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IDENTIFICATION OF POORLY CRYSTALLINE SCORODITE IN URANIUM MILL TAILINGS

R.Frey, J. Rowson, **K. Hughes**.
AREVA Resources Canada Inc.
Saskatoon, SK, Canada

J. Warner.
Canadian Light Source Inc.
Saskatoon, SK, Canada

ABSTRACT

The McClean Lake mill, located in northern Saskatchewan, processes a variety of uranium ore bodies to produce yellowcake. A by-product of this process is an acidic waste solution enriched in arsenic, referred to as raffinate. The raffinate waste stream is treated in the tailings preparation circuit, where arsenic is precipitated as a poorly crystalline scorodite phase. Raffinate neutralization studies have successfully identified poorly crystalline scorodite using XRD, SEM, EM, XANES and EXAFS methods, but to date, scorodite has not been successfully identified within the whole tailing solids. During the summer of 2008, a drilling program sampled the *in situ* tailings within the McClean Lake tailings management facility. Samples from this drilling campaign were sent to the Canadian Light Source Inc. for EXAFS analysis. The sample spectra positively identify a poorly crystalline scorodite phase within the McClean tailings management facility.

1 INTRODUCTION

The McClean Lake uranium mill, owned by AREVA Resources Canada Ltd, was envisaged to process a variety of ore bodies, including the McClean, Midwest, Cigar Lake and SUE ore deposits. A wide range of arsenic concentrations, from approximately 250 ug/g to 100,000 ug/g, are encompassed by these ore bodies. During the processing of these ores, a substantial amount of arsenic is liberated. During the design phase of the McClean Lake tailings preparation circuit, the mitigation of aqueous arsenic in mill solutions was a driving factor in the process conception. The tailings preparation process required an effective arsenic removal process that produced chemically stable tailings of sufficiently low solubility to be protective of the environment for the long term.

The necessity of such a process was due to the permanent disposal of tailings within the tailings management facility (TMF). The TMF is a previously mined out open pit that has been engineered to control arsenic release to surrounding ground and surface waters. Under current operating conditions, hydraulic containment is achieved by active processes, including de-watering and reclaim wells. Upon completion of milling activities and decommissioning of the TMF, passive controls for maintaining containment have been engineered. An inherent component of that design is that deposited tailings pore waters will have arsenic concentrations of less than 5 mg/L. With this as a primary consideration, a process was designed to ensure arsenic was removed as a chemical precipitate, and the subsequent precipitate would be thermodynamically stable for the long term under the present conditions in the McClean Lake TMF.

At the time the McClean Lake mill was conceived, conventional tailings treatment involved the liming of tailings solutions to increase the solution pH above 10. This process removes metal cations, however arsenite (AsO_3^{-3}) and arsenate (AsO_4^{-3}) tend to de-sorb from specific solids surfaces at elevated pH (Stumm & Morgan, 1996).

Laboratory tests and geochemical modelling performed by Langmuir et al. (1999) examined processes to reduce arsenic and nickel concentrations in TMF pore waters, so as to minimize release from deposited tailings. These large scale laboratory tests were completed to optimize the primary tailings preparation control parameters of ferric sulphate addition rate and terminal pH.

Tailings solids prepared during the laboratory scale tests were then used in aging tests. These tests were meant to simulate the long term conditions in the TMF. Of the nominal pH values used, pH 7 had unacceptably high nickel concentrations in the pore water, whereas pH 9 resulted in high arsenic concentrations. Further research then focused on nominal pH values in the range of 7.5 to 8 (Langmuir et al., 1999).

After completion of laboratory studies, samples were submitted for X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), electron microprobe (EM) and petrographic work. The XRD and optical results indicated that there were two mineral modes: crystallized major and minor phases comprised of both primary and secondary minerals, and poorly crystalline or amorphous mineral analogues precipitated as secondary minerals (Langmuir et al., 1999).

Further analysis found that arsenate was predominantly associated with iron, in an equal molar relationship (Langmuir et al., 1999). The EM analysis and XRD patterns suggested three possible ferric arsenate phases; scorodite, kankite and an amorphous phase (Krause & Ettel, 1988), possibly a composition between kankite and scorodite. Conclusions drawn at the time, based on XRD analysis, suggested the presence of a relatively amorphous scorodite-like phase (Langmuir et al., 1999).

