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AGING OF REDUCED ARSENIC MINERALS IN URANIUM MILL TAILINGS AT THE MCCLEAN LAKE OPERATION

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ABSTRACT

The primary arsenic minerals in the uranium ore processed at the McClean Lake Operation are rammelsbergite, niccolite and gersdorffite. During processing, a large fraction, typically (80 - 95%), of these reduced minerals is oxidized and dissolves primarily as As^{5+} in the leachate solution. In the tailings preparation circuit the dissolved As^{5+} is precipitated as a poorly crystalline form of the mineral scorodite. Following subaqueous deposition in the tailings management facility, a temporal rise and fall in arsenic pore water concentrations has been observed. This is due to the oxidation of the residual quantities of reduced arsenic minerals initially present in the tailings sediment. The XANES (x-ray absorption near edge spectrometry) technique has shown that As^{1-} is gradually oxidized to As^{3+} and then finally to As^{5+} in the tailings sediment. This oxidation process results in a temporary accumulation of As^{3+} in solution and is the source of the rise and fall in arsenic concentration observed.

1. INTRODUCTION

The McClean Lake Operation is an uranium mine and mill facility operated by AREVA Resources Canada Inc. It is located 700 km north of Saskatoon on the eastern edge of the Athabasca Basin. At McClean Lake, the JEB mill has been in operation since 1999. It was designed to process ore from various uranium deposits in the region. Co-mineralized arsenic is commonly associated with uranium deposits in the region [9] and the arsenic content of the ore can range from 0.025% to 4%. Therefore, the mill process had to be capable of treating waste solutions with a wide range of arsenic concentrations. The tailings produced from the mill are ultimately disposed of in the JEB Tailings Management Facility (TMF). This permanent, below grade, subaqueous disposal of a large volume of tailings presents technical challenges because the potential for constituent release from this facility to affect water quality in nearby lakes and streams over the long term exists.

To control long term release of potential constituents of concern to the surrounding groundwater flow system, the JEB TMF is dependent on two principal design parameters. The first principal design parameter is a fine-grained tailings material that, when consolidated, has a hydraulic conductivity at least two orders of magnitude less than the surrounding sandstone. Under these conditions for the long term, the consolidated tailings represent a low-permeability zone and groundwater is expected to preferentially flow around the tailings mass through the surrounding host rock as illustrated in Figure 1.

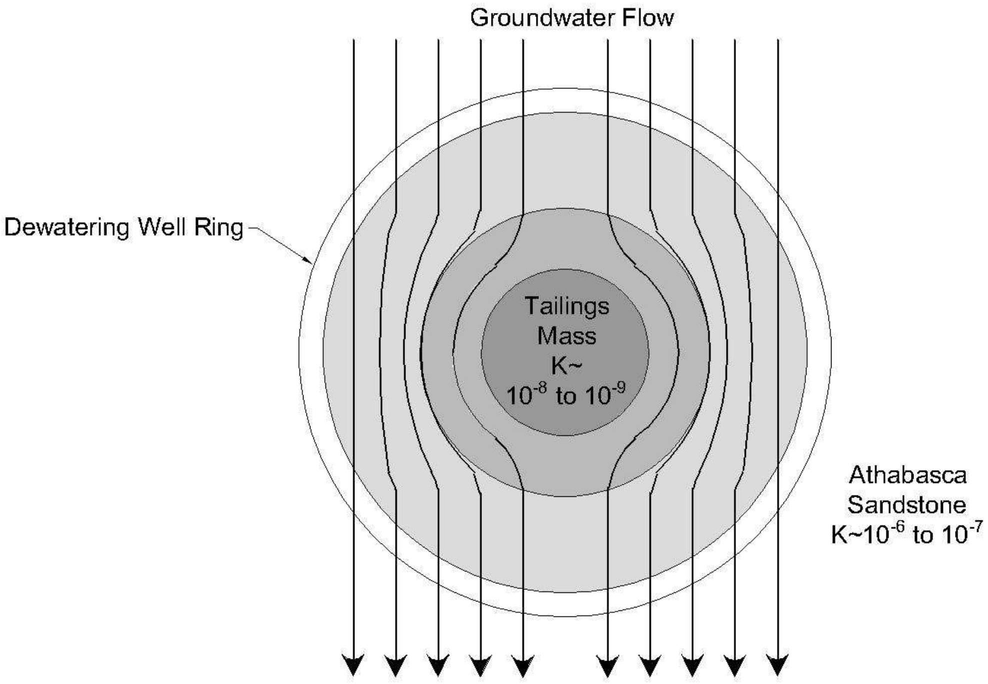


Figure 1. Plan view depicting the principle physical containment control of the JEB TMF.

2. DESIGN OF THE TAILINGS PREPARATION CIRCUIT

The preliminary design of the tailings preparation circuit began with a comprehensive literature review and initial scoping tests where fixation of arsenic by ferric iron was selected as the most promising option for consistent treatment of tailings and raffinates. This was followed by larger scale test work conducted at AREVA’s pilot plant facility by Service d’Etudes de Procédés et Analyses or SEPA. SEPA Protocol 1 was developed to optimize the impact of iron and lime additions on dissolved arsenic concentrations in tailings raffinate and SEPA Protocol 2 applied an accelerated aging test to estimate the long term arsenic pore water concentration within tailings placed in the TMF. A summary of the SEPA protocols is provided, while the details can be found in Langmuir et al. [4].

The SEPA Protocol 1 was designed to define optimum conditions for removal of arsenic from the raffinates during processing of the tailings by adjusting the Fe/As ratio of tailings raffinates and adjusting the final pH due to slaked lime addition. The procedure simulated the reactions that take place in the mill tailings preparation circuit. Representative tailings were produced in a pilot plant from all ores intended to be processed through the JEB mill. Varying amounts of ferric sulphate and slaked lime were added to reaction vessels that contained 1 kg of tailings and 6.0 L of raffinate solution. These tests were preformed in contact with atmospheric oxygen for three hours duration, the expected residence time of the tailings during processing.

