

A method to measure arsenic readily released to pore waters from uranium mill tailings

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Abstract. A method to quantify the amount of readily released arsenic in uranium mill tailings was developed using a technique known as Equilibrium Partitioning In Closed Systems (EPICS). The method employs a gentle leaching solution that, except for its arsenic (As) concentration, is identical to the neutralized raffinate that contacts the tailings. Prior to implementation, the experimental design and mathematical approach were verified in geochemical models using PHREEQC. Laboratory experiments using tailings from the Athabasca Basin of Northern Saskatchewan demonstrated that As that could be readily released to pore waters is about 0.2 % of the total As in the tailings.

Introduction

Predicting the mobility of contaminants such as arsenic (As) 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 As in uranium ore (up to 10% by weight) have required that studies be conducted to assist in designing methods to reduce pore water concentrations of As in the neutralized tailings that are disposed in a tailings management facility (TMF).

At the JEB mill at McClean Lake, uranium is extracted from the ore using sulfuric acid. The leach residue from the ore consists chiefly of unreacted quartz and illite, with lesser amounts of kaolinite and chlorite. After uranium extraction, the leach residue solids are mixed with the barren leach solution (raffinate), which commonly has a pH below 2.0. To reduce dissolved As concentrations, which often reach 700 mg/L in the acid raffinate, the raffinate has its molar Fe/As ratio in-

creased to 3/1, if necessary, by the addition of ferric sulfate (Langmuir et al. 1999). The raffinate and leach residue slurry is then neutralized by lime addition to pH 4 and subsequently to pH 7-8. After neutralization, concentrations of As in slurry pore waters from the mill are typically less than 1 mg/L. Precipitated phases that contain important amounts of As include the arsenate mineral scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) in a poorly crystalline matrix, a possible oxyhydroxide coprecipitate with a variable Fe/As ratio, and As that may be surface precipitated or adsorbed onto ferrihydrite and other mineral surfaces. Solids in the neutralized tailings are typically comprised of 50-70% leach residue minerals with the remainder as precipitated solids. The slurry is pumped into the JEB TMF for disposal using subaqueous emplacement. Underdrains allow for removal of pore water expelled by settling and compaction in the TMF. The pore water is pumped to a water treatment facility. Canadian regulatory agencies have expressed concern that significant concentrations of adsorbed As might be released over time from the tailings. This study was performed to determine the amount of readily releasable As.

EPICS method and model

Fuller et al. (1988) and Darland and Inskeep (1997) among others, suggest that readily desorbable As is a small fraction of total adsorbed As, and that most adsorbed As is strongly bound to mineral surfaces. In our study, readily desorbed As has been measured using a method that involves the successive addition, to the neutralized raffinate and tailings, of aliquots of the same raffinate, but free of As, and measuring the As released to solution following each addition. This method is less aggressive than others (c.f. Shiowatawa et al. 2003, Kim et al. 2003), and avoids dissolution of amorphous arsenate phases. In this study it is assumed that desorbable As does not include As from dissolution of arsenate minerals, Fe/As oxyhydroxides precipitates or surface precipitates.

Mathematical derivation

To quantify the readily desorbable As in the tailings, a series of laboratory measurements were performed using a procedure based upon a methodology described by Gossett (1987), which he called Equilibrium Partitioning in a Closed System (EPICS). Conceptually, the method is simple. By changing the liquid to solid ratio in a slurry, while keeping the amount of desorbable As plus dissolved As and the mass of solids constant, the amount of desorbable As can be calculated based upon changes in the dissolved As concentration.

The following example explains the method. A sample of 1 L of solution with a concentration of 1.0 mg/L of dissolved As is diluted to 2 L. The As concentration is thus reduced to 0.5 mg/L. If releasable As is available to the solution, some of it will be released and As concentrations will exceed 0.5 mg/L. When the system undergoes further dilution, As concentrations will not decrease in accordance with

a simple dilution process, but rather additional releasable As will transfer from the solids to the solution. As infinite dilution is approached, the amount of potentially releasable As approaches zero. All of the As is in solution but, the concentration becomes too low to measure. In this study we extrapolate from measured As concentrations to calculate the releasable amount.

