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LONG-TERM FATE AND TRANSPORT OF ARSENIC IN AN IN-PIT URANIUM MINE TAILINGS FACILITY

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ABSTRACT

An important environmental issue facing the uranium mining industry in Saskatchewan is the quantification of the long-term migration of arsenic from its tailings facilities to the adjacent groundwater system. Decommissioning of these arsenic-rich tailings requires that the long-term arsenic source term for the tailings to the groundwater be defined. To meet this need, arsenic-rich uranium mine tailings from one in-pit tailings facility (tailings emplaced in a mined out open pit) were studied in detail. The tailings facility selected for study was the Rabbit Lake in-pit tailings management facility (RLITMF) in northern Saskatchewan, Canada. The tailings body in the RLITMF is 425 m long x 300 m wide x 100 m deep at its center and mill tailings were deposited in layers between 1985 (base) and 2004 (top). Associated with the low-level radioactive tailings is approximately 23,000 tonnes of arsenic. The in-pit design limits solute transport in these fine-grained tailings to diffusion. Because the layers of tailings have varying chemical characteristics (controlled by the ore being milled at the time), the total arsenic concentrations in the layers and their associated pore fluids range from 56 to 9,871 μg/g and 0.24 to 140 mg/l, respectively. As was the case for arsenic, the concentration of iron present in the layers was also variable (ranging from 8,967 to 30,247 μg/g). Synchrotron-based studies show that the arsenic in these tailings is strongly attenuated by adsorption to secondary 2-line ferrihydrite through inner sphere bidentate linkages. Single reservoir diffusion cell testing shows that the effective diffusion coefficient for arsenic in the tailings is 4.5×10^{-10} m^2 s^{-1}. Based on results from our field- and laboratory-based studies, the redistribution (via diffusion) and attenuation (via adsorption) of arsenic in the RLITMF was modelled using a one-dimensional geochemical reactive transport model to provide a source term for arsenic migration from the tailings to the regional groundwater systems over the next millennia.

I. INTRODUCTION

Arsenic contained within uranium mine tailings is a primary contaminant of concern in terms of its potential to affect downstream receptors. It can exist in four oxidation states (As^{5+}, As^{3+}, As^0, and As^{3-}). In most groundwaters, arsenic exists primarily as As^{3+} and As^{5+} with As^{3+} being up to 60 times more toxic and generally more mobile than As^{5+} (KORTE and FERNANDO, 1991). Surface adsorption or direct precipitation of arsenic with ferric oxyhydroxide, commonly known as ferrihydrite, is a dominant control on the solubility of arsenic in natural aquatic systems (PIERCE and MOORE, 1982). Ferrihydrite, a short ordered poorly crystalline solid, has a high adsorption affinity for the arsenate anion because of its reactivity and large specific surface area (>200 m^2/g) (FULLER et al., 1993). The degree of crystallinity of ferrihydrite determines its ability to effectively adsorb arsenic with the lowest ordered ferrihydrite (two-line ferrihydrite) having the greatest sorption affinity for arsenic (SWASH and MONHEMIUS, 1995).

The degree of arsenic adsorption on ferrihydrite (forming an arsenical ferrihydrite) is greater in solutions where arsenic and iron are co-precipitated simultaneously as compared to surface adsorption of arsenic after the formation of ferrihydrite. This is attributed to the strong adsorption of the arsenate anion to the surface of ferrihydrite, preventing Fe-O-Fe polymerization within the ferrihydrite lattice, thereby reducing the degree of crystallinity. In conditions where arsenic is introduced after the precipitation of ferrihydrite, much less adsorption occurs because polymerization has already progressed (WAYCHUNAS et al., 1993). Formation of stable arsenical ferrihydrite requires conditions where the Fe/As molar ratio in the original solution is greater than four. An increase in the Fe/As molar ratio in the solutions from which precipitation occurs results in an increase in the stability of the arsenical ferrihydrite as evidenced by lower solubility (KRAUSE and ETTEL, 1985). In contrast, arsenical ferrihydrite formed in conditions with low Fe/As molar ratios (<4) results in an increase in the solubility of arsenic by a factor of 100 to 1000 times (KRAUSE and ETTEL, 1985).

