Mechanisms of Arsenic (As) Release and Retention During Fenton Rreatment of Nine Wastewater

Norberto Jr Aquino[1], Musah Salifu[1], Ksenia Novikova[2], Erik Månsson[2], Erik Ronne[2], Lena Alakangas[1]

[1]*Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, SE-971 87 Luleå, Sweden*

[2]*Boliden AB, SE-101 20 Stockholm, Sweden*

Abstract

This study investigates the mechanisms controlling arsenic (As) removal and retention during Fenton treatment of mine wastewater from 2015 to 2025. Results show a substantial decrease (sevenfold) in dissolved As concentrations during treatment accompanied by an increase in particulate As (sixfold), indicating transfer of As from aqueous to the solid phase. Sequential extraction results suggest that As is proportionally associated with Fe oxide phases (≈13.2%). These observations indicate that As removal is primarily controlled by adsorption and co-precipitation with Fe(III) (oxyhydr)oxide precipitates formed during the Fenton reaction and subsequent liming. The findings provide insights into the geochemical processes governing As stabilization in mine wastewater treatment systems and highlight implications for the long-term management of treatment residues.

Keywords: Arsenic, Fenton reaction, wastewater, sludge, adsorption, co-precipitation

Introduction

Arsenic (As) is a toxic and carcinogenic metalloid commonly released from mining activities, posing risks to aquatic ecosystems and human health. The environmental behavior, mobility, and toxicity of As are generally governed by its speciation and geochemical conditions, particularly pH and redox state (Jomova *et al.* 2011). In aqueous systems, As primarily occurs as arsenite [As(III)] and arsenate [As(V)], with As(III) generally being more mobile and toxic (Wang *et al.* 2015), while As(V) exhibits stronger affinity for adsorption onto iron (Fe) hydroxides (Liu *et al.* 2024).

Mine wastewaters often contain elevated concentrations of As with complex mixtures of dissolved metals and reduced sulfur species (i.e. thiosalts). Treatment of such waters remains challenging at full scale due to the complexity of geochemical characteristics and interactions among multiple contaminants. For wastewaters with high thiosalts concentration, advance oxidation processes (AOPs), such as Fenton treatment (addition of H_2O_2 and $FeSO_4$), have been applied to promote oxidation and degradation (Olvera-Vargas *et al.* 2021). Fenton reactions generate reactive oxidants (e.g., hydroxyl radicals) and Fe(III) species, while subsequently form iron hydroxide precipitates upon pH adjustments and flocculation (liming and clarification).

While Fenton treatment is primarily implemented for oxidation of thiosalts, the simultaneous redox cycling of iron and formation of Fe(III) solids can influence As mobility. Acidic conditions during the Fenton stage may promote temporary As release, whereas subsequent liming and precipitation of Fe(III) hydroxides may enhance As retention through sorption and co-precipitation. In addition, Fenton reaction may oxidize As(III) to As(V), reducing its toxicity (Hug and Leupin 2003; Wang *et al.* 2015). With these complex mechanisms of As release and retention, it is therefore important to understand its behaviour, especially during full-scale Fenton treatment that will contribute to long-term management of As contamination in mine wastewater.

This study investigates the mechanisms controlling As release and retention during full-scale Fenton treatment and subsequent liming of mine wastewater by integrating long-term water quality monitoring data (2015–2025) with As partitioning and stability in the sludge.

Methods

Fenton Wastewater Treatment Process

Inflow wastewater originating from the mine tailings impoundment was subjected to full-scale Fenton treatment. Hydrogen peroxide (H_2O_2) was added with ferrous sulfate ($FeSO_4$), where Fe^{2+} catalyzed the decomposition of H_2O_2 and generated reactive oxidants. Following oxidation stage, slaked lime ($Ca(OH)_2$) was added to increase the pH and promote precipitation of iron hydroxides. The outflow water was then passed through a clarification area to enhance solid-liquid separation. The treated water was discharged to receiving tributaries, with a portion recycled within the mine site. The separated solids were classified as sludge.

Water Quality Monitoring

From 2015 to 2025, water samples were collected at three locations within the treatment system: (i) inflow (prior to Fenton treatment), (ii) outflow (after Fenton treatment and liming), and (iii) final discharge (after clarification). Samples were filtered (0.45 µm) to determine dissolved concentrations and analyzed unfiltered for total concentrations. Arsenic concentrations were quantified using Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) at ALS Scandinavia, Luleå, Sweden.

