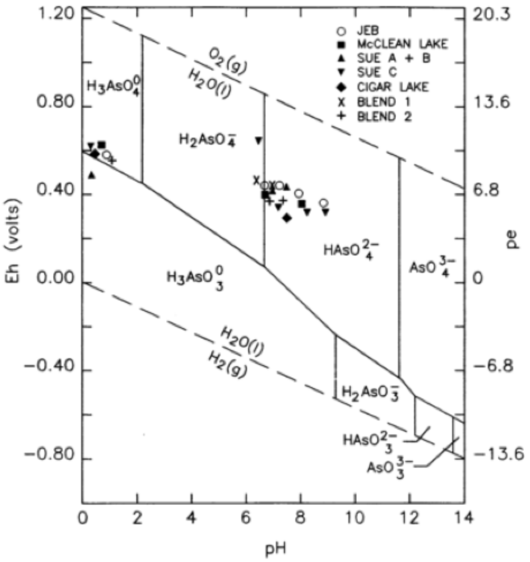

Figure 2.2.: The As-$H_2O$ system [2]

As(III) solutions at pH=7 [39]. In another study the heterogeneous oxidation of As(III) was observed in soils that contained oxides of manganese, aluminum and iron [40]. In hydrometallurgical systems there are different oxidants used for As(III) of which $H_2O_2$ is the most common [41]. Because of its cost however Demopoulos and co-workers have studied and proposed the use of $SO_2/O_2$ instead [42].

The reduction of arsenate to arsenite by dissolved sulfide was reported to be faster at pH=4 than at pH=6.8, but the reduction at neutral pH is very slow ($k_{sp}$ = 1.04 $M^{-1}h^{-1}$ [43, 44]. Rochette *et al.* found the primary reduction products with sulfide to be thioarsenites. Thioarsenates have been identified in the geothermal waters of Yellowknife as intermediate products between arsenite oxidation and arsenate reduction [45].

## 2.3. Co-precipitation and Stability Considerations

### 2.3.1. Co-precipitation of Arsenic with Ferric Iron

According to the US EPA, the co-precipitation of As(V) with ferric iron by lime neutralization is the 'Best Demonstrated Available Technology (BDAT)' [46]. Arsenic is preferably in its pentavalent state because Arsenic(V) co-precipitates with Fe(III) to form environmentally stable products with Fe(III)/As(V)$\geq$3 [2, 5, 47]. Furthermore As(V) is less toxic to most human cells as shown by Styblo *et al.* [48]. Arsenates are also less mobile [49] because they adsorb stronger on iron, aluminum and silica matrices [50]. *Jia et al.* and *De Klerk et al.* were able to show that lime as base improved arsenic removal in the co-precipitation process by up to a factor of 100 [6, 51]. Additionally the staging of the reaction into multiple tanks resulted in higher arsenic removal. On the laboratory scale a two-tank operation was shown to work best [6, 7, 51, 52]. For the sake of completeness it should be mentioned that arsenite co-precipitation has also been demonstrated by Nenov and co-workers. They used an initial As(III) concentration of 3775mg/L. Best arsenite removal was achieved at pH = 9 with a molar ratio of Fe(III)/As(III) = 11 [53]. However such a high molar ratio would be very costly for an industrial operation. Therefore arsenic should be oxidized to As(V) before co-precipitation.

### 2.3.2. Nature of Co-precipitates

#### Poorly Crystalline Ferric Arsenate

The characterization of the solids, that form during co-precipitation, was a difficult task due to their amorphous nature. The prevailing opinion until recently was that ferrihydrite was the most important arsenate controlling phase (more in section 2.3.2). Recent results, however, show that the nature of solids forming during neutralization is dependent on the final neutralization pH. Chen *et al.* were able to characterize tailings from the McClean Lake mine with the aid of EXAFS at the Canadian Light Source [54]. They found that below a pH of 7.5 the solids are co-precipitates of ferric and arsenate with a similar local structure to that of scorodite ($FeAsO_4 \cdot 2\,H_2O$): $FeO_6$ octahedra with bridging $AsO_4$ tetrahedra. This similarity is why ferric arsenate (also: poorly crystalline ferric arsenate - $FeAsO_4 \cdot xH_2O$) is called 'poorly crystalline scorodite' as it possesses less long range order than crystalline scorodite. These findings were later challenged. It was claimed that Chen *et al.* had used false parameters for their fitting for the As K-Edge XAFS and hence came up with a false structure [55, 56]. However Mikutta *et al.* recently published their XAFS results for the local structure of ferric arsenate, which confirms the results of Chen *et al.* [57]. These findings are supported by experimental results from LeBerre *et al.* that demonstrated the rapid transformation from ferric arsenate to scorodite at low pH. They suggested the formation of scorodite within the small range ordered precursor rather than a dissolution-precipitation mechanism [58]. Jia *et al.* were able to show the transformation of arsenate adsorbed on ferrihydrite to surface precipitate of ferric arsenate in acidic conditions (pH 3-5) [59]. Ferric arsenate can be distinguished from ferrihydrite with the aid of 'Powder X-Ray Diffraction'. The two broad peaks of ferrihydrite (34 & 61 degrees 2theta with Cu-K$\alpha$ radiation) are shifted to 28 and 69 degrees respectively in the case of ferric arsenate(see Fig. 2.3).

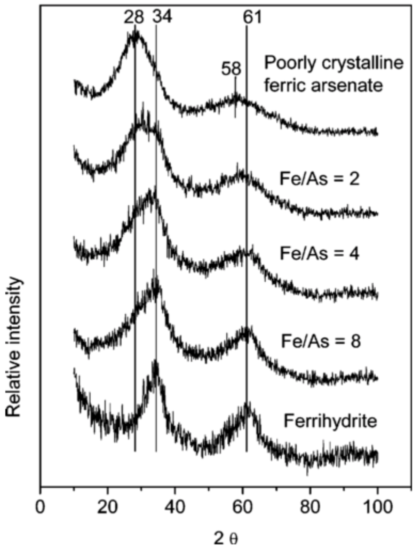

Figure 2.3.: XRD patterns of various co-precipitates compared to ferric arsenate and ferrihydrite with Cu-K$\alpha$ radiation [59]

### Arsenical Ferrihydrite

Ferrihydrite was given a variety of different chemical formulae because of its nanocrystallinity (lack of long-range order). Especially the amount of crystal water varies significantly. For simplicity, this review will use $FeOOH \cdot \frac{1}{2} H_2O$ to describe ferrihydrite [60, 61]. Cornell and Schwertmann published a simple method for ferrihydrite synthesis involving rapid neutralization of a ferric nitrate solution to pH=7 with NaOH [29]. A typical XRD pattern can be found in Figure 2.3.

Due to the excess amounts of ferric (Fe(III)/As(V)$\geq$3) in the co-precipitation process (refer to section 2.3.1) ferrihydrite will precipitate alongside ferric arsenate at pH$\leq$7 or as the main arsenic controlling phase above pH$\geq$7. Ferrihydrite is an excellent sorbent for arsenate. Because of its nanocrystallinity ($\leq$5nm crystallite size [62]) it can have BET surface areas of over 340 $m^2/g$ [63]. Fuller *et al.* measured adsorption densities as high as 0.7mol As(V) per mol of Fe(III) for ferrihydrite [32]. Arsenate adsorbs onto ferrihydrite via mono- and bidentate surface complexation [64]. However there are concerns that ferrihydrite transforms into the thermodynamically more stable goethite or hematite, which has been demonstrated to be a function of time, temperature and pH by Cornell and Schwertmann [65]. The transformation to hematite was complete at 25℃ and pH=4 in only four hours. A transformation to goethite showed reduction in surface area of at least 50%. This reduction of surface area would result in arsenate desorption, because the free and the adsorbed species are in equilibrium and depend on available sorbent as well as on pH [66].

### 2.3.3. Environmental Stability of Fe(III)/As(V) Phases

#### Oxic Conditions

Long-term stability or environmental stability are terms to describe the resistance of the solids against influences from the surrounding environment. These usually consist of chemicals like oxidizing or reducing agents that govern different $E_h$ milieus. A system that is rich in oxidizing agents will display a high $E_h$ and that system will easily accept electrons. These are 'oxic conditions' which are herein defined as $E_h \geq 250$mV at pH=7 (refer to Figure 2.2). Since $E_h$ and pH are correlated, a corresponding oxidizing $E_h$ for pH=10 would be lower ($\approx$ 150mV). Anoxic conditions are the exact opposite ($E_h \leq 0$mV at pH=7). The intermediate region with oxygen starvation is hereafter called 'sub-oxic' or 'oxygen starved' milieu.

The conditions inside the tailings pond are usually slightly oxidizing as reported for the JEB Tailings Management Facility ($E_h \geq 300$mV, pH=7.1)[2]. In the Rabbit

Lake In-Pit Tailings Management Facility on the other hand, the pH is higher (mean pH=9.79) and the $E_h$ averages 162mV [67]. This pH difference plays an important role with regards to which phase is controlling arsenate concentration in the pore water.

In 1981 Robins published thermodynamic estimates for M-arsenate-water systems (M = Fe, Ca, Mg). He concluded that these phases were less stable than previously assumed by incorporating more possible reactions into his model. Namely the $Fe\text{-}AsO_4\text{-}H_2O$ system reached a minimum of $a(AsO_4)=10^{-3}$ moles at pH=2.2. According to his thermodynamic model the activity of arsenate rapidly increases when the pH is de- or increased, reaching 1 molar at pH 0.1 and 5.3 respectively [68]. His results imply a very high arsenate solubility under sub-aqueous disposal conditions, as the pH values are significantly higher than 5.3. However the arsenate concentrations that are found inside the JEB Tailings Management Facility (at $7 \leq$ pH$\leq 8$) are measured as below 2 mg/L [69, 70]. This means that arsenate control in the actual tailings is far more complex and stable than predicted by the model from Robins. This review will attempt to present a variety of factors and observations to explain this discrepancy.

Langmuir *et al.* used PHREEQC, a geochemical modeling software, to re-evaluate thermodynamic data with regards to arsenate solubility from poorly crystalline ferric arsenate, scorodite and ferrihydrite in the tailings [70]. They suggested scorodite to pick up 90-98% of the arsenate during neutralization. Near neutral pH they found scorodite (or more likely poorly crystalline ferric arsenate) and ferrihydrite to be the arsenate controlling phases with log $K_{sp}$ of -25.74 and -37.03 respectively. This is surprising to some degree, as experimental results for congruent dissolution of scorodite, find 50 mg/L arsenate (up to 25 times more than in the actual tailings) at pH=7 [5]. Ferric arsenate, due to its amorphous nature, is up to 100 times more soluble than scorodite at pH=4 according to Krause and Ettel (see Fig. 2.4). There is other published work that finds lower solubilities for ferric arsenate, although this group used models with higher Fe/As ratios than one. [71]. As mentioned in Chapter 2.3.1, a molar ratio of Fe(III)/As(V)≥3 is used for the co-precipitation and therefore ferrihydrite will always be a major (by mol-%) Fe(III) phase in the resulting precipitate. Ferrihydrite plays an important role in arsenate retention especially at discharge pH≥7 because of the high affinity of arsenate towards Fe(III) [72] combined with the high specific surface area of ferrihydrite (refer Chapter 2.3.2).

In their experimental study, Robins *et al.* showed that arsenate removal from solution improved with increasing Fe(III)/As(V) molar ratio. Similarly, the pH range for arsenate removal got wider [73]. This shows the provided stability from ferrihydrite (excess Fe(III) forms ferrihydrite).

Poorly crystalline ferric arsenate and scorodite are the main arsenate controlling phases below pH=7. These phases account for up to 98 % of the arsenate. The rest of the arsenate is associated with ferrihydrite. This observation was also made by Moldovan *et al.* although they did not account for ferric arsenate as their publication was before the findings from Chen *et al.* in 2009. Furthermore they investigated the tailings from the Rabbit Lake mine, which are discharged at a pH=10.8 where all ferric arsenate is re-dissolved [74].

A couple of studies have been conducted on the long-term stability of ferric arsenate and ferrihydrite. De Klerk found less than 1 mg/L of arsenate at a fixed pH=8 and oxic conditions over 1.5 years with Fe(III)/As(V)=4 [6]. Jia and Demopoulos found roughly 0.01mg/L As(V) after 250 days with lime as base under similar conditions as de Klerk [51]. However most laboratory studies [5, 68, 71] exposed freshly produced solids to a variety of conditions (mostly pH)

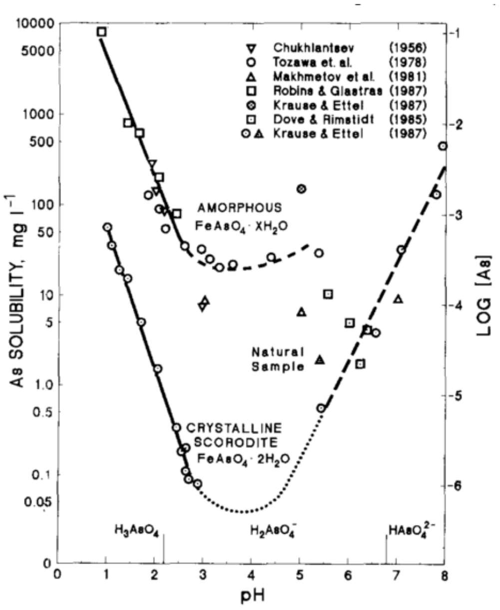

Figure 2.4.: solubilities of ferric arsenate and scorodite [5]

to determine immediate and/or short-term solubility. These tests are important but do not necessarily reflect all possible reactions in the actual sub-aqueous deposited tailings.

In an attempt to predict As release from buried mine tailings Mahoney *et al.* used an EPICS model combined with a laboratory study. They found a mean 0.2% of total As in solids could be readily released, which according to them would not exceed a couple of mg/L [75]. Several studies tried to identify the As-bearing phases in old tailings. Pantuzzo and Ciminelli investigated 9-23 year old gold mining tailings and found up to 75 % of As to be ferric arsenate with the rest being adsorbed onto ferric oxyhydroxides (Fe(III)/As(V)=1.6-4.5, initial discharge pH=8 and pH=13) [76]. Donahue *et al.* found the majority of As to be calcium arsenate in the high pH tailings of the Rabbit Lake In-Pit Tailings Management Facility [77]. Calcium arsenates are known to be unstable due to formation of the thermodynamically more stable calcite with atmospheric $CO_2$ [78]. In 2003 Moldovan *et al.* updated Donahue *et al.'s* findings from the Rabbit Lake In-Pit Tailings Management Facility. According to the new study As(V) was associated with ferrihydrite in the iron rich parts of the tailings [67]. Paktunc *et al.* investigated the Ketza River Mine Tailings and found similar results to those of Pantuzzo and Ciminelli, namely that arsenic is mainly in the form of ferric arsenate and also adsorbed onto ferric oxyhydroxides. They could also detect small quantities of a Ca-Fe-As phase (yukonite) [79].

Summarizing this chapter up to this point, it can be said that ferric arsenate and scorodite are the main arsenate carrier phases up to pH=7. These phases were identified in the actual mine tailings. Although these phases where found to have somewhat higher solubility in laboratory experiments, this is not the case in the tailings, because of the presence of excess ferrihydrite which is needed for optimal arsenate retention. Therefore it can be concluded that arsenate immobilization is achieved by a complex synergy of those phases, whose mixture exceeds the stability of any single phase alone.

Another reason for the great stability of the tailings is the presence of co-ions. Especially $Ca^{2+}$ is crucial not only for the co-precipitation process (refer Chapter 2.3.1) but also for the stability of the co-precipitates. Jia and Demopoulos could show up to 25 times less arsenate in solution after 300 days when lime was used for neutralization instead of NaOH [51, 72]. The same observations were made by de Klerk and Wilkie *et al.* [6, 80]. A possible explanation could be the charge neutralization of $Ca^{2+}$ for adsorbed arsenate. Furthermore it was indicated that $Ca^{2+}$ seems to support bidentate surface complexation of arsenate on ferrihydrite making it less likely to desorb [9] aluminum has also been shown to improve arsenic retention. In a batch experiment Jia *et al.* added a solution of $Al^{3+}$ to a Fe(III)/As(V)=2 co-precipitate at pH=4. Then they raised the pH to 8. The solids with aluminum had approximately eight times less arsenate in solution after 120 days compared to no aluminum present. They did not use lime as base for the co-precipitation hence the high concentration of arsenate (4-33 mg/L) [81]. In a co-precipitation experiment Robins *et al.* demonstrated very efficient arsenate removal with aluminum present, but they only investigated up to 10mg/L $As(V)_{initial}$ [82]. Although Al(III) is known to desorb As(III,V) faster than a corresponding Fe(III) site, the presence of Al(III), for example by substitution into the ferrihydrite matrix, has a very interesting perspective in reducing environments [83, 84].

The role of ferrous that also is found in effluents and tailings [2] has not been extensively studied. Daenzer [7] began investigating the role of ferrous during co-precipitation and long-term stability tests. His results show that up to 50% of ferric can be replaced by ferrous in oxic stability tests and during co-precipitation (with Fe(tot)/As(V)=4) without losing arsenic stability. In oxidation experiments (initial Fe(II)/As(V)=4) with intentional air-sparging, two different rates of Fe(II) oxidation were found. A slow oxidation rate could be attributed to a ferrous arsenate phase and it was concluded that ferrous arsenate has better stability than arsenate adsorbed ferrihydrite and ferric arsenate at pH=8 [7]. Mukiibi *et al.* looked at the effect of Fe(II) on arsenate adsorption onto ferrihydrite. It was found that Fe(II) increased the sorption capacity of ferrihydrite by providing additional soprtion sites [85]. Catalano *et al.* identified symplesite ($Fe_3(AsO_4)_2 \cdot 8\,H_2O$) formation on arsenate adsorbed goethite/hematite under Fe(II) supersaturated conditions [86]. Symplesite has a very low solubility product according to Johnston and Singer and could play a major role in stabilizing $AsO_4^{3-}$ in reducing environments [87]. Another compound of interest is green rust(GR), which is a partially reduced iron hydroxide. Sulfate green rust has the formula $[Fe^{II}_4Fe^{III}_2(OH)_{12}]^{2+} \cdot [SO_4 \cdot mH_2O]^{2-}$ [88]. $FeO_6$-octahedra form a layered structure. Because of the mixed valence Fe(II)/Fe(III) there is excess positive charge, that is countered by incorporating anions between those layers (like $SO_4^{2-}$) [89]. Green rust can be found in mildly reducing soils. Its surface point of zero charge was determined to be at pH=8.3 by Guilbaud *et al.*. Below pH=8.3 the surface has a positive charge, meaning it could adsorb more anions additionally to those in between the layers [90]. Green rust can be synthesized by either oxidation of $Fe(OH)_2$ or co-preciptation of Fe(II) and Fe(III) [91, 92]. As mentioned, anions are incorporated into the green rust structure namely sulfate. Theoretically sulfate could be exchanged with arsenate. This however has yet to be demonstrated. Randall and Sherman investigated the sorption capabilities of sulfate green rust when exposed to arsenate. They found As(V) to adsorb onto the GR surface. They used an initial As(V) concentration of ca. 50*mg/L with a molar ratio of Fe/As(V)≥250* (*numbers derived by this author) and found arsenic to quickly adsorb with levels going below detection limit after less than 20 hours. This observation led them to the conclusion that As(V) was not reduced by GR, because As(III) is less prone to adsorb and therefore As(tot) levels would have increased or at least stayed above the detectable limit [89].

### Anoxic and Oxygen-Starved Conditions

The conditions inside the TMF could change from oxic to anoxic (oxygen depleted) due to microbial/bacterial activity. By-products of the metabolism can be sulfides for sulfate reducing bacteria [93], which would induce locally reducing conditions (≅anoxic). These reducing conditions may become an issue for arsenic retention, because Fe(III) containing solids could undergo a so-called reductive dissolution:

$$\mathrm{FeAsO_4 \cdot xH_2O + e^- \rightleftharpoons Fe^{2+} + AsO_4^{3-} + xH_2O} \tag{2.1}$$

This would release arsenate into the pore waters and increase risk of contaminating adjacent groundwater drastically. McCreadie *et al.* identified this exact problem at the Campbell Mine in Balmertown, Canada, where up to 100 mg/L As (mostly As(III)) were found in aged tailings. The spike in As concentration was linked to free organic carbon that would reduce sulfate and As-carrying hematite:

$$SO_4^{2-} + 2\,CH_2O \longrightarrow 2\,HCO_3^- + HS^- + H^+ \tag{2.2}$$

$$2\,Fe_2O_3 \cdot xH_3AsO_3 + CH_2O + 7\,H^+ \longrightarrow 4\,Fe^{2+} + HCO_3^- + 4\,H_2O + 2\,xH_3AsO_3 \tag{2.3}$$

Ferrous and sulfide precipitate to form FeS. The pH in the reducing zone dropped from 8.3 to 6.6 due to the release of protons during the reaction. The authors concluded that the addition of organic carbon should be avoided in the tailings [94].

