Identifying calcium-containing mineral species in the JEB Tailings Management Facility at McClean Lake, Saskatchewan

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ABSTRACT

The JEB Tailings Management Facility (TMF) is central to reducing the environmental impact of the McClean Lake uranium mill facility that is operated by AREVA Resources Canada. This facility has been designed around the idea that elements of concern (e.g., U, As, Ni, Se, Mo) will be controlled through equilibrium with precipitants. Confirming the presence of calcium-containing carbonates in the JEB TMF is the first step in determining if gypsum ($CaSO_4 \cdot 2H_2O$) controls the concentration of HCO_3^- (aq), limiting the formation of soluble uranyl bicarbonate complexes. A combination of X-ray diffraction (XRD), X-ray absorption near-edge spectroscopy (XANES), and microprobe X-ray fluorescence (XRF) mapping was used to analyze a series of tailings samples from the JEB TMF. Calcium carbonate in the form of calcite ($CaCO_3$), aragonite ($CaCO_3$), and dolomite ($CaMg(CO_3)_2$) were identified by analysing Ca K-edge μ-XANES spectra coupled with microprobe XRF mapping. This is the first observation of these phases in the JEB TMF. The combination of μ-XANES and XRF mapping provided a greater sensitivity to low concentration calcium species compared to the other techniques used, which were only sensitive to the major species present (e.g., gypsum).

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1. Introduction

AREVA Resources Canada (AREVA) operates the JEB Tailings Management Facility (TMF) to manage and dispose of elements of concern generated in the U ore milling operations located at McClean Lake, Saskatchewan. A location map showing the JEB mill and TMF, as well as some of the ore bodies that feed the mill is presented in Fig. S1 in the Supporting Information (SI). The JEB TMF is designed to reduce the migration of water-soluble elements that co-mineralize with U ore (i.e., As, Ni, Mo, and Se) by promoting the formation of water-insoluble mineral species, effectively "trapping" these elements of concern (AREVA, 2015). The concentration of the solutes are out of equilibrium with the desired mineral phases when initially added to the TMF and may require a long period of time to reach a stable mineralogical end-point. Mineralogical evolution is limited by low temperatures (+6 °C), low hydraulic conductivity, and low liquid/solid ratios that reduces mass transport

(AREVA, 2015). A table that identifies a selection of the primary and secondary minerals present in the tailings before being placed in the TMF can be found in the SI (Table S1).

AREVA has been investigating the long-term formation of solid phases containing several elements of concern in the TMF (e.g., As, Ni, Mo) (Langmuir et al., 2006; Mahoney et al., 2007; Chen et al., 2009; Hayes et al., 2014; Blanchard et al., 2015). However, there is little known about the behaviour of U in the JEB TMF. The process of separating yellow cake ($U_3O_8(s)$) from the ore consumes small amounts of hydrocarbon material. The largest sources of hydrocarbons used in the mill are organic flocculent (polyacrylamide) and kerosene. Small amounts of kerosene are lost to the raffinate solution that reports to the tailings preparation process. This hydrocarbon material adsorbs onto the surface of the tailings solids and is subsequently deposited in the TMF. Hydrocarbons in the tailings are gradually converted to soluble $HCO_3^-(aq)$ (bicarbonate) in the tailings pore water, which is facilitated by the presence of bacterial communities. Under the oxic conditions of the TMF (Eh ~ +290 mV; pH ~ 7), U oxide (e.g., UO_2, U_3O_8, $U(SiO_4)_{1-x}(OH)_{4x}$) in the tailings may react with bicarbonate to form an undesirable water-soluble uranyl-carbonate complex. Dissolved bicarbonate

can be removed from the TMF pore water by co-precipitating with dissolved $Ca^{2+}(aq)$ as calcium carbonate $(CaCO_3(s))$. The concentration of dissolved $Ca^{2+}(aq)$ is relatively high in the TMF (~550 mg/L), as the TMF is saturated with gypsum $(CaSO_4 \cdot 2H_2O(s))$ that forms from the addition of sulfuric acid and lime during the leaching and tailings preparation stages, respectively. Overall, the conversion of gypsum to calcium carbonate (calcite or aragonite) can be written as (AREVA, 2015):

$$CaSO_4 \cdot 2H_2O(s) + HCO_3^-(aq) + OH^-(aq) \rightarrow CaCO_3(s)$$
$$+ SO_4^{2-}(aq) + 3H_2O(l) \tag{1}$$
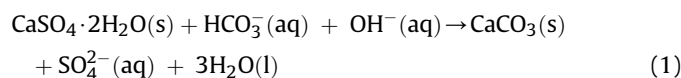
Although there is some indirect evidence of calcium carbonate precipitation as observed by the decrease in concentration of $Ca^{2+}(aq)$ in the pore water collected at lower elevations (i.e., deeper depths) of the TMF (AREVA, 2015), calcium carbonate has not been directly observed. Identifying calcium-containing carbonate is an essential first step to understanding how the $HCO_3^-(aq)$ concentration is controlled in the TMF. Our recent X-ray diffraction (XRD), X-ray absorption near-edge spectroscopy (XANES), and X-ray fluorescence (XRF) microprobe studies have proven useful in identifying Mo-bearing mineral species in the TMF, particularly at low concentrations (Hayes et al., 2014; Blanchard et al., 2015). In the current study, the calcium mineralization in the JEB TMF has been investigated using a combination of these techniques. Detailed micro powder XRD and bulk XANES analyses indicated that the major Ca-containing mineral species in the TMF are gypsum and possibly anhydrite $(CaSO_4)$. Micro XANES (μ-XANES) analysis was able to identify several minor calcium-containing mineral species, including calcite, aragonite, and dolomite $(CaMg(CO_3)_2)$. Overall, this investigation has demonstrated that μ-XANES coupled with XRF mapping is the most effective way to identify low concentration calcium species in the TMF.