Tailings derived from the nominal pH of 8 were used to predict arsenic concentrations in tailings pore water after 10,000 years. Using a TMF temperature of 4°C, it was concluded that arsenic concentrations in tailings pore water were not expected to exceed 2 mg/L over a 10,000 year span (Langmuir et al., 1999).

Following the start up of the McClean Lake mill, extensive studies on actual mill raffinate solutions were initiated. It was confirmed that dissolved arsenic could be minimized in treated tailings pore waters if prior to treatment, raffinate solutions had a ferric iron to arsenic molar ratio greater than three (Mahoney et al., 2007). Following this preparation procedure, the final concentration of arsenic in tailings pore water was generally less than 1 mg/L.

Mineralogical examination of prepared tailings samples continued to further elucidate the mineral structure of the iron-arsenic precipitate. This characterization involved XRD analysis of powered samples, SEM with energy dispersive analysis and qualitative EM and XM scans at Argonne National Laboratory's Advanced Photon Source. Quantitative mineralogical analysis of all samples were performed using the proprietary computer model QMAS (Slaughter, 1985, 1990), which combines the XRD, EM and XM results and sample chemistry using linear programming. This analysis determined that the arsenic in the raffinate precipitated with ferric iron as a poorly crystalline scorodite phase (Mahoney et al., 2007).

Chen et al (2009) conducted extensive Extended X-ray Absorption Fine Structure (EXAFS) studies of the solids produced by Mahoney et al. (2007). The arsenic and iron K-edge spectra were used to characterize the chemical structure of the neutralized tailings solid samples. The arsenic was determined to be bound to iron in a molar ratio of 1: 1 (Chen et al., 2009). The comprehensive analysis of the EXAFS spectra was compared to synthetic model compounds, including crystalline scorodite, $FeAsO_4 \cdot 2H_2O$ (Singhania et al, 2005), iron (III)-arsenate co-precipitates (Jia et al., 2003), and poorly crystalline scorodite (Jia et al., 2003). It was concluded that the observed spectra, obtained from the laboratory neutralized raffinate solutions, identified a poorly crystalline scorodite mineral phase (Chen et al., 2009).

In 2008, an *in situ* sampling program for the McClean Lake TMF was undertaken. A drilling rig was used to sample representative regions of the tailings facility. Samples obtained from this program were processed to collect pore waters and solid tailings samples. Solid samples were sent to the Canadian Light Source Inc. (CLSI) for analysis by synchrotron based X-ray absorption techniques.

1.1 Tailings Preparation Process

The McClean Lake milling process employs sulphuric acid, as a lixiviant, and hydrogen peroxide, as an oxidant, to liberate uranium from ores. In addition to uranium, this process liberates approximately 80% of the arsenic in the ore. Upon completion of the leaching process, uranium is separated from the acidic leach solution through contacting an organic matrix in the solvent extraction process. The residual arsenic remains in the acidic 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 McClean Lake mill tailings preparation process.

The tailings preparation circuit employs a pre-treatment stage and a two stage neutralization process. The pre-treatment involves the addition of ferric iron to the raffinate waste stream to achieve a molar ratio greater than or equal to 3 parts ferric iron to 1 part arsenic (Fe (III) / As molar ratio ≥ 3). A barium chloride solution is also added to remove radium from the tailings solution. 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 tailings 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 process has a residency time of 90 minutes. Upon completion of Stage 1, the tailings slurry is transferred from the primary to the secondary reaction vessel. During Stage 2, slaked lime addition increases the pH from 4 to a terminal pH of 7.5, within a residency time of 90 minutes. The tailings slurry is then pumped to a high rate thickener, where the slurry is settled and subsequently deposited in the TMF. This preparation process reduces aqueous arsenic concentrations to less than 2 mg/L (Rowson and Tremblay, 2003). Figure 1 provides a representation of the tailings preparation process.