In the neutralized tailings slurry, the precipitated forms of As, which are defined as $AS_{(ppt_form)}$, include arsenate minerals such as scorodite, Fe/As oxyhydroxide coprecipitates or surface precipitates. Adsorbed As that is not readily desorbed is also considered part of $AS_{(ppt_form)}$. Desorbable As is termed $AS_{(desorb_form)}$. Possible sorbent phases may include ferrihydrite, hydroxysulfate minerals, clays and gypsum. The third form of As is dissolved in solution ($AS_{(aq_form)}$). These forms make up the total As ($AS_{(total)}$).

$$AS_{(total)} = AS_{(ppt_form)} + AS_{(desorb_form)} + AS_{(aq_form)} \quad (1)$$

The term “form” provides a conceptual description of the different types of arsenic in the system. Equations 1 and 2 do not explicitly describe concentrations. Total and aqueous As concentrations can be readily determined using standard analytical methods. The desorbable As plus dissolved As in equation (1) may be defined as the readily released As ($AS_{(rr)}$),

$$AS_{(rr)} = AS_{(desorb_form)} + AS_{(aq_form)} \quad (2)$$

Desorbable As responds rapidly to changes in conditions such as temperature, pH or liquid to solid ratio. Arsenic in precipitated form, or irreversibly bound to surfaces, will respond to such changes at a much slower rate or not at all.

There are several mathematically equivalent approaches to estimate the amount of readily released As in the tailings. The most straightforward is based upon the EPICS method (Gossett, 1987). In Gossett’s work, the EPICS methodology was used to measure Henry’s Law Constants for volatile organic compounds. We use a similar approach here to measure the distribution coefficient for readily released As (K_d^{rr}).

For a fixed mass of slurry ($M_{(solid)}$), the readily released As ($AS_{(rr)}$) is operationally defined by Equation 3:

$$AS_{(rr)} = AS_{(desorb)}M_{(solid)} + AS_{(aq)}V_{(aq)} \quad (3)$$

Where $AS_{(desorb)}$ is the desorbable As concentration associated with slurry solids, and $AS_{(aq)}$ and $V_{(aq)}$ are the aqueous As concentration and volume of the aqueous phase.

The distribution coefficient for readily released As is defined as:

$$K_d^{rr} = \frac{AS_{(desorb)}}{AS_{(aq)}} \quad (4)$$

The superscript *rr* distinguishes this distribution coefficient from the total distribution coefficient, K_d^{total} , which is defined by

$$K_d^{total} = [AS_{(ppt)} + AS_{(desorb)}] / AS_{(aq)}. \quad (5)$$

Substituting Equation 4 into Equation 3, we obtain:

$$As(rr) = As(aq) [V(aq) + K_d^{rr} M(solid)] \quad (6)$$

If samples 1 and 2, prepared with different volumes of liquid, both contain the same total amount of readily releasable As and mass of solid, then

$$As(aq1)[V(aq1) + K_d^{rr} M(solid)] = As(aq2)[V(aq2) + K_d^{rr} M(solid)] = As(rr) \quad (7)$$

Where the subscripts 1 and 2 represent the As concentrations and volumes at specified steps. Solving for K_d^{rr} gives:

$$K_d^{rr} = \frac{As(aq1)V(aq1) - As(aq2)V(aq2)}{[As(aq2) - As(aq1)]M(solid)} \quad (8)$$

This equation shows that K_d^{rr} can be determined by experimentally changing the proportions of water to solid in a system in which $As(rr)$ and $M(solid)$ are fixed.

The simplest method of computing K_d^{rr} from such experimental data, is to plot the inverse of the As concentrations ($1/As(aq)$) versus the volume of solution for two or more measurements. It can be demonstrated (Mahoney et al. 2005) that K_d^{rr} then equals the intercept (b) of the line, divided by the slope (m) of that line times the mass of solid, or

$$K_d^{rr} = b / [mM(solid)]. \quad (9)$$

Because all of the concentrations used in these calculations are derived from solution analyses, the proportion of liquid to solid is not explicitly required, so a dimensionless K_d^{rr} is commonly obtained. This can be converted to a true distribution coefficient (in units of V/M) when the mass of solids and initial volume of solution are known.

One method to estimate the amount of readily released As is to calculate $F_{(desorb)}$, the fraction of As that is readily desorbed:

$$F(desorb) = \frac{As(desorb)M(solid)}{As(desorb)M(solid) + As(aq)V(aq)} \quad (10)$$

The readily released As is then calculated:

$$As(rr) = \frac{[As(aq)V(aq)]}{[1 - F(desorb)]} \quad (11)$$

Model simulations

A series of model simulations were performed to verify that the assumptions and the computational method could be applied to the more complicated system of As desorption from ferrihydrite. Desorption reactions were modeled using PHREEQC (Parkhurst and Appelo, 1999), and the diffuse layer model (Dzombak and Morel, 1990). PHREEQC was used because the distribution of the different forms of As

can be determined at each modeling step. Therefore, the amount of readily released As measured using the EPICS calculation could be directly compared to the amount estimated using PHREEQC.