The results of the SEPA Protocol 1 tests indicated that by adding ferric sulphate and slaked lime in the tailings preparation circuit to give a raffinate Fe/As molar ratio of at least three and a nominal pH of 7.5, arsenic concentrations of 2 mg/L or less were consistently achieved.

Mineralogical analyses of the laboratory processed tailings concluded that tailings solids include largely unaltered mineral phases from the original ore and a roughly equal amount of solids precipitated by neutralization of the acid raffinate solutions. The majority of the arsenic was precipitated as a poorly crystalline form of the mineral scorodite as the pH was increased by lime addition. All arsenic present in the solids was in the As^{5+} oxidation state.

The accelerated aging portion of the SEPA tests (Protocol 2) were designed to help predict long term arsenic concentrations in TMF pore water after disposal. The tests used the reaction products from the Protocol 1 tailings preparation tests as initial starting materials. The tests were carried out in sealed vessels and continued for 5-6 days to maximum of 49 days, under anaerobic conditions at three different temperatures: 50 °C, 25 °C, and 4 °C. The reactions were accelerated by agitating the vessels on a shaker table.

Predictions from the accelerated aging tests gave consistent results and showed that arsenic concentration in pore waters was unlikely to exceed 2 mg/L in the long term for all ores expected to be processed by the JEB mill.

3. OVERVIEW OF MILLING PROCESS

The JEB mill employs both sulphuric acid, as a lixiviant, and hydrogen peroxide, as an oxidant, to liberate uranium from ores mined in the Athabasca Basin. This same process liberates approximately 80% of the arsenic in the ore. The uranium is then removed from the acidic leach solution through contacting an organic matrix in the solvent extraction process. The arsenic remains in the acidic sulphate waste solution, referred to as raffinate.

The raffinate reports to the tailings preparation circuit for precipitation of elements of concern and pH adjustment. All process waste streams, both solid and liquid, are treated concurrently by the JEB mill tailings preparation process. After neutralization, the tailings are placed in the JEB tailings management facility.

The results of the SEPA tests defined the parameters to be used in the tailings preparation portion of the mill process. The preparation circuit employs a pre-treatment stage and a two stage neutralization process (Figure 2). The pre-treatment involves the addition of ferric iron to the raffinate waste stream to achieve a molar ratio greater than or equal to three parts ferric iron to one part arsenic. (Fe/As molar ratio ≥ 3). During vigorous mixing, washed residual solids from the leach circuit are added to the raffinate and ferric iron solution, now referred to as tailings feed solution. The tails feed solution is then directed to the primary reaction tank, where slaked lime addition increases the solution pH from 1 to 4. The stage 1 neutralization tank has a residency time of 90 minutes where slaked lime addition increases the solution pH to 7.5. The slurry from the primary tank is then transferred to the secondary reaction vessel. The secondary neutralization tank also has a residency time of 90 minutes. The arsenic is precipitated with ferric iron as a poorly crystalline form of the mineral scorodite – $FeAsO_4 \cdot 2H_2O$ as identified by XRD, SEM, EM, and EXAFS analyses of the solids [1, 5].

The neutralized slurry is then pumped to a high rate thickener, where the slurry is settled and subsequently deposited in the tailings management facility (TMF) for long term disposal. Tailings lines from the mill run down the TMF ramp onto a floating walkway leading to the placement barge. The discharge pipe is suspended below the barge and the tailings are placed within a fluidized bed of tailings using a shallow injection tremie method. The deposited tailings flow in a laminar motion outwards from the deposition point to the outer edges of the TMF.

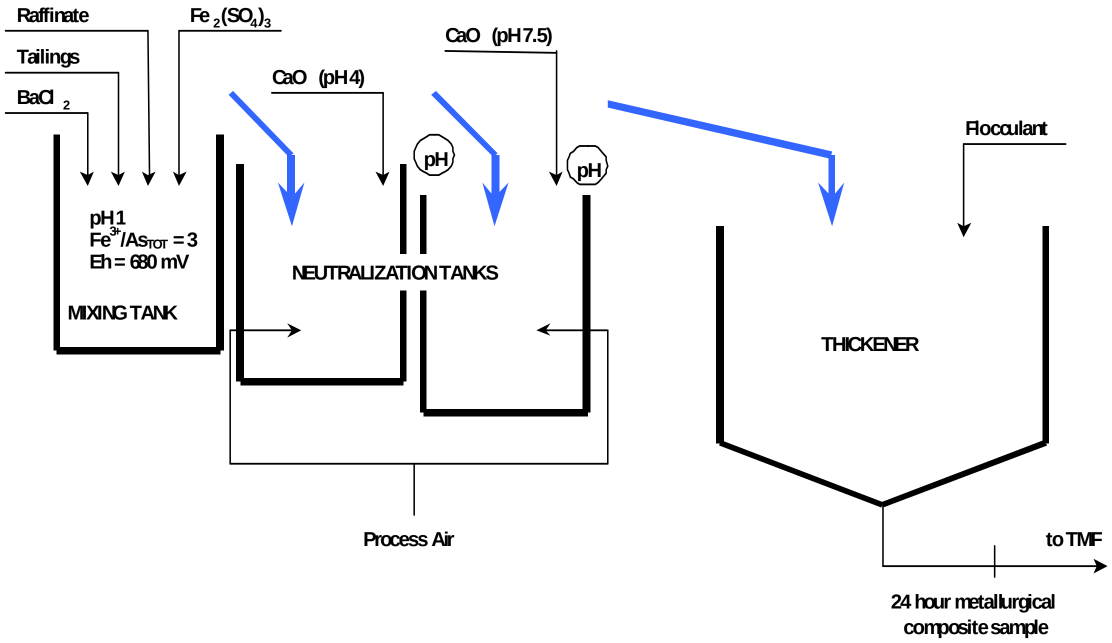


Figure 2. Schematic diagram of tailings preparation process.