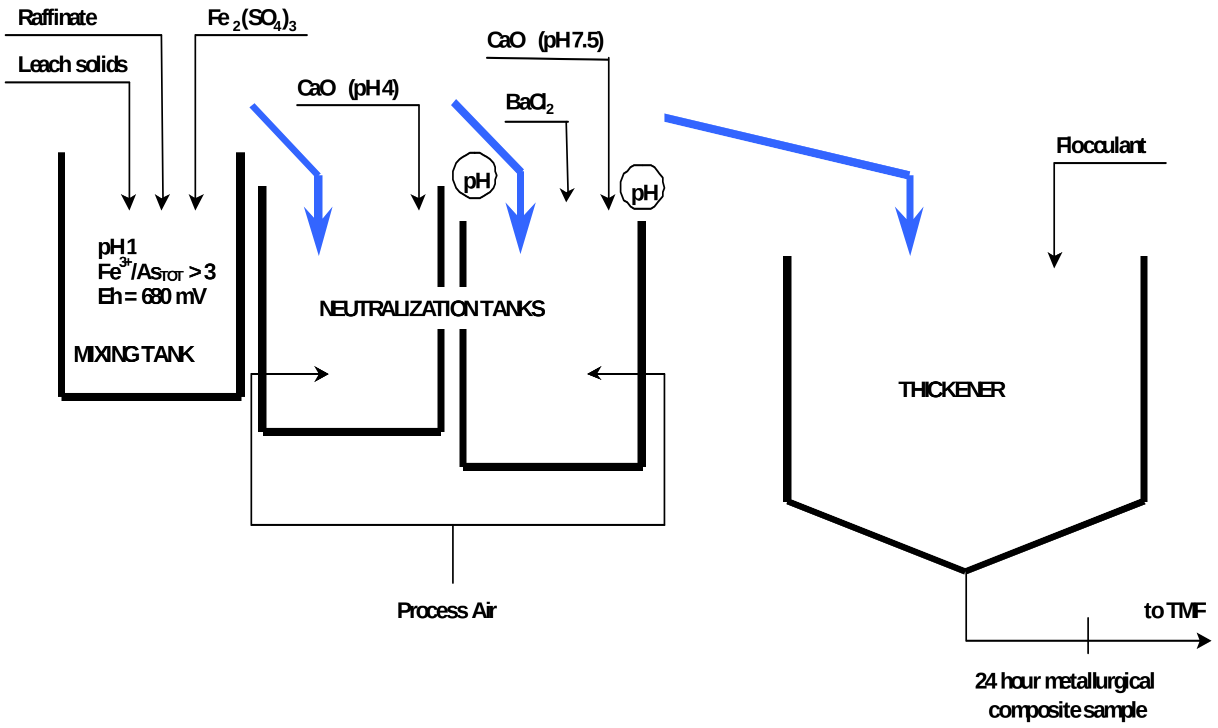

Figure 1 - McClean Lake tailings preparation process

2 EXPERIMENTAL

2.1 TMF Sample Collection

The 2008 McClean Lake TMF *in situ* sampling program collected both geotechnical and geochemical samples. The geochemical samples were collected from 4 locations in the TMF, consistent with previous annual sampling programs (Figure 2).

Samples were collected by positioning a drilling rig, mounted on a floating barge, above the co-ordinates from previous intrusive sampling programs. Every effort was made during the sampling program to place the bore holes in the same co-ordinate locations and to sample at the same elevations as in past drill sampling campaigns so that aging of the tailings sediments and pore water can be monitored.

The drilling program obtained samples in 3 meter intervals from the base of the TMF (364 masl), corresponding to tailings places in July 1999, to tailings recently placed in June 2008 (420 masl) at the surface of the tailings mass. Refer to Figure 3 for tailings placement and elevation during the operations to date of the McClean Lake mill.