For the primary leaching solution, which was arsenic-free, the assumed major ion concentrations were 400 mg/L Ca, 230 mg/L Na, 243 mg/L Mg and 2400 mg/L SO₄. Arsenic, at 0.1, 1.0 and 10.0 mg/L, was added to the primary solution to produce the starting solutions. Diffuse layer model weak sites (Hfo_wOH) at 0.001 mol/L were used. For each step, the 1 L of As bearing solution was mixed with a volume of the “As-free” leaching solution, and the mixture equilibrated with the adsorption sites.

To obtain the data required for the EPICS calculation, leaching solution was added to the initial 1-L system, changing the solution/sorbent ratio. In these simulations the final volumes were 1.2, 1.4, 1.6, 1.8, 2.0, 3.0, 4.0 and 5.0 L. In the PHREEQC models, the leaching solution is added using the MIX keyword, which calculates the changes in volume as solutions are added together. This makes the PHREEQC program ideally suited to verifying the EPICS method.

Table 1 lists some of the verification calculations and provides a comparison of EPICS and PHREEQC site concentrations. Readily released As concentrations, using the EPICS methodology, and the initial values used in PHREEQC are in close agreement. The simulations show that the method is computationally sound.

Fig. 1 shows As concentrations for two simulations. The theoretical dilution lines show As concentrations if simple dilution is the only process. Departures of model-simulated lines from the dilution lines indicate that a significant reservoir of As buffers dissolved As concentrations. The data are replotted as inverse concentrations, which linearizes both the data and the dilution lines (Fig.2). By definition, the dilution lines correspond to a K_d^{rr} of 0.0. These lines have an intercept of zero, and a slope equal to the inverse concentration of the first data point.

Table 1. EPICS procedure verification by comparison with PHREEQC results.

Initial As (mg/L)	pH	As(aq) (moles/L)	K_d^{rr}	$F_{(desorb)}$	Readily Released As (moles/L)		Agreement % EPICS vs PHREEQC
					EPICS	PHREEQC	
0.1	7	9.14×10^{-10}	5725	1.00	1.34×10^{-6}	1.34×10^{-6}	100
1	7	1.03×10^{-8}	123	0.99	1.34×10^{-5}	1.34×10^{-5}	100
10	6	2.69×10^{-6}	28.4	0.93	1.30×10^{-4}	1.34×10^{-4}	97.3
10	7	6.45×10^{-7}	53.5	0.96	1.30×10^{-4}	1.34×10^{-4}	97.4

For the pH 7.0 data, the K_d^{rr} was 54, for the pH 6.0 data the K_d^{rr} was 28. In simple systems the K_d^{rr} for As should decrease as pH increases. The apparently unusual behavior is because of the large sulfate concentrations. Desorption of sulfate with increasing pH increases the number of sites available for As adsorption, which increases K_d^{rr} .

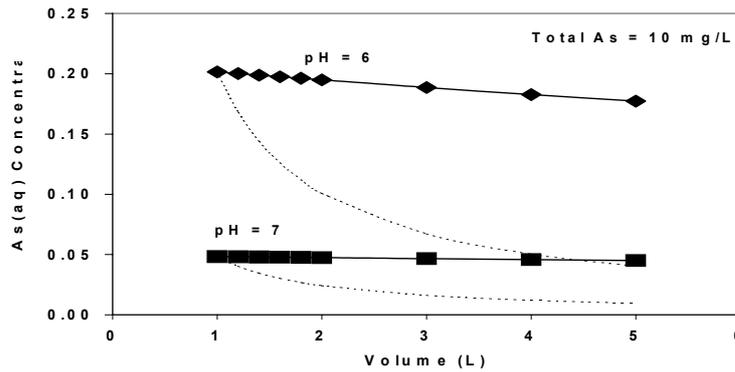


Fig. 1. PHREEQC model derived concentrations of EPICS procedure assuming As adsorption on hydrous ferric oxide. Dilution lines are dashed.