Arsenic-rich tailings produced at the Rabbit Lake uranium mine located in northern Saskatchewan, Canada are deposited in the Rabbit Lake in-pit tailings management facility (RLITMF). In-pit disposal of tailings is a preferred method, as compared to above ground tailings storage facilities, in that the presence of a more permeable zone surrounding the pit minimizes the hydraulic gradient across the tailings thereby greatly reducing the advective transport of contaminants from the tailings. Limiting the mechanism of mass flux to diffusion was done to minimize the flux of contaminants into the regional groundwater. The design of the RLITMF included the placement of a highly permeable (1.0×10^{-7} m/s) layer of rock in combination with a low permeability sand filter (1×10^{-10} m/s) , called a pervious surround, around the outside of the mined out pit. The geochemistry of the pore fluids contained within the tailings is very different from that of the regional groundwater. As well, there is variability of the aqueous geochemical parameters within the tailings pore fluids through depth in the tailings body (DONAHUE et al., 2000; MOLDOVAN et al., 2000). In both instances a concentration gradient exists and diffusion of solutes within the tailings body itself is possible as well as the potential for diffusion of solutes from the tailings body to the regional groundwater.

The objectives of the current study were to: (1) determine the chemical composition of the tailings solids and their associated pore fluids through the depth of the tailings body; (2) identify the mineralogical composition of arsenic present in mine tailings precipitated from iron-rich (Fe/As molar ratio >4) hydrometallurgical solutions; (3) assess the long-term stability of the arsenic precipitates in these mine tailings; (4)

provide an estimation of the diffusion coefficient (D*) and adsorption (distribution/partition) coefficient (K_d) of arsenic in uranium mine tailings and (5) use a one-dimensional diffusive transport model to assess the long-term evolution of arsenic within the mine tailings and the resulting source term of arsenic to the regional biota over the next millennia.

The objectives of this study were met by collecting tailings material through depth in the tailings body and analyzing the collected tailings solids and associated pore fluids for elements of interest. The tailings in the RLITMF provided a well-constrained system to study the long-term (10,000 yr) evolution of Fe^{3+}/As^{5+} compounds because the vertical distribution of iron and arsenic concentrations in the tailings corresponded to that in the mill feed, thus providing age-defined stratigraphic layers in the tailings management facility (DONAHUE et al., 2000). Mineralogical characterization of the arsenic-bound species in both fresh and aged mine tailings (up to 10 years) collected from the RLITMF was completed using synchrotron radiation based X-ray absorption techniques. Determination of the diffusion coefficient and adsorption coefficient of arsenic in the mine tailings was completed using single reservoir diffusion cell test work. Using results from field- and laboratory-based studies, the redistribution (via diffusion) and attenuation (via adsorption) of arsenic in the RLITMF was modelled using a one-dimensional mass transport model (MT3DMS) to provide the source term (mass flux) of arsenic migration from the tailings to the regional groundwater systems over the next millennia.

II. SITE BACKGROUND

The Rabbit Lake mine site is located approximately 800 km north of Saskatoon, Saskatchewan, Canada (58^0 15N and 103^0 40E). The climate is sub-arctic with a mean annual temperature of 4 ^{0}C (ranging from –45 ^{0}C to 25 ^{0}C) (CAMECO, 1992). The mine site is situated within the Athabasca Basin, which contains the world's richest uranium deposits. The Rabbit Lake mine began production in 1975, making it Canada's longest operating uranium mine. By September 1999, in excess of 10 million tonnes of ore were milled resulting in the production of 150 million pounds of yellowcake (U_3O_8).