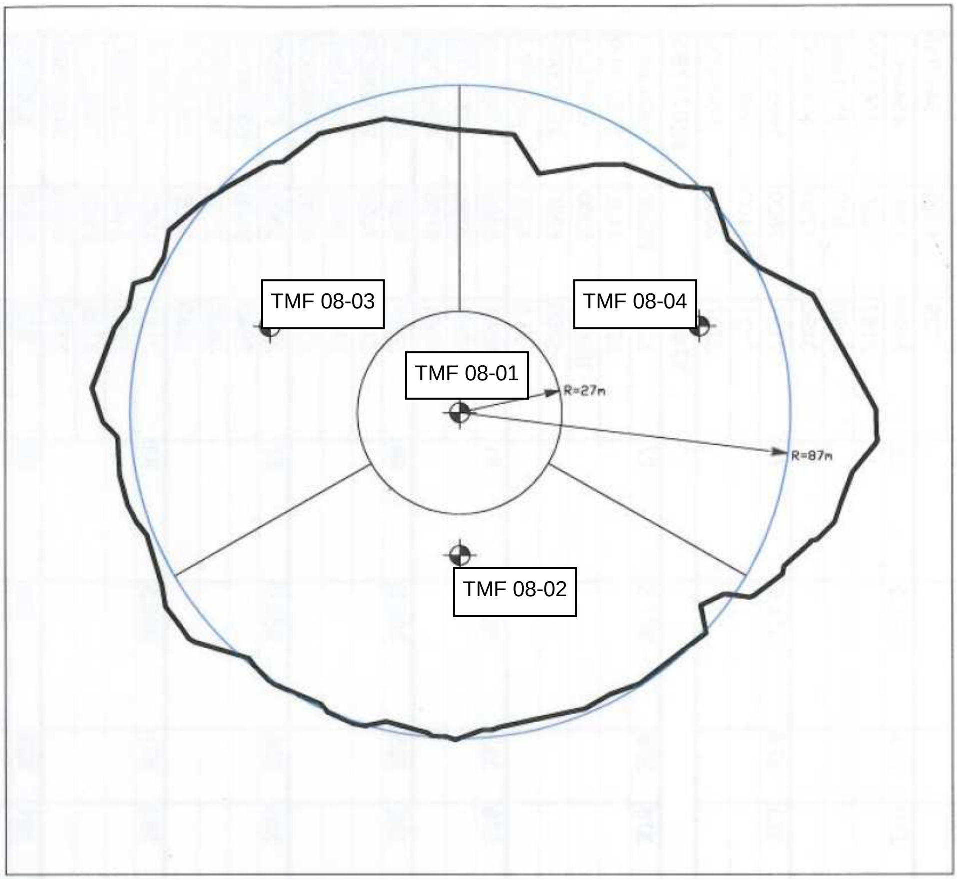

Figure 2 - McClean Lake TMF *in situ* sampling program – Geochemical borehole locations

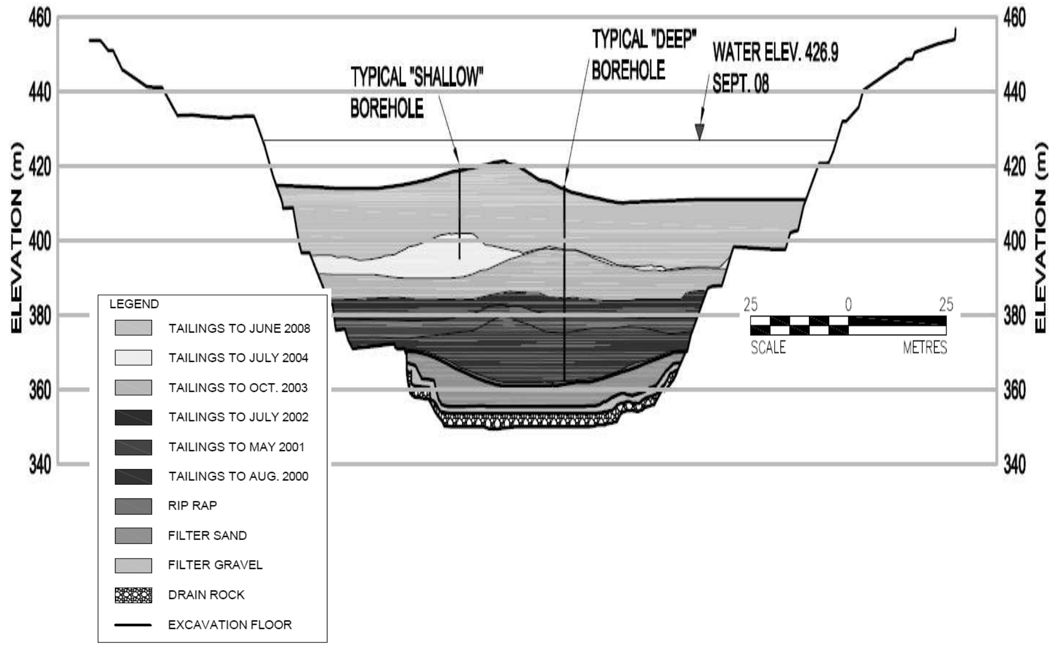

Figure 3 - Tailings placement within the McClean Lake TMF – June 2008

The collected samples were sealed and stored sub-aqueously to minimize oxidation. An extraction device was used to collect pore waters from the core samples. Solid samples were then extruded and vacuumed sealed to preserve the sediment samples from oxidation. Figure 4 provides a schematic diagram of the tailings pore water extraction device. Figure 5 is a picture of an extruded core sample.