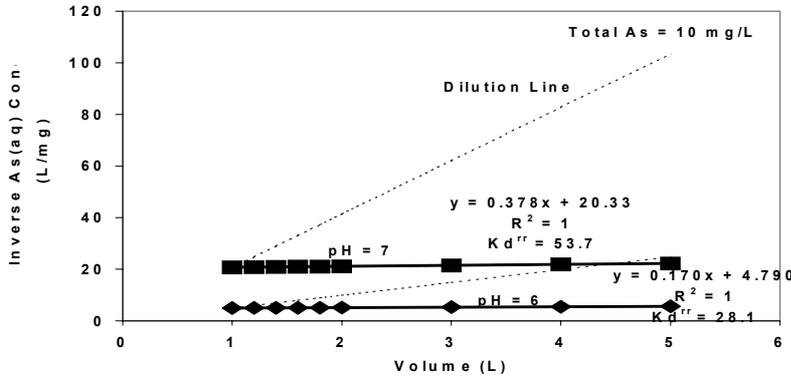


Fig. 2. Inverse concentrations of PHREEQC modeled EPICS process, showing regression fit and calculation of K_d^{rr} .

Experimental methods and measurements with tailings

A pre-weighed container (approximately 7-L size, wide-mouth plastic bucket) was partially filled with approximately 1 L of neutralized tailings slurry. The pH and mass of the slurry were measured. The initial volume was defined as V1. The slurries typically contained 400-600 g of solids. The remainder of the slurry was neutralized raffinate. Solids were allowed to settle and an aliquot of supernatant solution was carefully drawn off. This and subsequent aliquots were kept as small as possible, and were always less than 25 mL. The large initial volumes and small aliquots was necessary to keep the system 'closed' with respect to total As. The aliquot was filtered (0.45 μ m) and analyzed for total As. After each aliquot was drawn off, the container was reweighed to estimate the mass of solution removed.

The starting solution was the neutralized and unmodified raffinate, which typically has an As concentration of <1 mg/L. The second water was the "As-free" leaching solution, which retained the pH and major ion composition of the neutralized raffinate. In the leaching solution, arsenic concentrations were required to be less than 0.01 mg/L.

Because of the large volumes required by the procedure, the amounts of solution and masses of solids in the mixtures were measured gravimetrically. To start the experimental procedure, approximately 1 L of "As-free" leaching solution was added to a liter of the tailings slurry. The new volume was defined as V2. The slurry was mixed, and the pH was measured. The slurry was mixed again and the solids allowed to settle. In most experiments settling times were limited to 1 hr. The pH was rechecked, and a sample was withdrawn for analysis. Because dissolved As concentrations are a strong function of pH, the pH was kept constant throughout the process.

The process of adding leach solution, measuring the weight and volume of the new mixtures, and extracting aliquots for analysis was repeated two more times (V3 and V4). Finally, the water in the slurry was removed by filtration. The solids were weighed and analyzed for As.

Results and discussion

Initial desorption experiments were run with one hour between extractions. Some examples are shown on Fig. 3. Values for K_d^{rr} were estimated using the regression derived slopes and intercepts from the inverse concentration data. Compared to the dimensionless K_d^{total} values, which range from 600 to 1400 for the experiments, the values for K_d^{rr} are small and range from 0.44 to 2.77. In spite of an up to five-fold dilution in some experiments, only slight changes in pH were noted and corrections to the pH of the slurries were not required.

The results of the first series of tests indicated that little As was released from the solids when extraction times were limited to approximately 1 hr, and the complete procedure took less than 4 hrs. A short time for the extractions was used because of concerns that other processes such as mineral dissolution could release additional As. The low amounts of readily released As demonstrated that dissolution from other phases was not an issue. Additional tests were run using longer times between dilutions. Two tests were run with 12 hrs between measurements, with samples gently mixed every two hours. One test was run as a control, with one hour between measurements.

Fig. 4 shows that there was no difference in the results between the 12-hr leaching/sampling times and the one-hour steps. The fact that additional As was

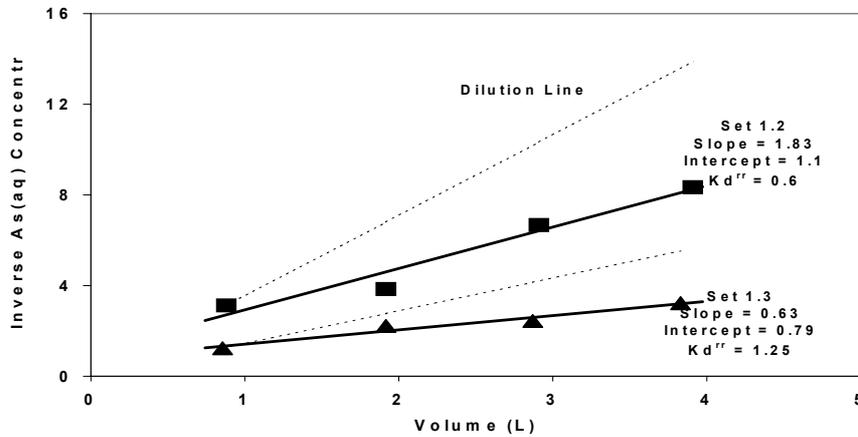


Fig. 3. Inverse concentrations for EPICS experiments using 1 hour between extractions.