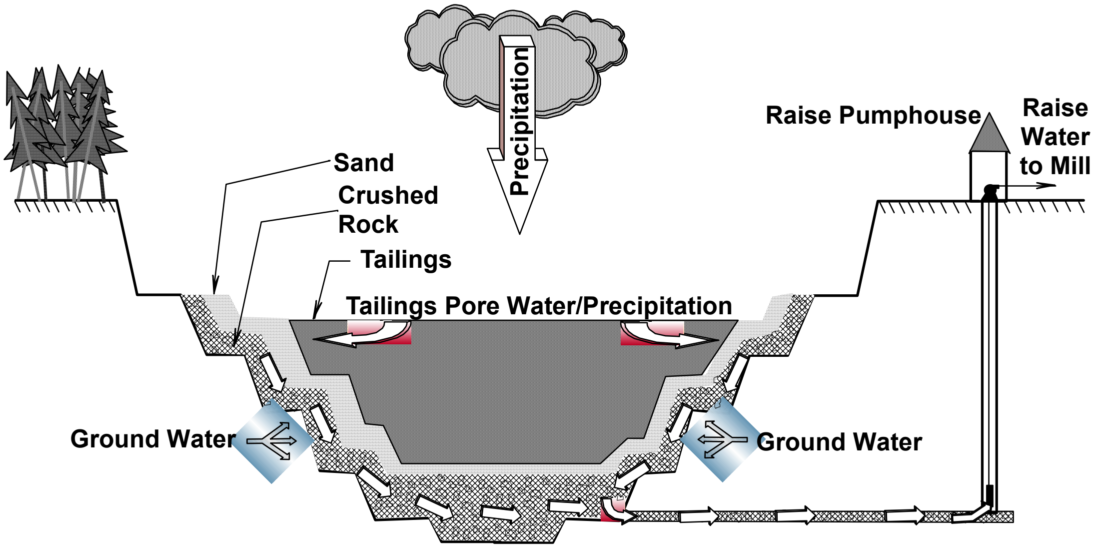

Figure 1. Design of the RLITMF. The pervious surround system consists of an outer coarse-grained rock and an inner sand filter pack installed between the pit wall and the tailings.

The RLITMF was developed in the mined out Rabbit Lake open-pit mine and tailings were deposited in the RLITMF since 1985. The design of the RLITMF included a pervious surround consisting of coarse-grained rock and sand filter pack that was placed between the pit wall and the tailings (Figure 1). Mine tailings are composed of residues from the ore leach process and precipitates from acid neutralization. The mine tailings ranged from a toothpaste-like consistency to fully consolidated, with 45% of the tailings solids passing through a 75 µm sieve (BHARADWAJ et al., 1995). As of January 2001, more than 5 million tonnes of tailings solids were emplaced in the RLITMF and the dimensions of the tailings body were about 425 m long and 300 m wide with a depth of 98 m at the centre. Contained within these tailings was approximately 23,000 tonnes of arsenic.

Groundwater conditions around the RLITMF are controlled through the dewatering of the pervious surround by pumping from a raise well connected to the pit bottom drain via a horizontal dewatering drift (Figure 1). The contaminated water from the dewatering drift is pumped to the Rabbit Lake mill for treatment. Groundwater levels are drawn down approximately 110 m below the original level and the resulting drawdown cone extends 500-800 m from the RLITMF.

III. RESULTS AND DISCUSSION

III.A. Geochemistry of the Uranium Mine Tailings

Core samples (n = 42) of tailings were collected to a depth of 70.6 m below the surface of the tailings near the centre of the pit in September 1999 using a sonic drill rig mounted on a barge. A detailed description of the sampling techniques, field measurements and analytical techniques for arsenic speciation of dissolved arsenic are described elsewhere (MOLDOVAN et al., 2000). Total arsenic concentrations in the mine tailings and their associated pore fluids ranged from 56 to 9,871 μg/g and 0.24 to 140 mg/l, respectively. The mean Eh, pH and temperature of the tailings were +161 mV (standard deviation = ± 53 mV; range from –64 to +316 mV), 9.94 (standard deviation = ± 0.53; range from 8.39 to 11.14), and 3.7^{0}C (standard deviation = ± 2.4^{0}C; range from –0.1 to 10.1^{0}C).