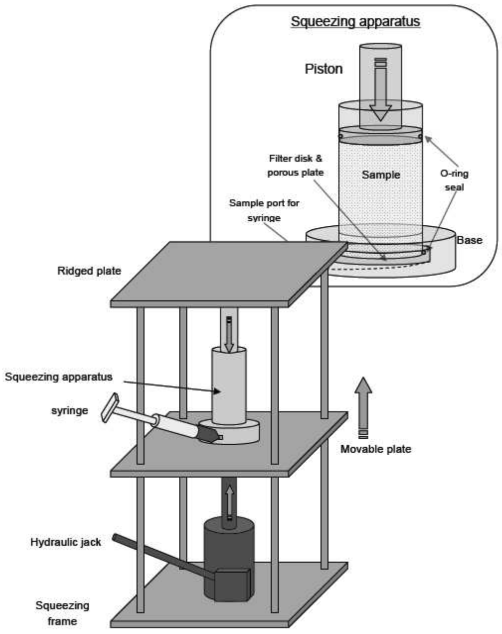

Figure 4 - McClean Lake TMF *in situ* sampling program - Pore water collection apparatus

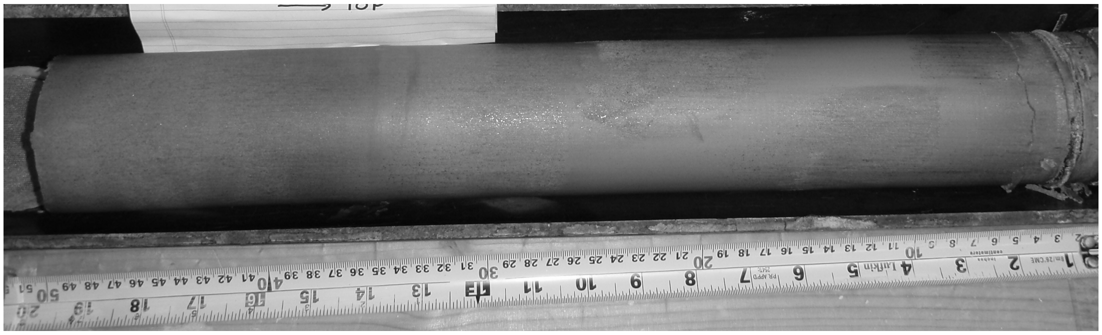

Figure 5 - McClean Lake TMF *in situ* sampling program – Extruded core sample

2.2 EXAFS Measurements at CLSI

Extruded tailings solid samples were sent to the CLSI for an initial screening by X-ray Absorption Near Edge Structure (XANES) analysis. Based on the XANES results, samples containing 100% As(V) species were selected for EXAFS analysis. The results from the tailings samples detailed apparent scorodite features in all the initial EXAFS spectra. These preliminary results allowed the selection of two samples for extended EXAFS exposure time and detailed fitting.

The detailed EXAFS measurements were collected on beamline 6ID2, Hard X-ray Micro Analysis (HXMA) at the CLSI. The HXMA beamline uses a superconducting wiggler operating at 1.9 T as a source magnet and a double crystal monochromator for wavelength selection, equipped with Si(111) crystals for measurements. Entrance slits defined the beam size at 1.0 mm vertical height for all samples. The incident beam was detuned 50% to limit the harmonic content at the As K-edge (11867 eV). Sample spectra were collected in fluorescence mode and reference compound spectra were collected using transmission geometry.

