Raffinate Neutralization Experiments at the McClean Lake Mill – Removal of Arsenic and Nickel

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Abstract. Uranium ores at the McClean Lake Operation in the Athabasca Basin of Northern Saskatchewan can produce elevated levels of arsenic (up to 700 mg/L) and nickel (up to 500 mg/L) in acidic ($pH<1.5$) spent leaching solutions (raffinates). Prior to neutralization, if necessary, ferric sulfate is added to tailings slurries to increase their Fe/As (molar) ratio to greater than 3. The slurries are then neutralized with lime to pH 4, and subsequently to pH 7-8. After neutralization, As and Ni concentrations average less than 1 mg/L. Solids from bench scale experiments demonstrate that As is associated primarily with scorodite and annabergite, with small amounts adsorbed onto or co-precipitated with ferrihydrite.

Introduction

Predicting the mobility of contaminants such as arsenic in ground water has become increasingly important as risk assessment plays a greater role in the licensing of waste disposal facilities. In the Athabasca Basin of northern Saskatchewan, elevated concentrations of arsenic (up to 10% by weight) and nickel (approximately 5 %) in uranium ores have required that detailed studies be conducted to assist in designing methods to reduce pore water concentrations of As and Ni in the tailings (Langmuir et al. 1999).

At the JEB Mill at McClean Lake, uranium is extracted from ore using sulfuric acid. The leach residue consists chiefly of unreacted quartz and illite, with lesser amounts of kaolinite and chlorite. After extraction, the leach residue solids are mixed with the barren leach solution (raffinate), which commonly has a pH below

2.0. To control dissolved As concentrations, which often reach 700 mg/L in the acid raffinate, a tailings neutralization circuit was included in the mill (Fig. 1). Prior to neutralization, the raffinate has its molar Fe/As ratio increased to a minimum of 3 by the addition of ferric sulfate. The raffinate and leach residue slurry is then neutralized by lime addition in the first neutralization tank to pH 4, and subsequently to pH 7-8, in a second neutralization tank. Residence times in each neutralization tank are approximately 90 minutes. After neutralization, As and Ni concentrations in slurry pore waters are typically less than 1 mg/L. Extensive laboratory work has demonstrated that a pH of approximately 7 is optimum to minimize both Ni and As concentrations. This pH was selected because, as an oxyanion As is least soluble under low pH conditions, whereas cationic Ni is least soluble at alkaline pH values (Jones et al., 1997). Neutralization also causes the precipitation of gypsum [$CaSO_4 \cdot 2H_2O$], hydrobasaluminite [$Al_4SO_4(OH)_{10} \cdot nH_2O$, n = 2–3], ferrihydrite [an Fe(III) hydroxide] and theophrastite [$Ni(OH)_2$]. Precipitated phases that contain important amounts of As include the poorly crystalline arsenate minerals scorodite or ferric arsenate [$FeAsO_4 \cdot 2H_2O$], and annabergite [$Ni_3(AsO_4)_2 \cdot 8H_2O$], a possible oxyhydroxide coprecipitate with a variable Fe/As ratio, and surface precipitated or adsorbed As (cf. Mahoney et al., 2005).

Solids in the neutralized slurry are typically comprised of 50-70% leach residue with the remainder as precipitated (secondary) solids. The slurry is pumped into the JEB Tailings Management Facility (TMF) for final disposal using a subaqueous emplacement process. Underdrains in the TMF allow for the removal of the pore water expelled by settling and compaction. The drain water is pumped to a water treatment facility for final processing before being released to the surface environment.

Neutralization tests using mill-produced raffinate were performed to: 1) study changes in solution composition as a function of pH; 2) evaluate the influence of different neutralizing agents on dissolved arsenic concentrations; 3) produce arse-

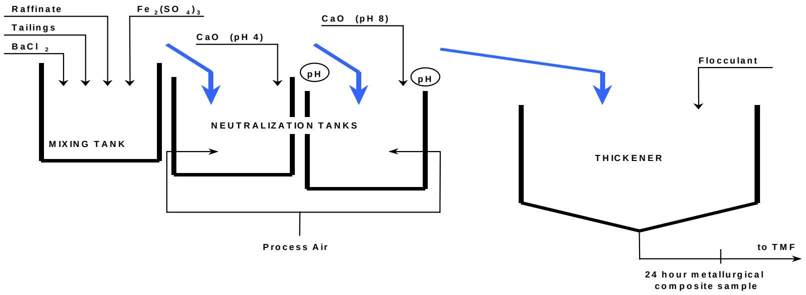

Fig. 1. Diagram of Tailings Neutralization Circuit – JEB Mill.

nic and nickel-rich solids for quantitative mineralogical analysis, including x-ray diffraction and spectroscopic analyses using x-ray absorption fine structure (XAFS) techniques; and 4) develop a geochemical model of the neutralization process.