2. Experimental

2.1. Tailings sample description

The samples studied were collected during the 2013 sampling campaign of the JEB TMF. Samples were collected from two borehole locations in the TMF. A total of six samples were provided for this study, with three samples collected from the central borehole (TMF13-01-SA12, TMF13-01-SA19, TMF13-01-SA22) and three samples from a periphery borehole (TMF13-03-SA12, TMF13-03-SA15, TMF13-03-SA19) located approximately 55 m from the centre. A figure showing a schematic of the TMF and the location of the bore-holes in plan view is shown in Fig. S2 in the SI. The tailings are placed in the TMF using a floating barge and tremie piping system in a way that minimizes particle size segregation at the point of placement; however, it does not eliminate it. As a consequence, the particle size distribution of the tailings solids is not homogenous in the TMF with the central bore hole possessing a coarser particle size distribution than bore holes located at the periphery of the TMF. More information on the sampling of the tailings can be found in the SI.

2.2. Micro powder XRD

Micro powder X-ray diffraction (μ-XRD) patterns of the tailings samples were collected to determine which crystalline phases are present in the bulk material. Measurements were performed using a PANalytical Empyrean powder X-ray diffractometer equipped with a Cu K$\alpha_{1,2}$ X-ray source, and powder XRD patterns were analyzed using the PowderCell software package (Kraus and Nolze, 1996). Unground grains from each tailings sample was measured

instead of finely ground powder in an attempt to increase the possibility of detecting minor phases by μ-XRD. More information on these experiments can be found in the SI.

2.3. Bulk XANES

2.3.1. Bulk Ca K-edge XANES

Bulk Ca K-edge XANES measurements were collected on the Soft X-ray Microcharacterization Beamline (SXRMB; 06B1-1) at the CLS (Hu et al., 2010). Finely powdered (i.e., homogenized) tailings samples and standards were lightly dusted onto carbon tape mounted onto a multi-sample holder. A single layer of Kapton foil covered the tailings samples. More details on the experimental set-up can be found in the SI. All XANES spectra were analyzed using the Athena software program (Ravel and Newville, 2005). A quantitative analysis of the XANES spectra was performed using principle component analysis (PCA) followed by linear combination fitting (LCF) using the spectra from the standards. The energy range used for PCA and LCF analysis was −20 and + 40 eV relative to the
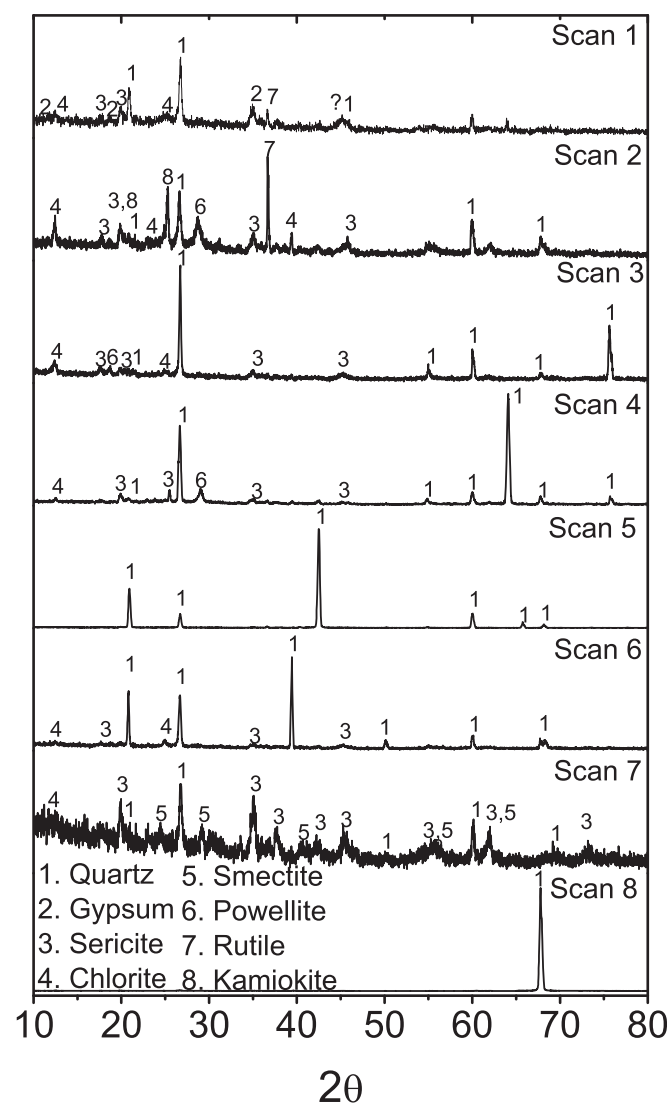

Fig. 1. μ-XRD patterns collected from tailings sample TMF13-01-SA19. Evidence of gypsum is highlighted in scan 1 while evidence of powellite is highlighted in scan 3. The high 2θ diffraction peaks corresponding to quartz shown in the diffraction patterns collected in scans 4 and 8 are so intense due to preferred orientation effects.