All k^3–weighted samples were Fourier transformed over the k-space range 2-12.7 $Å^{-1}$ using a Hanning window function. Fits in R-space extended from 1 – 3.5 Å (uncorrected for phase). EXAFS parameters ΔE_0 and S_0^2 were obtained from a fit to scorodite and used as global parameters. Debye-Waller factors, σ^2, for multiple scattering paths within the arsenate tetrahedron were constrained to keep the number of variable EXAFS parameters to half the total number of independent points (N_{idp}, Lytle et al., 1989). EXAFS analysis was performed using the program Artemis (Ravel and Newville, 2004).

3 DISCUSSION

Samples TMF 08-01 SA05 and TMF 08-01 SA07 were selected for extended exposure and detailed fitting at the CLSI. Sample TMF 08-01 SA05 was collected from the central geochemical borehole in the TMF, at a depth of 408 meters above sea level (masl). Tailings were deposited at the SA05 location during the late fall of 2004. Sample TMF 08-01 SA07 was also collected from the central geochemical borehole in the TMF, at a depth of 402 masl. Tailings deposited at the SA07 location occurred during the summer of 2004. TMF 08-01 SA05 and SA07 contained arsenic in concentrations of 583 ug/g, and 294 ug/g respectively.

As K-edge spectra were collected for TMF 08-01 SA05 and TMF 08-01 SA07. Samples were processed with neutralized raffinate data collected previously (Chen et al., 2009) in order to establish the peak position of arsenic-iron single scattering in the pseudo radial distribution plot of arsenic in samples collected from the TMF.

Of the two samples sent to the CLSI, initial analytical efforts concentrated on the samples of greater arsenic content. As such, this discussion focuses on the results from sample TMF 08-01 SA05. The Fourier transform of the k-space data are presented in Figure 6. For comparison, the transformed data from two selected samples, labelled as pH 7.08 and 6.09, from the laboratory prepared tailings experiment (Mahoney et al., 2007) are included. These laboratory samples were generated following the McClean Lake mill tailings preparation process, but with different terminal pH values. They were the subject of extensive EXAFS analysis and have been previously reported (Chen et al., 2009). The similarities in R-space for all the sets of data are evident. The first major peak at approximately 1.3 Ǻ is due to scattering from the nearest As-O shell within the arsenic-oxygen tetrahedron. A second peak of interest, between 2.5 to 3.0 Ǻ, consists of several components but a significant contribution is the result of scattering from the As-Fe shell in a scorodite structure.

Figure 7 provides a comparison of the Fourier transform magnitude in the region of the As-Fe shell for the laboratory produced tailings and actual tailings from the McClean Lake TMF. Two principal components are present under the main feature; the multiple scattering (MS) from the oxygen atoms in the arsenic-oxygen tetrahedron, and the As-Fe scattering from the scorodite orientation. These are marked with heavy arrows to indicate their approximate locations. From Figure 7, it is readily apparent that a significant contribution to the main EXAFS feature is due to an orientation of iron around arsenic, as described by the scorodite structure.