Sequential Extraction for Sludge Sample

Arsenic partitioning in sludge was determined using a six-step sequential extraction procedure (Dold 2003; Hall *et al.* 1996). One gram of dried and powdered sludge was subjected to a sequential extraction procedure to operationally define As partitioning among different geochemical fractions. The extraction steps targeted the following fractions: (1) water-soluble fraction extracted with ultrapure water (MQ-H_2O); (2) acetate-soluble fraction extracted with 1 M $NH_4CH_3CO_2$, representing exchangeable and carbonate-bound phases; (3) easily reducible fraction extracted with 0.25 M $NH_2OH{\cdot}HCl$, corresponding to amorphous oxide phases; (4) moderately reducible fraction extracted with 1 M $NH_2OH{\cdot}HCl$, representing crystalline oxide phases; (5) oxidizable fraction extracted using 0.75 g $KClO_3$ and 12 M HCl to target sulfide-bound phases; and (6) residual fraction determined by complete digestion of the remaining solids using HCl, HNO_3, and HF.

Results and Discussion

Arsenic Behavior during Fenton Wastewater Treatment Process

Changes in As concentrations were evaluated across the treatment process (Figure 1) to assess As removal and retention in the wastewater. The untreated inflow wastewater contained dissolved As concentrations averaging around 14 µg/L, with an average pH of approximately 8.7 prior to entering the Fenton reactor. Following Fenton treatment and subsequent liming (pH ≈ 10), average dissolved As concentrations decreased by about seven (7) times compared to the inflow. In contrast, average particulate As concentrations increased substantially during this stage (from 3 µg/L to 18 µg/L), likely reflecting the formation and suspension of newly precipitated solid phases. After clarification, the final discharge waters (pH≈ 8.4) exhibited a decrease in particulate As concentrations, indicating effective removal of suspended particles. Dissolved As concentrations remained relatively similar between the outflow and discharge stages despite pH differences (from ≈10 to 8). This behavior suggests that remobilization of As from the particulate phase was limited during the clarification step, indicating relatively stable retention of As within the solid phases formed during the treatment.

The distribution of As in the sludge sample was evaluated using a six-step sequential extraction procedure targeting operationally defined geochemical phases (Figure 2) to assess the stability of As in the treatment sludge. The results indicate that As is predominantly associated with the residual (58.2%) and sulfide-bound (15.8%)

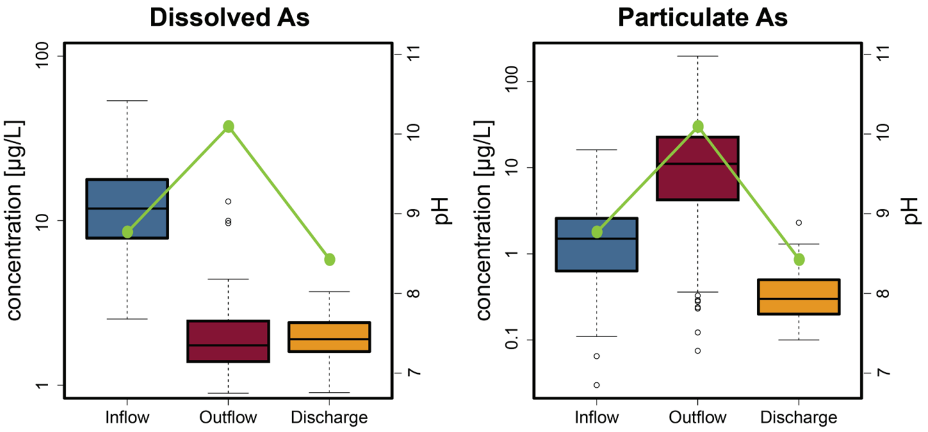

Figure 1 *Dissolved and particulate arsenic (As) concentrations across treatment stages. Boxplots show dissolved (left) and estimated particulate (right; calculated as total minus dissolved) As concentrations in inflow, post-treatment outflow, and final discharge waters. Boxes represent interquartile range (IQR), center lines indicate medians, whiskers denote 1.5x IQR, and empty circles represent outliers. Green circles and lines represent average pH across treatment stages (right Y-axis). Note the logarithmic left Y-axis scaling.*

fractions, suggesting its potential association with structurally stable mineral phases such as silicates and sulfide minerals (e.g., Arsenopyrite) likely from the mine tailings. This indicates that it is not only water that enters the Fenton reactor but also includes particulates and sand from the mine tailings impoundment. Comparable proportions of As were also associated with the crystalline oxide (12.6%) and carbonate-bound (12.8%) fractions, suggesting adsorption and co-precipitation with secondary iron hydroxide minerals formed during treatment as well as incorporation into carbonate phases generated during the liming step. Only minor amounts of As were detected in the amorphous oxide fraction (0.6%), while the water-soluble fraction was negligible (<0.1%).

