THE EVOLUTION OF ARSENIC IN THE URANIUM MILL PROCESS AT MCCLEAN LAKE MINE, SASKATCHEWAN, CANADA

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Abstract

The McClean Lake Uranium Mill in Northern Saskatchewan was designed to accommodate the wide variation in the percentage or arsenic which occurs naturally within uranium ore bodies of the Athabasca Basin without producing adverse environmental effects. After over 15 years of mill operations and the direct study of arsenic through the mill process and in the tailings, a detailed understanding of the geochemical evolution of arsenic has been achieved.

Arsenic enters the mill as reduced arsenide minerals such as niccolite (NiAs), rammelsbergite ($NiAs_2$) and gersdorffite (NiAsS) which are not always fully oxidized during the leaching process. Residual primary arsenic mineralization is, therefore, transferred to the tailings preparation process in an unstable form. It undergoes oxidation to secondary mineral phases controlled by the final circumneutral tailings geochemistry in the Tailings Management Facility (TMF). The oxidation of arsenides to stable arsenates is a two-step process: there is a rise in As^{3+} values in the tailings pore water and then a subsequent fall as As^{3+} is oxidized to As^{5+} and precipitated as the mineral scorodite.

Verifying this model of arsenic mineral speciation in the tailings is essential to predicting the long-term evolution of arsenic mineralization in the TMF and ensuring that the process is protective of the environment. Most recently, X-ray Absorption Near-Edge Structure (XANES) spectroscopy was used to analyze fifty samples from three boreholes through the TMF. Overall, as predicted, scorodite in equilibrium controls the release of arsenic in the tailings, maintaining As^{5+} pore water concentrations at < 1 mg/L.

1. Introduction

AREVA resources Canada Inc. (AREVA) is the principal owner of the McCLean Lake Operation (MLO) that operates a uranium mill in the Athabasca basin of northern Saskatchewan, Canada. Operations at the MLO commenced in 1999 with an anticipated operating life of approximately five decades, over which several different ore bodies will have been processed. Most uranium ore bodies in the Athabasca basin are co-mineralized with arsenic and nickel bearing phases principally including gersdorffite (NiSAs), niccolite (NiAs), rammelsbergite ($NiAs_2$) and skutterudite ($NiAs_3$). There is a wide variation in the arsenic co-mineralized content in the ore bodies investigated to date: the average ore body

As content ranges from about 300 µg/g to as much as 50,000 µg/g. Localized zones within each ore body can possess significantly higher values than the average. With this in mind AREVA must ensure that the MLO produces no harmful long-term environmental effects.

Arsenic is of primary importance when considering long-term environmental effects because of its known environmental and human toxicity when in solution [1,2,3]. Early in the development of the MLO Tailings Management Facility (TMF) federal and provincial regulators expressed concerns that significant concentrations of adsorbed arsenic and nickel might be released with time from the tailing solids to the pore water within the TMF and ultimately to the surrounding groundwater flow system. This lead to the initiation of a long term tailings optimization and validation program (TOVP) to ensure that all constituents of concern are sequestered over the long term as a solid chemical precipitates. Scorodite, which is formed with the most oxidized form of arsenic (As^{5+}), was identified as the most stable iron arsenic mineral under the geochemical conditions present in the TMF [4,5]. Over the course of the TOVP it has been shown that, through optimization of the tailings preparation process at the MLO, all the arsenic in the pore water of the tailings will gradually oxidize over time and be sequestered as scorodite [6]. When this process is complete the long term pore water value of arsenic (As^{5+}) in solution will be <1 mg/L, well below the established environmental objectives required for long term arsenic pore water concentrations of less than 5 mg/L.

2. Leaching

The MLO utilizes a hydrometallurgical leaching process to extract the uranium from the ore, where it is principally found as uraninite (UO_2). Because of the mill constraints needed to optimized uranium leach efficiencies (typically 99%); the arsenic leaching efficiency is lower, typically 70-95%. The arsenic that is leached is oxidized to soluble arsenite ($[AsO_3]^{3-}$; As^{3+}) and finally to arsenate ($[AsO_4]^{3-}$, As^{5+}) which eventually report to a waste solution with a pH<1.5 (raffinate). The concentration of arsenic in the raffinate solution can range from <100 mg/L to >10,000 mg/L depending on the initial arsenic concentrations in the ore and is approximately 99.5% As^{5+}. Arsenic that did not oxidize and dissolve remains in the leach residue solids as very minor (<1%) primary mineralization (gerdorffite and occasionally rammelsbergite). The bulk of the leach residue solids are composed of unreacted quartz and clays when it is finally deposited as tailings.

