Forecasting opportunities for co-management of Cu-Ni tailings with byproducts of iron ore mining

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Abstract

Legacy tailings produced in taconite iron ore mining in Northeastern Minnesota are rich in iron oxides and have strong carbonate-derived pH buffering capacity. These properties make taconite tailings an attractive candidate for attenuating trace metals and metalloids via surface complexation to iron oxides and/or co-precipitation of solid solutions. The proposed development of copper-nickel resources in the Duluth Complex of Minnesota represents an opportunity for beneficially re-using legacy taconite tailings to control metal mobility from newly created Cu-Ni tailings.

To probe the geochemical interactions between Cu-Ni and taconite tailings, a unique set of laboratory-scale kinetic tests were conducted. The test program placed modified humidity cells in series with leachate from cells with Cu-Ni tailings being fed as influent into cells containing taconite tailings. The tests remained in operation for thirteen years. The data show distinctive geochemical signatures of (i) surface area normalized release for conservative ions such as SO_4^{2-}, (ii) approach to an equilibrium solubility limit for carbonate forming cations such as Ca^{2+}, and (iii) sorptive attenuation for trace metals and metalloids such as AsO_4^{3-}. The sorptive attenuation was observed to increase over time as the taconite cells aged over the course of the test, consistent with ongoing precipitation of iron oxyhydroxide solids from iron produced via ankerite (in taconite) dissolution.

A geochemical model was developed and calibrated against the data to test the plausibility of potential interaction mechanisms expected for a hypothetical full-scale tailings co-management scenario. Simulations with the model demonstrate the potential for non-linear scaling of water quality with respect to water-to-rock ratio and highlight the critical importance of assumptions that influence model predictions of pH on metals mobility. Results highlight the role of the in-situ pH on geochemical processes in both kinetic tests and in field-scale tailings facilities. Both kinetic test data and modelling results suggest an opportunity for beneficial reuse of byproducts from the established taconite and developing Cu-Ni mining industries in Northeastern Minnesota.

Keywords: Tailings, adsorption, modelling, geochemistry, beneficial re-use

Introduction

The Duluth Complex is a mafic intrusion emplaced during the Mid-continent rift approximately 1.1 billion years ago. Intrusions along the western edge of the Duluth Complex host mineralization comprising sulfide minerals containing copper, nickel, and platinum group elements (Miller and Nicholson 2013). Taconite iron ore mining has been conducted in Northeastern Minnesota since the 1950s. The tailings produced from taconite pelletizing are typically managed in facilities consisting of a ring dike constructed from coarse tailings inside of which fine tailings are deposited in a fluvial manner (Bavin et al. 2016). Owing to their ankerite content, taconite tailings can buffer pH and precipitate iron oxide solids. Because iron oxides are able to attenuate a variety of metals at circumneutral pH, legacy taconite tailings have potential for beneficial re-use in the co-management of new tailings produced from the Duluth Complex.

To characterize the geochemical implications of co-managing Duluth Complex tailings in legacy taconite tailings management facilities, a novel and long-term kinetic testing program was conducted wherein leachate generated from Duluth Complex tailings was fed into a series of reactor cells containing taconite tailings as depicted in Fig. 1. In this way, the tests simulated deposition of Duluth Complex tailings on top of a pre-existing bed of taconite tailings. A geochemical transport model, reported here, was developed to test the plausibility of geochemical mechanisms proposed to explain observations in the evolution of drainage chemistry observed during the over 13 years of testing.

Methods

Experimental Design

An interaction test program was conducted with connected cells of Duluth Complex and taconite tailings as depicted in Fig. 1 (SRK 2007). All tests were conducted at SGS Canada Inc. (SGS) in Burnaby, Canada. Analyses were performed by SGS or its contractors. In four of the tests, leachate generated from experimental weathering of Duluth Complex-derived tailings was directed through three sequential cells containing taconite tailings. Both fine and coarse taconite tailings were

tested. Two controls were comprised of three sequential taconite cells only. The Duluth Complex and taconite cells each contained 5 kg and 2 kg of tailings, respectively.