4. PERFORMANCE OF TAILINGS PREPARATION CIRCUIT

When actual production tailings became available, the Tailings Optimization and Validation Program or TOVP aging tests were developed and carried out to validate the performance of the tailings preparation circuit. Initial TOVP aging tests used relativity high arsenic JEB ore which contained about 0.5 to 0.8 wt % arsenic. The Fe/As molar ratio of the acid raffinates was approximately 4. The acid raffinates held about 1100 mg/L arsenic and 1200 mg/L iron. Tailings and raffinates were neutralized with lime in two stages; to pH 4 and 7.5. Samples for the aging tests were obtained by sampling the tailings thickener underflow over a 24 hr period. The samples were split into separate 1 L sample containers for storage at 4 °C, 20 °C, and 50°C for successive time periods ranging up to 320 days. Sample containers including solids and neutralized raffinate were stored at temperature without mixing until sampled for chemical and mineralogical analysis.

The results of the TOVP aging tests exhibited a temporary rise and fall of arsenic concentration in the pore water, which was not evident in the SEPA aging tests. The arsenic concentration increased immediately after tailings preparation and then decreased over time to the original concentration as shown in Figure 3. The time to reach an equilibrium concentration was dependent on temperature, with the lower temperature series taking the longest time and the higher temperature series taking less time.

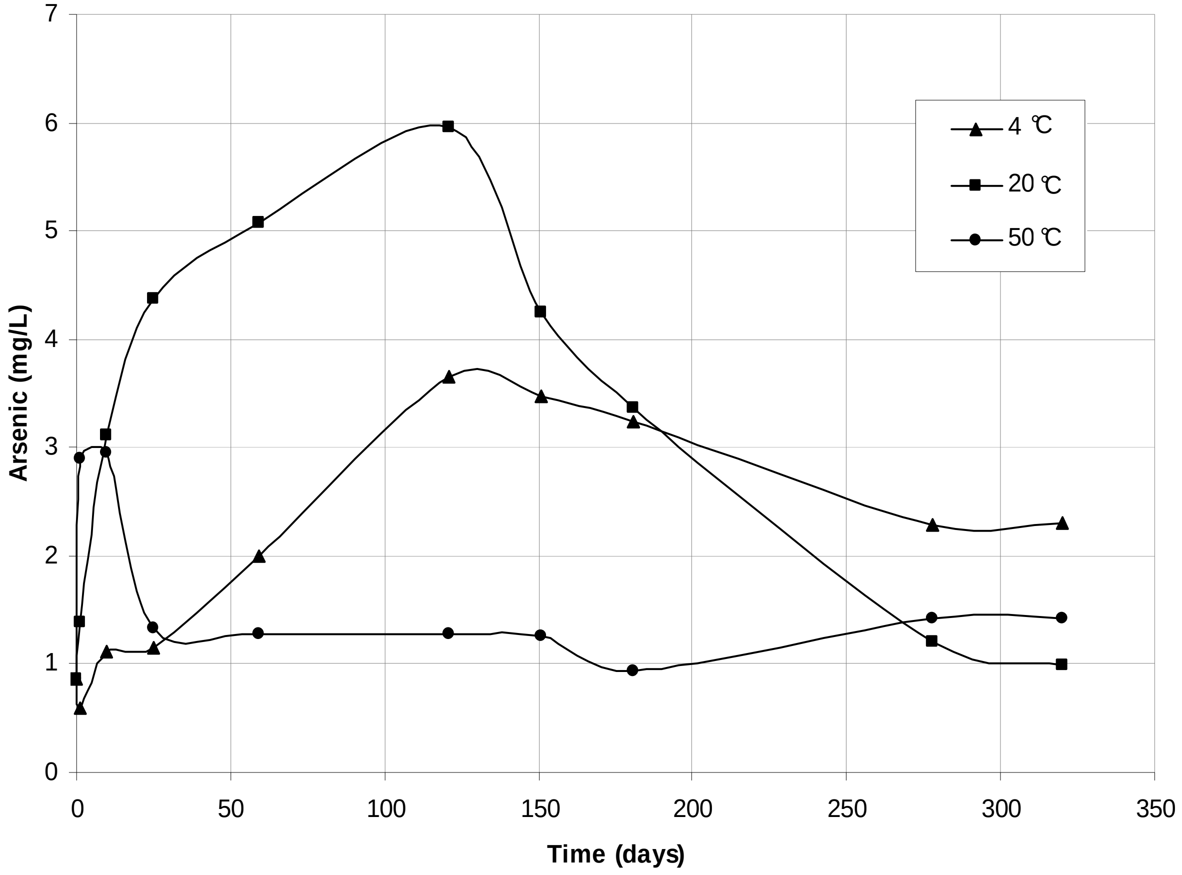


Figure 3. JEB ore TOVP aging test results - arsenic concentration in tailings pore water.

Figure 4 provides a comparison of arsenic pore water concentrations generated by the two techniques. For the SEPA aging technique, the arsenic pore water concentration reach its terminal value within the first day of aging and remained at the same value for the 63 day aging period. Arsenic concentrations in the TOVP test case gradually rose for about seven days and then declined slightly for 14 days. After 21 days, until the end of the aging period, both tests produced very similar results.

There is a significant difference between the SEPA and TOVP aging test techniques with respect to reaction kinetics. The SEPA tests were continuously agitated on a shaker table, while the TOVP aging tests were static in the sample container, only being vigorously agitated upon final sampling. By agitating the samples the reaction kinetics were increased in the SEPA tests, while diffusion controlled kinetics dominated the TOVP aging tests.