3. The Tailings Preparation Process

After leaching, all the waste solids (leach residue) and solutions (raffinate) from the uranium process are directed to tailings preparation process for final processing before they are discharged to the JEB tailings management facility (TMF), **Figure 1**. Primary minerals report as part of the leach residue, as previously discussed, while secondary minerals are present as precipitated phases from the neutralized raffinate solution. The secondary minerals are generally poorly crystalline and/or amorphous mineral analogues of secondary minerals such as scorodite or ferrimolybdite, except for gypsum which makes up a large portion of the tailings (20-40%). Most of the solid arsenic content in the tailings

slurry a part of the secondary mineralization from the raffinate. The leach residue and raffinate are combined in a mixing tank where the pH and Eh are controlled to approximately 1 and +680 mV respectively. A Fe^{3+}/As molar ratio of at least 3 is maintained through the continuous addition of ferric sulphate ($Fe_2(SO_4)_3$). The pH is then raised from pH 1 through the controlled addition of lime ($Ca(OH)_2$) in two reactor tanks first to pH 4, and then to the terminal pH of 7.5. As the pH is raised to 4 in the first neutralization reactor tank, arsenic (As^{5+}) is almost entirely co-precipitated with Fe^{3+}. A large quantity of Fe^{3+} remains in solution which is precipitated as hydrous ferric oxide (HFO) as the pH is increased to the terminal pH in the second reaction tank. The near neutral discharge pH and the controlled addition of Fe^{3+} to co-precipitate arsenic in the tailings preparation process at the MLO are unique to the uranium mining industry [7].

