Coordination of arsenic and nickel to aluminum and magnesium phases in uranium mill raffinate precipitates

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ARTICLE INFO

ABSTRACT

The Key Lake U mill uses a stepwise neutralization process (pH 4.0, 6.5, 9.5, and 10.5) to treat raffinate (acidic, metal-rich wastewater) prior to safely releasing effluent to the environment. This process generates a complex mixture of precipitates that are deposited to a tailings facility. In this study, the coordination environments of As and Ni with respect to Al-Mg phases precipitated in the presence and absence of Fe in mill-generated and synthetic precipitates were defined using bulk X-ray absorption spectroscopy complemented with bulk X-ray diffraction. In low pH (pH 4.0–4.6) samples, As(V) precipitates as ferric arsenate and adsorbs to $AlOHSO_4$ (an amorphous hydrobasaluminite-like phase) and ferrihydrite via bidentate-binuclear complexes. Nickel(II) predominantly adsorbs to amorphous $Al(OH)_3$ via edge-sharing bidentate-mononuclear complexes. In high pH (pH 9.5–9.9) samples, As(V) adsorbs to amorphous $Al(OH)_3$, ferrihydrite, and MgAlFe-hydrotalcite (bidentate complex). Nickel(II) octahedra adsorb to amorphous $Al(OH)_3$ and likely form a Ni-Al layered double hydroxide (LDH) surface precipitate on MgAlFe-hydrotalcite via Al dissolution-precipitation. In the final solids (blended low and high pH precipitates) discharged at ~ pH 10.5, As(V) adsorbs to amorphous $Al(OH)_3$, ferrihydrite, and MgAlFe-hydrotalcite. Nickel(II) adsorbs to amorphous $Al(OH)_3$ and forms Ni-Al LDH surface precipitates on hydrotalcite. This study demonstrates that neutralization of chemically complex wastewater precipitates multiple phases capable of controlling dissolved As and Ni concentrations. Knowledge gained from this study will aid investigations in understanding the long-term fate of these potential contaminants in the environment and can be applied to other industries and environmental systems with similar conditions.

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1. Introduction

The milling of metallic ores often results in the generation of acidic wastewater (raffinate) rich in metal(loid)s that are liberated from minerals in the host rock during processing. Raffinate must be treated before releasing the final effluent to the environment. The most common neutralization process used in the metal processing industry is hydroxide precipitation, in which metal hydroxides precipitate from the raffinate due to the addition of a base such as $Ca(OH)_2$ (Blais et al., 2008; Djedidi et al., 2009; Langmuir et al., 1999). Neutralization of acidic waters and soils are common processes observed in the environment and include the neutralization of acid mine drainage by natural sources (e.g., circumneutral pH river water or limestones) and the liming of acidic, metal(loid) rich soils affected by smelters (Adra et al., 2013; Nkongolo et al., 2013).

Due to the ubiquitous occurrence of these neutralization processes, it is critical to characterize the mineralogical and chemical composition of the resulting precipitates. Understanding mineral/chemical compositions of these precipitates will aid studies in understanding the long-term fate of uranium tailings.

The milling of uranium (U) at Key Lake (KL) in northern Saskatchewan, Canada is one example of an industrial activity that acid-leaches primary minerals (such as kaolinite, chlorite, arsenopyrite, and gersdorffite) associated with U ore and uses a neutralization process to precipitate the dissolved metals (e.g., Al, Mg, Fe) and elements of concern (EOCs; e.g., As, Ni, Se, and Mo) from raffinate prior to discharging the effluent to the environment (Shaw et al., 2011). The KL neutralization process uses slaked lime (hydrated CaO) to raise the pH in a stepwise manner. The resultant precipitates are collected in low pH (~4.0) and high pH (~9.5) thickeners, termed the Se-Mo and Lamella thickeners, respectively. The two sets of precipitates are mixed in a separate tank and the pH of the mixture is increased to 10.5 using slaked lime. This final

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slurry is sent to the in-pit Deilmann Tailings Management Facility (DTMF) as a portion of the overall tailings (details of the process are given in Fig. S1; Robertson et al., 2014). The mineralogy and geochemistry of these and other similar tailings (e.g., Au and other U tailings facilities) have been actively studied to gain an understanding of any potential risk EOCs may pose to the surrounding groundwater (Corriveau, 2006; Craigen, 2006; Douglas et al., 2010; Essilfie-Dughan et al., 2013; Gomez et al., 2013; Mahoney et al., 2007; Moldovan et al., 2003; Pichler et al., 2001; Robertson et al., 2016). These studies show that secondary metal-oxyhydroxide phases with adsorptive properties are the dominant controls on aqueous concentrations of EOCs. Based on high concentrations of Fe in the raffinate and resulting tailings, previous studies focus on Fe-oxyhydroxides and their adsorption of EOCs through inner- and outer-sphere surface complexation in the neutralized precipitates (Essilfie-Dughan et al., 2013, 2011; Mahoney et al., 2007; Moldovan et al., 2003). Calcium arsenate precipitates have also been a focus in previous studies due to the addition of excess $Ca(OH)_2$ (Donahue et al., 2000; Donahue and Hendry, 2003; Pichler et al., 2001). These studies, however, were not able to directly quantify the presence of Ca-arsenates, and it was suggested that Ca-arsenates will not precipitate when the Fe/As molar ratio is elevated (>4). At ratios as high as Fe/As = 4, batch synthesis experiments show Ca-arsenates begin to form from Ca-Fe-As slurries at 75—85 °C after 336 h (Paktunc et al., 2015). Given that Fe/As ratios are frequently elevated beyond 4 at the KL mill and the tailings temperature is ≈ 4 °C, Ca-arsenates were not considered for this study.