Pedersen *et al.* investigated the reduction of ferric matrices with adsorbed arsenate. Only when the provided surface from the ferric matrix for ferrihydrite and goethtie became too small, arsenate was released into the pore water. However lepidocrocite instantaneously released arsenic upon reduction of Fe(III). Fe/As molar ratios of 200 and less were used [95].

Saalfield and Bostick investigated the effect of sulfate reducing bacteria in ferrihydrite rich, artificial groundwater on Fe and S speciation. Magnetite and FeS formation were found without drastic increases in arsenic concentration. Arsenate reduction was found (up to 35% of total As) but the arsenite was not released from the solid phase [96]. In contrast to those results, Burton *et al.* found 'high' arsenite release from goethite covered sand under sulfate reducing conditions compared to abiotic in column eluent experiments at near neutral pH [97]. The abiotic results of that group show 70 % arsenite release into the porewater after 60 days compared to 100 % in the presence of sulfide.

The sulfide was able to reduce 70 % of the goethite and quartz by itself is a bad sorbent for As(III,V). Furthermore, the goethite coated sand only had 460 nmol/g sand of arsenic loading so these results are more interesting for arsenic in the environment outside of a tailings persepctive.

So it is to be noted that when talking about reducing conditions it has to be differentiated between sulfate, arsenate and iron reducing conditions for bacteria (different strains) or when chemicals are used from a thermodynamic perspective for the long-term results. Tufano *et al.* investigated both arsenate and iron reducing conditions on arsenic loaded ferrihydrite and goethite. Iron reducing conditions were found to release minimal arsenic, while arsenate reducing conditions showed the most arsenic released to the porewater. Somewhat surprising is that both effects combined did not result in even higher arsenic release. Overall ferrihydrite exhibited better arsenic retention when exposed to bacterial reduction. The authors proposed a dissolution precipitation mechanism to form magnetite which then scavenges arsenic [98].

Ferrous arsenate reduction was demonstrated with an ANA-3 strain, which resulted in As(III) release at first with subsequent formation of a ferrous arsenite phase [99].

Arsenate-adsorbed ferrihydrite and aluminum substituted ferrihydrite were shown to release minimal amounts of arsenic as arsenite, when exposed to arsenate reducing bacteria. Molar ratios of (Fe+Al)/As=100 were chosen with a final neutralization pH=7.3. The aluminum substituted ferrihydrite released 10 times more arsenite than ferrihydrite (0.08mg/L and 1mg/L respectively). Aluminum hydroxide alone wasn't a sufficient arsenic sink [100]. However, aluminum hydroxides, as they cannot be reduced under naturally occurring conditions, provide stable surfaces for arsenic adsorption in reducing environments. As mentioned above, they are not sufficient for arsenic retention alone and are particularly weak for arsenite adsorption, but nonetheless, their abundance will provide stability by providing additional surface. Even arsenate reduction on the surface of $Al(OH)_3$ does not seem to result in quick arsenite release [101].

Mine tailings from the Delnite goldmine in northern Ontario were characterized by Paktunc in a recent publication (2013) to investigate the influence of a biosolid (≅organic) cover on a tailings management facility that is out of commission. He found most of the arsenic to be fixed in arsenopyrite with a goethite layer around the particles. This goethite layer was reductively dissolved under the biosolid cover because $O_2$ was consumed in the cover layer, which lead to arsenic release (13mg/L). The uncovered samples were stable in the TCLP (Toxicity characteristic leaching procedure) leaching tests [102].

To conclude this section it can be said that there is a lot of research available on bacterial reduction of Fe, S and As in groundwater. The possible reduction of tailings, identified as an issue with McCreadie *et al's* work in 2000 [94] and by more recent field studies, [101, 102] needs further attention. The complex tailings system imposes a lot of challenges in interpreting the various reactions and interaction effects. To this end parallel laboratory studies with simpler systems can provide insight useful in further understanding and optimizing our industrial arsenic waste management practices hence the undertaking of the present study.

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# 3. Long-Term Stability of Continuously Co-Precipitated Fe(II)/Fe(III)/As(V) Solids under Periodic Exposure to Reducing Agents

In this chapter, the first of two manuscript-based chapters, the effect of reducing agents on arsenate-bearing Fe(II)/Fe(III) co-precipitates was investigated. The stability of these co-precipitates against reducing agents is an important factor because a lot of metallurgical operations dispose arsenic by co-precipitation with excess ferric. Reducing conditions can develop in the tailings management facilities because of co-discharged reactive ore components like pyrrhotite, organic chemicals like solvent extraction or flotation reagents or by in-situ bacterial activity. This is potentially threatening for ferric containing solids as they can reductively dissolve. On the other hand, ferrous, as it is already reduced, can have a potentially stabilizing effect by forming insoluble ferrous arsenate and therefore this investigation is of importance for arsenate-bearing tailings.

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Fe(II)/Fe(III)/As(V) solids under periodic exposure to reducing agents”, *Waste Management* (to be submitted - **2013**). [1]

## 3.1. Abstract

Arsenic mobilized during ore processing necessitates its effective removal from process effluents and disposal in environmentally stable tailings. The most common method to accomplish this operation involves co-precipitation with excess ferric iron during lime neutralization. The precipitates produced are stable under oxic conditions. This may not be true, however, under sub-oxic or anoxic conditions that might develop in tailings management facilities. In this context, the potential stabilizing role of ferrous iron on arsenic removal/retention becomes important. As such, this work investigates the removal and redox stability of arsenic with ferrous, ferric and mixtures of both. The removal of arsenic is investigated in a 2-stage continuous co-precipitation circuit mimicking the industrial process and the stability of produced solids is monitored in terms of arsenic release over at least one year. It was found that ferrous is very effective for arsenic (V) removal with Fe(II)/As(V)=4 in the two-stage (pH 6 & 8) co-precipitation circuit reducing its concentration down to <15 ppb via the apparent formation of ferrous arsenate. During long-term stability testing without pH or $E_h$ adjustment it was found that oxidation of Fe(II)-containing co-precipitates goes through a minor spike in arsenic release before arsenic is stabilized through re-adsorption or ferric arsenate formation to below 1mg/L As. The presence of Fe(II) seems to favor an oxidation path towards goethtite (and possibly scorodite) formation in the aged bench-scale tailings. When pH

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[1] It is clarified that the text of the chapter is the same with that of the manuscript. However, occasionally reference is made to additional supporting data found in the form of an Appendix at the end of the thesis that was not included with the submitted manuscript.

and $E_h$ were regularly adjusted via the addition of lime and sulfite or sulfide, slightly higher arsenic amounts were released, ranging from 1 to 5mg/L; ferrous again was found to oxidize due to no air exclusion. Hence, it is concluded that Fe(II)/Fe(III)/As(V) co-precipitates are quite robust against incidental chemical reducing agent exposure like sulfide dosing.

## 3.2. Introduction

Management of voluminous waste tailings generated by the mining and metallurgical industries requires that pollutants are stable over the long term for the protection of the environment. While solidification/stabilization technologies can in principle be used [1] they are not considered economically feasible. Instead the co-precipitation of arsenic(V) with ferric by lime neutralization is a widely used method for arsenic removal from acidic sulfate containing effluents [2, 3]. According to the US EPA, it is the 'Best Demonstrated Achievable Technology (BDAT)' [4]. Laboratory scale research has shown that a molar ratio of Fe(III)/As(V)≥3 is needed for complete arsenic removal [5, 6]. Arsenic is preferably in its pentavalent state due to lesser mobility [7] (i. e. better adsorption on iron, silica and alumina matrices [8]) and lesser toxicity than As(III) [9]

Until recently, it was believed that arsenic was stabilized only through adsorption onto ferrihydrite ($FeOOH \cdot \frac{1}{2} H_2O$) because of the high molar ratio that was needed for arsenic removal [10]. Experimental results from low concentration solutions supported these considerations [11]. Chen *et al.* analyzed mine tailings from the McClean Lake Uranium Mill. They found that co-precipitation can lead to a stoichiometric ferric arsenate ($FeAsO_4 \cdot xH_2O$) phase depending on final neutralizing pH [12]. Other experimental studies support these findings [13, 14]. Ferric arsenate was also shown to precipitate on the surface of ferrihydrite following adsorption at lower pH [15].

Lime as base has been shown to increase arsenic removal by up to a factor of 100 compared to NaOH [16, 17]. Two mechanisms have been proposed how $Ca^{2+}$ ions can benefit arsenic stability:

1. $Ca^{2+}$ can form a Ca-Fe-As phase like yukonite to increase stability [17]
2. $Ca^{2+}$ ions can promote bidentate adsorption of arsenate onto ferrihydrite, increasing adsorption strength [18]

The charge neutralization of adsorbed arsenate by calcium and the additional surface for adsorption provided by gypsum could also play a role.

The discharged tailings are very complex mixtures of elements so many of potentially beneficial or deleterious ions already present can impact on the stability of the tailings and their role has to be investigated. Not much is known about the effect of ferrous, although widely present in acidic leaching effluents and tailings [2, 19].

As shown by the work of McCreadie, reducing conditions can form in the tailings management facilities [20]. These are threatening regarding arsenic remediation as ferric containing solids can undergo reductive dissolution reactions leading to high arsenate concentrations in the pore water and potentially to contamination of surrounding groundwaters. In this context, co-precipitating ions like ferrous, as it is already reduced, are interesting to be looked at, because Fe(II)-As(V) interactions can potentially stabilize arsenic in reducing environments.

There have been some previous studies on Fe(II)-Fe(III)-As(V) systems. Mukiibi *et al.* investigated the effect of pre-adsorbing Fe(II) onto ferrihydrite with subsequent arsenate adsorption. It was found that Fe(II) increased sorption capacity of ferrihydrite [21]. Similar results were obtained by Roberts *et al.* [22]. Proposed stabilizing mechanisms are similar to those of $Ca^{2+}$ [23].

Therefore, the scope of this work is to investigate the release of arsenic from ferrous-containing Fe(II)/Fe(III)/As(V) co-precipitates, produced in a two-stage continuous circuit by lime neutralization [17], when exposed to doses of different reducing agents such as $SO_3^{2-}$ and $S^{2-}$.

## 3.3. Materials and Methods

### 3.3.1. Co-precipitation Circuit and Procedures

For the production of solids, a bench-scale 2-reactor continuous co-precipitation (CCPTN) circuit was used, as descirbed elsewhere [24]. Two reactors with 2L volume (working volume was limited to 1.6L) each were put in series. A 17L feed solution was prepared for each experiment with varying Fe(II)/Fe(III)/As(V) molar ratios between experiments (see Table 3.1) and fed at fixed flow rate to give 1 hour mean tetention time per reactor. For each condition duplicate tests were run as shown in Table 3.1. The pH was kept constant at pH=4 (Tests CD3 and 4) or 6 (CD2) in reactor 1, and 8 in reactor 2, with the aid of peristaltic pumps, which pumped 2M $Ca(OH)_2$ slurry into the reactors. The circuit needed 6.5 hours to reach steady-state [16] after which the slurry was collected for long-term stability tests. pH and $E_h$ values were logged on a computer by pyConsort, an open source software developed by Philippe Tetreault-Pinard. The software can be obtained at http://consort.sourceforge.net.

Table 3.1.: List of continuous co-precipitation experiments with targeted Fe/As molar ratios and initial arsenic concentration

| Exp. name | Fe/As combination used | Molar ratio | As conc. [g/L] |
|---|---|---|---|
| CD2 | Fe(II)/As(V) | 4 | 1.4 |
| CD2b | Fe(II)/As(V) | 4 | 1.4 |
| CD3 | Fe(II)/Fe(III)/As(V) | 2/2/1 | 1.4 |
| CD3b | Fe(II)/Fe(III)/As(V) | 2/2/1 | 1.4 |
| CD4 | Fe(III)/As(V) | 4 | 1.4 |
| CD4b | Fe(III)/As(V) | 4 | 1.4 |

### 3.3.2. Stability Testing Procedure

Solids produced in the co-precipitation experiments were exposed to stability testing under various pH and $E_h$ conditions. After the steady-state solids were collected in the form of a slurry, they were allowed to settle in a 4 L graduated cylinder. Half of the aqueous phase was decanted to double the solid/liquid ratio. Then the slurry was homogenized and filled into four 500 mL wide-mouth nalgene bottles (Fig. 3.1). Every co-precipitation experiment therefore had four samples, which initially were equivalent and then treated differently during stability testing as per Table 3.2. For this series of stability testing three co-precipitation experiments (CD2b, CD3b and CD4b) have been used.

**Sampling**

The slurries were agitated with magnetic stirring for a total of 7.5 minutes. During this time frame the slurries were, depending on the sample type, sampled only, pH adjusted and sampled or pH and $E_h$ adjusted and sampled. Table 3.2

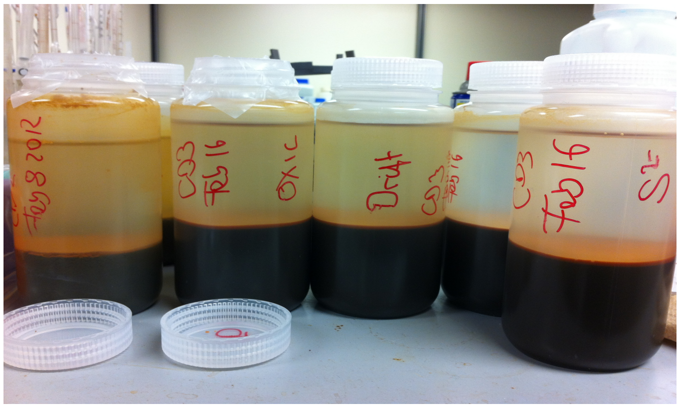

Figure 3.1.: Nalgene bottles used in stability testing

summarizes the adjusted conditions. pH adjustment was done with 1M slaked lime. [2] Table 3.2 shows the adjusted conditions.

Table 3.2.: Stability testing adjustment levels

| Sample | pH | Base | Target $E_h$ | Reducing Agent (0.1M) |
|---|---|---|---|---|
| Drift | - | - | - | - |
| Oxic | 8 | CaO | - | - |
| Sulfite | 8 | CaO | 250 mV | $SO_3^{2-}$ |
| Sulfide | 8 | CaO | 0 mV | $S^{2-}$ |

### pH/$E_h$ adjustment

The slurries were sampled before and after adjustment giving rise to two data points for all samples with the exception of the 'Drift' sample, which was not subject to chemical exposure after production. An example for pH and $E_h$

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[2] The NaOH series data that were essentially the same with the lime series are summarized in the Appendix

progression (with both data points) can be found in Figure 3.2 and Fig. A.11-Appendix.

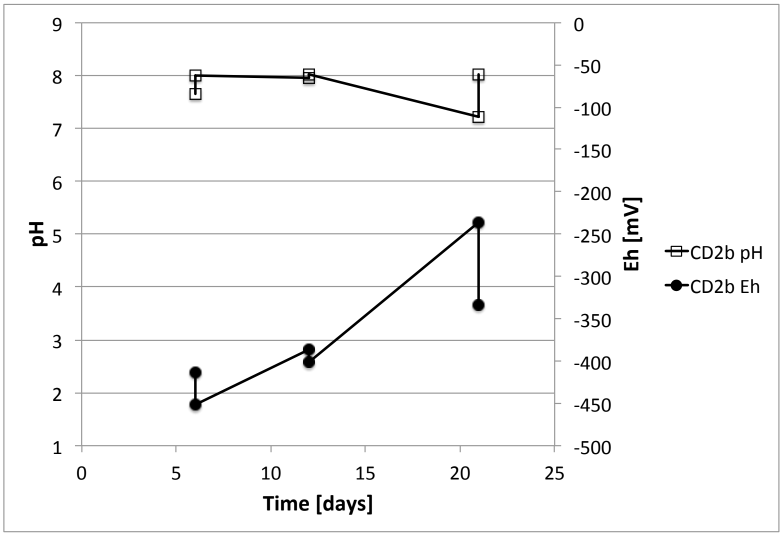

Figure 3.2.: Example for opposite trends in pH-$E_h$ progression with the used before/after adjustment sampling technique (CD2b 'Oxic')

This body of work will focus on the 'after-adjustment' samples to evaluate immediate effects of the added chemicals. [3]

### 3.3.3. Analysis and Characterization

Fe(II) concentration was determined by a modified dichromate titration method. For total Fe(II) a 5mL slurry sample was digested in 20mL concentrated HCl. The solution was diluted with 25mL $H_2SO_4{-}H_3PO_4$ buffer and 50mL DI water. 3 drops of a 0.001N diphenylamine sulfonate indicator were added and titrated with 0.01N $Cr_2O_7^{2-}$ until the color changed to purple.

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[3] All other data can be found in the Appendix.

Total arsenic and iron were analyzed in a Thermo ICAP-6500 axial/radial inductively coupled plasma optical emission spectrometer equipped with Meinhard K-type nebulizer, 50mL cyclonic non-baffled spray chamber and a 2.5mm injector. The radiofrequency generator was set at 1100W. Sample flow rate was 75rpm.

Before conducting characterization of the solids, the final aged solids were washed with water to remove gypsum and avoid thus its interference with co-precipitated product identification (dominant XRD gypsum pattern). For washing about 1.5g of dried solids were immersed in 500mL DI water for one day. It was then filtered and dried for two days at 40℃. XRD patterns for aged solids were recorded on a Bruker Discover D8-2D area detector and Co-K$\alpha$ radiation. [4]

## 3.4. Results and Discussion

### 3.4.1. Co-Precipitation Performance

The feed composition of the various continuous co-precipitation experiments performed using the two-reactor circuit is given in Table 3.3. By following the iron and arsenic concentrations, especially As(V), the effectiveness of the process in removing arsenic below environmentally set limits (in this case 1mg/L) can be evaluated. The target As(V) concentration in all feed solutions was 1.4g/L and the molar ratio of [Fe(II,III)]/[As(V)]=4. Fe(III)/As(V)=4 is used as

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[4] XRD of the Fe(II)-containing feed solids could not be done due to air oxidation of the samples. Similarly as sampling of aged samples was done without excluding air - despite the use of reducing agents during $E_h$ adjustment - ferrous was found to get oxidized. In a subsequent series discussed in the next chapter samples were handled in a glovebox and the oxidation problem was avoided.

a reference sample because it is the standard Fe(III)/As(V) molar ratio in most industrial co-precipitation processes [17]. There are some deviations for the initial concentrations and the molar ratios from the targeted values, which can stem from dilutions for the ICP-OES sample, oxidation of ferrous sulfate and the hygroscopic nature of $As_2O_5 \cdot xH_2O$. Overall the experiments are very close to the targeted values and show good reproducibility.

Table 3.3.: Feed composition for all CCPTN experiments

| | Concentration [mg/L] | | | Molar Ratios | | |
|---|---|---|---|---|---|---|
| Name | Fe(III) | Fe(II) | As(V) | Fe(II)/As(V) | Fe(III)/As(V) | Fe(tot)/As |
| CD1 | - | 4267 | - | - | - | |
| CD2 | - | 4021 | 1420 | 3.8 | - | 3.8 |
| CD2b | - | 3875 | 1295 | 4.0 | - | 4.0 |
| CD3 | 2256 | 1675 | 1410 | 1.6 | 2.1 | 3.7 |
| CD3b | 1792 | 2022 | 1282 | 2.1 | 1.9 | 4.0 |
| CD4 | 3696 | - | 1354 | - | 3.7 | 3.7 |
| CD4b | 3904 | - | 1345 | - | 3.9 | 3.9 |

Figure 3.3 shows an example of iron (in this case ferrous) and arsenic concentration profiles during a co-precipitation test (here: CD2, Fe(II)/As(V)=4). The equivalent plots from the other experiments can be found in the Appendix. As it can be seen in Figure 3.3 the circuit has reached steady-state after 5 hours of operation. For the subsequent stability testing work only solids, generated after steady-state (≥6.5hours) was reached, were used. The two solid black lines are total ferrous concentrations in reactor 1 (triangles) and reactor 2 (circles) respectively. The initial Fe(II) concentration was 4021mg/L. Roughly 10% loss of ferrous per reactor can be attributed to oxidation due to air intake by the agitated reactors. The dashed lines represent ferrous concentrations in the

filtrate. The difference of Fe(tot) and $Fe(II)_{filtrate}$ is the amount of ferrous that precipitated. Almost 90% of the ferrous precipitated. The dotted lines represent arsenic concentrations. Less than 0.5mg/L As was left in solution at the end of the experiment (R2 filtrate). These plots are useful to evaluate not only that steady-state has been reached but also the co-precipitation of As(V) with iron (in this case Fe(II); similar evaluations can be done for the other co-precipitation tests (Table 3.3)). [5]

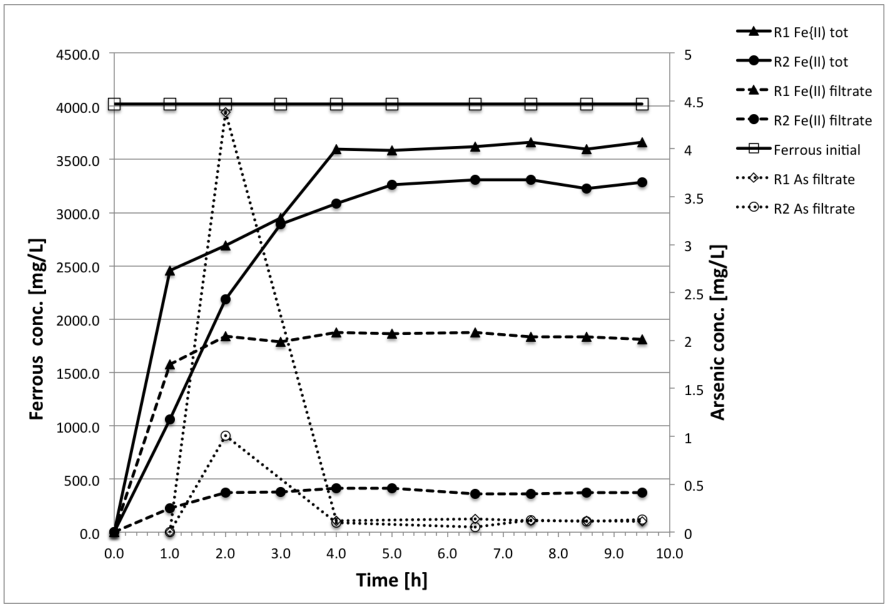

Figure 3.3.: CD2 (Fe(II)/As(V)=4): Ferrous and arsenic concentration profiles during co-precipitation

First of all the amount of ferrous and arsenate precipitated in reactor 1 should be noted (Table 3.4 and Figure 3.3). As a reminder, the pH in reactor 1 was 6. As it can be seen ca. 50% of ferrous precipitated in reactor 1 alongside all arsenate. The Fe(II)/As(V) molar ratios that precipitate in reactor 1 were 1.70 and

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[5] These plots are given in the Appendix.