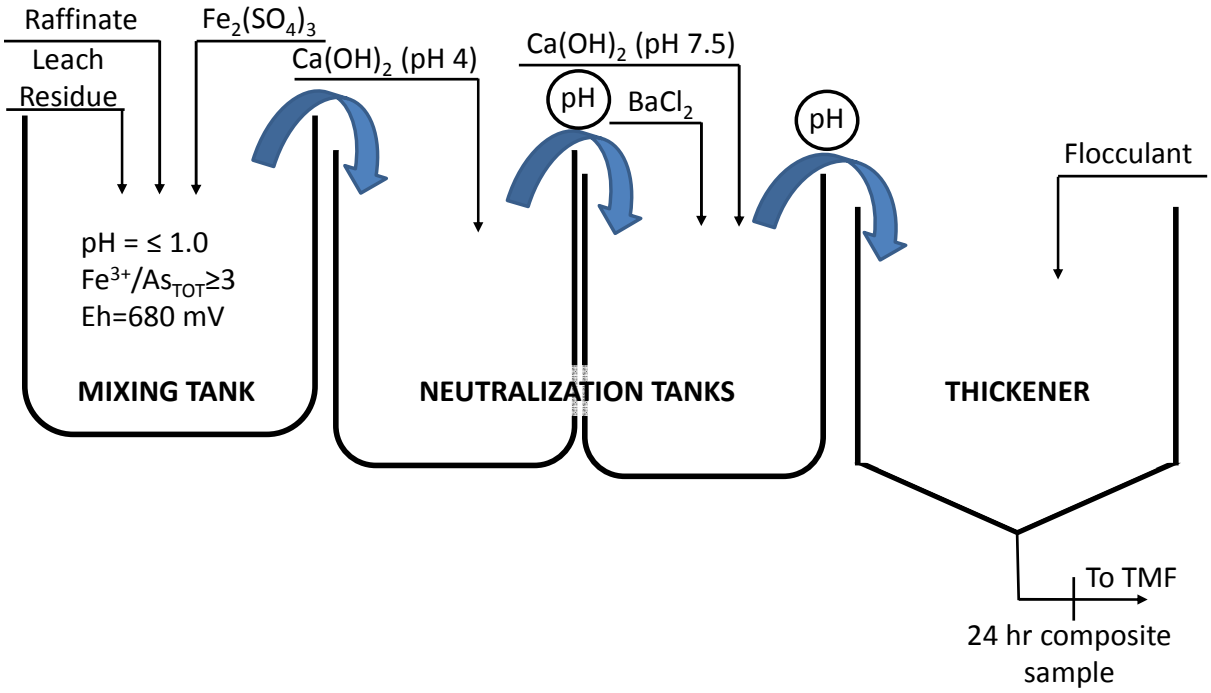

Figure 1 Schematic of the MLO tailings preparation process

4. Initial Raffinate Solids Testing to Identify Arsenic Mineralization

Large-scale test work was conducted from 1997-1999 to support initial licensing of the MLO and develop the tailings preparation process [8,9]. The test work demonstrated that by maintaining a Fe^{3+}/As molar ratio of ≥3 in solution by varying the quantity of ferric ion added to the mix tank, arsenic mineralogy was consistent irrespective of the arsenic content of the ore being processed. Testing showed that arsenic was primarily sequestered in poorly crystalline scorodite ($FeAsO_4 \bullet 2H_2O$) with secondary adsorption onto ferrihydrite (AsO_4–FeOOH). All arsenic present in the laboratory generated tailings was as As(V).

A series of laboratory batch neutralization tests were performed using actual plant raffinate solutions, following the startup period at the MLO. The co-precipitation process of arsenic with iron of the actual tailings preparation circuit was followed [10,11]. Typical results indicated that, up to pH 3.23, essentially all of the arsenic had co-precipitated with Fe^{3+} in a near 1:1 molar ratio as poorly crystalline scorodite. As the pH was raised further the majority of the ferric ion remaining in solution precipitated initially as HFO. These observations replicated the results of the large-scale laboratory test work conducted prior to start up [9] and demonstrated that: (1) neutralization to pH 4 with a retention time of 90 minutes in the first reactor tank optimized the precipitation of As(V) in poorly crystalline scorodite, and (2) significant poorly crystalline scorodite was present at the terminal pH 7-7.5.

To further substantiate the existence of poorly crystalline scorodite at pH 7 in the neutralized raffinate solids at the MLO, synchrotron based X-ray absorption spectroscopy (XAS) techniques [6] were applied to selected neutralized raffinate samples. An EXAFS study [12] concluded that a poorly crystalline scorodite appears to characterize the bulk of arsenic speciation in neutralized raffinate solids well into the pH 7 range. This was the first concrete mineralogical evidence of the occurrence of a scorodite-like (amorphous) phase in ferric arsenate co-precipitates produced by neutralization of strongly acidic solution with an Fe^{3+}/As molar ratio >1.

5. Long-term Monitoring and Placed Tailings Research

A long-term tailings monitoring and research program, known as the "Tailings Optimization and Validation Program" (TOVP), is a requirement of the operating licence granted to the MLO by the Canadian Nuclear Safety Commission. The TOVP validates that the predicted long-term environmental effects from the TMF fall within what was originally assessed, approved and licensed. The program investigates arsenic containing mineral phases produced by the tailings preparation process and conducts regular sampling of the emplaced tailings solids to verify that these arsenic mineral phases i.e. scorodite and arsenical ferrihydrite, are present.

Synchrotron based XAS techniques were utilized in the identification of ferric-arsenate structure in the co-precipitates formed in the neutralized raffinate solids. This methodology was also applied to whole tailings collected from the TMF during an intrusive drilling campaign in 2008. Using the Hard X-ray Micro Analysis end station at the Canadian Light Source synchrotron facility, EXAFS spectra was collected from the 2008 tailings samples to compare with the EXAFS collected from the neutralized raffinate solids. In both systems, the data is consistent; there is a significant contribution to the peak at 2.5-3.0A from the As-Fe shell in the scorodite structure [12]. Bulk arsenic in the system was identified as poorly crystalline scorodite, based on the peak position of arsenic-iron scattering (**Figure 2**).