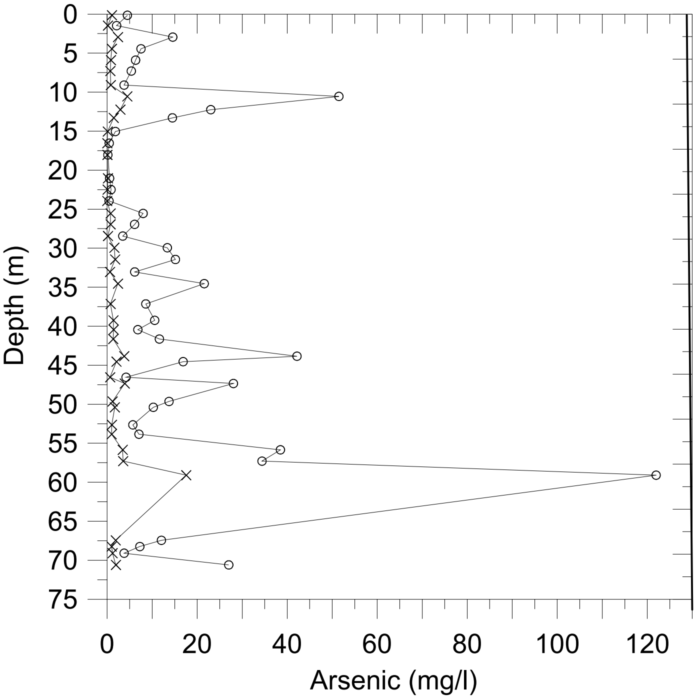

Figure 2. Concentration profile of dissolved As^{3+} (represented as x) and As^{5+} (represented as o) through depth of the RLITMF.

A summary of the vertical distribution of dissolved As^{3+} and As^{5+} in the tailings pore fluids is provided in Figure 2. The concentration of dissolved As^{3+} in the tailings pore fluids ranged from 0.03 to 3.57 mg/l. The concentration of As^{5+} in the tailings pore fluids ranged from 0.19 to 122 mg/l. The concentration of these dissolved arsenic species was directly related to the ore type milled at the time of tailings deposition (MOLDOVAN et al., 2000). In addition, greater than 95% of the dissolved arsenic in the tailings pore fluids existed in the As^{5+} state and was due to the oxidative conditions present during the milling process (Eh maintained at +660 mV during the leaching process). The variability in the concentration of As^{3+} and As^{5+} through depth of the tailings indicates a concentration gradient, which will be the driving mechanism for diffusive transport of arsenic within the tailings body.

III.B. Mineralogical Characterization of Arsenic-Bound Species in the Mine Tailings

Mineralogical characterization of the mine tailings was completed using synchrotron-based X-ray absorption studies. A detailed description of the analysis is presented elsewhere (MOLDOVAN et al., 2002). Synchrotron-based X-ray absorption spectroscopic studies of tailings samples, fresh mill precipitates, and reference compounds showed that the arsenic in iron-rich areas of the tailings existed as the stable As^{5+} and was adsorbed to 2-line ferrihydrite through inner sphere bidentate linkages. Furthermore, under the conditions in the RLITMF, the 2-line ferrihydrite did not undergo any measurable conversion to more crystalline goethite or hematite, even in tailings discharged to the RLITMF 10 years prior to sampling.

III.B. Determination of the Long-Term Evolution of As in the RLITMF

Single reservoir diffusion cell test work in conjunction with geotechnical procedures were used for the determination of the diffusion coefficient (D*), adsorption coefficient (K_d), mass loading capacity of As on ferrihydrite as well as porosity, specific yield, specific storage and bulk density. A description of this test work and the diffusive transport modeling is provided in MOLDOVAN et al., 2005.

Table 1. Input variable for simulation of diffusive flux of arsenic through the RLITMF tailings body with adsorption to ferrihydrite.