2.08 for CD2 and CD2b respectively. By comparison in the case of experiment CD1, where only Fe(II) was used, barely any ferrous precipitated without As(V) present, namely 304mg/L of ferrous equalling 8.05% of total Fe(II). When this percentage is removed from the ferrous precipitating in CD2 and CD2b, corrected molar ratios of 1.42 and 1.65 are obtained. This is an indirect indication of precipitation of arsenic as ferrous arsenate corresponding to the formula of symplesite ($Fe_3(AsO_4)_2 \cdot 8\,H_2O$, Fe(II)/As(V)=1.5).

Table 3.4.: Amount of Fe(II) and As(V) For CD1, CD2, CD2b precipitated in Reactor 1 (at pH=6) [mg/L]

| Experiment | Fe(II) | As(V) | Fe(II)/As(V) Molar Ratio |
|---|---|---|---|
| CD1 | 304 | - | - |
| CD2 | 1837 | 1420 | 1.70 |
| CD2b | 1421 | 1295 | 2.08 |

The arsenate removal for Fe(II)/As(V)=4 was as effective as for Fe(III)/As(V)=4 (see experiments CD4/CD4b in Table 3.5) with ≤0.121mg/L of As(V) remaining in solution, which means that well above 99.9% of initial arsenate co-precipitated. When 50% of the ferric is substituted by ferrous (CD3, CD3b) less than 0.1mg/L of arsenate was found in reactor 1, in par with the levels of CD2/CD2b and CD4/CD4b. However in reactor 2 the arsenate values of 1.3mg/L and 1mg/L were surprisingly relatively high. Previous work with the same experimental conditions only found 0.1mg/L As in reactor 2, which fits better into the stability range of CD2/CD2b and CD4/CD4b [19]. The observed somewhat high amounts of arsenate in these experiments (CD3/CD3b) cannot be explained at this point. Since the main scope of this work was the generation of co-precipitates to evaluate their stability under reducing conditions no further investigation was attempted.

Of interest are the widley different $E_h$ values in the various tests (Table 3.5). Thus by focussing on reactor 2 values, it can be seen the higher the Fe(II) concentration the lower the $E_h$ to be: ~-450mV (CD1,CD2,CD2b;Fe(II)= 4g/L), ~-150mV (CD3 and CD3b;Fe(II)=~2g/L) and ~+400mV(CD4,CD4b;Fe(II)=~0g/L, Fe(III)=4g/L). Despite the high variation in $E_h$ co-precipitation of arsenate with iron is very effective. In the next sections, the role of $E_h$ on stability of the co-precipitates was investigated.

Another issue that needs to be commented on is the pH of the first reactor. As described elsewhere the standard pH profile of the two-stage co-precipitation process is 4 in reactor 1 and 8 in reactor 2 [16, 24]. This was the case for experiments CD4/CD4b and CD3b. However, in the case of ferrous containinig feed solutions a higher pH in reactor 1, namely 6, was applied based on the work by Daenzer [19]. In the latter work it was determined that precipitation of ferrous arsenate takes place at pH>5 hence the selection of pH=6 for reactor 1 [25] that proved indeed very effective (Table 3.5 and Figure 3.3). The test with mixed Fe(II)/Fe(III) feed solution (CD3/CD3b) was run with either having pH 4 in reactor 1 (CD3b) or pH 6 (CD3). As it can be seen in Table 3.5 in either case arsenic removal was complete in reactor 1 (≤0.1mg/L As) but there was slightly more arsenic in reactor 2 filtrate in test CD3 (1.3mg/L vs. 1mg/L As in CD3b). It is not clear at this point if this is a significant trend or not and further research is required.

Table 3.5.: Average steady-state values for all CCPTN experiments

| Experiment | Ions | Molar Ratio | R1 As | R2 As | R1 $E_h$ | R2 $E_h$ | R1 pH | R2 pH |
|---|---|---|---|---|---|---|---|---|
| CD1 | Fe(II) | - | - | - | 227.7 | -430.8 | 5.76 | 8.02 |
| CD2 | Fe(II)/As(V) | 3.8 | 0.121 | 0.113 | 84.5 | -478.4 | 6.11 | 7.95 |
| CD2b | Fe(II)/As(V) | 4.0 | * | 0.009 | 45.5 | -457.2 | 6.00 | 7.87 |
| CD3 | Fe(II)/Fe(III)/As(V) | 1.6/2.1/1 | 0.091 | 1.321 | 118.6 | -140.5 | 5.91 | 8.10 |
| CD3b | Fe(II)/Fe(III)/As(V) | 2.1/1.9/1 | 0.095 | 0.976 | 420.4 | -189.4 | 3.96 | 7.78 |
| CD4 | Fe(III)/As(V) | 3.7 | * | * | 734.7 | 393.0 | 3.73 | 7.84 |
| CD4b | Fe(III)/As(V) | 3.9 | 0.017 | 0.013 | 749.1 | 401.5 | 4.02 | 7.99 |

*below detection limit, ≤0.009mg/L

## 3.5. Stability Performance

Steady-state co-precipitates from the different tests were subjected to long-term stability testing by equilibration with water whose pH and $E_h$ conditions were monitored/adjusted on a regular basis. The various stability testing-conditions are summarized in Table 3.2. In the first series labelled 'pH-drift' there was no pH or $E_h$ adjustment applied. In the 'oxic' series, samples were maintained at pH 8 with regular lime (1M) addition without the $E_h$ being adjusted. Finally in the other two series in addition to pH adjustment (pH=8, with lime), 'sulfite' ($SO_3^{2-}$) and sulfide ($S^{2-}$) reagents (0.1M) were added regularly for the purpose of maintaining $E_h$ at a 'sub-oxic' environment (250mV) and an anoxic environment (0mV) respectively. In a previous study Daenzer [19] had considered the long-term stability of similar Fe(II)/Fe(III)/As(V) co-precipitates but only under pH-drift conditions, otherwise the other three series 'oxic' at pH 8, 'sulfite' and 'sulfide' constitute new stability investigations.

### 3.5.1. Stability Performance - pH Drift Series

As mentioned Daenzer [19] has previously investigated the stability of Fe(II) containing co-precipitates under pH drift conditions. For the purpose of continuation and comparison with the present study Table 3.6 summarizes Daenzer's results. As can be seen with increasing Fe(II) the pH drifted towards more acidic values while arsenic release increased marginally exceeding the 1mg/L limit, when Fe(II)/As(V)>2. Similar trends were observerd in the present study that are discussed in detail below.

Table 3.6.: Long-term arsenic release levels from Fe(II)/Fe(III)/As(V) co-precipitates under pH drift conditions reported by Daenzer [19]

| Experiment | Fe(II)/Fe(III) (Fe(tot)/As(V)=4) | [As] Release after ageing at 20℃in mg/L (days) |
|---|---|---|
| RD5 ($pH_{drift}$ 7.1) | 0/1 | 0.1 (550) |
| RD6 ($pH_{drift}$ 6.6) | 1/3 | 0.6 (520) |
| RD7 ($pH_{drift}$ 5.1) | 2/2 | 0.8 (550) |
| RD8 ($pH_{drift}$ 4.6) | 3/1 | 9.0 (520) |
| RD11 ($pH_{drift}$ 5.0) | 4/0 | 2.2 (720) |

The pH and $E_h$ drift as a function of time during stability testing (room temperature ageing) of the various co-precipitates can be seen in Figure 3.4. The Fe(II)/As(V)=4 sample was seen to stabilize at pH=7 after roughly 3 months, a pH that was also reached in the corresponding experiment by Daenzer (see Table 3.6). When ferrous was introduced into the system, the aged samples became more acidic. The drop in pH was proportional to the amount of ferrous present as also observed by Daenzer. Thus the Fe(II)/Fe(III)/As(V)=2/2/1 (CD3b) system stabilized at pH=5 (same as Daenzer - see Table 3.6) while the Fe(II)/As(V)=4 (CD2b) system drifted to a lower pH=3.5.

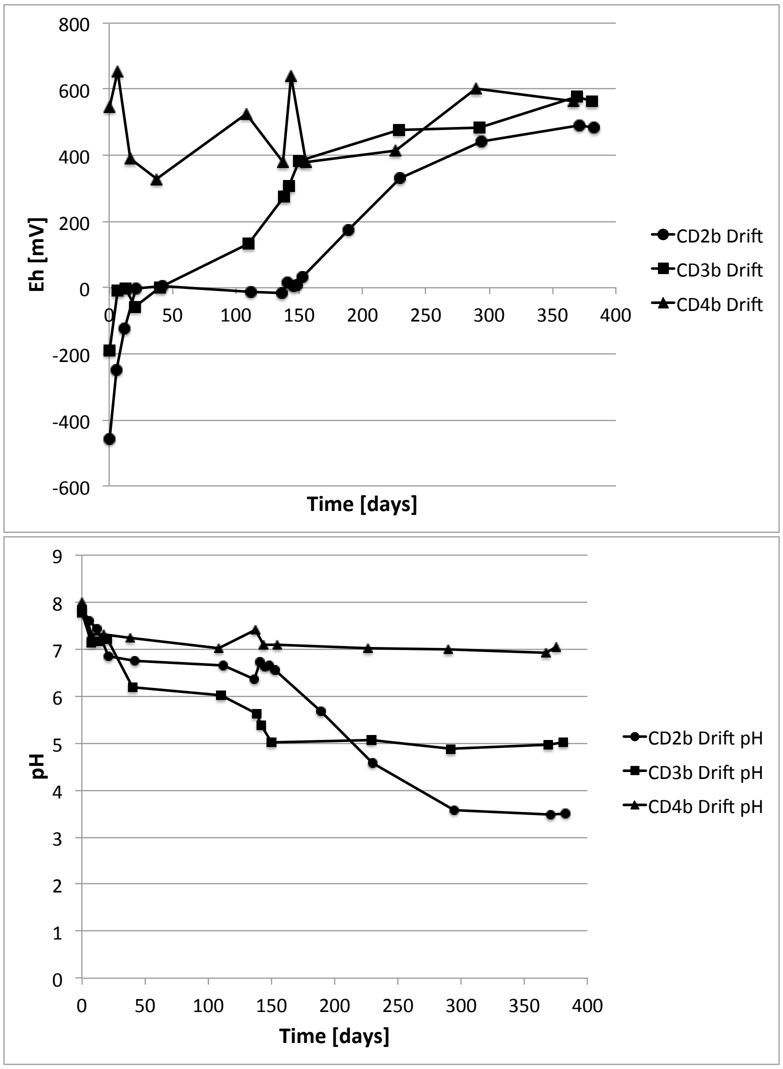

Figure 3.4.: pH-'Drift' series: pH drift (top) and $E_h$ drift (bottom) as a function of time

At the same time monitoring of the total ferrous concentration (data shown in Figure 3.5) revealed its gradual decrease apparently due to oxidation. There was evidence of variable rate of oxidation between soluble ferrous and precipitated ferrous. Thus the CD2b filtrate was found to contain 0.67g/L Fe(II) after 383 days, when the total ferrous remaining was only 0.78g/L, i.e. only about 15% of the non-oxidized iron being in the solids. This means that overall the solids had only 1.5% of total iron as ferrous left after 383 days. The rest has been oxidized to Fe(III). A similar observation can be made for CD3, where after 381 days only 1% of ferrous was left with all of it being in solution.

Looking more closely at the data it can be seen that in CD2b (Fe(II)/As(V)=4) the solid oxidation was complete after 300 days and the pH stayed constant thereafter. In CD3b (Fe(II)/Fe(III)/As(V)=2/2/1), the oxidation was almost complete after 150 days and then the pH stabilized at pH=5. CD4 (Fe(III)/As(V)=4) also experienced a drop in pH down to pH=7 without any ferrous being present. This could be associated with a hydrolysis reaction that is associated with incongruent dissolution of ferric arsenates like scorodite as discussed elsewhere [26].

Both CD2b and CD3b lost approximately 4g/L of ferrous in 150 days. There seems to be an initial phase of rapid oxidation of Fe(II). Afterwards the oxidation slowed down, which could be an indication for different Fe(II) phases in the solids, e.g. association of Fe(II) to As(V) and an arsenate-free Fe(II) phase. In the following reaction sequence the oxidation of symplesite with $O_2$ will be used as an example to show how solid oxidation can lead to a decrease in pH.

$$2\,\mathrm{Fe_3(AsO_4)_2 \cdot 8\,H_2O} + \tfrac{3}{2}\,\mathrm{O_2} \longrightarrow 2\,\mathrm{Fe(OH)_3} + 4\,\mathrm{AsO_4^{3-}} + 4\,\mathrm{Fe^{3+}} + 13\,\mathrm{H_2O} \tag{3.1}$$

The subsequent hydrolysis of $Fe^{3+}$ releases protons:

$$\mathrm{Fe^{3+}} + 3\,\mathrm{H_2O} \longrightarrow \mathrm{Fe(OH)_3} + 3\,\mathrm{H^+} \tag{3.2}$$

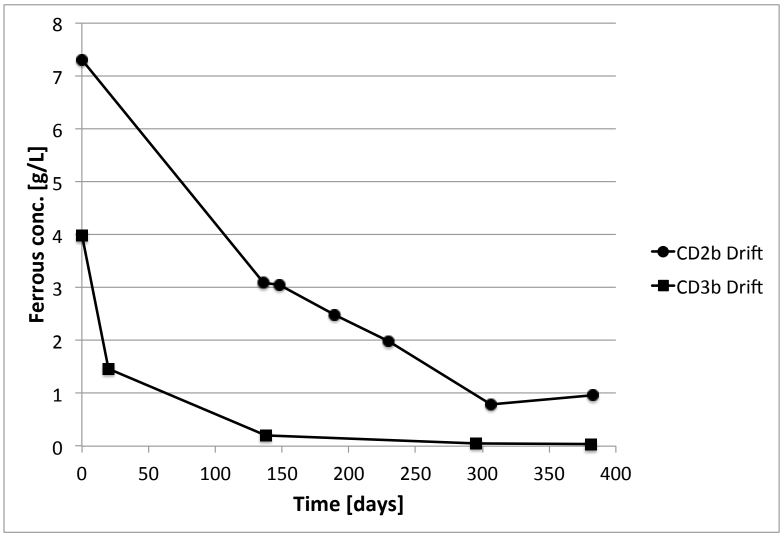

Figure 3.5.: Ferrous concentrations for the 'pH-Drift' series CD2b and CD3b during ageing

Arsenate re-adsorbs on ferrihydrite or precipitates with ferric to form ferric arsenate (FA) without the release of protons:

$$\mathrm{Fe^{3+} + AsO_4^{3-} \longrightarrow FeAsO_4} \tag{3.3}$$

The released arsenic concentration data for the three different drift samples can be found in Figure 3.6. At termination of the experiments, CD2b (Fe(II)/As(V)=4) and CD4b (Fe(III)/As(V)=4) have a similar arsenic concentration of just below 0.5mg/L. However while arsenic release from CD4b gradually increased to reach that point, CD2b exhibits an initial period of approximately 150 days with exceptional arsenic retention. After that point there was a spike in arsenic concentration release, which then lowered to below 0.5mg/L. On the other hand, CD3b (Fe(II)/Fe(III)/As(V)=2/2/1) despite the almost 1mg/L As reported during co-precipitation in reactor 2 (Table 3.5) for over 100 days had its arsenc release stabilized below 0.1mg/L at the same level as the other two co-precipitates (CD2b and CD4b). After that arsenic release increased and stayed more or less stable at the 2-2.5mg/L level, i.e. a bit higher than the other two co-precipitates.

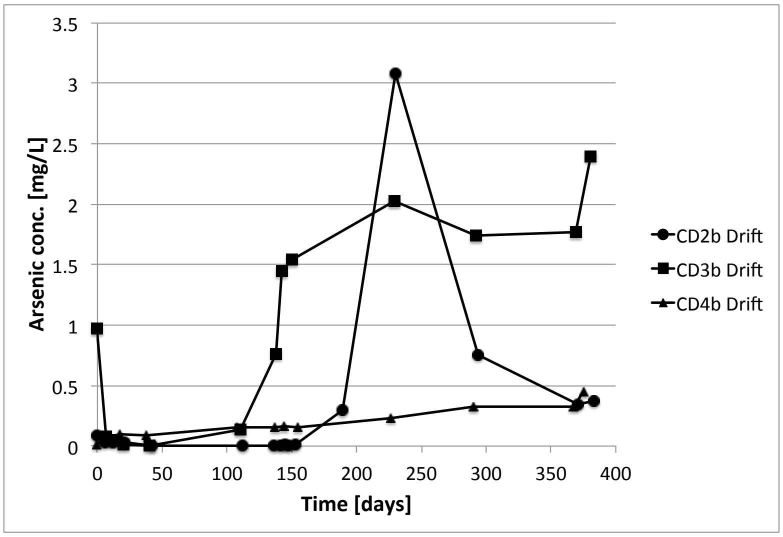

Figure 3.6.: Arsenic concentration for the 'Drift' series

The origin of the 'jump' by CD3b is not clearly understood. After all ferrous is oxidized the sample should behave like CD4b and CD2b at day 385. The spike in arsenic concentration for CD2b after day 189 is interesting, if it is indeed real and not an artifact of a single erroneous sampling point. Arsenic concentration begun to increase after day 149. The same day the total ferrous concentration (slurry digestion) was measured to be 3.05g/L with 0.56g/L of ferrous in solution.

The molar ratio of the resulting 2.49g/L Fe(II) in the solids to 2.59g/L of As(V) equals 1.29. [6] As established in the co-precipitation section 3.4.1 this is very close to symplesite (1.5). Hence it is possible that the oxidation of the ferrous arsenate precipitate that formed during co-precipitation led to arsenic release (spike over the period 200-300 days). The subsequent drop can reflect arsenic scavenging by Fe(III) to form ferric arsenate and/or arsenical ferrihydrite (see Equations 3.1, 3.2 and 3.3). For CD3b, the arsenic concentration increased drastically after all the ferrous was oxidized. Despite certain differences in the final arsenic release levels (especially in the case of CD3b) the generated results suggest that ferrous or mixed ferrous/ferric can essentially stabilize arsenate over the long term the same way as ferric alone, as long as the molar ratio is Fe(II,III)/As(V)≥4 and drift oxic conditions prevail.

The oxidation of the ferrous-containing co-precipitates to ferric equivalent compounds was also confirmed by XRD analysis as shown in Figure 3.7. Reference patterns for ferrihydrite synthesized as described elsewhere [23] and yukonite synthesized in our facilities are included. Other reference spectra retrieved from the PDF-cards given, are goethite, 6-line ferrihydrite and scorodite.

Distinction between arsenical ferrihydrite and poorly crystalline ferric arsenate is not straight-forward because of their similar two broad peaks [14, 27]. Comparing CD4b (Fe(III)/As(V)=4) to the reference spectra shows that the aged sample has the main ferrihydrite features. However, the presence of the shoulder at 35° 2-theta along a slight peakshift of the two broad peaks to the left may be taken as evidence of co-existence of poorly crystalline ferric arsenate [14]. The small, sharp peaks in CD4b are background peaks from the aluminium sample holder due to inadequate sample amount.