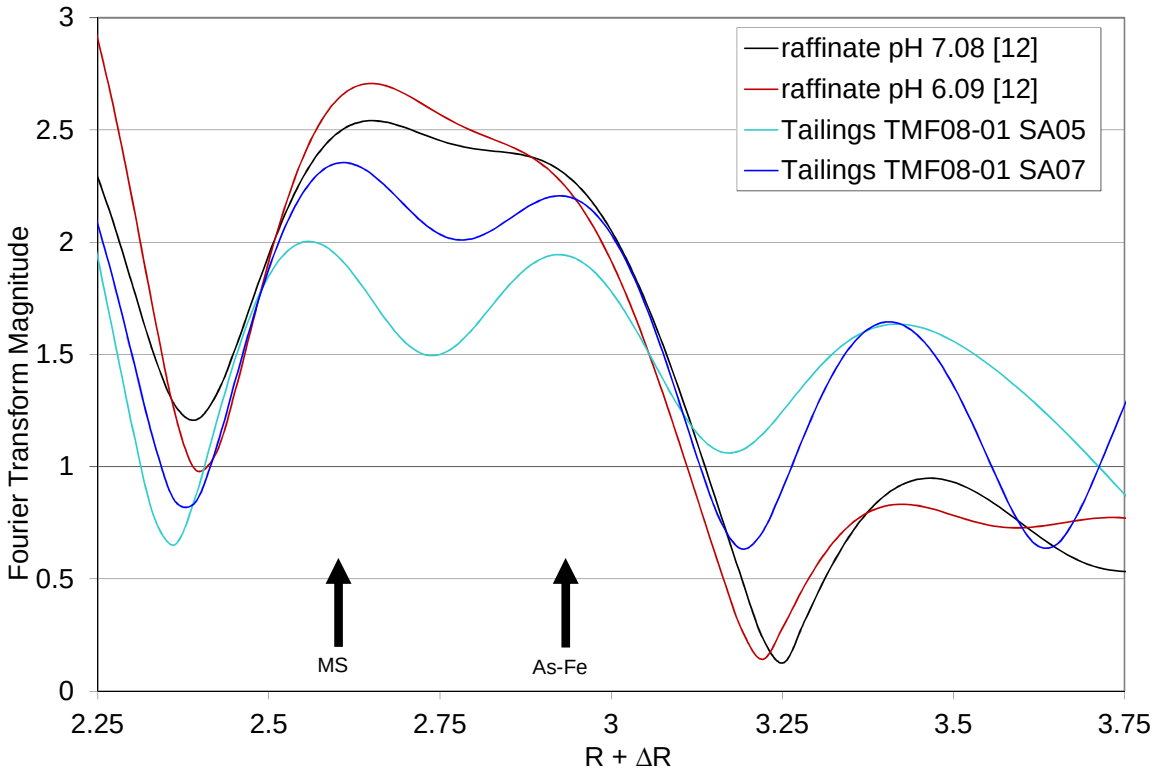

Figure 2 Comparison of the Fourier transform magnitude in the region of the As-Fe shell for laboratory produced tailings [11] and actual tailings from the MLO TMF sampled during the 2008 TOVP.

This work has led to an understanding of the long-term equilibrium of arsenic in the tailings pore water which is used to predict any post-decommissioning environmental effects. The long-term tailings pore water concentration of As(V) is predicted to be <1mg/L. Scorodite, when placed in water at near neutral pH, such as in the tailings, will begin to dissolve incongruently i.e. the Fe/As molar ratio in the solution is different from the solid. The Fe^{3+} released into solution will precipitate as ferrihydrite and initially the AsO_4^{-3} will remain in solution. However, as the As concentrations increase in the solution AsO_4^{-3} will be adsorbed onto the ferrihydrite initiating the process of mineral evolution to scorodite [13,14]. It is apparent that the dissolution is reversible via a mechanism involving an assemblage of these three Fe^{3+} - AsO_4^{-3} phases. Eventually, an equilibrium will be established with scorodite dissolving at the same rate as it is formed (**Figure 3**). A distinct amount of AsO_4^{-3} would be distributed among the three phases, which was supported by observations using bulk XANES combined with linear combination fitting (LCF) on samples from the 2013 TOVP sampling campaign (**Figure 4**). Looking at this typical tailings sample the XANES technique is unable to distinguish between AsO_4^{3-} adsorbed on ferrihydrite or amorphous FeAsO4 so the spectrum identified as amorphous FeAsO4 represents the total of these two species. At this sample location a majority of the AsO_4^{3-} has partitioned as scorodite with smaller amounts present as adsorbed or amorphous $FeAsO_4$. Amorphous $FeAsO_4$ is considered a short-term transitional phase as the mineralogy of the tailings ages and more crystalline scorodite is produced. The presence of As^{3+} is also noted as As_2O_3 which is also expected as a transition phase while As^{3+} continues to oxidize to As^{5+}.