Parameter	Value
Diffusion Coefficient (D*) (m^2/yr)	0.0126
As loading capacity (moles As^{3+}/mole ferrihydrite)	0.00
As loading capacity (moles As^{5+}/mole ferrihydrite)	0.50
Adsorption coefficient (K_d) (l/mg) for As^{5+}	4
Effective porosity	0.3
Total porosity	0.4
Specific storage	0.001
Specific yield	0.1
Bulk density	2.37

Table 1 summarizes the results of the single reservoir diffusion cell test work and the geotechnical characterization of the mine tailings. Results of the single reservoir diffusion cell test work show that the diffusion coefficient for arsenic was 0.0126 m^2/yr. It was also observed that As^{5+} contained in the tailings pore fluids was strongly attenuated to the surface of ferrihydrite with a maximum loading capacity of 0.5 moles As^{5+}/mole ferrihydrite. Conversely, As^{3+} did not adsorb to the surface of ferrihydrite (or any other species in the tailings solids) and behaved as a conservative species.

It can be concluded that the long-term evolution of As^{5+} within the tailings will be controlled by the redistribution (diffusive flux/concentration gradient) and retardation (adsorption of As^{5+} to ferrihydrite). Because As^{3+} behaves as a conservative species it can be concluded that the long-term evolution of As^{3+} will be controlled by diffusion only.

Geotechnical test work completed on the tailings showed that the effective and total porosity were 0.3 and 0.4. The specific storage and specific yield were 0.001 and 0.1. Finally, the bulk density of the tailings solids was determined to be 2.37.

The data summarized in Table 1 along with the concentration profile of As^{3+} and As^{5+} through depth in the tailings (Figure 2) were used as input into the hydrogeological model Modflow (version 3.0.0). Constant head (zero advective flow) was used as the boundary condition for the model. The transport engine used for simulating diffusive transport (with attenuation) was MT3DMS. The model was set to run for 10,000 years with is in keeping with the requirements of the regulatory agencies for proven stability of mine tailings containing low-level radionuclides. Observation wells were incorporated in the model to monitor the evolution of dissolved arsenic through depth in the tailings.

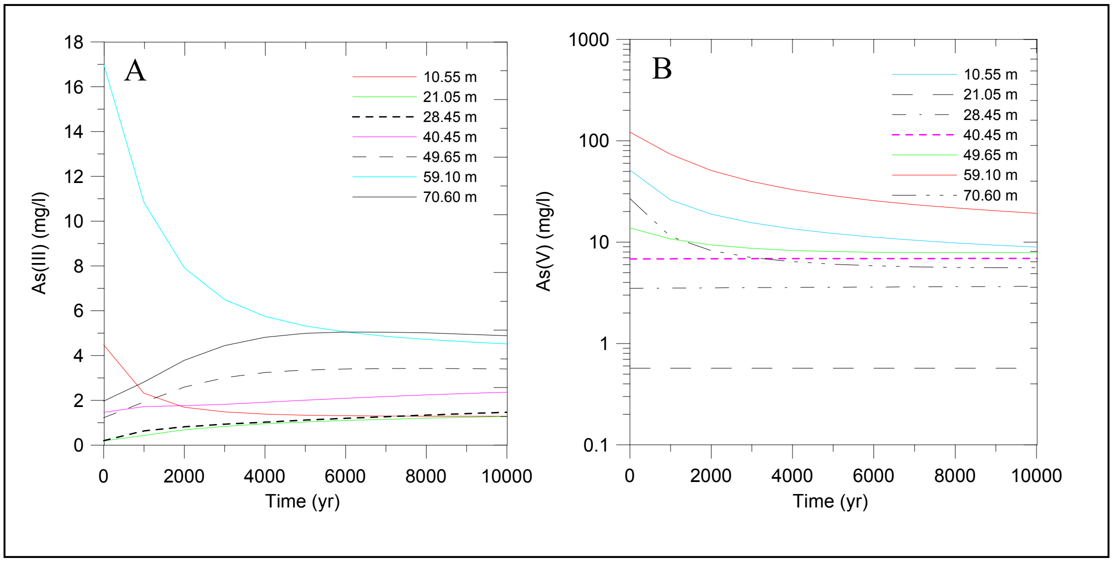

Figure 3. Long-term evolution (10,000 yr) of As^{3+} (Figure 3A) and As^{5+} (Figure 3B) through depth in the tailings.