During testing, tailings were allowed to react under laboratory conditions for 6 days. On the seventh day, approximately 1 L of deionized water was dripped into the top of each of the Duluth Complex cells and allowed to drain through the bottom. Approximately 250 mL was collected from a port at the base of the Duluth Complex cell for analysis. The remaining 750 mL was directed through to the top of the second cell and allowed to drain. Approximately 250 mL was collected from a port at the base of the second cell for analyses. The remainder was directed through to the top of the third cell, and so on. The control columns are operated in the same manner, with the exception that approximately 750 mL of deionized water was dripped into the first taconite cell. Collected leachate was analysed by ICP-MS for dissolved metals and IC for sulfate.

Two different Duluth Complex samples were used in these tests. Both samples are bulk tailings (not size segregated) and were produced from a pilot plant. Initial sulfur concentrations were 0.1% (DC-A) and 0.15% (DC-B). Taconite tailings consisted of fine and coarse samples, with silty and sandy textures, respectively. Both the coarse
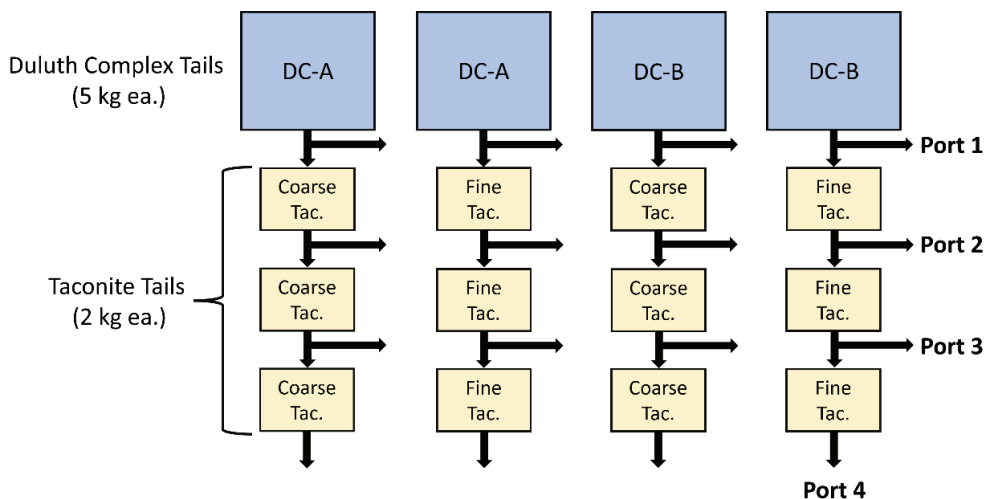

Figure 1 Reactor configuration for interaction tests. Two controls were run without Duluth Complex cells

and fine fractions are primarily composed of quartz, amphibole, iron oxides, chlorite, ankerite, and calcite.

Numerical Modelling

Cell leachate was modelled by coupling a geochemical reaction model for water-rock interactions within the cell with a mixing model to represent weekly flushing events that remove reaction products from the cell. Flushing was treated as an instantaneous mixing process between the flushing water and a volume of residual pore water containing reaction products accumulated over the prior week. Cells were modelled as a series of reactors with the flushing volume decreased between cells to account for the sampled volume.

Geochemical reactions considered include metal and metalloid release in both Duluth Complex and taconite tailings, dissolution of ankerite (a Ca-Mg-Fe carbonate) in the taconite tailings, and surface complexation of metals and metalloids to oxide surfaces. Constituent release was modelled as an irreversible processes described by a constituent release rate law and sorption was modelled with a linear isotherm. A mass balance analysis on mixing in the i-th cell gives:

$$C_f^i(n \cdot \Delta t) = \frac{C_f^{i-1}(n \cdot \Delta t) \cdot V_f^i + C_r^i(n \cdot \Delta t) \cdot (V_r^i + K_d^i \cdot M_s^i)}{V_f^i + V_r^i + K_d^i \cdot M_s^i}$$

(1)

where $C_f(t)$ and $C_r(t)$ represent the concentration of a solute at time t in the the effluent and residual pore water, respectively. The time-period between flushing events (i.e. one week) is denoted by Δt and n is an integer representing the number of flushes. The superscript i indicates the cell such that C_f^{i-1} represents the effluent concentration from the prior cell in the series which serves as influent to cell i. V_f and V_r represent the flushing and residual volumes following the same superscript notation for cells. K_d represents the linear partitioning coefficient to a mass of sorbent denoted by M_s.