Experimental Methods

The testing program was designed to evaluate the influence of factors including pH, selection of neutralizing agent, and the presence or absence of leach residue on the concentration of arsenic in the solution and the mineralogy of the precipitated phases. To perform the first experiments, approximately 60 liters of raffinate (Raffinate 1) were collected and spiked with As, Ni and Fe(III) (Table 1). Additional experiments, which consumed approximately 20 liters of raffinate (Raffinate 2), were performed primarily to assess redox reactions. Both raffinates were spiked with anhydrous As_2O_5 and $NiSO_4{:}5H_2O$. Ferric sulfate (Triron® solution) was added to increase the Fe/As ratio.

The experiments were designed to evaluate the behavior of As and Ni over the pH range of 2.0 to 8.0. Various neutralizing agents were used including dry $Ca(OH)_2$, NaOH pellets, and slaked lime (CaO) slurry. The procedure involved adding a neutralizing agent (base) to all of the beakers while continuously stirring. The pH was monitored and more base was added to successive beakers. After reaching their target pH values, the slurries were filtered and the solutions analyzed.

Table 1. Raffinate compositions, concentrations in mg/L.

Parameter	Raffinate 1 Unspiked	Raffinate 1	Raffinate 2 Unspiked	Raffinate 2
pH		1.5		1.1
Total As	362	732 (920)		693 (729)
Sum of As (III+V)			351	668
As(III)			100	447
As (V)			251	221
Fe Total	629	2,400 (2,700)	808	1,854 (2,400)
Fe (II)			640	685
Al		420		200
Ca		760		589
Cl		14		13
K		210		357
Mg		260		229
Na		48		23
Si		260		190
Sulfate		14,100		21,430
Ni	203	560 (550)	230	515 (529)
Eh (mv)				668
Fe/As(molar)	NA	4.4	NA	3.6
Fe/Ni(molar)	NA	4.5	NA	3.8

Concentrations in ( ) represent rapid turnaround time semi-quantitative analyses
NA – Fe/As and Fe/Ni ratio are not calculated for unspiked raffinate

The Raffinate 2 experiments placed particular emphasis on redox measurements including nearly continuous readings with a platinum electrode as the neutralizations proceeded. Laboratory analyses included total As, and analyses for As(III) and As(V). Iron measurements included total Fe and Fe(II), with Fe(III) estimated by difference.

To further concentrate As-bearing phases, one set of experiments was performed using approximately 5 liters of spiked raffinate (Raffinate 2) and a single "beaker". The neutralization procedure was similar to the batch experiments except that when the neutralized raffinate was filtered, the solution, less an aliquot for analysis, was returned to the "beaker" for additional neutralization and filtration. These experiments removed previously precipitated solids, thus separating the different solids as the pH increased.

Results and Discussion

Fig. 2 shows the concentration of total arsenic as function of pH during the tests. Results for the different experimental conditions are generally similar. The experiments that used Raffinate 2 show higher arsenic concentrations in the higher pH ranges. This is caused by the smaller Fe/As ratio in Raffinate 2 than in Raffinate 1. The figure includes data sets that used slaked lime or sodium hydroxide as neutralizing agents. Arsenic concentrations do not significantly differ, regardless of which base is used. The overall similarity of the As concentrations for the Raffinate 2 experiments, which contained accumulated solids, and the single beaker experiments, in which solids were removed, suggests that, at least for arsenic, the precipitated solids do not continue to react with the solution.

Fig. 3 shows the concentration of Ni as a function of pH during the neutralization experiments. As was observed for arsenic, the different neutralizing agents do not influence dissolved Ni concentrations. Separately, at similar pH values, concentrations of Ni in the three samples from the single beaker experiment were

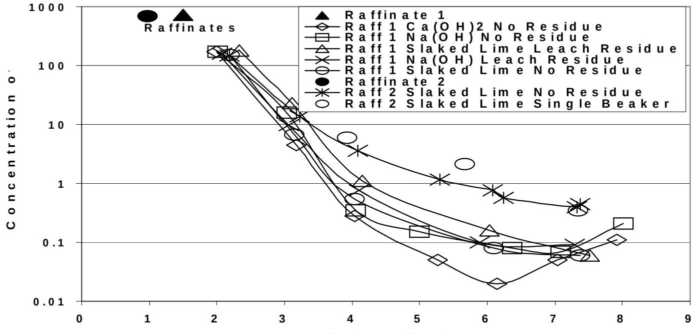

Fig. 2. Arsenic concentrations during raffinate neutralization experiments.

greater than in samples from the batch tests. The differences are most significant at higher pH values. This suggests that Ni concentrations may be influenced by the presence of previously precipitated solids.