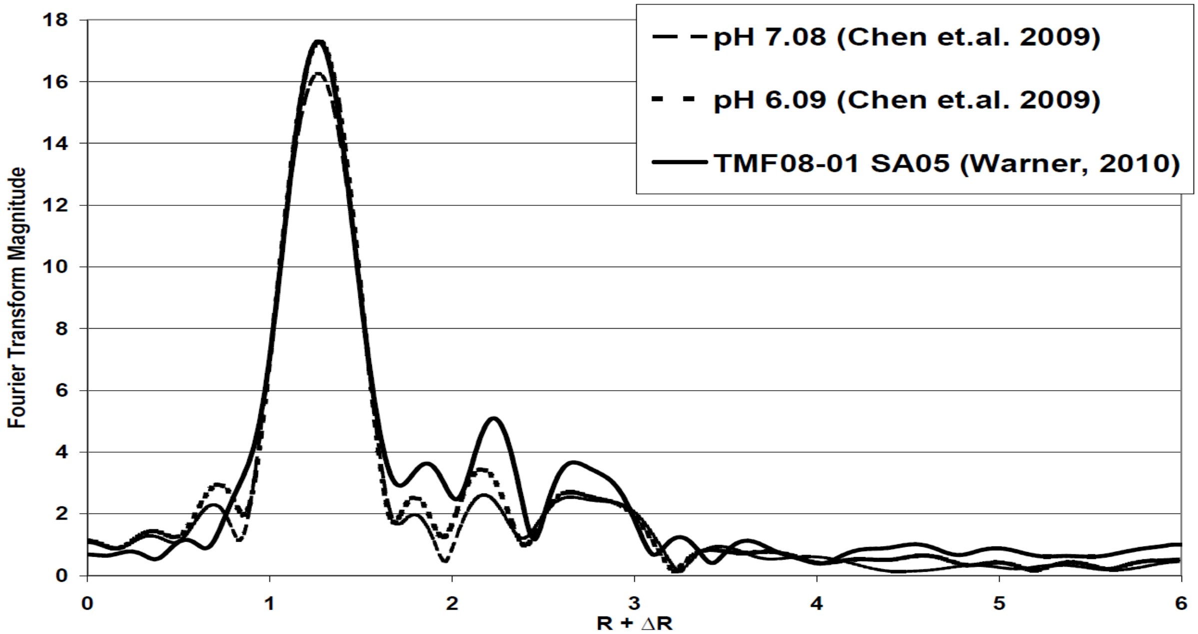

Figure 6 - Detailed EXAFS expanded plot of laboratory prepared tailings solids and TMF *in situ* tailings solid sample TMF 08-01 SA05

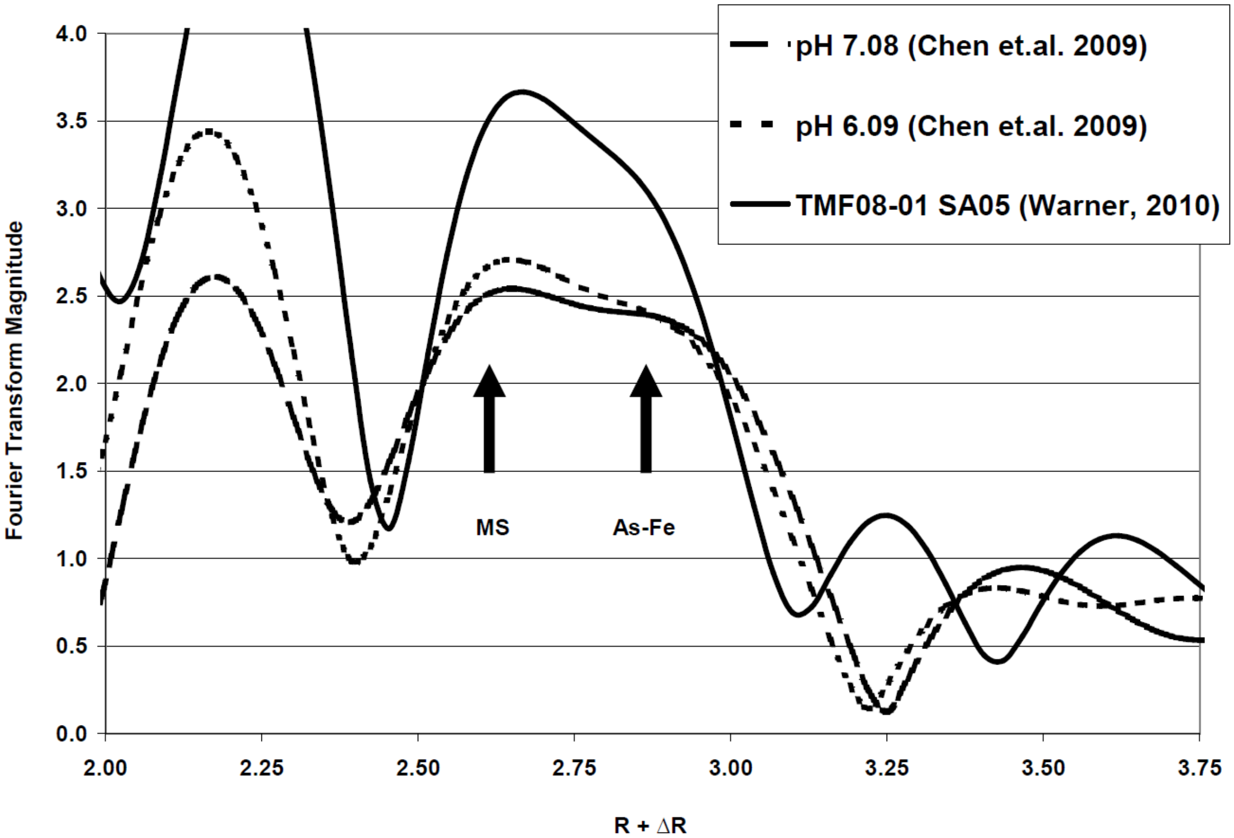

Figure 7 – Comparison of the Fourier transform magnitude in the region of the As-Fe shell for laboratory produced tailings and actual tailings from the McClean Lake TMF.