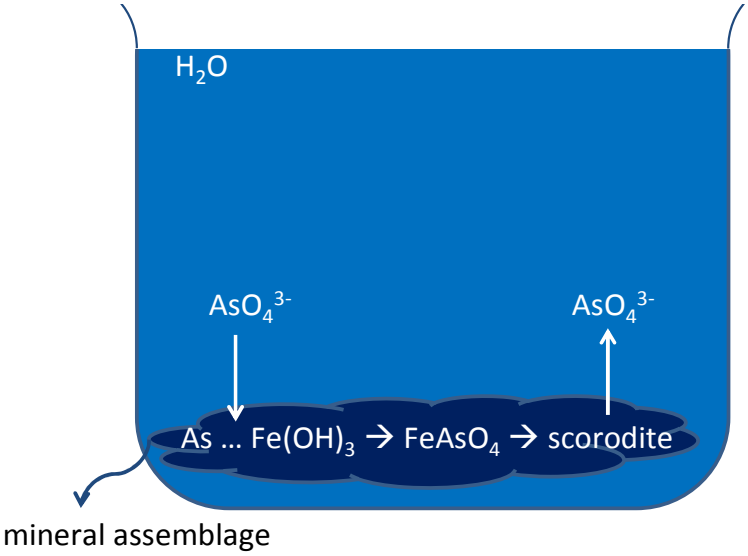

Figure 3 Simplified illustration of the control of As^{5+} solutions concentration by equilibrium with synergistic Fe^{3+} - AsO_4^{3-} mineral assemblage.

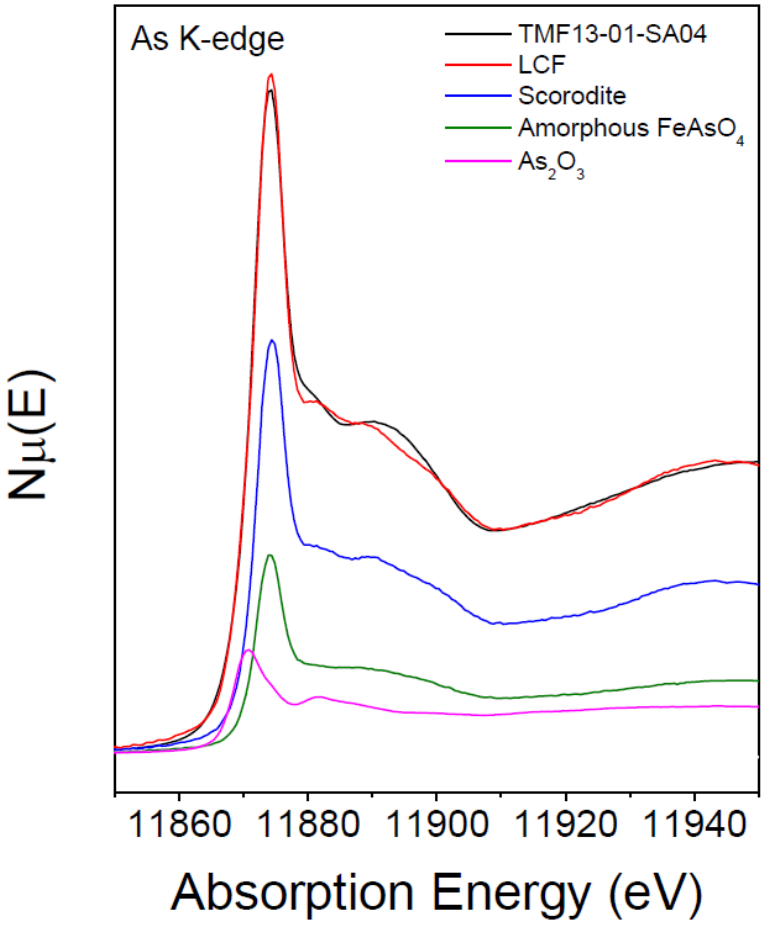

Figure 4 As K-edge XANES spectrum of tailings sample TMF13-SA04 from the 2013 TOVP [Scorodite (59± 4%,), Amorphous $FeAsO_4$ (23±5 %), As_2O_3 (186%)]

6. Conclusions

Since 1997 the processes in place at the MLO to sequester arsenic over the long-term have been carefully tested though a continuously evolving series of experimental initiatives. Early testing indicated that arsenic is sequestered as the mineral scorodite and subsequent synchrotron-based XAS investigations of the placed tailings have supported this initial work. The ongoing TOVP continues to increase the evidence for scorodite sequestration of arsenic in the tailings and this work will be continued to develop the data set of this unique approach to tailings and to ensure long-term protection of the environment.

7. References

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