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[6] The use of g/L as a unit stems from the direct subtraction of the values mentioned above to avoid altering the results with the incorporation of solid/liquid ratios that were complicated to determine due to ferrous oxidation during drying of the solids.

CD2b and CD4b feature the two broad peaks as well but this time there are additional small sharp peaks revealing the appearance of crystalline phase features. As such, goethite has been identified to be present possibly resulting from crystallization of ferrihydrite and scorodite crystallizing from ferric arsenate [28]. There seem to be more crystalline phase peaks present the higher the initial ferrous content. Most of these peaks appear to indicate goethite formation as well as 6-line ferrihydrite and for CD2b (pH=3.5) possibly scorodite. The amount of initial Fe(II) seems to be the determining factor as to how much goethite is formed (compare CD2b and CD3b). Although all ingredients were present for the formation of yukonite, this phase was not found in the XRD probably because of the low sample pH (Figure 3.4) [17, 26].

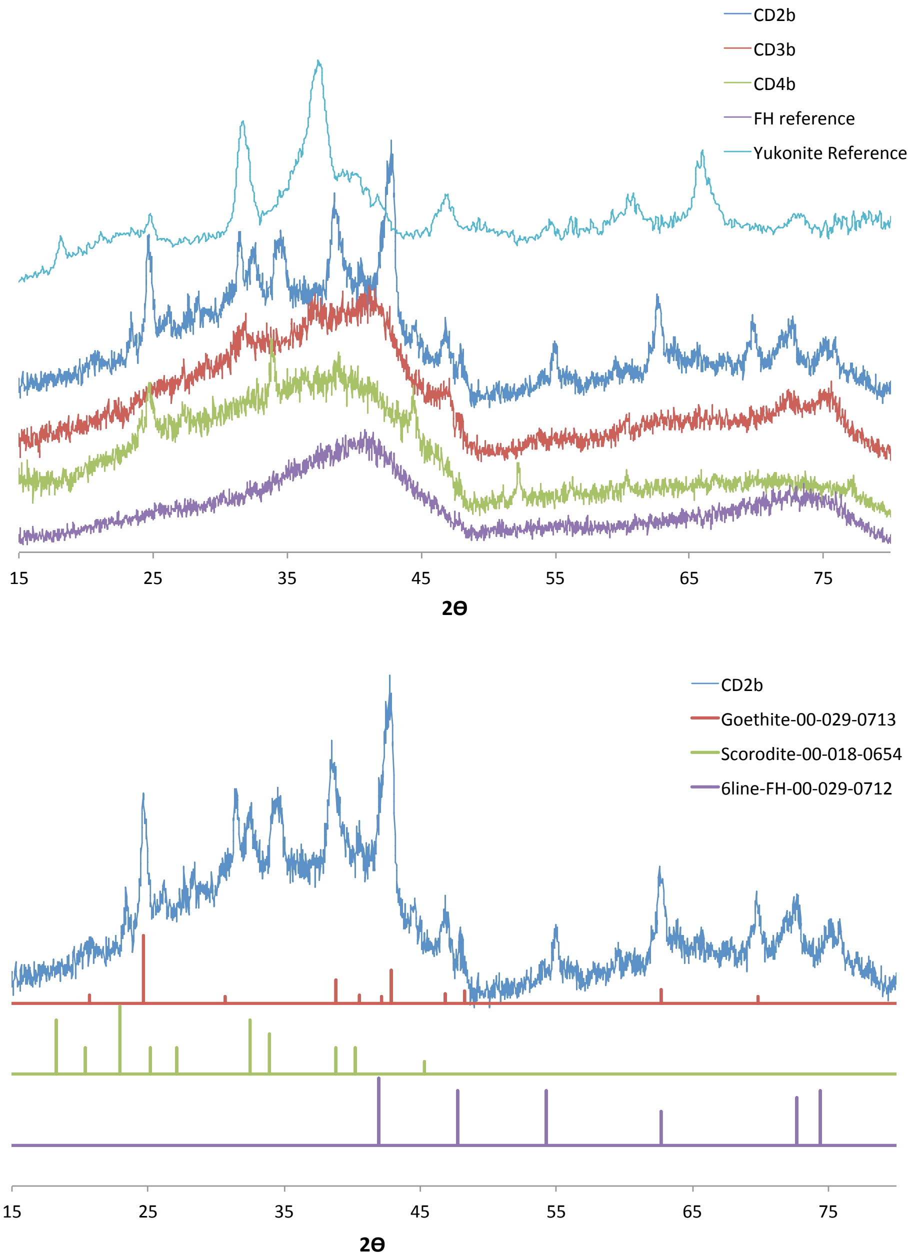

Figure 3.7.: XRD patterns for CD2b/CD3b/CD4b 'Drift' series at termination of experiments vs. ferrihydrite(FH) and yukonite reference (Top) and CD2b 'Drift' series vs. goethite, scorodite and 6line-ferrihydrite (Bottom)

### 3.5.2. Stability Performance - Oxic Series at pH=8

The 'Oxic' stability series involved adjustment to pH=8 with slaked lime. Samples were taken before and after adjusting the pH. The variation of pH as a result of this pH adjustment sequence is described in Figure 3.8. [7]

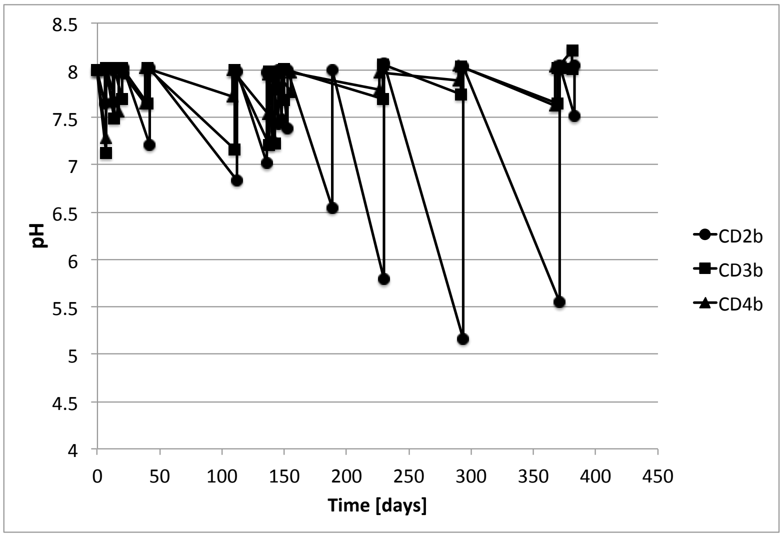

Figure 3.8.: pH progression for the 'Oxic' series

As it can be seen similar to the data presented in the previous 'pH-drift' series section, the pH drifted towards the acidic region. Apparently the pH decreased due to proton release via the incongruent dissolution mechanism already described. This was more pronounced in the case of Fe(II)-containing co-precipitates. It is obvious that pH adjustment results in higher arsenic release than the case of free pH drift (section 3.5.1) but the system shows considerable capacity for 'self-control' following pH adjustment. As the arsenic release values following pH adjustment represent the 'worst-case' scenario,

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[7] The corresponding variation in $E_h$ is presented in Figure A.7-Appendix.

here we will compare the stability performance of the three different composition co-precipitates on that basis. The relevant data are presented in Figure 3.9.

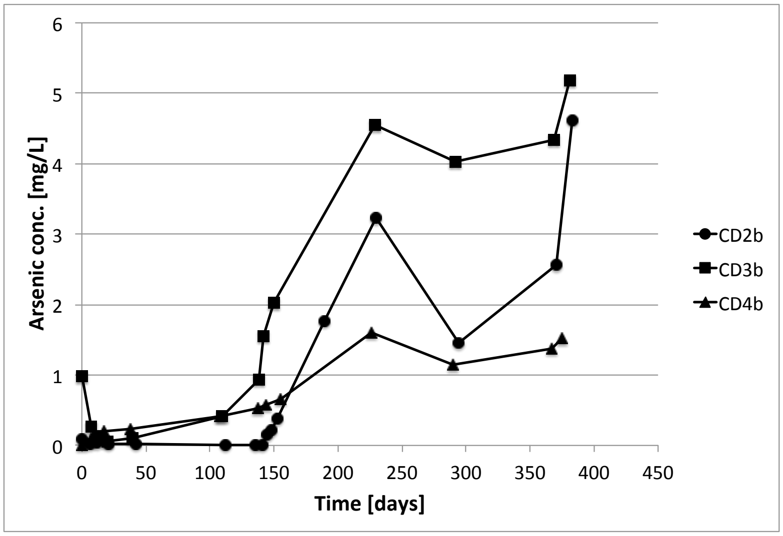

Figure 3.9.: Arsenic concentration for all 'Oxic' (pH=8) samples

As it can be seen in this case the release of arsenic increased over time for all co-precipitates. The trends are initially very similar to the 'Drift' series (section 3.5.1) just the amount of released arsenic concentration is higher. For CD2b (Fe(II)/As(V)=4) the spike in arsenic concentration after day 148 is similar to the corresponding 'Drift' test with the exception that arsenic stays in a plateau (stabilized at 2-3mg/L As) and not dropping. CD4b (Fe(III)/As(V)=4) follows the trend of the same 'Drift' co-precipitate from the same series with roughly 2.5 times more arsenic at termination of the experiment. CD3b 'Oxic' also exhibits a similar trend compared to the CD3b 'Drift' co-precipitate with 2.5 times more arsenic in solution. Here it is necessary to comment on the last data points of CD2b and CD4b that show a relatively high increase in [As]. These should not be used as indication of progressive climbing in arsenic release. More likely they represent analytical difficulties because of ICP instrument problems that could not be rectified on time for the needs of this project.

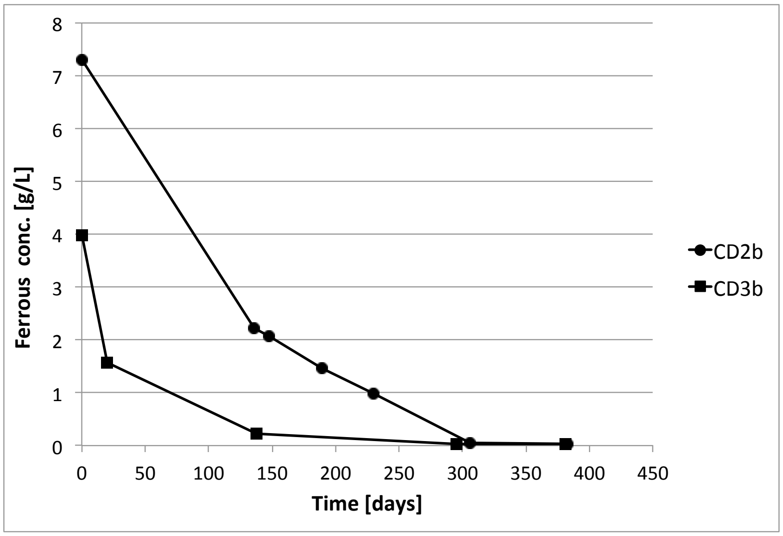

Figure 3.10.: Oxidation of ferrous in CD2b/CD3b 'Oxic' samples

Overall the reference system CD4b (Fe(III)/As(V)=4) had the best arsenic retention but it should be pointed out that CD2b (Fe(II)/As(V)=4), before undergoing oxidation of more than 66% Fe(II), had exceptional stability (day 136 and before). Figure 3.10 shows the oxidation of ferrous during the long-term stability testing. It can be seen that both co-precipitates needed about 300 days to completely oxdize. After day 136 the arsenic concentration for CD2b begun to spike as a result of oxidation of ferrous arsenate. Analysis of Fe(II) in the solids (by digestion) and solution (day 136) indeed indirectly confirmed the initial presence of ferrous arsenate as the composition was 2.23g/L of ferrous that gives a molar ratio of 1.15 when compared to 2.59g/L of arsenic. The oxidation of the solids was further evidenced by XRD analysis. [8] Similar patterns as with the 'pH-drift'

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[8] Relevant patterns are shown in the Appendix A.8.

series were obtained although in this case the goethite formation signs were less pronounced apparently due to the adjustment of pH and therefore higher pH over time.

### 3.5.3. Stability Performance - Effects of Sulfite $SO_3^{2-}$ Addition

Additionally to adjusting the pH with slaked lime, in this series the co-precipitates were exposed to frequent sulfite (0.1M $SO_3^{2-}$) addition. Sulfite is a modest reducing agent at pH~8 and this experiment therefore represents a sub-oxic environment, an intermediate between the 'Oxic' and 'Sulfide' series. In particular in this series the target $E_h$ was 250mV. The evolution of $E_h$ for the three co-precipitates during stability testing (after adjustment with sulfite addition) is shown in Figure 3.11. The detailed $E_h$ data before and after adjustment are given in Table A.2 in the Appendix. As it can be seen in Figure 3.11, the $E_h$ increased with time because of the inevitable exposure to air during sampling. Initially up to 150 days for CD3b and 300 days for CD2b the $E_h$ remained below the target 250mV. The CD4b had an $E_h$ varying between 250 and 350mV almost the same with that of the 'Oxic' series. [9]

The progression of the released arsenic concentration can be found in Figure 3.12. Again the trends are the same as for the 'Drift' and 'Oxic' series, but just as before the arsenic concentrations vary. For CD2b (Fe(II)/As(V)=4) the arsenic levels are a bit lower (~2.5 vs. 3.5mg/L) than without $SO_3^{2-}$ present but almost the same for the CD3b series. On the other hand there was more arsenic released in the $SO_3^{2-}$ series for CD4b (Fe(III)/As(V)=4) than in the 'Oxic' series, namely 2.5 vs. 1.5 mg/L. Overall however no drastic destabilizing effects were introduced by exposing the co-precipitates to periodic sulfite dosing under non-air exclusion conditions.

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[9] Refer to Figure A.7-Appendix

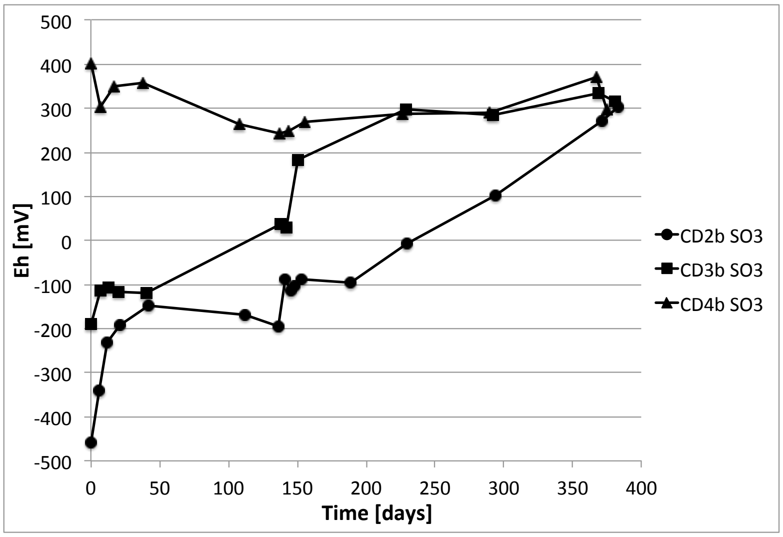

Figure 3.11.: $E_h$ progression for all 'Sulfite' samples after-adjustment samples in mV

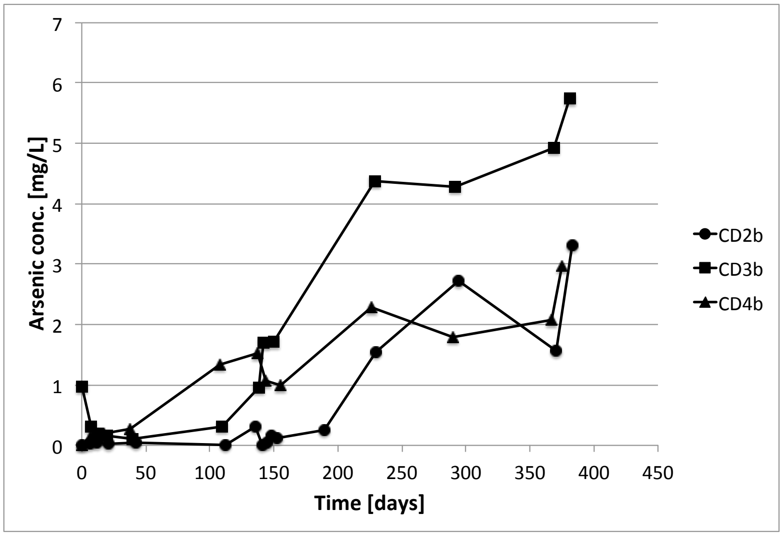

Figure 3.12.: Arsenic concentration for the 'Sulfite' samples during long-term stability testing

As suggested by the $E_h$ data of Figure 3.11 the environment became progressively more oxidizing. This was confirmed by chemical analysis. [10] It is apparent that the addition of sulfite did not prevent the oxidation of ferrous. Similarly, the XRD patterns for the 'Sulfite' co-precipitates were found to match those of the 'Oxic' co-precipitates. [11] Therefore it can be concluded that $SO_3^{2-}$ does not have any significant adverse impact on the co-precipitates' stability, when air is not excluded. Moreover this implies high stability of the produced solids, because regardless of chemical and mechanical agitation the released arsenic levels are still comparably low, especially if we take into account, that the slurries contain ~2.8g/L of As(V) which is all co-precipitated in the solids. [12]

### 3.5.4. Stability Performance - Effect of Sulfide $S^{2-}$ Addition

This series of long-term stability testing was conducted with sulfide (0.1M) addition and the pH was adjusted to pH=8 with slaked lime. The adjustment of $E_h$ and pH coincided with sampling points. Sulfide is a strong reducing agent, stronger than sulfite, and in this case the target $E_h$ was 0mV. The evolution of $E_h$ for the three co-precipitates during stability testing (after adjustment with sulfide addition) is shown in Figure 3.13. [13] As it can be seen in Figure 3.13 the target $E_h$ of 0mV was consistently achieved after sulfide addition proving the reducing effectiveness (much stronger than sulfite) of this reagent. However, between adjustments - coinciding with sampling - the $E_h$ tended to increase (as also happened with sulfite) with time due to air infiltration. A good measure of

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[10] The ferrous concentration-time data can be found in Figure A.9 in the Appendix.

[11] Data in Figure A.10-Appendix.

[12] Here g/L is the total concentration obtained by digestion of the slurry's solid phase. Subtraction with filtrate concentration determines the amount of As(V) that is co-precipitated.

[13] The detailed $E_h$ data before and after adjustment are given in Table A.3 in the Appendix.

the ’up-and-down’ $E_h$ variation can be obtained by reviewing the actual data for the CD2b test, shown in Figure 3.13 (Right). Up to ~200 days the $E_h$ did not rise above 100mV. This was helped by the relatively frequent addition of sulfide but also the presence of large excess of ferrous. Despite this frequent sulfide addition however oxidation of Fe(II) in CD2b (and CD3b) occurred even then the $E_h$ was <100mV as it can be seen in Figure 3.13. Thus after 200 days more than 70% of Fe(II) in CD2b has been oxidized. The oxidation was essentially complete after 150 days in the case of CD3b and after 300 days in the case of CD2b - note double the time required for double the ferrous quantity. The full oxidation of the solids was also evident from the XRD patterns that had the same features as found previously for ’Oxic’ and ’Sulfite’ solids. [14]

The arsenic concentration released from the different co-precipitates during the $S^{2-}$ stability testing series is presented in Fig.3.14 (Note that all these data are from samples collected after $E_h$ adjustment to 0mV. [15]

At completion of the stability testing after one year, CD4b (Fe(III)/As(V)=4) had the highest arsenic concentration at 1.74mg/L, a concentration that is almost the same with the CD4b ’Oxic’ sample. Similar values were obtained for CD2b (Fe(II)/As(V)=4). CD3b (Fe(II)/Fe(III)/As(V)=2/2/1) had the lowest arsenate release with about 0.77mg/L, which is also a lot lower than the CD3b ’Oxic’ sample (5.18mg/L). Before these low values were attained, all co-precipitates went through a spike in arsenic release, similar with that observed in the ’Drift’, ’Oxic’ and ’Sulfite’ series. This apparently as already discussed is most likely linked to oxidation of the ferrous arsenate phase with subsequent arsenate fixation via adsorption on ferrihydrite and ferric-arsenate

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[14] Data provided in Figure A.13-Appendix.

[15] There was a small difference between arsenic release data before and after adjustment (see Fig. A.12-Appendix).