Fig. 4 shows major component concentrations during the neutralization of Raffinate 2, including the three single beaker samples. As just noted, concentrations of As and Fe both decrease with rising pH at low pH values. Ni concentrations also consistently show small decreases from pH 2 to approximately 5. Aluminum begins to precipitate near pH 4.

Fig. 5 shows the number of moles precipitated for As, total Fe, Ni and Fe(II) at each neutralization step. The figure demonstrates that Fe and As are removed at a one to one proportion at pH of 2.18, which provides strong evidence that scorodite is formed under these conditions. As the pH increases to 3.22 much of the remaining As is removed as scorodite. Approximately 98 percent of the total As is removed from solution by a pH of 3.22. A significant amount of additional Fe is also removed in this pH range.

Small amounts of Ni are also removed even under low pH conditions. It is believed that strong pH gradients are formed during the addition of slaked lime, and that these gradients, coupled with the abundance of As and Ni, allow for the formation of annabergite [$Ni_3(AsO_4)_2 \cdot 8H_2O$]. Saturation index calculations demonstrate that annabergite is not in equilibrium with the solution at any pH of the bulk solution during neutralization. However mineralogical studies indicate that the phase is present. With increasing pH (greater than 5) significant amounts of Ni are removed.

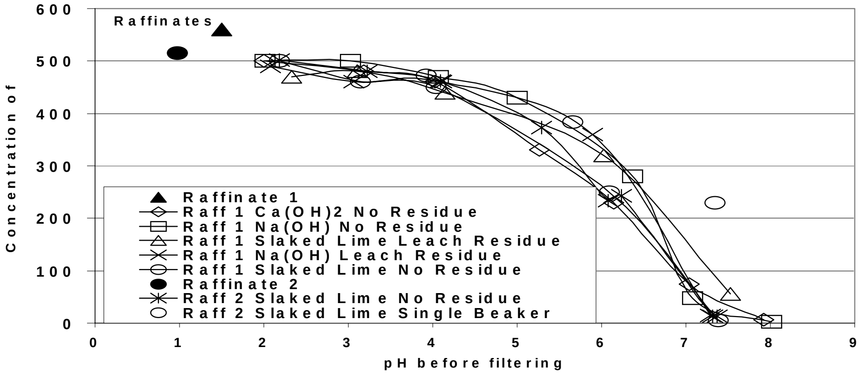

Fig. 3. Nickel concentrations during raffinate neutralization experiments.

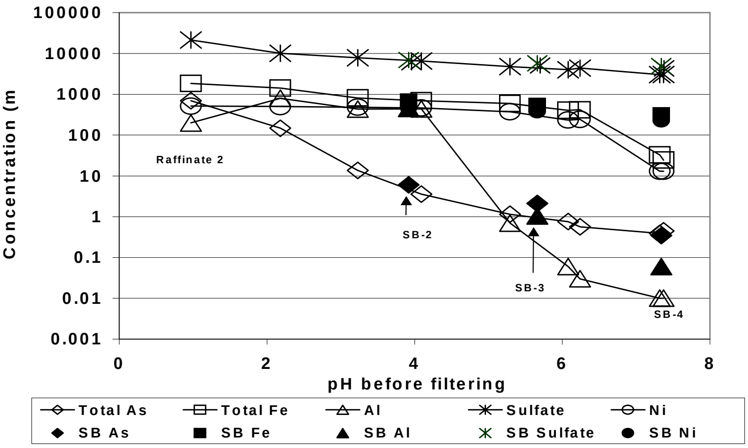

Fig. 4. Changes in major components during slaked lime neutralization of Raffinate 2.