The simulated concentration of arsenic through depth in the tailings over a period of 10,000 years is illustrated in Figure 3. Figure 3A illustrates the long-term evolution of As^{3+} from 10.55m below the tailings surface to 70.60 m below the tailings surface. At 59.10 m below the surface of the tailings the concentration of As^{3+} at time zero was 17.6 mg/l. Following 10,000 years the concentration was reduced to 4.52 mg/l via diffusive transport. At 70.60 m below the surface of the tailings the concentration of As^{3+} at time zero was 2.0 mg/l. Following 10,000 years the concentration increased to 4.90 mg/l via diffusive transport. From these data it can be concluded that the long-term (10,000 year) source term concentration of As^{3+} within the tailings body will be approximately 3 mg/l.

Figure 3B illustrates the long-term evolution of As^{5+} from 10.55m below the tailings surface to 70.60 m below the tailings surface. Results from this modeling scenario were based on maximum loading (attenuation) of As^{5+} of 0.5 moles As/mole ferrihydrite. The concentration of As^{5+} at time zero 10.55 m below the tailings surface was 51.5 mg/l. Following 10,000 years the simulated concentration was reduced to 8.92 mg/l. The concentration of As^{5+} at time zero 59.10 m below the tailings surface was 122 mg/l. Following 10,000 years the simulated concentration was reduced to 19.3 mg/l. Areas within the tailings where the initial concentration of As^{5+} was below 10 mg/l the concentration remained relatively constant. It can be concluded that following 10,000 years equilibrium of As^{5+} within the tailings body was not attained and the diffusion/attenuation process would be on-going.