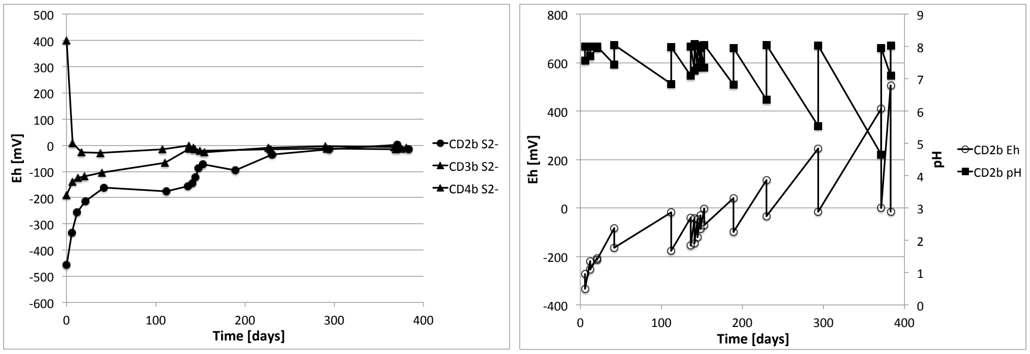

Figure 3.13.: $E_h$ progression for all 'Sulfide' after-adjustment samples in mV (Left) and $E_h$-pH progression before and after adjustment for CD2b $S^{2-}$ (Right)

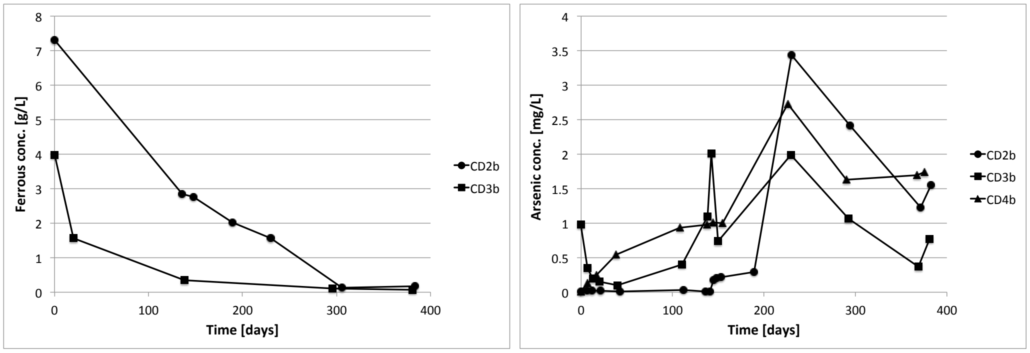

Figure 3.14.: The oxidation of Fe(II) for all 'Sulfide' samples (Left) and the arsenic concentrations during stability testing for all 'Sulfide' samples (Right)

formation.

Overall the arsenic release data are truly remarkable considering that an aggressive reducing agent like sodium sulfide was used and the $E_h$ potential was kept below 0mV for at least 200 days-see Figure 3.13(Right). The 'sulfide' samples overall show surprisingly low arsenic release. It is possible that the added $S^{2-}$ actually helped 'stabilize' arsenate rather than releasing more for CD2b and CD3b. Although the sulfide could precipitate arsenic to form $As_2S_3$ the latter is unstable in oxidizing environments and relatively soluble [29], therefore expected to redissolve eventually. Although mechanistically a number of questions remain, the fact is that the Fe(II)/Fe(III)/As(V) co-precipitates remained essentially unaffected by exposing them to a strong reducing agent ($S^{2-}$) in a non air-tight environment.

## 3.6. Conclusions

From the data presented in the previous sections the following general trends/-conclusions can be drawn:

- Arsenate co-precipitation with ferrous iron is very effective and achieves comparable levels as Fe(III)/As(V) co-precipitation with well above 99.9% arsenate removal.
- Comparing the two-reactor continuous co-precipitation tests with Fe(II)/-As(V)=4 to Fe(II) only reveals possible symplesite formation in reactor 1. Ferrous arsenate co-precipitate remains stable until it is oxidized.
- Drift pH leads to more stable precipitates (due to lower attained pH) than adjusted/fixed pH (at pH=8) even when only Fe(II) is used.

- Maintenance of anoxic conditions via frequent reducing agent addition without strict air exclusion is difficult; in both systems ($SO_3^{2-}$ and $S^{2-}$), $E_h$ shifts to higher values. As a result Fe(II) tends to oxidize over time even when $S^{2-}$ is used as reducing agent.
- Oxidation of Fe(II)-containing co-precipitates goes through a minor spike in arsenic release before arsenic is stabilized through re-adsorption or ferric arsenate formation. The presence of Fe(II) seems to favor an oxidation path towards goethite (and possibly scorodite) formation in the aged bench-scale tailings.
- Arsenic release is higher (but still) 'reasonable' when reducing agents are used, e.g. arsenic release remains below 2 mg/L even after one year ageing proving that Fe(II)/Fe(III)/As(V) co-precipitates are quite robust against intermittent chemical reducing agent exposure like sulfides.

## 3.7. References

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# 4. Stability of Arsenate-Bearing Fe(III)/Al(III) Co-Precipitates in the Presence of Sulfide as Reducing Agent under Anoxic Conditions

In the previous chapter a variety of Fe(III)/Fe(II)/As(V) co-precipitates were produced in a two-stage continuous circuit and subjected to long-term stability testing by exposing them to infrequent dosing with sulfite and sulfide reducing agents. It was found that pure Fe(II)/As(V) co-precipiates compared very well in terms of arsenic removal to their ferric counterparts. The ferrous/ferric mixtures also gave satisfactory results. During their subsequent stability testing it was discovered that the ferrous content of the co-precipitates progressively decreased via oxidation by air during sampling despite the use of reducing agents. The $E_h$ in other words could not be kept at reducing conditions continuously under normal air atmosphere. Ultimately with minor differences all Fe(III)/Fe(II)/As(V) co-precipitates were found to oxidize and provide effective arsenic stability. However, the question remains what will happen to the co-precipitates in terms of stability if air is completely excluded, i.e. if a truly anoxic environment is maintained. To answer this question the work reported in this chapter was undertaken in which Fe(III)/Al(III)/As(V) co-precipitates are subjected to stability testing using excess sulfide as reducing agent under inert gas in a glove-box. Two types of co-precipitates were tested, which again were produced via the two-stage continuous circuit, one with the standard Fe(III)/As(V)=4 molar ratio and one with mixed Fe(III)/Al(III)/As(V)=2/2/1 molar ratio. In the latter aluminium was incorporated as it cannot be reduced, hence it was of interest to evaluate its stabilizing role in an anoxic environment. No ferrous was initially added as its formation by reduction of Fe(III) in-situ during stability testing had to be monitored.

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## 4.1. Abstract

Currently, the co-precipitation of arsenate with ferric iron at molar ratio Fe(III)/As(V)$\geq$3 by lime neutralization produces tailings solids that are stable under oxic conditions. However not much is known about the stability of these hazardous co-precipitates under totally anoxic conditions. Anoxic conditions can develop in tailings storage sites by the action of co-discharged reactive sulfides, organic reagent residuals or bacterial activity. The ferric matrix can then

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[1] It is clarified that the text of the chapter is the same with that of the manuscript. However, occasionally reference is made to additional supporting data found in the form of an appendix at the end of the thesis that was not included with the submitted manuscript.

undergo reductive dissolution reactions which are potentially harmful triggering arsenic release to the surrounding groundwaters. Co-ions like hydrolyzed aluminium could provide a redox-immune sink to scavenge any mobilized arsenic as a result of reduction of ferric. As such, in this work Fe(III)/As(V)=4 and aluminium substituted Fe(III)/Al(III)/As(V)=2/2/1 co-precipitates were produced in a mini continuous co-precipitation process circuit and subjected to excess sulfide ion addition under inert gas to evaluate their stability. It was found that the ferric-arsenate co-precipitate could retain up to 99% (30mg/L in solution) of its arsenic content despite the high pH (10.5) and extremely reducing ($E_h$ <-200mV) environment generated by the sulfide addition. There was only 45% of ferric reduced although enough reduction equivalent was present to reduce all Fe(III) present. Further there was no significant reduction of arsenate by sulfide, nor evidence of arsenic sulfide formation. Partial aluminium substitution was found to cut the amount of mobilized arsenic by 50% (15mg/L) hence mixed Fe(III)/Al(III)-arsenate co-precipitates may offer better resistance to reductive destabilization over the long term than all iron co-precipitates.

## 4.2. Introduction

Mine tailings have to be stable for thousands of years after the mining operation ceases. This requires the discharged tailings to be stable under a variety of storage conditions. For arsenic the stabilizing phases, produced by co-precipitation with lime neutralization, are ferric arsenate ($FeAsO_4 \cdot xH_2O$) and arsenate adsorbed ferrihydrite ($FeOOH \cdot \frac{1}{2} H_2O$ [1–3]. Several studies have investigated their stability in oxic conditions in terms of pH and Fe(III)/As(V) molar ratio [4–6] as well as neutralization medium and conclcuded the co-precipitates to be stable under oxic conditions [7, 8]. However, organic matter acting as complexing or reducing agent [9, 10] or inorganic or biologically-generated reducing species like sulfides can cause the destabilization of the iron(III)-arsenate containing tailings solids. Although solidification/stabilization technologies [11] are available for arsenical hazardous wastes, they are not suitable for voluminous mine tailings such as those generated by uranium mines in Northern Saskatchewan, Canada [12]

McCreadie *et al.* [9] found high arsenic concentrations in old mine tailings pore-waters at the Campbell Mine in Balmertown, Canada, where according to the authors residual organics caused the destabilization of iron(III)-arsenate containing solids via reduction of ferric and arsenate to ferrous and arsenite respectively. The concurrent sulfate reduction resulted in the release of protons and therefore a drop in pH [9]. Harris in a review paper [13] raised the possibility of reductive destabilization of ferric arsenate tailings, like the ones considered by McCreadie *et al.* [9], by co-deposited reactive sulfides such as pyrrhotite. So far it appears that mainly the reduction of ferrihydrite and ferrihydrite loaded with arsenic has attracted research attention. Arsenical ferrihydrite, for example, has been shown to reductively dissolve by chemical reducing agents such as hydroquinone [14]. Co-precipitated arsenate and ferrihydrite were shown to release less arsenate compared to arsenate-adsorbed on pre-prepared ferrihydrite. Ferrihydrite has been further shown to be reductively dissolved by bacteria at high pH (9.5) [15] and neutral pH (7.1) [16]. Bacterial sulfate reduction was also shown to lead to formation of ferrous sulfide. Arsenate, however, was not released from the solids in the process. The authors suggest reduction to arsenite being a crucial step for arsenic release into solution [17].

In the context of co-precipitation and stability of arsenic with iron(III), it is also important to consider the possible role of aluminium that is a common cation in ore leaching operations and which upon hydrolysis can provide reductionimmune co-precipitates. Thus arsenate adsorbed on aluminium-substituted ferrihydrite has been shown to release minimal amounts of arsenic as arsenite, when exposed to arsenate reducing bacteria, but in that study, a rather large excess of Fe and Al was used, namely (Fe+Al)/As=100 and pH=7.3 [18], therefore it has yet to be proven if this scenario holds true in metallurgical tailings with significantly smaller (Fe+Al)/As ratios. Aluminium hydroxide alone was not a sufficient arsenic sink [18], but arsenate reduction on the surface of $Al(OH)_3$ does not seem to result in quick arsenite release [19]. Recently Jia *et al.* reported the batch co-precipitation of arsenate in a 2-step process with ferric (first step from pH1 to 4 at Fe(III)/As(V)=2 and aluminum (second step from pH 4 to 8 at Al/As=2). It was found that aluminum increases arsenic rentention in oxic, sulfide reducing and bacterial reducing conditions.

In this study, continuous two-stage co-precipitation of Fe(III)/Al(III)/As(V) was conducted and the produced solids were exposed to excess sulfide reducing agent under inert gas (ensuring a complete anoxic environment) to evaluate the stability of the solids. The slurry samples were placed on a shaker table to keep the solids in suspension and thereby accelerate the tailings aging process and the attainment of pseudo-equilibrium/long-term trends.

## 4.3. Materials and Methods

The production of solids was achieved by continuous co-precipitation by lime neutralization using a two-reactor circuit as described in the previous chapter and reported in detail elsewhere [8]. Two types of co-precipitates were produced: the standard one with a molar ratio of Fe(III)/As(V)=4 and the alternative mixed Fe(III)/Al(III)/As(V)=2/2/1 system. The feed solutions were prepared by dissolving the required amounts of ferric and aluminum sulfate salts along arsenic pentoxide to give 1.4g/L As(V), [Fe+Al]/[As]=4 and pH=1.5 The exact feed compositions for both co-precipitation experiments can be found in Table 4.1. The mean retention time for each reactor was 1 hour and the circuit was operated for 9.5 hours; steady-state operation was achieved after 6.5hours.

Table 4.1.: Feed composition for all CCPTN experiments

| | Concentration [mg/L] | | | Molar Ratios | |
|---|---|---|---|---|---|
| Name | Fe(III) | As(V) | Al(III) | Fe(III)/As(V) | Al(III)/As(V) |
| CD4c | 3905 | 1495 | - | 3.5 | - |
| CD5 | 1966 | 1504 | 1132 | 1.8 | 2.1 |

The slurries were used in stability testing as obtained from the co-precipitation process (steady-state produced co-precipitates only), except the solid/liquid ratio was doubled by decanting an appropriate amount of water. Sulfide was used as the reducing agent (0.33/0.66M, $Na_2S \cdot 9\,H_2O$). [2] The two co-precipitates (Fe(III)/As(V)=4 and Fe(III)/Al(III)/As(V)=2/2/1) were exposed to one equivalent of sulfide per mole of iron. The slurry samples were placed (all handling was done in a glove-box) in inert gas-filled septum bottles secured on a shaker table that was set to 180 oscillations per minute to keep the slurries fully mixed and the solids in suspension. The bottles were continuously shaken for different times up to a maximum of 4 weeks. Each bottle represented one sample, i.e. a simple sampling point thus avoiding potential risk of air infiltration because of excessive handling.

**Stability testing of sulfide samples**: 80mL of Fe(III)/As(V)=4 or Fe(III)/Al(III)/-As(V)=2/2/1 co-precipitate slurry was filled in 125mL tinted septum bottles.

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[2] In another series sulfite (1.2M, $Na_2SO_3$) instead of sulfide was used and the results are reported in the Appendix.

30mL of a 0.33M/0.66M sulfide solution was added to obtain $S^{2-}$/Fe(III)=1. The sulfide solution was adjusted to pH=8 with 50% concentrated $H_2SO_4$ just prior to addition to the co-precipitate slurry. Ten samples per co-precipitate series were generated in this manner to be sampled every third day. Used samples were discarded. They were evacuated right after sulfide addition and the atmosphere replaced with nitrogen in a glovebox.

**Drift samples**: Four 'Drift' samples per series were produced without the addition of reducing agent but put under a nitrogen atmosphere to act as reference. These were sampled every six days.

Fe(II) was analyzed by a modified dichromate titration method. For total Fe(II) a 1mL slurry sample was digested in 5mL concentrated HCl. Since elemental sulfur is not soluble in concentrated HCl the slurry was filtered with a 0.2$\mu$m filter and the solids washed with an addition 5mL DI water. The solutions were then combined and diluted with 25mL $H_2SO_4$–$H_3PO_4$ buffer and 50mL DI water. 3 drops of a 0.001N diphenylamine sulfonate indicator were added and titrated with 0.01N $K_2O_7^{2-}$ until the color changed to purple. Filtrate samples were first diluted with 50mL DI water, then buffer and concentrated HCl were added. Arsenite, sulfite and sulfide solutions were titrated to see if these ions interfere with the method. No significant interference was found.

pH and $E_h$ were obtained by a Consort Multichannel R305 Controller with Cole-Parmer pH electrode and Accumet Platinum Ag/AgCl ORP combination electrode.

A Thermo ICAP-6500 axial/radial inductively coupled plasma optical emission spectrometer equipped with Meinhard K-type nebulizer, 50mL cyclonic non-baffled spray chamber and a 2.5mm injector was used to determine total arsenic. The radiofrequency generator was set at 1100W. Sample flow rate was 75rpm.

189.9nm line was used as a principal line, 193nm line used as a confirmation line

In order to separate/identify/characterize the various arsenic species (arrsenate vs. arsenite) a Thermo Accela HPLC equipped with a quaternary pump, a diode array detector and an autosampler capable of injecting 125$\mu$L was used. A Hamilton 10u PRP-X100 0A (250x4.1mm) anion exchange column with prefilter (KrudKatcher Classic HPLC In-Line Filter) separated the analytes of interest. A mmoles phosphate buffer at pH=6.2 was used as the mobile phase.

The drain from the detector of the HPLC was coupled with a Y-junction from the ICP-OES. The resulting analyte was diluted by 50% with the 4% nitric acid normally used in the ICP. A time scaled measurement applying a first order differential equation to recorded intensity was utilized to quantify arsenic species concentration. A standard bracketing technique was employed to compensate for instrument drift.

## 4.4. Results and Discussion

### 4.4.1. Co-precipitation of Fe(III)/Al(III)/As(V)

The Fe, Al and As concentrations in each reactor at steady-state are summarized in Table 4.2. The corresponding concentration profiles as a function of circuit operating time are presented in the Appenxid (Figures A.18 and A.19). Focussing first on the CD4c test (Fe(III)/As(V)=4) it can be seen that the steady-state concentration results compare well to those obtained in the previous chapter (tests CD4 and CD4b). Essentially in both reactors the ferric and arsenic values were below 0.1mg/L. When half of the ferric was replaced by Al(III), the arsenic and iron concentrations were higher in reactor 1 at ~0.5mg/L but dropped below 0.05mg/L in reactor 2 (0.046mg/L As), i.e. half of the As concentration in CD4c (the corresponding Al concentrations in reactors 1 and 2 were 65.1 and 0.592mg/L respectively). These results indicate that Al as per work by Jia *et al.* [7] has the capacity at higher pH (pH=8 in reactor 2) to remove arsenic more effectively than iron. The opposite was true at pH=4 (reactor 1) despite the fact that over 90% of aluminum precipitated in reactor 1. This may suggest that arsenic was removed via formation of ferric arsenate in reactor 1 (pH=4) with the residual soluble arsenate fraction further removed in reactor 2 (pH=8) via adsorption on ferrihydrite and aluminum hydroxide.

Table 4.2.: Average steady-state values (in mg/L) for all CCPTN experiments

| Experiment | Ions | Molar Ratio | R1 $E_h$ | R2 $E_h$ | R1 pH | R2 pH |
|---|---|---|---|---|---|---|
| CD4c | Fe(III)/As(V) | 3.5 | 700.0 | 361.5 | 4.10 | 8.01 |
| CD5 | Fe(III)/Al(III)/As(V) | 1.8/2.1/1 | 635.3 | 347.5 | 4.06 | 7.94 |

| Experiment | R1 As | R2 As | R1 Al | R2 Al | R1 Fe | R2 Fe |
|---|---|---|---|---|---|---|
| CD4c | 0.021 | 0.088 | - | - | 0.021 | 0.006 |
| CD5 | 0.532 | 0.04 6 | 65.1 | 0.592 | 0.414 | 0 |

### 4.4.2. Stability Testing

After addition of the sulfide solution, that was previously adjusted to pH=8, to the co-precipitate slurry (pH=7-8) the pH drastically increased to pH~11 for CD4c (Fe(III)/As(V)=4) as can be seen in Figure 4.1. This means that a reaction took place that scavenged a lot of protons e.g. by released hydroxide ions. A possible reaction would be the dissolution of ferrihydrite (or ferric arsenate) by reduction to ferrous:

$$2\,\mathrm{FeOOH} + \mathrm{S}^{2-} + 2\,\mathrm{H}^{+} \longrightarrow 2\,\mathrm{Fe}^{2+} + \mathrm{S}^{0} + 4\,\mathrm{OH}^{-} \tag{4.1}$$

Ferrous can form black FeS with excess sulfide. A color change from the rusty ferrihydrite/ferric arsenate co-precipitate colour to a black precipitate was observed right after sulfide addition

$$\mathrm{Fe}^{2+} + \mathrm{S}^{2-} \longrightarrow \mathrm{FeS}\downarrow \tag{4.2}$$

The reduction of arsenate to arsenite would also lead to an increase in pH

$$\mathrm{H_2AsO_4^{-}} + \mathrm{S}^{2-} + \mathrm{H}^{+} \longrightarrow \mathrm{H_2AsO_3^{-}} + \mathrm{OH}^{-} + \mathrm{S}^{0} \tag{4.3}$$

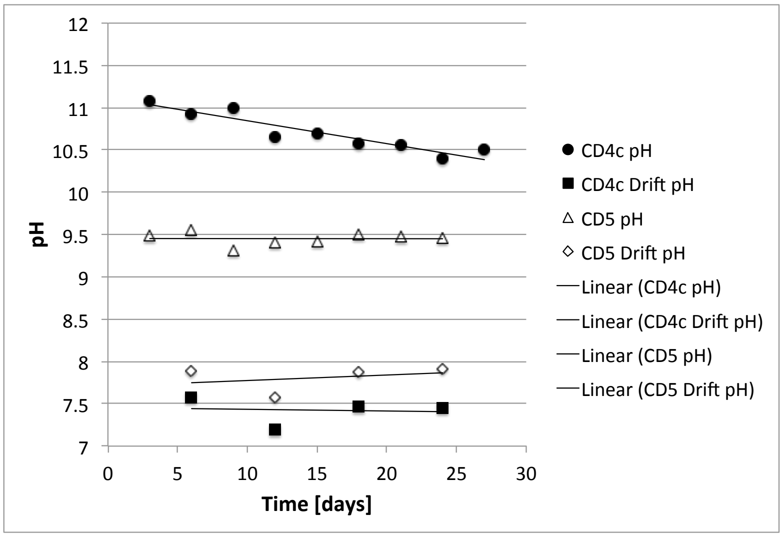

Figure 4.1.: pH progression for CD4c (Fe(III) / As(V)=4) and CD5 (Fe(III) / Al(III) / As(V)=2/2/1) during anoxic stability testing with and without added sulfide reagent

The pH decreased with time and stabilized after 18 days at pH=10.5. CD5, where half of the ferric was substituted by aluminum, shows a stable pH reading at pH=9.5. The 'Drift' samples on the other hand stayed close to the final production pH of just below 8 for CD5 and 7.5 for CD4c. The big discrepancy in pH among the various samples may indicate a reaction taking place in the bulk of the sample when sulfide was added. If we take a look at the $E_h$ (see Figure 4.2) it is apparent that the 'Drift' samples, although under inert gas atmosphere, stayed very oxidizing around $E_h$=600mV for CD4b and just slightly lower at $E_h$=580mV for CD5.