Irreversible reactions were modelled as releasing mass to the residual water volume during the time period Δt between flushes. Assuming that the concentration in the residual water at the beginning of the week-long reaction period is equal to the effluent concentration of the previous flush, mass balance over the reaction period gives:

$$C_r^i(n \cdot \Delta t) = C_f^i((n-1) \cdot \Delta t) + \int_{(n-1) \cdot \Delta t}^{n \cdot \Delta t} r^i(t) \cdot dt \cdot \frac{V_r^i}{V_r^i + K_d^i \cdot M_s^i}$$

(2)

where $r^i(t)$ represents the (instantaneous) release rate of mass to the residual water and sorptive equilibrium has again been assumed.

A rate law must be specified in order to use equations (1–2) to simulate effluent concentrations. Results discussed below indicate effects of both material age and solution composition so a general rate law in the form of equation (3) was used (Rimstidt 2014):

$$r(t) = r_0 \cdot \left(\frac{m(t)}{m_0}\right)^\gamma \cdot (1 - S_R)$$

(3)

where r_0 represents a far-from-equilibrium rate for fresh material, $m(t)$ and m_0 represent the mass of material at time t and at time zero, respectively, S_R represents the saturation ratio ($S_R = 1$ when the solution reaches equilibrium with respect to the dissolving phase). The term $(m(t)/m0)^\gamma$ represents the effect of material aging. A shrinking particle model was used by setting $\gamma = 2/3$ (Levenspiel 1998).

The geochemical model was implemented in a Python script and fit to data using Levenberg-Marquardt square error minimization (Press et al. 2007). Because the test design included several combinations of Duluth Complex and taconite tailings as well as controls with taconite tailings only, a shared parameter approach was used (Bandstra and Brantley 2008) wherein all datasets were used to refine each fitting parameter. Each rate parameter was assumed to take a unique value for each material, but a common value was forced for any cell containing the same material (including data from the control tests).

Results

Several constituents showed conservative behavior across cells as exemplified by sulfate in Fig. 2. In the interaction test (Fig. 2A), sulfate released in the Duluth Complex cell appears to be superimposed on sulfate released in the taconite cells. Net sulfate increases across Ports 2–4 and sulfate in the interaction tests were systematically greater
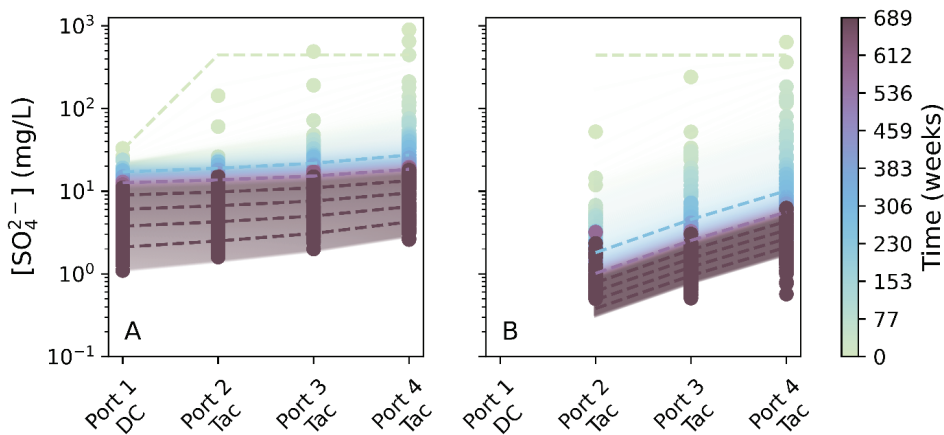
Figure 2 Sulfate concentration plotted across cells for Duluth Complex/taconite interaction tests (A) and taconite only control (B). Data depicted by markers, shared parameter fitting results depicted by lines. Color indicates time and heavy dashed lines represent model increments of 100 weeks

than the sulfate released from the control (Fig. 2B). This holds throughout a pronounced temporal decrease in sulfate release for both the Duluth Complex and taconite cells. Chloride, potassium, and sodium showed behavior similar to sulfate.