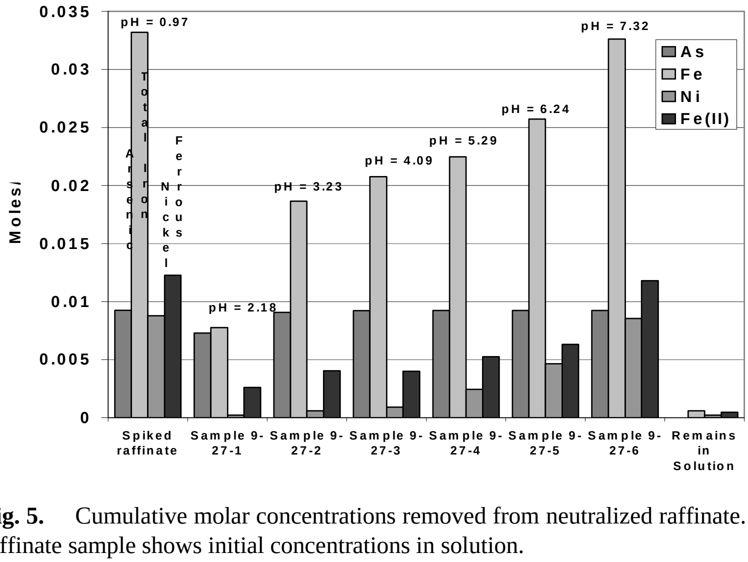

Fig. 5. Cumulative molar concentrations removed from neutralized raffinate. The spiked raffinate sample shows initial concentrations in solution.

Saturation Index Calculations

The geochemical modeling program PHREEQC (Parkhurst and Appelo, 1999) was used to calculate saturation indices for these samples. Saturation indices (SI) are defined as

$$SI = \log \frac{(IAP)}{(Ksp)} \qquad (1)$$

Where, IAP is the ion activity product of the mineral. At a saturation index of 0.0, the IAP equals the Ksp and the mineral is at equilibrium with the solution. Positive values mean that the IAP is greater than the Ksp and the solution is supersaturated with respect to the mineral. Baring kinetic constraints, the mineral should precipitate and concentrations in solution should decrease. Negative SI values mean that the solution is undersaturated and the mineral, if present, should dissolve.

Fig. 6 show saturation indices for gypsum, crystalline and amorphous scorodite, annabergite, ferrihydrite and theophrastite [$Ni(OH)_2$]. The raffinate is undersaturated with respect to amorphous scorodite, but oversaturated with respect to the crystalline form. The results from pH 3.0 to about pH 5.0 are particularly noteworthy; the solutions are at saturation with respect to amorphous scorodite. The crystalline form remains oversaturated. The bracketing of SI values between amorphous and crystalline scorodite suggests that scorodite of intermediate crystallinity limits As concentrations in these solutions.

For the other phases, the calculations demonstrate that gypsum is at saturation under all pH conditions. Ferrihydrite reaches saturation at a pH of approximately four. Theophrastite remains undersaturated until a pH of approximately seven is reached. Annabergite is always undersaturated.

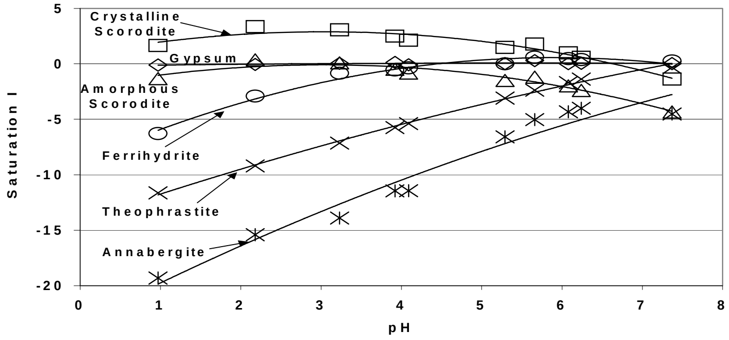

Fig. 6. Saturation indices for selected phases from Raffinate 2 measurements, speciated iron and arsenic activities based upon measured pe and total concentrations.

Table 2. Parameters used in geochemical model.

pH	-Log Ksp Al_Scorodite	Proportions	Measured As (mg/kg)	Modeled As (mg/kg)	Measured Ni (mg/kg)	Modeled Ni (mg/kg)
0.97			686		529	
2.18	22.31	0.96/0.04	150	181	510	510
3.23	22.66	0.87/0.13	13.6	13.1	487	486
4.09	23.16	0.82/.018	3.5	3	467	467
5.29	24.00	0.6/0.4	1.1	1	376	390
6.24	25.11	No Mix	0.56	0.55	245	390
7.32	25.11	No Mix	0.37	0.55	13.2	29

Geochemical Modeling Simulations

To understand the precipitation of minerals during the raffinate neutralization experiments, a geochemical model was developed using PHREEQC (Parkhurst and Appelo, 1999). The model was primarily designed to describe the changes in As, Ni and Fe concentrations.