It was suspected that the rise and decline of arsenic concentration was caused by the release of arsenic to solution from an unstable or metastable solid, followed by incorporation of the arsenic in a more stable solid with time. Arsenic was allowed to accumulate in the pore water before precipitating due to the slow reaction kinetics of a diffusion dominated system. Additional TOVP aging tests were conducted to confirm and further investigate this theory.

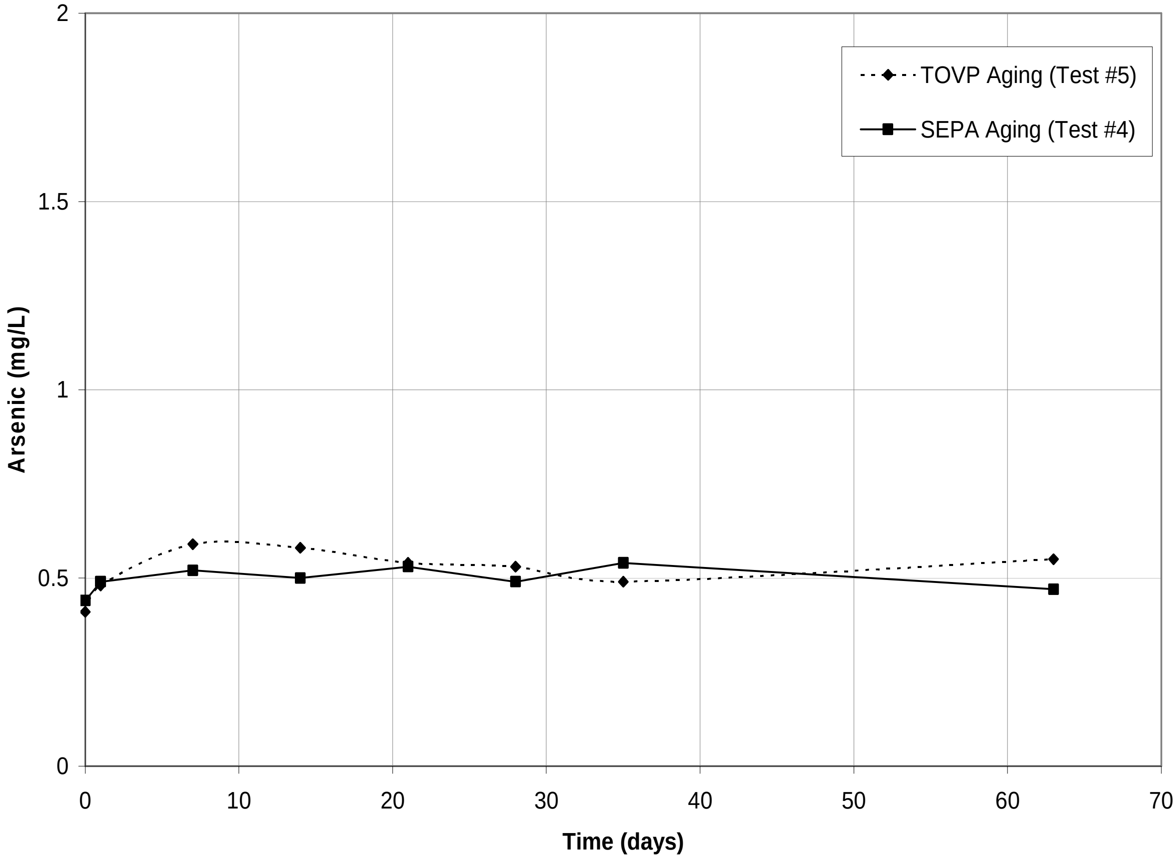


Figure 4. Comparison of arsenic pore water concentration generated by SEPA and TOVP aging techniques.

The additional TOVP aging tests compared the effects of different raffinate preparations. TOVP test #6 included a preliminary oxidation of the raffinate to achieve a As^{5+}/As_{TOT} ratio of 100% compared to TOVP test #8 which had a As^{5+}/As_{TOT} ratio of 62%. Figure 5 compares the pore water arsenic concentrations for TOVP tests #6 and #8. In pore water generated from fully oxidized raffinate, the arsenic concentration climbed slowly for approximately seven days and remained relatively constant until the termination of aging. In contrast, for the partly oxidized experiment, the arsenic concentration rose sharply to about three times the terminal value in two to three days, and then reduced to the terminal value within 21 days. Thereafter, until the end of aging, the pore water arsenic concentrations were similar for both tests #6 and #8.

For the partially oxidized arsenic tests, a small quantity of soluble As^{3+} is present at the start of aging. Within seven days of aging, As^{3+} is no longer detectable in the sample. This implies that during the early stage of aging with partially oxidized tailings, the small amount of As^{3+} entering the pore water is oxidized to As^{5+} by Fe^{3+} and precipitates. In summary, the additional TOVP tests identified As^{3+} in the initial raffinate as responsible for the transient arsenic concentration observed in the TOVP aging tests.