4 CONCLUSIONS

After the start up of the McClean Lake mill, raffinate solutions were processed on a laboratory scale. These experiments, using mill raffinate solutions, produced ferric arsenate precipitated solids by simulating the McClean Lake tailings preparation process. These solid samples were then subjected to synchrotron based EXAFS analysis. Further detailed fitting was conducted by Chen et al. Based on the results from the EXAFS As K-edge spectra, it was concluded that the chemical phase of the ferric arsenate precipitate was that of a poorly crystalline scorodite (Chen et al., 2009). Sample TMF 08-01 SA05, collected during the 2008 TMF *in situ* sampling program, exhibits identical EXAFS features with respect to scattering from the As-Fe shell, as reported by Chen et al. (2009) for the laboratory prepared tailings. It is concluded that arsenic in the McClean Lake TMF is present in a poorly crystalline form of the mineral scorodite. Based on laboratory test work, this structure was observed and predicted to exist within the TMF sediments. This presentation reports the first direct evidence of a "scorodite like" structure within the TMF tailings sediments.

5 ACKNOWLEDGMENTS

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6 REFERENCES

1. N. Chen, D.T. Jiang, J. Cutler, T. Kotzer, Y.F. Jia, G.P. Demopoulos, J. Rowson, "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 Acta, Vol. 73, 2009, 3260-3276.

2. Y.F. Jia, G.P. Demopoulos, N. Chen, J.N. Cutler and D.T. Jiang, "Preparation, characterization and solubilities of adsorbed and co-precipitated iron(III)-arsenate solids", Hydrometallurgy 2003 – Fifth International Conference in Honor of Professor Ian Ritchie, vol.2, C. Young, Ed., TMS, Warrendale, PA., 2003, 1923-1935.

3. E. Krause and V.A. Ettel. "The solubility of scorodite $FeAsO_4 \cdot 2H_2O$: new data and further discussion" American Mineralogist, Vol. 73, 1988, 850-854.

4. D. Langmuir, J. Mahoney, J. Rowson, "Predicting arsenic concentrations in the pore waters of buried uranium mill tailings", Geochimica et Cosmochimica Acta, 70, 1999, 2942-2956.

5. F.W. Lytle, D.E. Sayers, E.A. Stern, "Report of the international workshop on standards and criteria in X-ray absorption spectroscopy", Physica B: Condensed Matter, Vol. 158, 1989, 701-722.

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

7. B. Ravel, M. Newville, "ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT", Journal of Synchrotron Radiation, Vol. 12, 2005, 537-541.

8. J. Rowson and M. Tremblay, "COGEMA Resources Inc. – McClean Lake operations; tailings optimization and validation program (TOVP)", Program Status Report for 2002, COGEMA Resources Canada Inc., Saskatoon SK, Canada, 2003.

9. S. Singhania, Q. Wang, D. Filippou, G.P. Demopoulos, "Temperature and seeding affects on the precipitation of scorodite from sulphate under atmospheric-pressure conditions", Metallurgical and Materials Transactions B., Vol. 36B, 2005, 327-333.

10. M. Slaughter, "Method for determining composition and amount of minerals in rocks and soils", Nat. and International Clay Conference: Workshop Manual on Quantitative Analysis of Clays, 1985.

11. M. Slaughter, "Quantitative determination of clays and other minerals in rocks", Clay mineral society workshop lectures, Quantitative Mineral Analysis of Clays, Pevear D.R., Mumpton E.A., Eds., Clay Mineral Society, Evergreen, CO., 1990, 20-151.

12. W. Stumm, J.J. Morgan, Aquatic Chemistry – Chemical Equilibria and Rates in Natural Waters, 3rd ed., Wiley Interscience, New York, 1996.