Because Al and Mg are also prevalent in raffinate, recent studies characterized the Al and Mg solids in the neutralization process and resulting tailings (Gomez et al., 2013; Robertson et al., 2016). An amorphous phase bearing similar stoichiometry to hydro-basaluminite $(Al_4(SO_4)(OH)_{10} \cdot 15H_2O)$ was identified in pH 4.0 precipitates and is simply referred to as $AlOHSO_4$. Aluminum-bearing amorphous $Fe(OH)_3$ also precipitates at pH 4.0. Precipitates formed at pH 9.5 consist of MgAlFe-type hydrotalcite and amorphous $Al(OH)_3$. The final precipitates discharged to the DTMF (pH 10.5) are a complex mixture of amorphous $(Al,Fe)(OH)_3$, MgAlFe-type hydrotalcite, and amorphous $Al(OH)_3$. The non-Fe phases also appear to control the aqueous concentration of EOCs; however, the bonding characteristics of these Al and Mg minerals could not be determined using the methods applied by Robertson et al. (2016). The presence of these non-Fe sequestration mechanisms of EOCs is of interest because they could represent a secondary, long-term sequestration mechanism in metal (e.g., U and Au) tailings storage facilities as well as remediated acid mine drainage and acidic soil sites. Studies of Al-oxyhydroxides and mixed-metal layered double hydroxides (LDH), such as hydrotalcite, in other applications have identified EOC controls similar to Fe-oxyhydroxides (Douglas et al., 2010; Jobbágy and Regazzoni, 2013; Kappen and Webb, 2013). Few studies, however, have investigated the sequestration mechanisms exerted by Al-Mg phases on EOCs in the presence of Fe phases (Foster et al., 1998; Gomez et al., 2013; Moldovan and Hendry, 2005).

The objective of this study is to characterize the coordination environments of As and Ni in Al-Mg phases as an additional control to the well-known ferrihydrite controls present during raffinate neutralization. This is achieved using X-ray absorption spectroscopy (XAS) measured at the As and Ni K-edges on synthetic and field (mill process) precipitates in the absence and presence of Fe minerals by analyzing their extended X-ray absorption fine structure (EXAFS) regions. The samples are collected from three stages of neutralization: low pH (4.0—4.6), high pH (9.5—9.9), and mill discharge pH (10.5—10.9). The complexation mechanisms of Al-Mg phases that control concentrations of As and Ni are determined through EXAFS analysis of reference compounds. These results are

applied to the synthetic and mill samples using linear combination fitting (LCF) to determine the local coordination environment of As and Ni to Al, Mg, and Fe phases in the precipitates during and after neutralization. The relative distribution of As and Ni to these phases is also determined. The results of this study improve upon the current model of EOC sequestration in metallurgical tailings by describing the contributions of Al-Mg phases in these complex mineralogical systems. Because of the common occurrence of hydroxide neutralization of wastewaters and soils in industrial and environmental settings, this improved geochemical understanding of the precipitates in the KL system can be applied to other systems where acidic, metal(loid)-laden waters, tailings, and soils are neutralized to precipitate mixtures of metal-hydroxides to better predict the environmental impact of these processes and to better design remediation strategies.

2. Materials and methods

2.1. Preparation of samples and standards

Three sets of samples were used in this study. Two sets of samples were produced in a synthetic raffinate neutralization system (SRNS). The SRNS is a continuous-mode physical model (Fig. S2) of the neutralization process used at the KL mill that has been verified to reproduce the aqueous and solids geochemistry of the mill process (Robertson et al., 2014). The first SRNS experiment (termed R3) used synthetic raffinate devoid of Fe, while the second SRNS experiment (termed R4) used raffinate containing Fe. The composition of the two synthetic raffinates is shown in Table 1 and is based on a raffinate sample collected from the KL mill by in 2011 (Gomez et al., 2013). Concentrations of As, Ni, Se, and Mo were increased relative to the mill sample (approximately 10x for As and Ni, 75x for Mo, and 100x for Se) to aid in characterizing EOC-bearing phases. The detailed procedure and conditions used to synthesize the raffinate is presented by Robertson et al. (2014). Neutralized precipitates were collected from the Se-Mo (pH 4.0) and Lamella (pH 9.5) thickeners and equal volumes were mixed at pH 10.5 to simulate the treatment of the final tailings discharged from the KL mill to the DTMF (termed Combined samples). The third set of samples were field samples collected directly from the KL neutralization process in 2015 at pH 4.6 (Se-Mo), 9.9 (Lamella), and 10.9 (Combined) and are prefixed with "KL". A difference in synthetic and field raffinate compositions exists and is attributed to multiple process variables including variability in the composition of the current ore, upstream reagent addition, and operational parameters of the process. Field samples were collected every day for 3 days from the Se-Mo and Lamella thickeners. A composite sample was created by mixing equal volumes of each sample. The Combined sample was created from the composite Se-Mo and Lamella samples using the same method as for the synthetic samples. All samples were collected in 50 mL polypropylene centrifuge tubes and centrifuged at 2900 g for 20 min. The supernatants were decanted and the solids allowed to air dry for 3 d. The chemical composition of the solid samples as determined by inductively coupled plasma mass spectrometry (ICP-MS) is presented in Table 2 (the corresponding solution compositions are presented in Table S1).

Reference standards were synthesized, purchased, or obtained from collaborators to aid in characterizing the As- and Ni-bearing phases in the neutralized precipitates using XAS. These reference standards were chosen based on mineralogical characterization from previous studies using multiple techniques (e.g., XAS, X-ray diffraction (XRD), and scanning transmission electron microscopy (STEM)) (Gomez et al., 2013; Robertson et al., 2016, 2014). X-ray diffraction data for all synthetic samples and select standards are