Model fits shown in Fig. 2 capture the decrease in reactivity over time by setting γ to one in equation (3) and adjusting r_0 to fit the observations. Both sorption and inclusion of an equilibration term led to poor fits of the data so K_d in equation (2) and S_R in equation (3) were set to zero. These fitting results are consistent with the hypothesis that there are no chemical interactions between Duluth Complex tailings and taconite tailings for sulfate and, therefore, co-management of these tailings would be unlikely to alter the overall sulfate load released. A similar conclusion can be reached for chloride, potassium, and sodium.

The effect of a positive saturation ratio can be seen in Fig. 3 where calcium data are plotted for both an interaction test (Fig. 3A) and a control (Fig. 3B). The behavior of calcium is similar to sulfate in that release rates decline over time in all cells, but the calcium released in the Duluth Complex cell makes no more than minor additions to the calcium released by the taconite cells. When the interaction tests are compared to the control, calcium levels in the taconite cells are only 13 mg/L greater, on average, in the

interaction tests. Model fits where K_d was set to zero and S_R was computed as the ratio of the calcium concentration to a calcite solubility limit solid reinforce the notion that calcium in the taconite cell effluent is controlled by equilibrium saturation. Magnesium and strontium showed behavior similar to that of calcium.

The effluent pH data (not shown) were also consistent with equilibration with a carbonate solid in the taconite cells. After an initial adjustment, the Duluth Complex effluent sustained pH between 7 and 7.5 while all taconite cells showed a constant pH around 8.0 over the full time-course of the tests. The taconite tailings contain substantial quantities of ankerite and the observed pH values are consistent with ankerite saturation under open atmospheric conditions.

The observed pH is close to the zero point of charge for most iron oxy-hydroxides (Stumm 1992), under which conditions, a variety of both metal cations and oxy-anions can adsorb to iron oxide surfaces (Dzombak and Morel 1991). The arsenic data shown in Fig. 4 are suggestive of sorption control in the taconite cells. Unlike sulfate and calcium, the arsenic concentration decreases across the first taconite cell in Fig. 4A after about two years of test operation and the concentration remains suppressed across the other two taconite cells. Arsenic concentrations in the control follow a similar pattern within
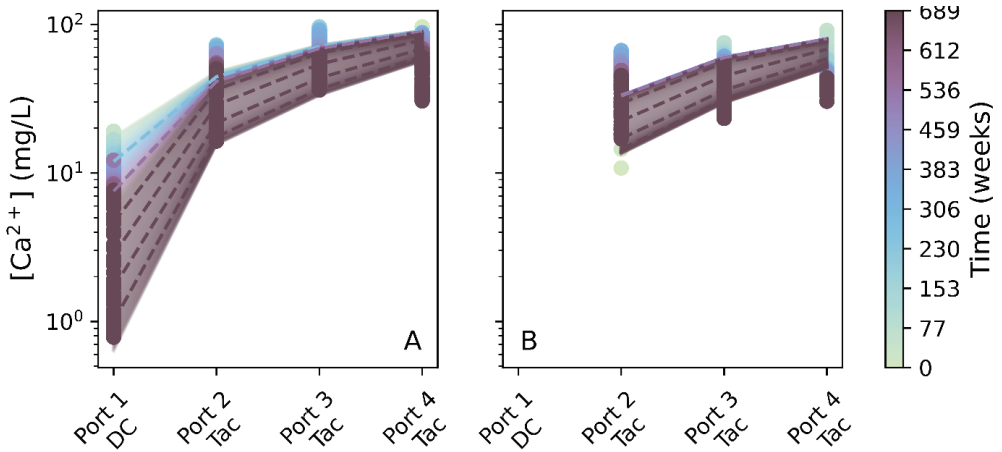
Figure 3 Calcium concentration plotted across cells for Duluth Complex/taconite interaction tests (A) and taconite only control (B). Data depicted by markers, shared parameter fitting results depicted by lines. Color indicates time and heavy dashed lines represent model increments of 100 weeks

the taconite cells but with arsenic values consistently lower (by a small amount) when compared to the interaction test.