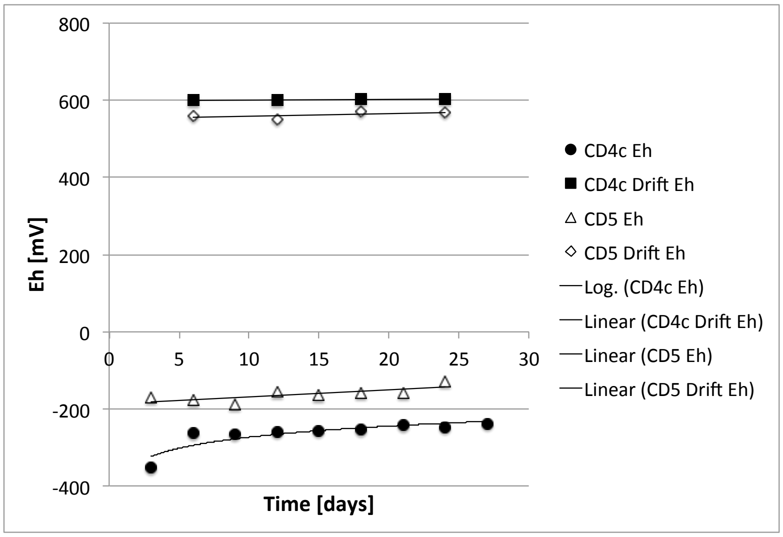

Figure 4.2.: $E_h$ progression for CD4c (Fe(III) / As(V)=4) and CD5 (Fe(III) / Al(III) / As(V) = 2 / 2 / 1) during anoxic stability testing with and without sulfide reagent addition

On the other hand, when sulfide ($S^{2-}$) was introduced into the system, the $E_h$ drastically dropped to almost -400mV for CD4c and close to -200mV for CD5. The $E_h$ slowly increased thereafter but stayed in a drastically reducing milieu. CD4c had more ferric initially and therefore more sulfide was added to reach the pre-set $S^{2-}$/Fe(III)=1 molar ratio. Therefore, a higher amount of ferric was reduced to ferrous, releasing more protons after reaction 4.1. The higher amount of $S^{2-}$ and Fe(II) were also responsible for the low $E_h$. Furthermore, the $E_h$ was reversely proportional to pH, which means an increase in pH would lead to a decrease in $E_h$.

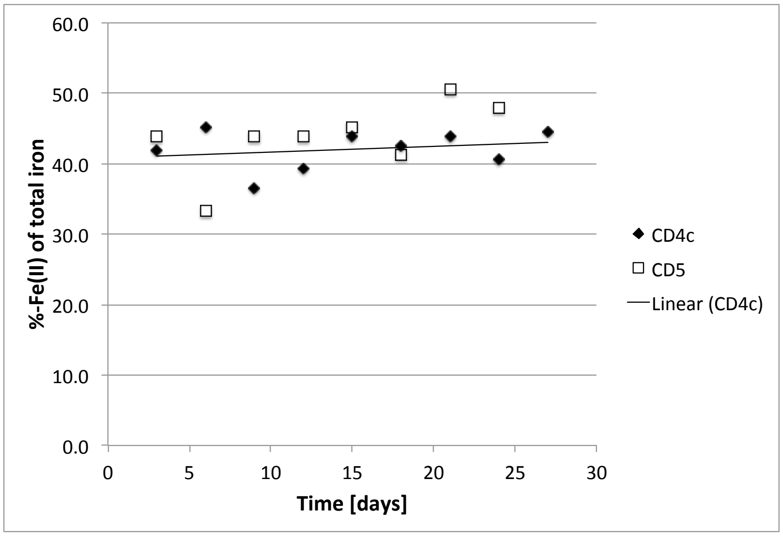

Figure 4.3.: Percentage of total iron as ferrous for CD4c (Fe(III) / As(V)=4) and CD5 (Fe(III) / Al(III) / As(V)=2/2/1) during sulfide-added anoxic stability testing

Figure 4.3 shows the fraction of ferrous concentration (in percentage of total iron) during the course of sulfide-added stability testing. It is interesting that for both co-precipitates, just above 40% of ferric has been reduced to ferrous. If we take into account that sulfide ($S^{2-}$) donates at least two electrons to form elemental sulfur (refer to reaction 3.1), then there were two reduction equivalents for every mole of iron present. Theoretically, the molar ratio of $S^{2-}$/Fe(III)=1 should be able to reduce twice the amount of ferric that is present in the co-precipitated solids. Part of the answer for this issue is the formation of

FeS. According to the combined stoichiometry of reactions 3.1 and 3.2, when 40% of the iron was reduced to form FeS this used 40% of the available sulfide. At this point it is not clear why the balance sulfide (more than 50%) did not reduce the remaining ferric. Several causes may be behind this behaviour. For example, the sulfide could comproportionate with sulfate to form S(0) and $SO_3^{2-}$; or part of the sulfide could have degassed as $H_2S$ during evacuation in the antechamber of the glove-box. There could also be a ferric phase present in the solid that is not prone to reduction such can be ferric arsenate, for example. Alternatively ferric reduction could be slowed due to mixed magnetite formation (mixed ferrous/ferric phase), which coincidentally is a black phase (as observed to precipitate) or formation of some sort of ferrite phase. XRD analysis of unwashed precipitate was conducted but the dominant gypsum phase made phase identification impossible. An amorphous underlying phase could be detected. XRD of washed precipitate could not be conducted in time for this thesis. Further, specialized characterization work involving air-tight sample handling in a facility like the Canadian Light Source has to be conducted.

The release of arsenic during the sulfide-added stability testing of the two co-precipitates is shown in Figure 4.4. These values are total arsenic measured by ICP-OES. Initially the CD4c test (Fe(III)/As(V)=4) recorded a high arsenic release level (70mg/L of arsenic in solution after 3 days). This may reflect the extremely high alkaline pH (above 11) and the strongly reducing $E_h$ (-352mV). Three days later, however, the arsenic concentration had dropped to 33mg/L and stayed more or less steady at that level for the rest of the stability test duration. This drop coincided with a lowering of pH down to 10.93 and $E_h$ rising to -262mV. Thermodynamically speaking, this is close to the stability region of magnetite. The ~30mg/L soluble arsenic fraction was just shy of 1.1% of the total arsenic- a rather tiny amount considering the very

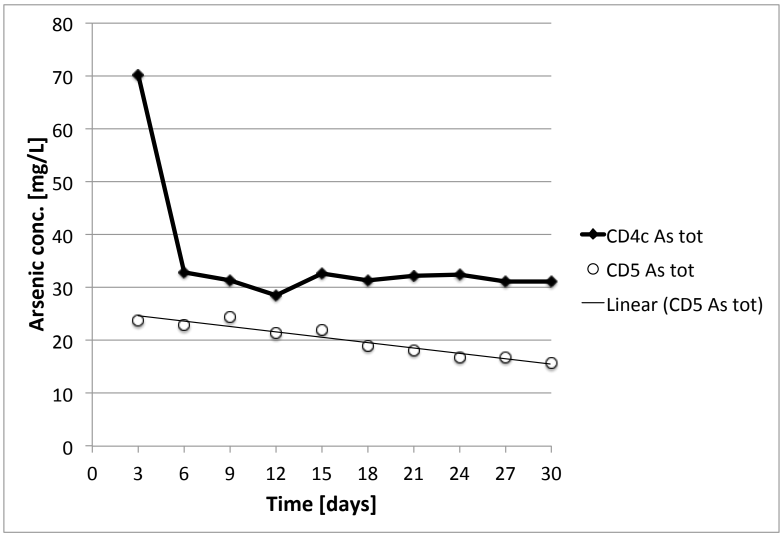

Figure 4.4.: Arsenic concentration release under sulfide-added stability testing of CD4c (Fe(III) / As(V)=4) and CD5 (Fe(III) / Al(III) / As(V)=2/2/1)

harsh reductive dissolution conditions. By contrast the soluble arsenic in the case of CD5 (Fe(III)/Al(III)/As(V)=2/2/1) was even lower than that of CD4c decreasing almost linearly with time from an initial 25mg/L down to 15mg/L after 30 days.

The question that this behaviour of arsenic raises is in what form the bulk of it remains insoluble. Since as discussed above, only 45% of ferric was reduced, one explanation could be that the bulk of ferric arsenate is not affected by sulfide and only ferrihydrite is reduced due to faster kinetics. Another reason could be that arsenic is retained in the form of ferrous arsenate (symplesite-like phase) as long as arsenate is not reduced (ferrous of course generated in-situ by the reduction of ferric - see Fig. 4.3). Alternatively, if arsenate is reduced to arsenite, then it is possible that arsenic sulfide ($As_2S_3$) forms; This could also explain the unaccounted equivalents of reducing agent ($S^{2-}$) as mentioned above. However the work by Young and Robins [20] found the solubility for orpiment (crystalline $As_2S_3$) in the pH range 2-5 to be 1.93mg/L. Amorphous $As_2S_3$, which is more likely to form in this case due to low temperature, has orders of magnitude higher solubility than orpiment according to the authors. Above pH=9.2 they suggest amorphous $As_2S_3$ to precipitate from the $As_3S_6^-$ ion:

$$As_3S_6^{3-} + H_2AsO_3^- + 2\,H^+ \rightleftharpoons 2\,As_2S_3(am) + 3\,H_2O \tag{4.4}$$

The minimum solubility for amorphous $As_2S_3$ was calculated to be 43.5mg/L below pH=6.5. For realgar ($As_4S_4$) only a small stability field between pH=8-9 was calculated [20]. However, the formation of arsenic sulfides is not only questioned because of the high pH in our samples, but more importantly that we did not find any significant reduction of arsenate to arsenite - a necessary precursor for precipitation of $As_2S_3$ to have occurred.

Initially the experiment was designed to stay at pH=8 where thermodynamically a reduction of As(V) to As(III) is feasible below $E_h$=0mV [21]. However, the actual pH increased anywhere between 9.5 to 11 (Figure 4.1) rendering the reduction of As(V) to As(III) thermodynamically less favorable [21]. Nevertheless arsenic speciation was conducted on soluble As with HPLC-ICP-OES to verify if any arsenic reduction had taken place.. The total arsenic concentrations obtained by ICP-OES vs. As(V) concentrations by HPLC-ICP-OES can be found in Figure 4.5 and 4.6. For CD4c, the As(V) concentration values almost match the As(tot) values. On the other hand, all As(V) values for CD5 are lower than As(tot) values suggesting some reduction to arsenite or thioarsenate/thioarsenite formation [22]. The detection limit for any arsenic species in the applied method was close to 2mg/L. Since there were no other peaks in the chromatograms apart from As(V) for the samples, even in scans as long as 30 minutes to verify the results, formation of other arsenic species in the solution can be ruled out. That leaves the question if the recorded lower As(V) values than the As(tot) values signal are indeed a reduction of a fraction of arsenate to arsenite below

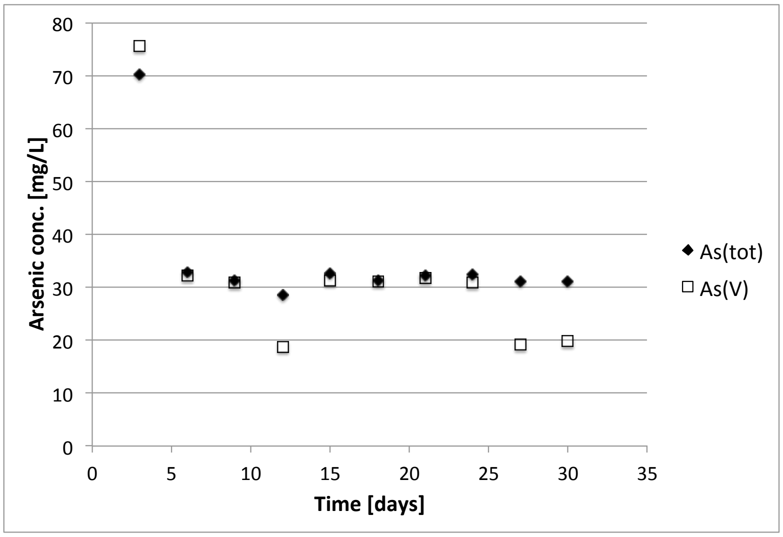

Figure 4.5.: Arsenic speciation data (As(tot) and As(V) for CD4c (Fe(III) / As(V)=4) under sulfide-added anoxic stability testing

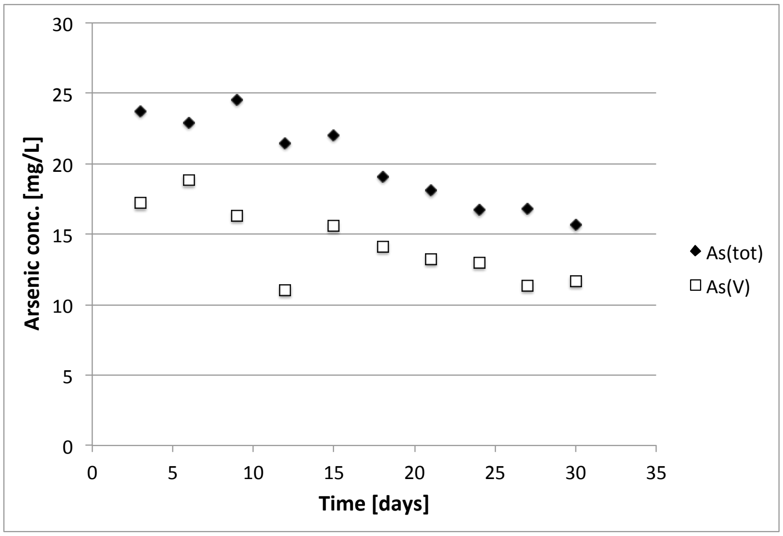

Figure 4.6.: Arsenic speciation data (As(tot) and As(V)) for CD5 (Fe(III) / Al(III) / As(V)=2/2/1) under sulfide-added anoxic stability testing

our detection limit or represent experimental difficulties (three data points in CD4c speciation (Fig. 4.5) are also lower than As(tot) values). The bracketing technique employed (measuring sample1, standard, sample2, standard, etc.) did not reveal issues with drift of the machine (i.e. carry-over between samples) and it is therefore difficult to pinpoint the reason of the discrepancy between As(tot) and As(V). A solid digestion analysis did not find any arsenite either. Due to the higher arsenic concentration the relatively high detection limit of the employed method should not have been an issue. Therefore it can be concluded that there was a only minor fraction of arsenate reduced by sulfide (i.e. $\leq$0.5% of total arsenic) and that the reduced arsenite was part of the soluble fraction.

The 'Drift' samples compare very well to previous long-term stability results (see previous Chapter). For CD4c (Fe(III)/As(V)=4) as per data summarized in Table 4.3, 0.346mg/L were found on average ($\sigma$=0.02803), meaning the solids are very stable even when agitated aggressively on a continuous basis. CD5 (Fe(III)/-Al(III)/As(V)=2/2/1) has an average of 0.193mg/L of arsenic in solution ($\sigma$=0.0468). CD4b (Fe(III)/As(V)=4, compare to data in previous chapter) released 0.453mg/L of arsenic over the course of a year. That sample however was not continuously agitated. Similarly RD5 (Fe(III)/As(V)=4, by Daenzer [23]) had even less arsenate in solution (0.1mg/L) after 550 days and again no agitation was employed during stability testing.

Table 4.3.: Drift experiments compared to previous long-term stability testing

| Exp. Name | Fe(III)/As(V) molar ratio, co-ions | pH | As [mg/L] (days) |
|---|---|---|---|
| CD4c | 4 | 7.45 | 0.346 (26) |
| CD5 | 2, Al(III) | 7.91 | 0.193 (26) |
| CD4b | 4 | 7.04 | 0.453 (375) |
| RD5 | 4 | 7.1 | 0.1 (550) |

For CD5, the lower arsenate concentration is surprising, as ferric arsenate is more soluble at higher pH [3], especially since Fe(III)/As(V) is smaller than three [5]. Therefore it can be concluded that Al(III) in the co-precipitates is not only effective for arsenic removal but also for the stability of the solids regarding arsenic remediation. Furthermore the trends for both co-precipitates do not rise, so arsenic is predicted to be stable in the long term around those levels or lower in the case of Fe(III)/Al(III) co-precipitates.

Of course here a chemical reducing agent was used while in natural tailings disposal sites bacterial reduction may provide different pathways for arsenic reduction and biotic anoxic stability testing will have to be undertaken as well.

## 4.5. Conclusions

- The strongly agitated 'Drift' co-precipitates under inert gas were very stable with less than 0.45mg/L As(tot) in solution at pH=7.97/$E_h$=600mV (CD5) and pH=7.45/$E_h$=600mV (CD4c) after 24 days. These results suggest the Fe(III)/As(V) or Fe(III)/Al(III)/As(V) co-precipitates are stable under air-starvation (no reducing agents added) anoxic conditions.

- In the presence of sulfide ($S^{2-}$/Fe(III)=1) up to 1% of the arsenic content was found to be dissolved, this being higher in the case of Fe(III)/As(V)=4 (~30mg/L As at pH~10.5/$E_h$=-220mV) than in the case of Al-containing co-precipitate (~15mg/L As at pH~9.5/$E_h$=-150mV). Of the soluble arsenic less than 30% was as arsenite, while no arsenite could be detected in the precipitated solids.
- Evidence was found that aluminum has a stabilizing effect both in the presence or absence of sulfide ions. There is less arsenate release in the 'Drift' sample when Al(III) is present.
- Sulfide ($S^{2-}$) was found to reduce 45% of the ferric in both co-precipitates. The formation of arsenic sulfide appears unlikely as sulfide hardly reduced any arsenate to arsenite (less than 0.5% of total As). This may suggest that ferrous arsenate had formed under such reducing environment helping prevent the uncontrolled release of arsenic.

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# 5. Global Conclusions

In a 2-reactor bench-scale continuous circuit, various arsenate-bearing co-precipitates from Fe(II)/Fe(III)/Al(III) solutions were prepared by lime neutralization. It was found that ferrous alone can remove arsenate effectively to the sub-$\mu$g/L range by co-precipitation in the circuit just like its ferric counterpart (Fe(III)/As(V)=4). When mixed ferric/ferrous or ferric/aluminum (Fe(II)/Fe(III) or Fe(III)/Al(III)=2/2) co-precipitation of arsenate ($M_{tot}$/As(V)=4) was performed, arsenic was also effectively removed within minor variation ($\leq$1mg/L As).

The main body of work was the exposure of the co-precipitates to reducing agents. In the first series of tests, Fe(II)/Fe(III)/As(V) co-precipitates were subjected to long-term stability testing ($\geq$1year) with frequent addition of sulfite ($SO_3^{2-}$) and sulfide ($S^{2-}$) (0.1M each) and adjustment of pH to pH=8 with lime. The undisturbed ('Drift' series) samples (no pH or $E_h$ adjustment) showed very low arsenate release independent of the presence of ferrous. Chemical manipulation of the other samples with either lime, or lime and one of the two reducing agents (sulfide or sulfite) resulted in generally higher arsenate release not exceeding a factor of 2.5 (compared to the 'Drift' series). This shows a great stability of the co-precipitates regardless of reducing agents being present or not. Ferrous was found to oxidize however under these conditions due to air infiltration because no air exclusion measures were taken. As a consequence the $E_h$ could not be kept at the target values of 0mV ($S^{2-}$) and 250mV ($SO_3^{2-}$) constantly. The more ferrous was present the more goethite, 6-line ferrihydrite and possibly scorodite was formed in all ageing samples additionally to ferrihydrite and ferric arsenate.