The results in Fig. 5 demonstrate that a scorodite-like phase is removed as the raffinate is first neutralized. Saturation index calculations provide supporting evidence that the phase is initially amorphous. Mineralogical analysis suggests that the scorodite has an approximate composition of: $Fe_{0.9}Al_{0.1}AsO_4 \cdot 2H_2O$. Accordingly, the model included precipitation of an initially amorphous Al-bearing scorodite. To improve the fit between measured and modeled arsenic concentrations, increasingly negative log K_{sp} values for amorphous Al scorodite were assumed with increasing pH. With slight adjustments to the K_{sp} for Al scorodite (Table 2), the simple equilibrium model did an excellent job of matching measured As and Fe concentrations.

To match nickel concentrations, a non-equilibrium sub-step was added to the model. In this sub-step a portion of the raffinate is neutralized to pH 7, which removes nickel either as annabergite or $Ni(OH)_2$. The pH 7 solution, less the precipitated solids, is then mixed back with the solution obtained from the previous step and equilibrated to produce a final concentration for the model defined pH. The sub-step reflects the disequilibrium, high pH conditions that must surround particles of incompletely reacted base. Such locally elevated pH values will cause minerals to precipitate that are not stable at the lower pH of the bulk solution.

The proportions of raffinate and pH 7.0 solution were estimated from measured changes in nickel concentrations in the bulk solution with increasing pH. For example, Raffinate 2 (pH 0.97) had an initial nickel concentration of 529 mg/kg (PHREEQC uses molalities, which are then converted to mg/kg of water). At pH 2.18, the nickel concentration was 510 mg/kg, indicating a loss of approximately 4 percent of the nickel between pH 0.97 and 2.18. A mixture of 96 percent raffinate and 4 percent neutralized raffinate (pH 7.0) produced a nickel concentration of approximately 510 mg/kg, an acceptable model fit. Proportions were increased with increasing pH (Table 2). Subsequent model steps used the previous equilibrated solution as the starting composition. Thus, in the first sub-step annabergite was removed, but with decreased As concentrations, annabergite became undersaturated and $Ni(OH)_2$ precipitated in the later steps.

The pH 5.29 solution was the starting solution for pH 6.09 and 7.38 steps. To model the pH 6.09 sample, the pH 5.29 solution was neutralized to a pH of 6.09. Only gypsum, hydrobasaluminite and ferrihydrite precipitated at this pH. At pH 7.32, the model predicted that gypsum, theophrastite and ferrihydrite would precipitate. The predicted concentrations for the Raffinate 2 experiments using this conceptual geochemical model for the raffinate neutralization process are provided in Fig. 7.

The complexity of the model reflects the fact that neutralization of the raffinate is a complicated process in which both equilibrium and nonequilibrium reactions take place. The model presented in this paper is obviously not unique. Numerous aspects, which have been arbitrarily defined, could be redefined and would still provide excellent fits to the data.

The equilibrium portions of the model suggest that precipitation of a scorodite phase of increasing crystallinity (smaller solubility product constant) with increasing pH, limits maximum arsenic concentrations up to pH 6-7. Adsorption reactions are not required to explain arsenic behavior. Mahoney et al. (2005) showed that reversible adsorption reactions have little impact on the concentration of arsenic.

The change in nickel concentrations with rising pH is explained by the precipitation of annabergite or theophrastite in local environments under the high pH conditions associated with unreacted base. Interaction with secondary solids may also play a role in the behavior of nickel. Nickel concentrations are lower than a mineral precipitation equilibrium model alone would predict, except at the highest pH values, when theophrastite [$Ni(OH)_2$] approaches saturation (Fig. 6).

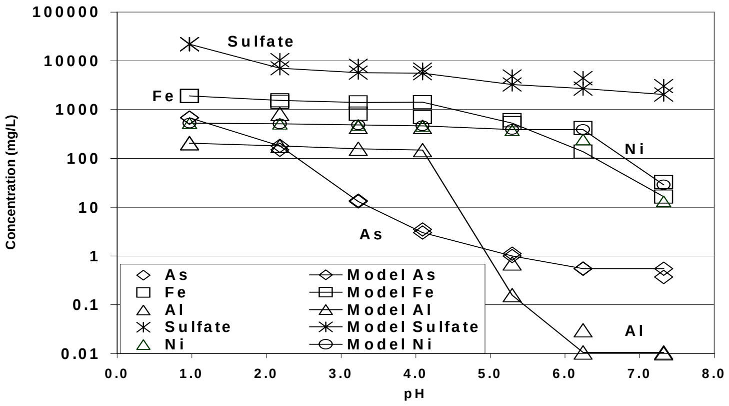

Fig. 7. Comparison of measured and modeled concentrations of some major species during the neutralization of Raffinate 2 using slaked lime.

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