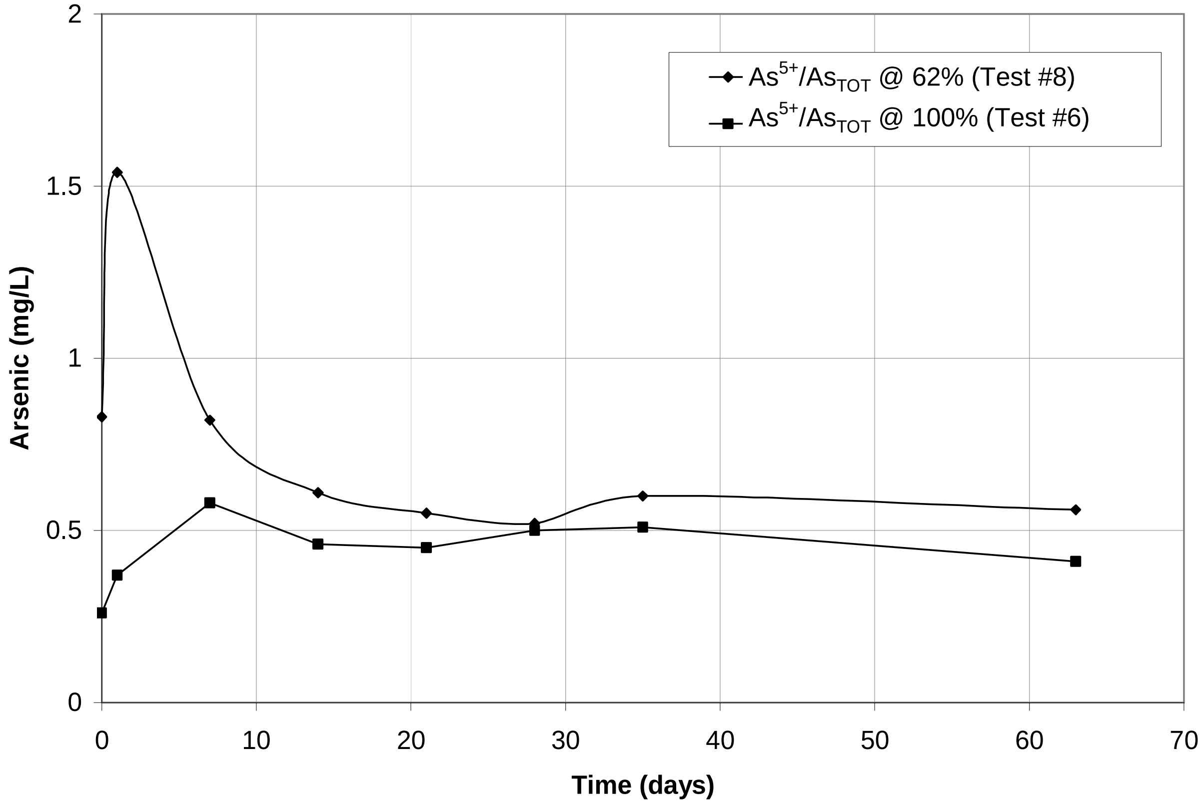


Figure 5. Effect of arsenic oxidation state in initial raffinate on arsenic concentration during TOVP aging tests.

Recent TOVP aging tests completed on Sue A tailings produces similar results to previous TOVP aging tests (Figure 6). In this case, arsenic concentrations reached a maximum of approximately 13 mg/L before declining to 2 mg/L. The arsenic concentration reaches equilibrium after approximately 350 days.

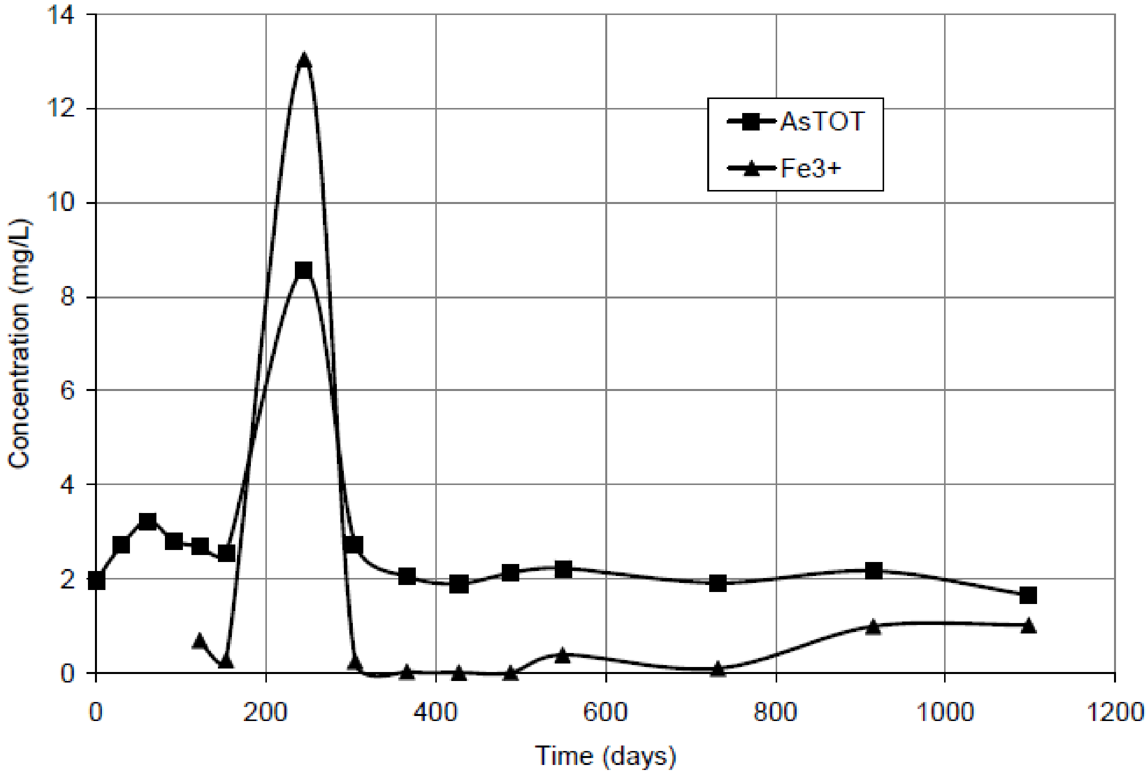
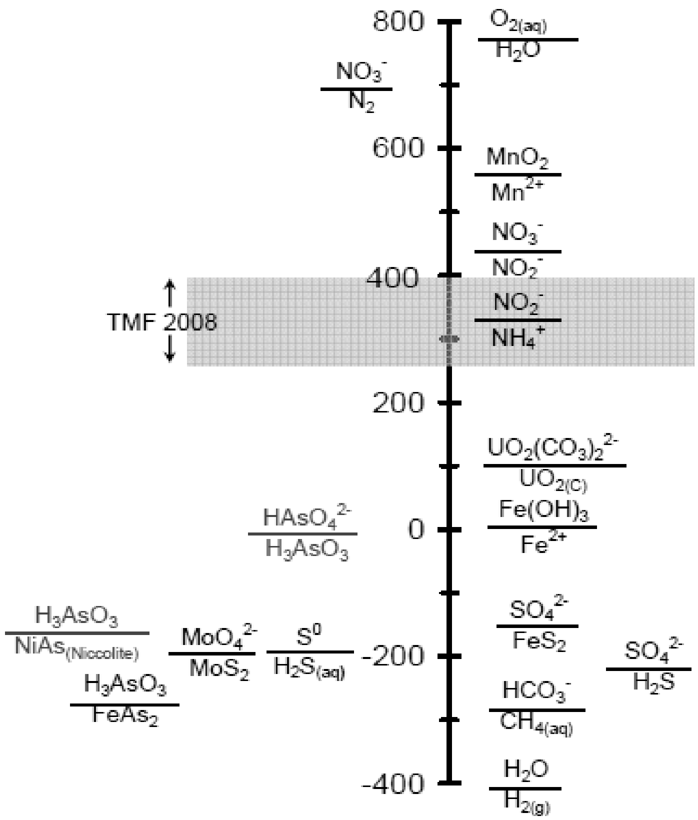