The second half of the stability experiments was conducted under inert atmosphere with the aid of a glove-box. Fe(III)/Al(III)/As(V)=2/2/1 and Fe(III)/As(V)=4 co-precipitates were exposed to excess amounts of sulfide ($S^{2-}$/Fe(III)=1). Ferrous was produced in situ by reduction of ferric with sulfide. However only 45% of total iron was found to be reduced although 200% of reduction equivalent in the form of sulfide was added. At the same time, no significant arsenate reduction was observed. The fate of the excess sulfide is unknown at this point. Arsenic sulfide formation does not seem feasible. A black precipitate was produced as a result of the exposure of the co-precipitates to sodium sulfide during stability testing. FeS and magnetite ($Fe_3O_4$) formation are likely. The Fe(III)/As(V)=4 series stabilized at 30mg/L while the aluminum-substituted series had an almost linear decrease in arsenate from 24 to 15mg/L. Less than 1.1% of total arsenate in the solids appeared to be soluble under these very harsh reducing conditions which shows the co-precipitates to resist arsenic release. This resistance is further enhanced when Al(III) is part of the co-precipitation system.

# A. Appendix

## A.1. Appendix A - Chapter 3 supplementary information

### Solid Digestion

The final aged co-precipitates were washed and dissolved in concentrated HCl to obtain the element composition by ICP-OES. The results can be found in Table A.1.

All samples had between 27.9 and 34.0 wt-% iron. The iron content in the CD2b (Fe(II)/As(V)=4) solids was the highest, as well as the arsenic concentration. The more initial Fe(III) was used for the co-precipitation the less iron and arsenic weight percentage is found in the final solids. This implies more $OH^-$ and crystal water in the ferric containing samples, as sulfur was found to be less than 0.6 wt-% in all samples, which is most likely residual gypsum, because sulfate adsorption is very weak compared to arsenate adsorption at pH=8. All samples had iron to arsenate molar ratios of less than 3, which means one equivalent of iron was washed out during ageing in the above described manner. This is very surprising because ferric is rather insoluble especially at higher pH. Ferrous being more soluble could be a reason for iron removal. The consistency of the results, even when no ferrous was present (CD4/CD4b), makes these considerations very unlikely. CD2b 'Drift' with a final pH of 3.49 had a lot of ferrous in solution, which explains the very low Fe/As molar ratio of 2.43. However for the other samples there is at present no reasonable explanation as to how the ferric iron could be removed from the sample.

Also very interesting are the high amounts of calcium that were incorporated into the ferric and ferrous arsenate co-precipitates during long-term stability testing. Up to 0.97 Ca/As molar ratios were found, although this sample also had the highest sulfur content, implying residual gypsum that overestimates the $Ca^{2+}$ that is actually in the solid. Nonetheless, the CD4b series incorporated the most calcium with approximately 0.6 Ca/As molar ratios, while CD3b has about 0.53 Ca/As molar ratios and CD2b has the least with an average of 0.36 (Drift sample excluded, which does not have any significant amount of $Ca^{2+}$). The ferrous containing co-precipitates incorporate the least amount of calcium probably because of the goethite formation.

In CD4b (Fe(III)/As(V)=4) $Ca^{2+}$ was easily incorporated. Ca-Fe-As solid solutions such as yukonite are known to exist but in this case due to low synthesis and ageing temperature they are unlikely. Moreover, the pH for yukonite formation should be above 8. The absence of the most intense XRD peak for Yukonite (37.2°, Co-K$\alpha$) supports these considerations. It is more probable that $Ca^{2+}$ adsorbs onto arsenate and ferrihydrite for surface charge neutralization [1].

Table A.1.: Solid composition of CD2b/CD3b/CD4b in wt-% and molar ratios

| Experiment | Fe [wt-%] | As [wt-%] | Ca [wt-%] | Fe/As | Ca/As |
|---|---|---|---|---|---|
| CD2b Drift | 34.0 | 18.7 | 0.2 | 2.43 | 0.02 |
| CD3b Drift | 33.1 | 15.5 | 1.6 | 2.86 | 0.19 |
| CD4b Drift | 24.9 | 12.1 | 6.2 | 2.77 | 0.97 |
| CD2b Oxic | 33.4 | 15.6 | 3.3 | 2.87 | 0.39 |
| CD3b Oxic | 34.0 | 15.6 | 4.4 | 2.93 | 0.53 |
| CD4b Oxic | 28.0 | 13.5 | 4.7 | 2.78 | 0.64 |
| CD2b $SO_3^{2-}$ | 35.1 | 16.5 | 2.7 | 2.86 | 0.31 |
| CD3b $SO_3^{2-}$ | 31.2 | 14.2 | 4.0 | 2.94 | 0.53 |
| CD4b $SO_3^{2-}$ | 27.9 | 13.4 | 4.0 | 2.80 | 0.56 |
| CD2b $S^{2-}$ | 33.9 | 15.9 | 3.1 | 2.87 | 0.37 |
| CD3b $S^{2-}$ | 31.0 | 14.0 | 4.2 | 2.97 | 0.56 |
| CD4b $S^{2-}$ | 28.1 | 13.5 | 4.6 | 2.79 | 0.63 |

## Co-Precipitation Experiments

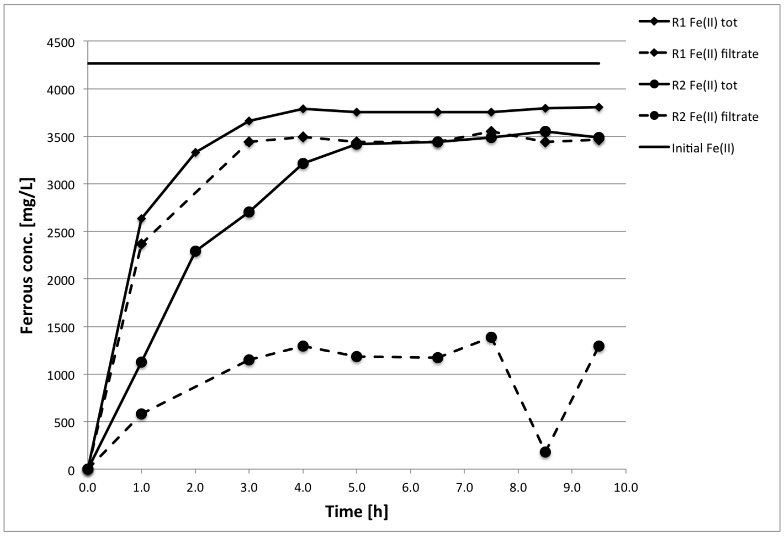

Figure A.1.: CD1 (Fe(II)): Ferrous precipitation in the CCPTN circuit

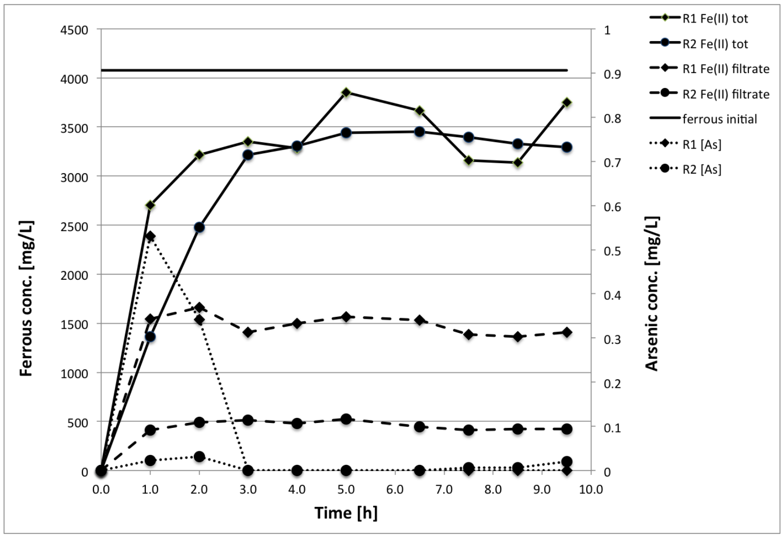

Figure A.2.: CD2b (Fe(II)/As(V)=4)

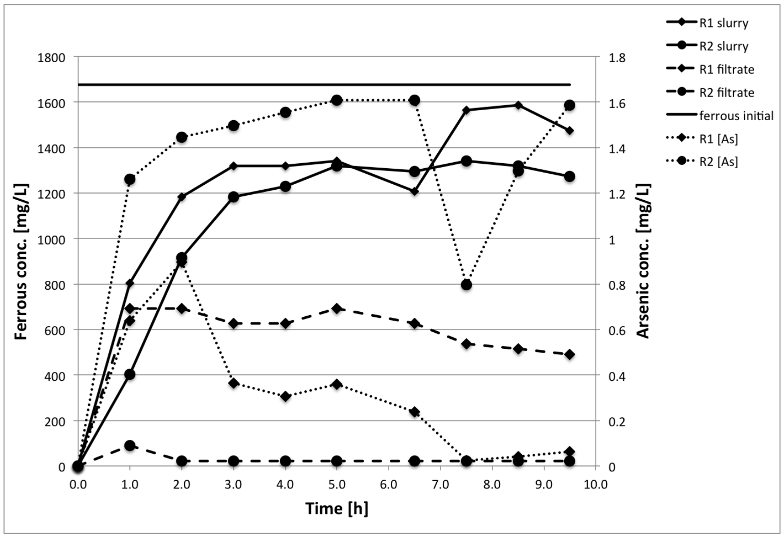

Figure A.3.: CD3 (Fe(II)/Fe(III)/As(V)=2/2/1)

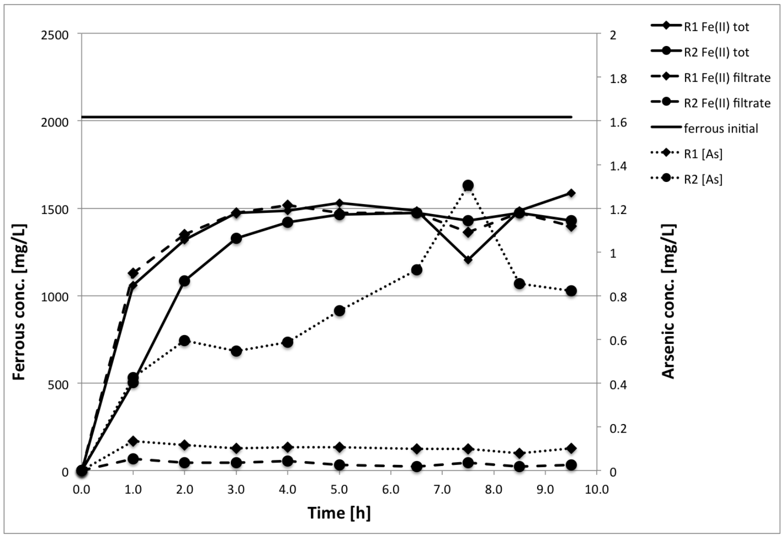

Figure A.4.: CD3b (Fe(II)/Fe(III)/As(V)=2/2/1)

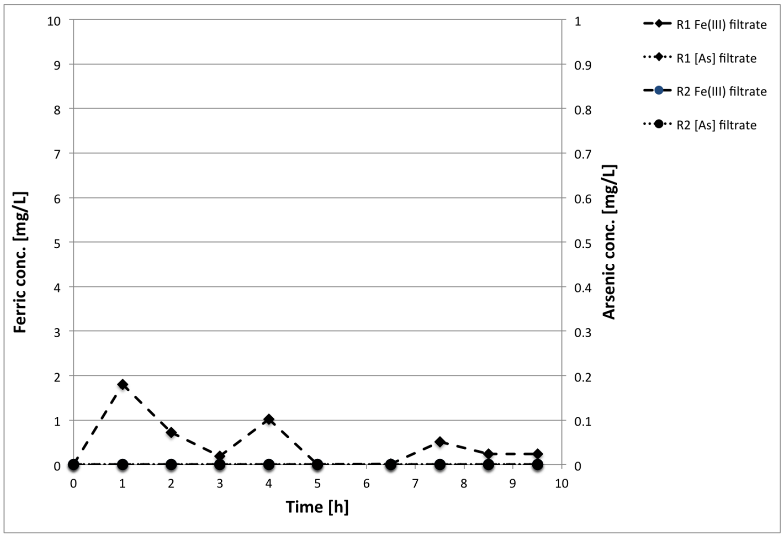

Figure A.5.: CD4 (Fe(III)/As(V)=4)

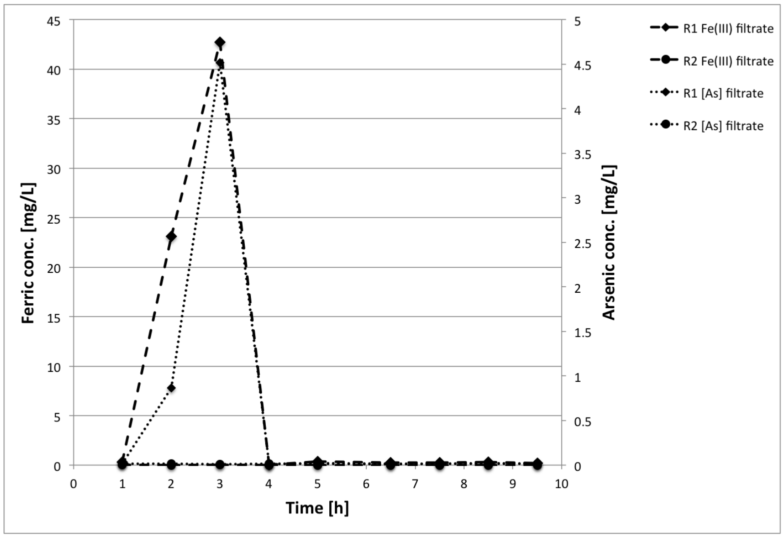

Figure A.6.: CD4b (Fe(III)/As(V)=4)

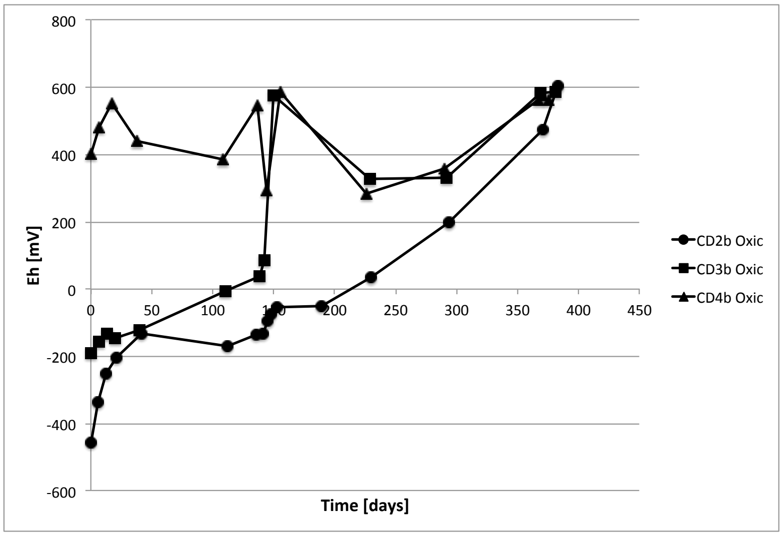

Figure A.7.: $E_h$ progression of the 'Oxic' series as a function of time

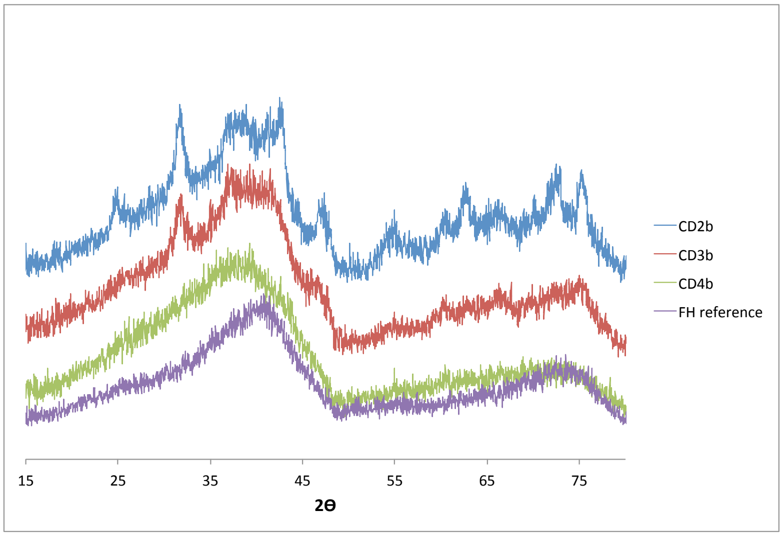

Figure A.8.: XRD patterns for CD2b/CD3b/CD4b 'Oxic' samples at termination of experiments vs. ferrihydrite reference

Table A.2.: $E_h$ [mV] for 'Sulfite' samples before (BA) vs. after adjustment (AA)

| CD2b | | | CD3b | | | CD4b | | |
|---|---|---|---|---|---|---|---|---|
| Time [days] | $E_h$ BA | $E_h$ AA | Time [days] | $E_h$ BA | $E_h$ AA | Time [days] | $E_h$ BA | $E_h$ AA |
| 0 | -457 | -457 | 0 | -189 | -189 | 0 | 401 | 401 |
| 6 | -282 | -341 | 7 | -12 | -114 | 7 | 550 | 303 |
| 12 | -166 | -230 | 13 | -57 | -107 | 17 | 515 | 351 |
| 21 | -185 | -193 | 20 | -87 | -116 | 38 | 366 | 358 |
| 42 | -43 | -148 | 40 | -72 | -119 | 108 | 379 | 264 |
| 112 | -6 | -168 | 110 | 63 | x | 137 | 315 | 243 |
| 136 | -41 | -195 | 138 | 112 | 37 | 144 | 276 | 248 |
| 141 | -43 | -89 | 142 | 82 | 29 | 155 | 291 | 269 |
| 145 | -50 | -114 | 150 | 199 | 183 | 226 | 343 | 287 |
| 148 | -41 | -103 | 229 | 343 | 297 | 290 | 360 | 290 |
| 153 | -25 | -88 | 292 | 366 | 286 | 367 | 603 | 370 |
| 189 | 44 | -96 | 369 | 579 | 334 | 375 | 574 | 297 |
| 230 | 114 | -7 | 381 | 562 | 315 | | | |
| 294 | 250 | 102 | | | | | | |
| 371 | 391 | 272 | | | | | | |
| 383 | 359 | 302 | | | | | | |

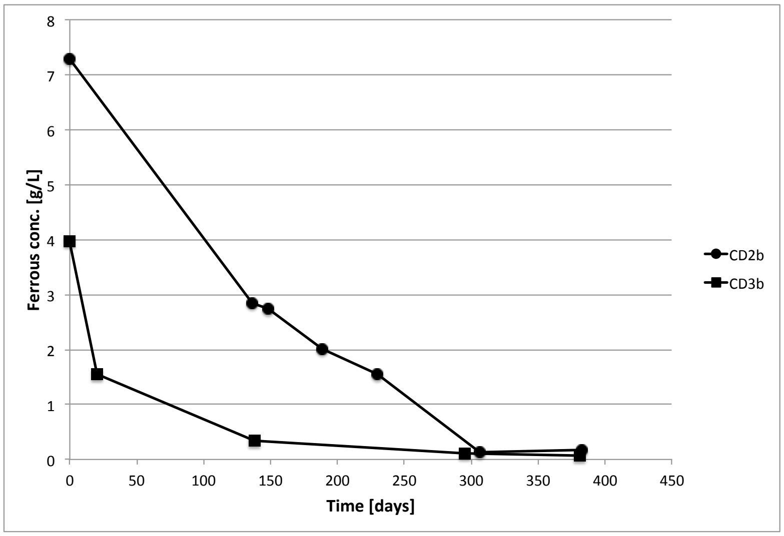

Figure A.9.: The oxidation of Fe(II) for all 'Sulfite' samples

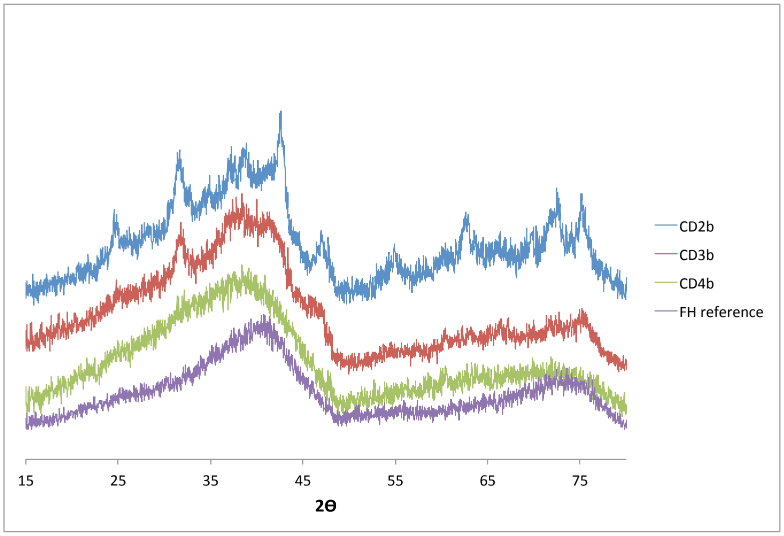

Figure A.10.: XRD patterns for CD2b/CD3b/CD4b 'Sulfite' samples at termination of experiments vs. ferrihydrite reference