Both the interaction test data and the control show a strong decrease in arsenic concentration over time, but the decrease is more pronounced in the taconite cells as compared to the Duluth Complex cell. All the taconite cells show a roughly 1000-fold decrease in arsenic concentration over the course of the test while the Duluth Complex cell shows only a 10-fold decrease and that mostly occurring in the first few months of operation. These data suggest that the taconite cells contain a sink for arsenic and that the strength of the sink is increasing over time.

A simple sorption model based on equation (2) with constant values of K_d and M_S is not able to reproduce the trends observed in the data (results not shown). This is because a sorbent of constant strength is only able to slow the temporal response of arsenic breakthrough from the taconite cells in a manner similar to that of retardation coefficient in a conventional continuous flow system (Freeze and Cherry 1979). The modelling results shown in Fig. 4 reflect conditions where the amount of sorbent is increasing over time. This could be due to the ongoing precipitation of iron oxyhydroxide solids from iron released to solution by ankerite dissolution.

In addition to arsenic, evidence for sorption was also observed for cobalt, copper, nickel, and vanadium. Data for other metals that might be expected to adsorb to iron oxides (e.g. cadmium, lead, zinc, chromium, selenium) were consistent with a sorption mechanism but were released in low amounts such that the observed trends were not definitive.

Results of post-mortem mineral characterization are consistent with the interaction mechanisms described above. Bulk solids chemical composition showed depletion of calcium and other carbonate-forming divalent metals in the first taconite cell relative to the other taconite cells. Arsenic and other sorbing metals and metalloids were relatively enriched in the first taconite cell with respect to both the downstream taconite cells and the control. Modal mineralogy indicated the presence of more than 10% iron oxides (by mass) in the taconite cells with the greatest amount accumulated in the first taconite cell.

Conclusions

These results suggest that legacy taconite tailings have favorable properties for beneficial reuse in the co-management of copper-nickel tailings such as those produced from the Duluth Complex. The high carbonate content of the taconite tailings can buffer pH and promote precipitation of iron oxides
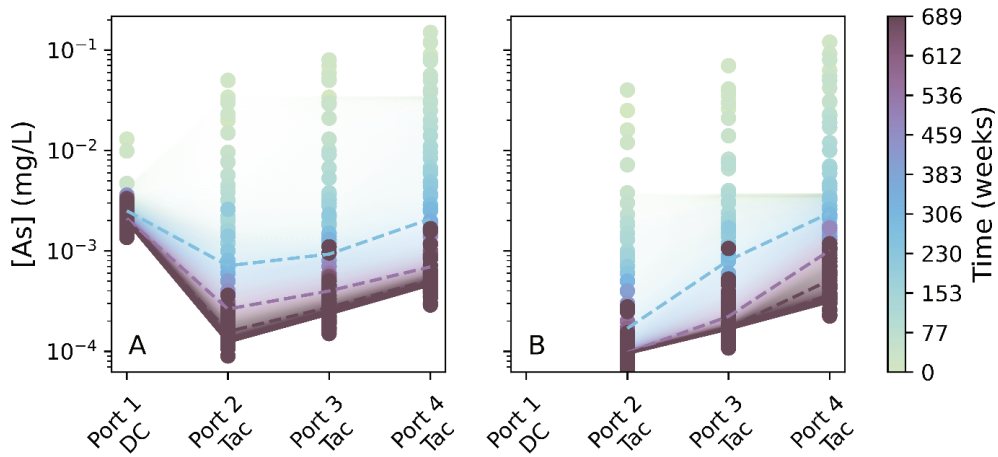
Figure 4 Arsenic concentration plotted across cells for Duluth Complex/taconite interaction tests (A) and taconite only control (B). Data depicted by markers, shared parameter fitting results depicted by lines. Color indicates time and heavy dashed lines represent model increments of 100 weeks

and sorption of both metal cations and oxy-anions to iron oxide surfaces. The taconite tailings appear able to continuously produce new sorbent surfaces over the thirteen-year time-course of the observed data such that attenuation of metals increased over time.

Application of the reported results will require a forecast of pH at the scale of a tailings management facility. Evidence here suggests that, given sufficient interaction between leachate and carbonate minerals in the taconite tailings, pH of leachate will be buffered by the carbonate minerals. However, the resulting pH from this reaction will be sensitive to hydrologic factors dictating the degree to which the carbonate system is open to atmosphere.

Acknowledgements

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