Figure 6. TOVP aging test of tailings and raffinate produced from milling of Sue A ore.

To help understand the oxidation of As^{3+} to As^{5+} in the tailings pore water, a redox ladder diagram from Langmuir [3] shows the Eh values at pH 7 that correspond to different oxidation reduction reactions at chemical equilibrium (Figure 7). The range of Eh measurements completed to date for TMF pore waters is indicated in this Figure (+200 mV to +500 mV). Between these Eh values, species found in the pore water that have a range of stability include NO_3^-, NO_2^-, NH_4^+, $[UO_2(CO_3)_2]^{2-}$, Mn^{2+}, MoO_4^{2-}, AsO_4^{3+}, Fe^{3+}, SO_4^{2-}, and HCO_3^-.

However in the TMF, minor concentrations of reduced species such as As^{3+} and residual amounts of initial arsenic minerals such as rammelsbergite and niccolite have been observed. These latter minerals were not dissolved during leaching and arsenic is present in the As^{1-} oxidation state. Figure 7 indicates that none of the latter species are thermodynamically stable within the more oxidizing Eh range measured in TMF pore waters. Over time, redox sensitive species are evolving to more stable forms within the TMF sediments. This evolution takes a long time because redox processes have very slow kinetics [2]. The pore water therefore contains a mixture of thermodynamically stable and unstable redox-sensitive species. Several redox environments are physically distributed in the TMF due to varying tailings characteristics. Within the pore water analytical data, evidence exists that these reduced species are being oxidized with time.



The theoretical Eh (mV) of some important oxidation reduction couples at equal molar ion concentrations except as indicated below at pH 7 and 25 °C. Other conditions are: NO_3^- /N_2(aq) at N_2(aq) = 14 mg/L, NO_3^- = 62 mg/L; MnO_2 (pyrolusite)/Mn^{2+} at Mn^{2+} = 1 mg/L; $UO_2(CO_3)_2^{2-}$/UO_2(uraninite) at 10^{-8} mol/L dissolve U(VI) and P_{CO2} = 10^{-2} bar; $Fe(OH)_3$/Fe^{2+} at Fe^{2+} = 1 mg/L assuming K_{sp} for $Fe(OH)_3$ = $10^{-38.5}$; SO_4^{2-}/FeS_2(pyrite) at Fe^{2+} = 1 mg/L and SO_4^{2-} = 96mg/L; MoO_4^{2-}/MoS_2 at MoO_4^{2-} = 10^{-6} mol/L and total S = $10^{-3.7}$ mol/L; and S° (native sulphur)/H_2S(aq) at H_2S(aq) = 108 mg/L (10-1.5 mol/L). Modified after [3]. Arsenic solids data from [7]. Data for FeS_2 from [3]. Data for niccolite (NiAs) from [6,8].

Figure 7. Eh ladder diagram for important redox sensitive species in TMF pore waters.

Laboratory testing has shown that small residual quantities of arsenic bearing minerals originally in the ore prior to processing, such as rammelsbergite, niccolite and gersdorffite, are present in the leach residue component of the tailings sediment.

Over a period of time, the As^{1-} is gradually oxidized in two steps from As^{1-} to As^{3+} and then finally to As^{5+} in the tailings sediment. The first oxidation step from As^{1-} to As^{3+} occurs more quickly and readily than the second step from As^{3+} to As^{5+}. This oxidation process results in a temporal accumulation of As^{3+} in solution until the As^{1-} source material has been depleted.

All laboratory aging tests to date concludes that the long term pore water concentration for arsenic will remain at 2 mg/L or less for tailings made from all ore bodies expected to be processed in the JEB mill.

5. TMF SEDIMENT AND PORE WATER SAMPLING

Pore water and sediment analytical results from the annual TMF sampling campaigns are being used to confirm that the laboratory aging test work predictions have provided a reliable basis for long term performance of deposited tailings. Four deep bore holes were sampled on five separate occasions. These four boreholes were located at approximately the same coordinates for each sampling campaign. Tailings sediments and pore water were sampled at the same elevations for each of the bore holes. This methodology has facilitated the observation of aging characteristics of the tailings sediment.