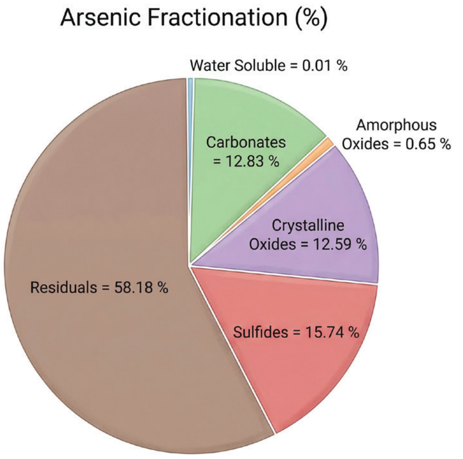

Figure 2 *Distribution of As among operationally defined geochemical fractions in sludge determined by sequential extraction.*

Potential Controls on Arsenic Removal and Retention from Mine Wastewater

Fenton reaction supports the oxidation of metastable sulfur species (e.g., thiosulfate) into a more stable form (e.g., sulfate). Moreover, it may also support oxidation of other species such as As(III) to As(V) as well as oxidation of sulfidic minerals hosting As (Noor *et al.* 2011). The behavior of As in a lab-scale Fenton system has been investigated by Hug and Leupin (2003), who demonstrated that the reaction between Fe(II) and H2O2 produces oxidizing species (e.g., hydroxyl radicals) capable of oxidizing As(III) to As(V). The oxidation of As(III) occurs in parallel with Fe(II) oxidation, facilitating removal through adsorption and co-precipitation with Fe(III) (oxyhydr) oxides. However, in the current study, almost all dissolved As concentration is in the form of As(V), which is estimated and calculated through PHREEQC (wateq4f.dat). Thus, the Fenton oxidation process has a minimal control on As stabilization in the wastewater. It should be noted that the presence of H2O2 during the Fenton process creates strongly oxidizing conditions that favor the formation of As(V). Consequently, the dominance of As(V) predicted by the PHREEQC calculations is consistent with the expected redox environment of the treatment system. However, because measured redox potential (Eh) data were not available, the PHREEQC model assumes equilibrium conditions, which may not fully represent the actual As(III)/As(V) distribution in the system.

Assuming that the system is dominated by As(V), this may suggest that dissolved As has a high affinity of adsorption to Fe(III) (oxyhyd)oxide surface (Liu *et al.* 2024). In the Fenton wastewater treatment system, Fe^{2+} oxidizes to Fe^{3+} (Zeliger 2022), which then go through hydrolysis and eventually form Fe(III) (oxyhydr)oxides precipitates (Figure 3) under alkaline conditions (pH ≈10). These newly formed Fe precipitates can provide sorption sites for different As species (Liu *et al.* 2024) (Figure 3). For instance, As(III) can adsorb onto Fe(III) hydroxide surfaces through inner-sphere surface complexation (e.g., adsorption to micropore, macropore, mesoporous). In contrast, As(V) occurs mainly as negatively charged oxyanions (e.g., $H_2AsO_4^-$ and $HAsO_4^{2-}$) that bind to positively charged surface sites on Fe (oxyhydr)oxide through electrostatic attraction in addition to its inner-sphere surface complexation. Due to its anionic property, As(V) generally exhibits a higher adsorption affinity to Fe (oxyhydr)oxide compared to As(III) under several environmental conditions. This interpretation is somehow reflected in the calculated average dissolved Fe/As ratios across the treatment stages. In the untreated inflow water, dissolved Fe/As is relatively low (≈1.76), suggesting limited availability of Fe sorption sites relative to dissolved As. Following Fenton reaction and liming treatment, the dissolved Fe/As ratio increases to ≈46, indicating a large excess of dissolved Fe that can hydrolyze and precipitate as Fe(III) hydroxides, thereby providing sorption sites for As. After flocculation, the dissolved Fe/As ratio decreases to ≈10, reflecting removal of Fe-bearing particulates from the water column, but still remains in a concentration sufficient to maintain As co-precipitation with Fe phases as compared to the inflow ratio. This is further supported by the sequential extraction result where a substantial proportion of As was associated with amorphous and crystalline Fe oxide phases (≈13.2%). Although As is mostly associated with the sulfide and residual phases, this does not necessarily indicate that all As in these fractions occurs exclusively as discrete sulfide or silicate minerals. Sequential extraction technique is a qualitative method and is operationally defined (Dold 2003; Hall *et al.* 1996). This may lead to challenges like non-specificity and incomplete dissolution. As a result, the residual and sulfide fractions