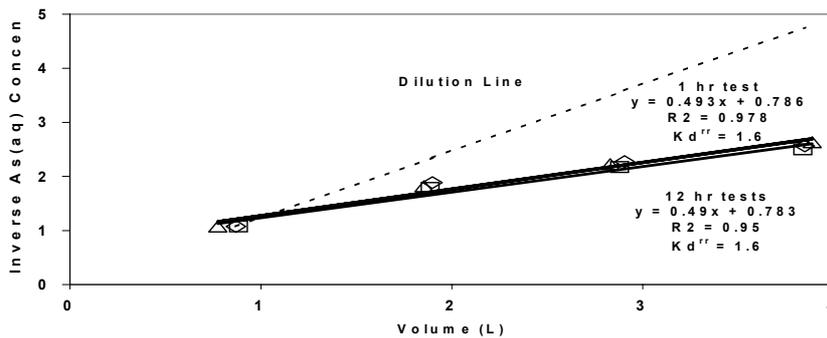


Fig. 4. Results of EPICS method comparing 1 hour (triangles) and 12 hour extraction times. The figure includes two sets of 12 hour-measurements (diamonds and squares).

Table 2. Calculation of readily released arsenic using the EPICS method.

Test	K_d^{rr}	$F_{(desorb)}$	Initial $As(aq)$ (mg/L)	As desorbed (mg/L)	Readily Released As (mg/L)
1.2 (1hr)	0.6	0.38	0.32	0.19	0.51
1.3 (1 hr)	1.25	0.56	0.81	1.01	1.82
2.1 (1 hr)	1.6	0.62	0.93	1.49	2.42
2.2 (12 hr)	1.6	0.62	0.93	1.49	2.42

not released over time demonstrates that the As associated with the solid phases is practically immobile.

The amount of readily released arsenic is calculated based upon the K_d^{rr} and $F_{(desorb)}$. Table 2 compares initial $As(aq)$ concentrations to the concentration of desorbed As, and to the total amount of readily released As. Among the eight sets of measurements (not all included in Table 2), initial $As(aq)$ concentrations constitute from 38 to 70% of the total readily released As in the slurry.

Upon completion of the leaching process, the solids were weighed and analyzed for As. When compared to the total As content in the tailings, only a very small percent of the total As is dissolved in solution or readily desorbed from the solids. Based upon an average of eight measurements, only $0.21 \pm 0.08\%$ of the total As is considered readily releasable. The low percentage of readily releasable As, demonstrates that processing of the tailings in the JEB mill to immobilize As has been optimized.

Conclusions

A method for measuring As desorption from mill tailings (or other solids) was developed based on the EPICS model of Gossett, (1987) The method: (1) is relatively gentle and avoids leaching the As from poorly crystalline arsenate solids and the strongly adsorbed As, and (2) simulates the composition of pore waters in the JEB TMF.

Prior to performing the desorption experiments, the mathematical derivation of the EPICS method was checked by comparing EPICS-predicted desorption results to the same results predicted using an adsorption model in the geochemical code PHREEQC. The comparison showed the EPICS method to be computationally sound.

The results indicate that the amount of As readily released from the tailings was small and was similar in magnitude to the concentration of As in the initial tailings solution. In all cases, the As desorbed by dilution was less than 3 mg/L. Previous work (Langmuir et al., 1999) indicated that the vast majority of the As in the tailings is strongly bound in solids, either as arsenate minerals or as specifically adsorbed arsenate on ferrihydrite. Of this total amount, the readily releasable As averaged only $0.21 \pm 0.08\%$. That 99.8% of the total As in the tailings is fixed and

not readily desorbed supports the efficacy of the procedures used for As immobilization in the JEB mill.

The method is applicable to desorption measurements not only from tailings, but also from other complex solids including soils and sediments. Additional details related to this work are given in Mahoney et al. (2005).

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