The XANES technique was used to analyze the sediment samples from the TMF sampling campaigns. XANES analytical data from the center bore hole with coordinates N11200; E5289 was plotted against sediment age in Figure 8. Measurable quantities of As^{1-} are found in the young sediments which appear to deplete to zero after about 700 days of aging in the TMF. The As^{1-} state is initially oxidized to As^{3+}. The As^{3+} content in the sediments is then observed, over a longer time frame, to deplete and become As^{5+} by a second oxidation step. Within 1,500 days of aging, the relative As^{5+} content has risen from 66% to 91%. This trend authenticates that the long term stable state for arsenic in the TMF sediments is As^{5+}.

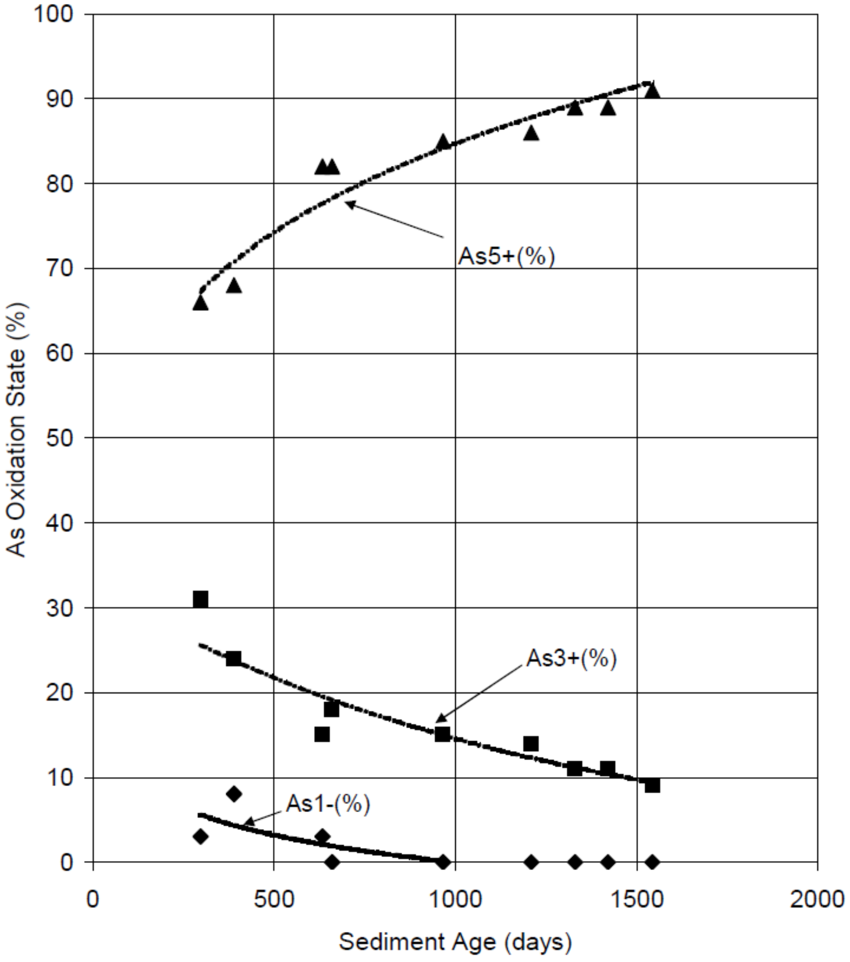


Figure 8. Relative arsenic oxidation state versus tailings sediment age bore hole coordinates N11200; E5289.