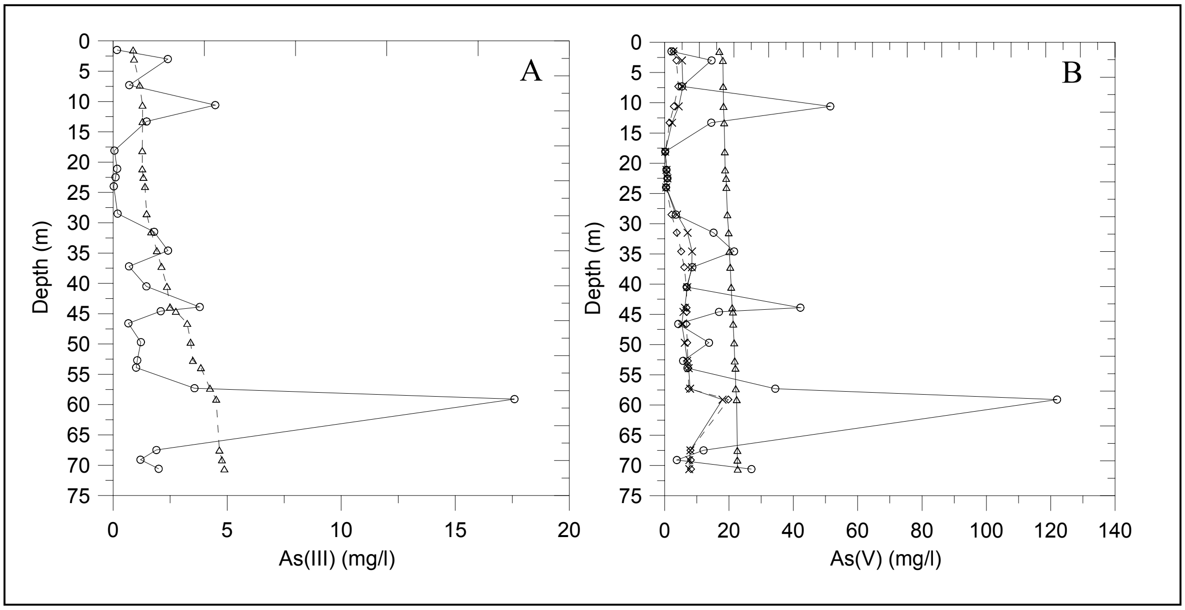

Figure 4. Concentration profile for arsenic through depth of the tailings at time zero and the simulated concentration profile for arsenic following 10,000 years of aging. Figure 4A illustrates the concentration of As^{3+} at time zero (represented by o) and the simulated concentration after 10,000 years (represented by Δ). Figure 4B illustrates the concentration of As^{5+} at time zero (represented by o). A sensitivity analysis was conducted for the adsorption of As^{5+} to the surface of ferrihydrite. The simulated concentration profile for 0.5 moles As^{5+} adsorbed/mole ferrihydrite is represented by ◊; 0.25 moles As^{5+} adsorbed/mole ferrihydrite is represented by x and 0.00 moles moles As^{5+} adsorbed/mole ferrihydrite is represented by Δ.

The simulated long-term evolution (10,000 yr) of As^{3+} through depth in the RLITMF is illustrated in Figure 4A. The mechanism controlling the redistribution of As^{3+} is diffusion alone (based on a concentration gradient) as As^{3+} behaved as a conservative species. Modelling results show that the overall long-term source concentration of As^{3+} in the RLITMF will be 2.51 mg/l.

The simulated long-term evolution (10,000 yr) of As^{5+} through depth in the RLITMF is illustrated in Figure 4B. The mechanism controlling the redistribution of As^{5+} is both diffusion (based on the concentration gradient) and attenuation (based on adsorption of As^{5+} to the surface of ferrihydrite). During the aging process of the mill tailings there is the potential for a decrease in the affinity that ferrihydrite will exhibit towards As^{5+}. Over time ferrihydrite was shown to become more crystalline (converting to goethite or hematite) resulting in a reduction in its absorption capacity of As^{5+}. Due to that premise the modelling exercise was completed using absorption capacities of 0.00, 0.25 and 0.50 moles of As per mole of ferrihydrite. Modelling results using an adsorption capacity of 0.5 moles As^{5+}/mole ferrihydrite showed that the overall long-term source concentration of As^{5+} in the RLITMF will be 5.40 mg/l; with 0.25 moles As^{5+}/mole ferrihydrite showed that the overall long-term source concentration of As^{5+} in the RLITMF will be 5.80 mg/l. If diffusion was the only mechanism for the redistribution of As^{5+} in the RLITMF and there was no adsorption of dissolved As^{5+} to the surface of ferrihydrite, model results show that the overall simulated long-term concentration of As^{5+} will be 20.3 mg/l. Based on these data it can be concluded that if the capacity for ferrihydrite to adsorb As^{5+} was reduced from 0.5 to 0.25 moles of As^{5+}/mole ferrihydrite the resulting increase in the long-term source concentration of As^{5+} would be negligible.

IV. CONCLUSION

Simulated diffusive transport modelling provided a means to evaluate the long-term source contaminant potential of arsenic within the RLITMF. Test work results showed that a concentration gradient for arsenic existed in the pore fluid within the tailings body and diffusion was the dominant mechanism for solute transport. In addition, results showed that As^{5+} was strongly attenuated by ferrihydrite contained within the tailings solids; As^{3+} was not attenuated in the tailings body and behaved as a conservative species. Model results showed that the long-term contaminant potential of dissolved As^{3+} and As^{5+} in the tailings pore fluid following 10,000 years aging were 2.51 mg/l and 5.40 mg/l. There is no biological activity in the tailings and a very low flux of carbon dioxide. It is therefore concluded that reductive dissolution of iron will not be a factor controlling the solubility of arsenic in the tailings pore fluids. In addition, pH changes in the tailings will be minimal due equilibrium attained with respect to the carbonate system. Further model development is currently being done to assess the long-term impact this arsenic will have on the regional groundwater.

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