Table A.3.: $E_h$ [mV] for ’Sulfide’ samples before (BA) vs. after adjustment (AA)

| CD2b | | | CD3b | | | CD4b | | |
|---|---|---|---|---|---|---|---|---|
| Time [days] | $E_h$ BA | $E_h$ AA | Time [days] | $E_h$ BA | $E_h$ AA | Time [days] | $E_h$ BA | $E_h$ AA |
| 0 | -457 | -457 | 0 | -189 | -189 | 0 | 401 | 401 |
| 6 | -273 | -333 | 7 | -28 | -138 | 7 | 586 | 7 |
| 12 | -219 | -255 | 13 | -71 | -123 | 17 | 399 | -26 |
| 21 | -208 | -214 | 20 | -86 | -118 | 38 | 428 | -29 |
| 42 | -84 | -163 | 40 | -59 | -105 | 108 | 307 | -14 |
| 112 | -19 | -175 | 110 | 47 | -68 | 137 | 308 | -1 |
| 136 | -41 | -155 | 138 | 85 | -13 | 144 | 280 | -16 |
| 141 | -42 | -145 | 142 | 79 | -9 | 155 | 367 | -27 |
| 145 | -45 | -120 | 150 | 247 | -20 | 226 | 296 | -10 |
| 148 | -31 | -87 | 229 | 305 | -16 | 290 | 352 | -5 |
| 153 | -2 | -72 | 292 | 378 | -11 | 367 | 479 | -6 |
| 189 | 42 | -97 | 369 | 444 | -15 | 375 | 449 | -12 |
| 230 | 116 | -34 | 381 | 476 | -10 | | | |
| 294 | 245 | -15 | | | | | | |
| 371 | 410 | 1 | | | | | | |
| 383 | 506 | -15 | | | | | | |

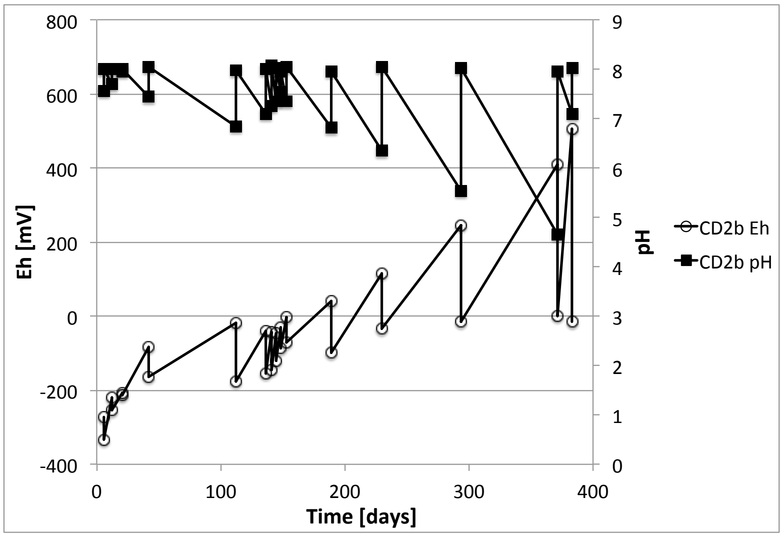

Figure A.11.: CD2b 'Sulfide' $E_h$ and pH progression before and after adjustment

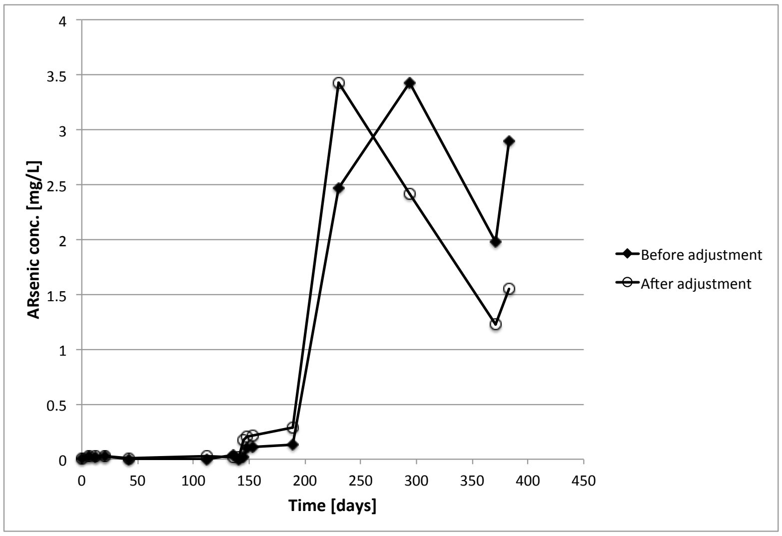

Figure A.12.: Before vs. after adjustment arsenic concentrations as a function of time (CD2b 'Sulfide'

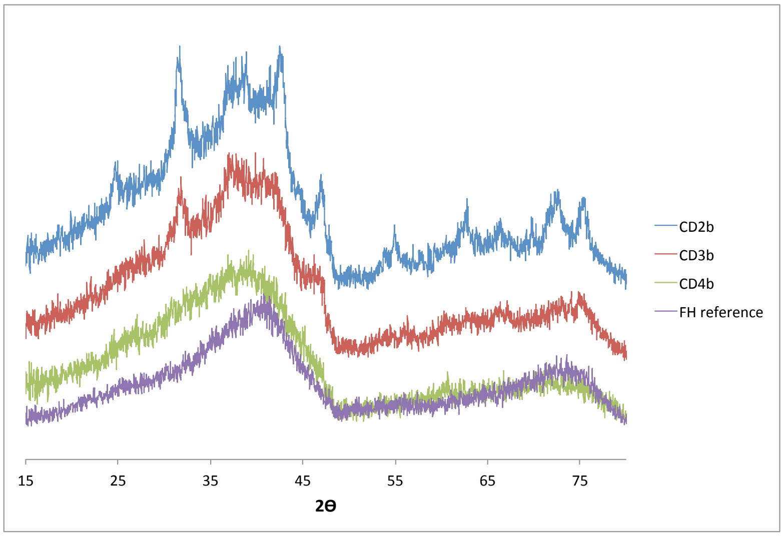

Figure A.13.: XRD patterns for CD2b/CD3b/CD4b 'sulfide' samples

The following diagrams show the corresponding ageing results to chapter 3 with the only difference that NaOH was used during ageing to adjust pH. In all co-precipitation series of this work lime was used as base for the production of solids.

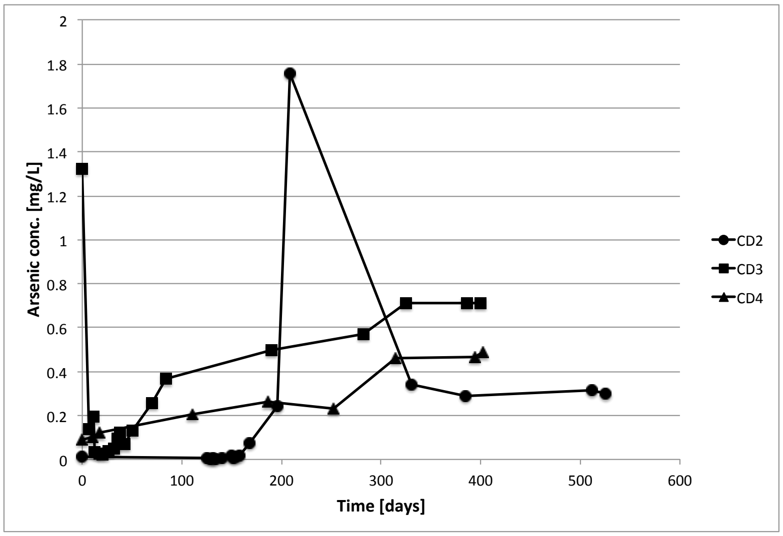

Figure A.14.: NaOH as base: As conc. during Drift stability testing

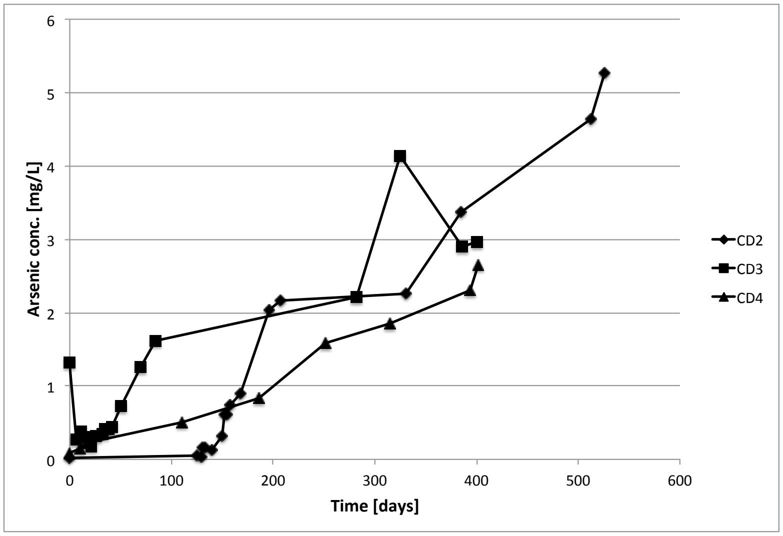

Figure A.15.: NaOH as base: As conc. during Oxic stability testing

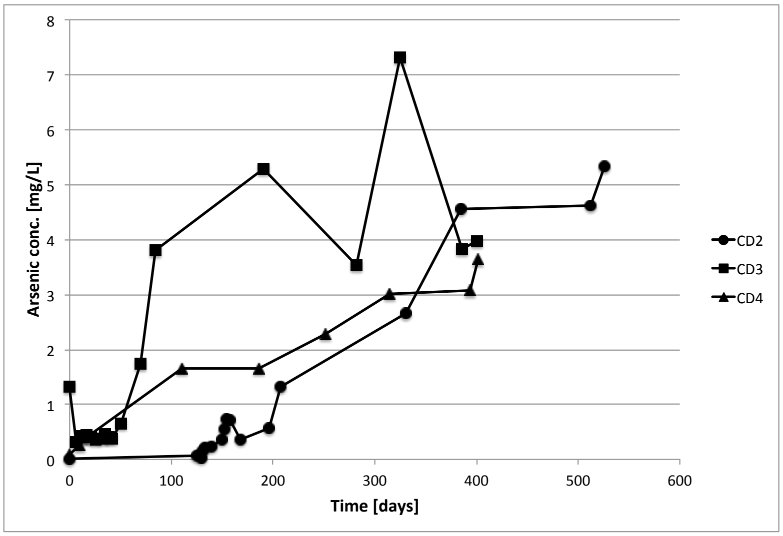

Figure A.16.: NaOH as base: As conc. during Sulfite stability testing

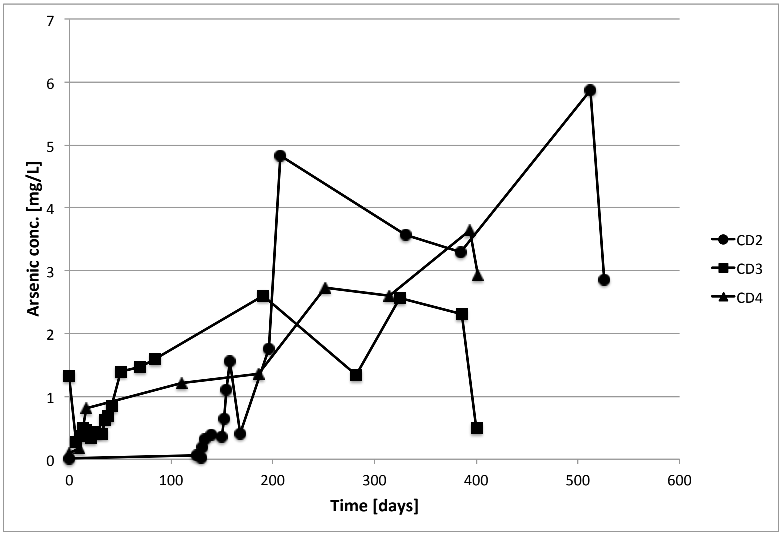

Figure A.17.: NaOH as base: As conc. during Sulfide stability testing

## A.2. Appendix B - Chapter 4 supplementary information

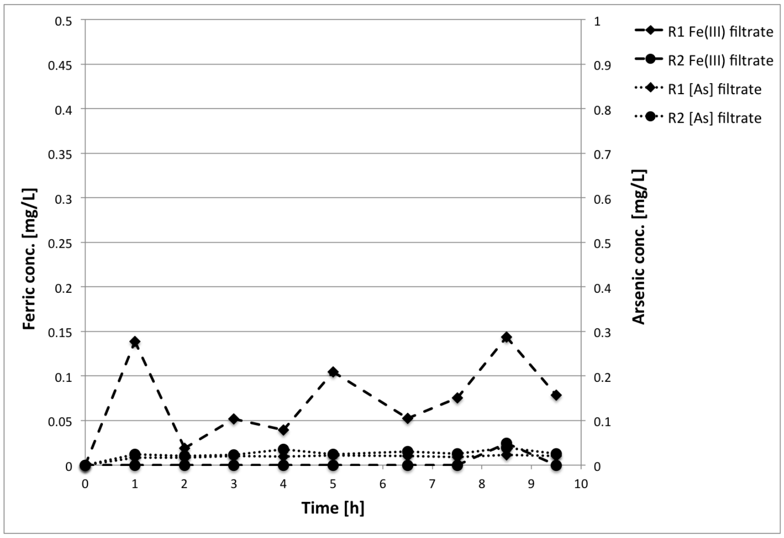

Figure A.18.: CD4c (Fe(III)/As(V)=4)

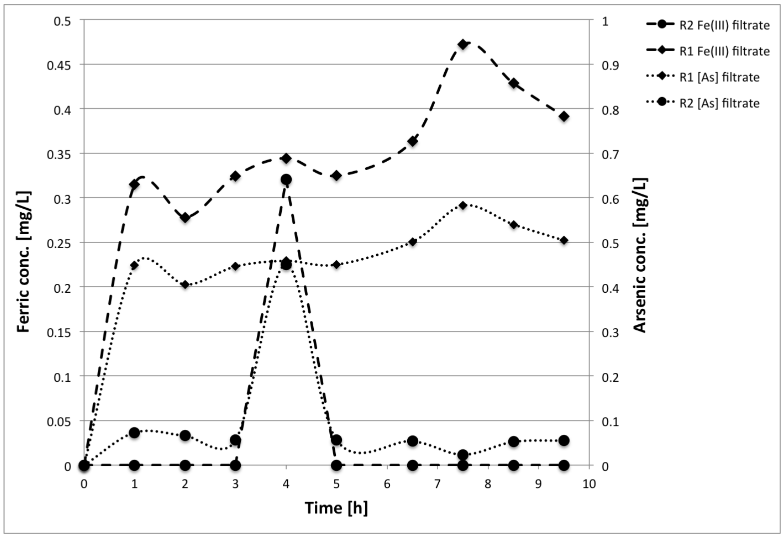

Figure A.19.: CD5 (Fe(III)/Al(III)/As(V)=2/2/1)

### A.2.1. Sulfite ($SO_3^{2-}$) Stability Testing

The same procedure with that used in Chapter 4 was followed. In this series the Fe(III)/As(V)=4 co-precipitate was exposed to three equivalents of sulfite per mole of iron. 80mL of the Fe(III)/As(V)=4 series were exposed to 30mL of sulfite solution (1.2M) to obtain $SO_3^{2-}$/Fe(III)=3. Seven samples were produced and sampled every day. Just as the sulfide samples these samples were evacuated right after sulfite addition and the atmosphere replaced with nitrogen in a glovebox. The pH during the one week long stability testing with permanent agitation from the shaker table was constant at pH=8.4 (see Figure A.20). The $E_h$ was also fairly constant around 155mV. The experiment seems to have reached equilibrium. These experiments are an intermediate between oxic and strongly reducing experiments, as sulfite is only a modest reducing agent which can be seen in the relatively high $E_h$ during the course of the experiment. The arsenic concentrations during the course of the experiment were slowly rising from

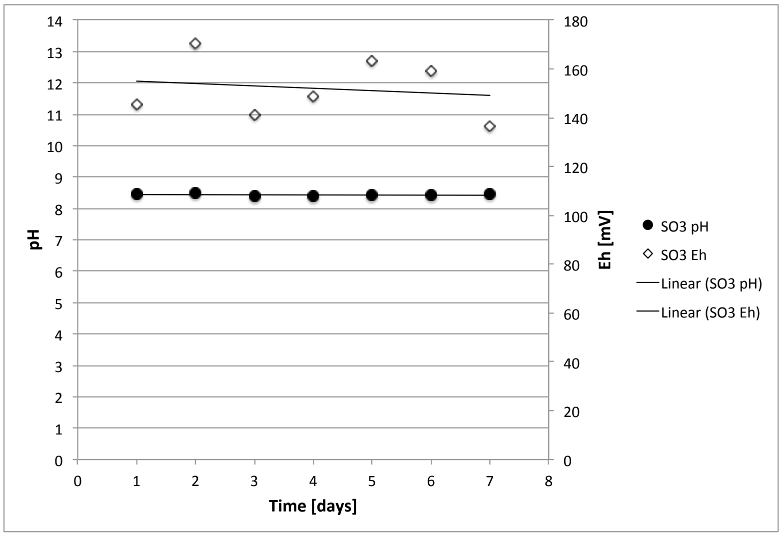

Figure A.20.: pH and $E_h$ progression for CD4c (Fe(III)/As(V)=4 under excess $SO_3^{2-}$-added stability testing

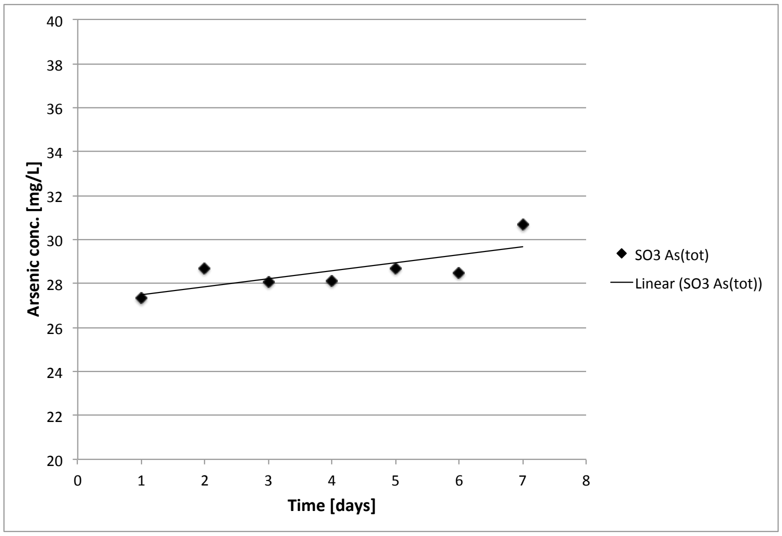

Figure A.21.: Arsenic concentrations for CD4c (Fe(III)/As(V)=4) in excess $SO_3^{2-}$

27.3mg/L to 30.7mg/L. The five data points in the middle were stable around 28.4mg/L. Since this was not a steady rise of all data points, it is hard to use the data to predict arsenic release over the long term. It might increase like the trendline shows. On the other hand it could, just as pH and $E_h$, be stable around 28.4mg/L and the data points (day 1 & 7) within the statistical highs and lows.
Titration with dichromate did not reveal any ferric reduction to ferrous. The ferric matrix stays intact. The mechanism for arsenic release is therefore difficult to explain. It is possible that sulfite adsorbs competitively with arsenate. Sulfate adsorption on ferric surfaces is very weak in the presence of arsenate, as arsenate adsorption experiments onto ferrihydrite from sulfate media show [2]. Sulfite adsorption is expected to be similar in strength. Hence this may seem unlikely. However the sheer amount of sulfite ($SO_3^{2-}$/As(V)=12) could shift the adsorption equilibrium towards release of arsenic.

**Conclusion:** Excess sulfite $SO_3^{2-}$ was not able to reduce arsenate to arsenite. It was further not able to reduce ferric. The release of arsenate in excess $SO_3^{2-}$ could be due to competitive adsorption.

## A.3. References

[1] Y. Jia and G. P. Demopoulos. “Adsorption of arsenate onto ferrihydrite from aqueous solution: influence of media (sulfate vs nitrate), added gypsum, and pH alteration.” In: *Environmental Science & Technology* 39.24 (2005), pp. 9523–7.

[2] C. Doerfelt, unpublished data, 2013.