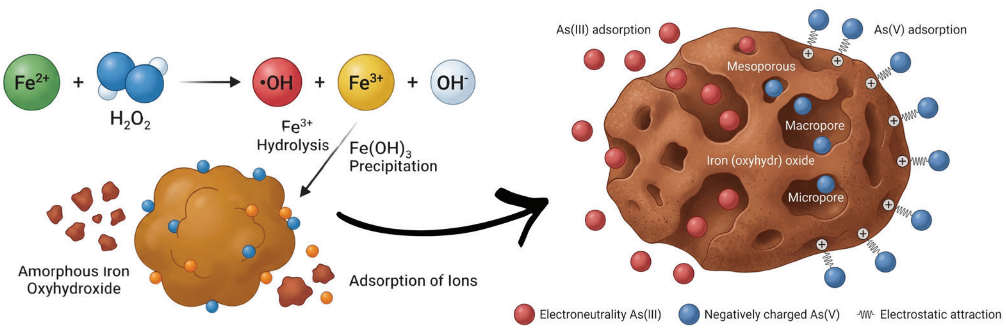

***Figure 3** Conceptual illustrations of arsenic removal and retention mechanisms during Fenton treatment of mine wastewater. Fenton reaction is modified and adapted from (Zeliger 2022) and As adsorption in Fe (oxyhydr)oxide is adapted from (Liu et al. 2024).*

may also include As incorporated within complex mineral matrices or strongly bound to mineral surfaces (e.g., strongly bound As to Fe hydroxide surface) that are not readily dissolved by earlier extraction reagents. Therefore, while the sequential extraction results suggest relative stability of As in the sludge, they should be interpreted cautiously and together with mineralogical analysis (e.g., SEM and XRD) after each extraction step.

Conclusions

Fenton treatment ideally promotes the oxidation of As(III) to As(V) in wastewater treatment system, although in the present system the untreated wastewater is already dominated by As(V) based on PHREEQC calculations. The addition of Fe during the Fenton process followed by the addition of lime leads to the precipitation of Fe(III) (oxyhydr)oxide which facilitates the removal of dissolved As in the system through adsorption and surface complexation. This process effectively removed dissolved As from the wastewater and transfer it to the resulting solid which is the treatment sludge.

Although this treatment reduced dissolved As concentrations in the treated effluent, the long-term stability of As retained in the sludge remains an important challenge. Arsenic associated with the Fe-rich sludge may remain stable under certain environmental conditions (e.g., alkaline with pH ≈8) but could potentially remobilized under changing environmental conditions such as strong reducing and oxidizing environments, pH fluctuations, or mineral transformation processes.

These findings highlight the importance of not only treating contaminated wastewater but also addressing potential As mobilization at the early stages of mine waste system. For instance, As stabilization or removal at the source can be considered through improved management of mine tailings, extraction of contaminated wastewaters, or early treatment of drainage streams. While such approaches do not eliminate the formation of As-bearing sludge, they can reduce the overall As load entering treatment systems and enable better-controlled handling of sludge, thereby lowering the risk of re-dissolution and unintended environmental release, particularly near discharge points. Nevertheless, treatment sludge generated from mine wastewater remains an ongoing environmental management challenge. Thus, sustainable stabilization and valorization techniques for sludge handling should be explored.

Acknowledgements

This project is co-funded by the European Union, the Swedish Agency for Economic and Regional Growth, and the Center of Advance Mining and Metallurgy (CAMM) at Luleå University of Technology.

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