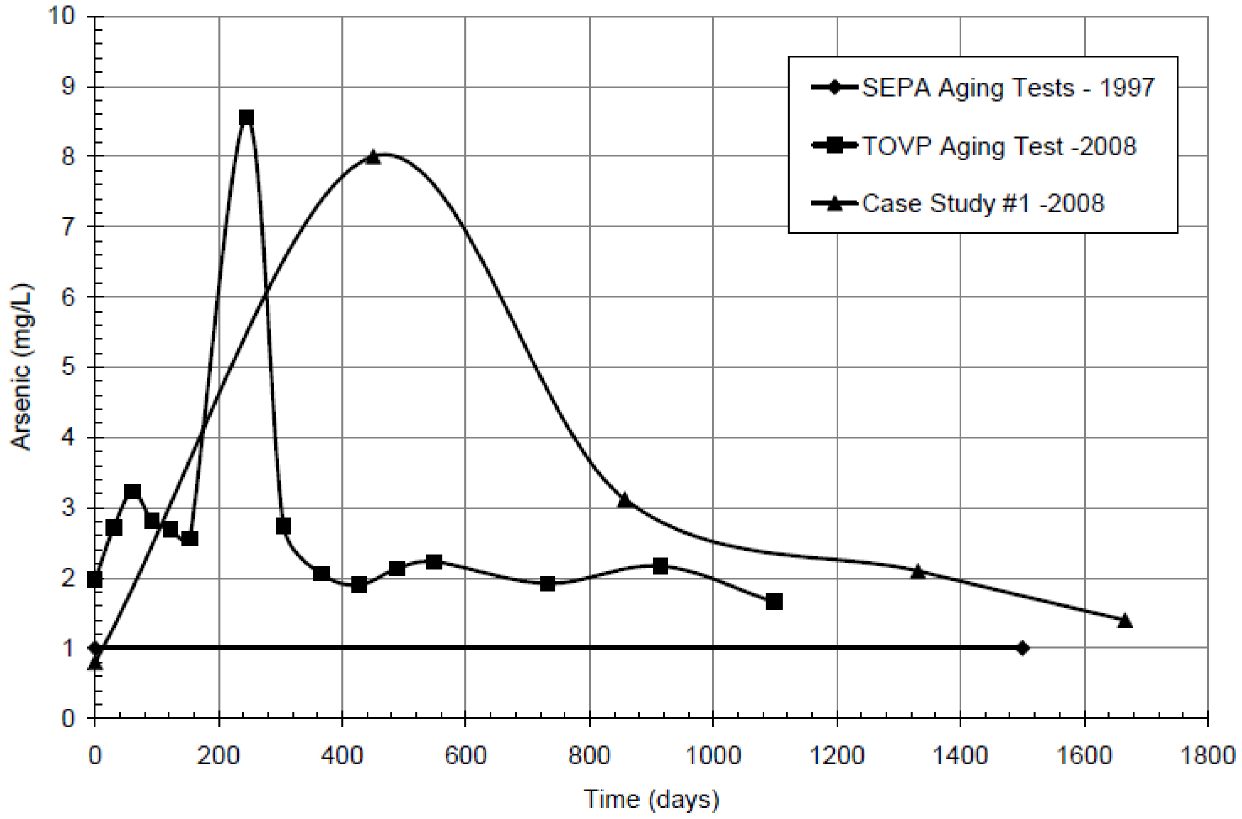


Figure 9. Arsenic pore water concentration comparison between SEPA aging tests, TOVP aging tests and TMF samples.

6. CONCLUSION

To protect the receiving environment, the JEB TMF at the McClean Lake Operation is dependent on physical as well as geochemical properties of tailings placed within it. The tailings are geochemically designed to maintain low concentrations of constituents of concern. Arsenic must be primarily contained in solid form within the TMF and the arsenic containing solids must be stable in an oxidized environment over the very long term.

Laboratory testing and TMF pore water and sediment sampling has confirmed the long term concentration of arsenic in the TMF pore waters to be 2 mg/L or less. The neutralized raffinate solids of the tailings sediment contain small amounts of arsenic in the As^{1-} and As^{3+} oxidation states. The As^{1-} state represents arsenic in the form of primary minerals of rammelsbergite and niccolite found in the initial ore. Partially oxidized remnants of these minerals are disclosed by the presence of the As^{3+} oxidation state in the leach residue solids. With reference to the Eh ladder diagram, Figure 7, neither of these oxidation states are thermodynamically stable within the more oxidizing Eh range in TMF pore waters. Over a period of several years, the As^{1-} is gradually oxidized by a two step process to As^{3+} and then finally to As^{5+} in the tailings sediments. The first oxidation step from As^{1-} to As^{3+} occurs more quickly and readily than the second step from As^{3+} to As^{5+}. If only As^{3+} were present, anticipated effects on arsenic pore water concentrations would be predicted to be minimal as the rate at which As^{3+} would go into solution would be governed by the rate at which As^{3+} can be oxidized to As^{5+} and removed from solution. However, the oxidation of As^{1-} generates an additional source of As^{3+} to the pore water at a rate faster than it can be oxidized to As^{5+} and removed from solution. This accumulation of As^{3+} in the pore water would be expected to exist until the source material had been depleted. The two stage arsenic oxidation process thus gives rise to the temporal rise and fall in As^{3+} concentrations predicted by the laboratory aging tests and observed in the TMF.

7. REFERENCES

1. Chen, N., Jiang, D.T., Cutler, J., Kotzer, T., Jia, Y.F., Demopoulos, G.P., and Rowson, J.W., "Structural Characterization of Poorly-crystalline Scorodite, Iron(III)-arsenate Co-precipitates and Uranium Mill Neutralized Raffinate Solids Using X-ray Absorption Fine Structure Spectroscopy", *Geochimica et Cosmochimica*, Vol. 73, 2009, pp.3260-3276.

2. Christensen, T.H, Berg, P.L., Banwart, S.A., Jakobsen, R., Heron, G., Albrechtsen, H., "Characterization of Redox Conditions in Groundwater Contaminant Plumes", *J. of Contaminant Hydrology*, Vol. 45, 2000, pp.165-241.

3. Langmuir, D., *Aqueous Environmental Geochemistry*, Prentice-Hall Inc., New Jersey, USA, 1997.

4. Langmuir, D., Mahoney, J., MacDonald, A., and Rowson, J., "Predicting Arsenic Concentrations in the Pore Waters of Buried Uranium Mill Tailings", *Geochimica et Cosmochimica Acta*, Vol. 63, 1999,pp. 3379-3394.

5. Mahoney, J., Slaughter, M., Langmuir, D., and Rowson, J., "Control of As and Ni releases from a uranium mill tailings neutralization circuit: solution chemistry, mineralogy and geochemical modeling of laboratory study results" *Applied Geochemistry*, Vol. 22, 2007, pp. 2758-2776.

6. Naumov, G.B., Ryzhenko, B.N., and Khodakovsky, I.L., *Handbook of Thermodynamic Data*. PB-226 722. Natl. Tech. Info. Serv., U.S. Dept. Commerce, Springfield, VA, USA, 1974.

7. Nordstrom, D.K. and Archer, D.G., "Arsenic Thermodynamic Data and Environmental Geochemistry", *in* Welch, A.H., and Stollenwerk, K.G., eds., *Arsenic in Ground Water: Geochemistry and Occurrence*: Academic Publishers, Boston, USA, 2002, pp.1-26.

8. Mah, A.D., and Pankratz. L.B., Contribution to the Data on Theoretical Metallurgy. XVI, *U.S. Bureau of Mines Bulletin 668*, Washington, D.C, USA, 1976.

9. Moldavan, B.and Hendry, M., "Characterizing and Quantifying Controls on Arsenic Solubility Over a pH Range of 1-11 in a Uranium Mill-scale Experiment", *Environ. Sci. Technol*., Vol. 37, 2005, pp.4913-4920.