



Arsenic readily released to pore waters from buried mill tailings

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Abstract

At the McClean Lake Operation in the Athabasca Basin of northern Saskatchewan, the untreated acid raffinate solutions associated with U mill tailings contain up to 700 mg/L dissolved As. To reduce the concentration of As and other contaminants in acid tailing slurries at the JEB mill at McClean Lake, ferric sulfate may be added to the acid raffinates to assure that their molar Fe/As ratio equals or exceeds 3. Tailings slurries are then neutralized with lime to pH 4, and subsequently to pH 7–8. The neutralized tailings contain minerals from the original ore, which are chiefly quartz, illite, kaolinite and chlorite, and precipitated (secondary) minerals that include gypsum, scorodite, annabergite, hydrobasaluminite and ferrihydrite. Most of the As is associated with the secondary arsenate minerals, scorodite and annabergite. However, a few percent is adsorbed and/or co-precipitated, mainly by ferrihydrite. Of major concern to provincial and federal regulators is the risk that significant amounts of As might be released from the tailings to pore waters after their subaqueous disposal in the tailings management facility. A laboratory study was performed to address this issue, measuring readily desorbed As using a method known as equilibrium partitioning in closed systems (EPICS). The EPICS method was selected because it employs a leaching solution that, except for its As concentration, is identical in composition to the neutralized raffinate in contact with the tailings. Laboratory experiments and modeling results demonstrated that the As that could be readily released to pore waters is about 0.2% of the total As in the tailings. Long-term, such releases may contribute no more than a few mg/L of dissolved As to tailings pore waters.

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1. Introduction

Predicting the mobility in ground water of contaminants such as As has become increasingly important as risk assessment plays a greater role in the licensing and permitting of waste disposal facilities. In the Athabasca Basin of northern Saskatchewan, elevated concentra-

tions of As in the U ore (up to 10% by weight) have required that detailed studies be conducted to assist in designing methods to reduce pore water concentrations of As in the neutralized tailings that are disposed of in contact with ground water in a tailings management facility or TMF (cf. Langmuir et al., 1999a,b).

At the JEB mill at McClean Lake, U is extracted from the ore using H₂SO₄. The leach residue from the ore consists chiefly of unreacted quartz and illite, with lesser amounts of kaolinite and chlorite. After U extraction, the leach residue solids are mixed with the barren

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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 increased to 3/1, if necessary, by the addition of ferric sulfate. The combined raffinate and leach residue slurry is then neutralized by lime addition to about pH 4 and subsequently to pH 7–8. After neutralization, As concentrations in slurry pore waters in the mill are typically less than 1–2 mg/L. Neutralization causes the precipitation of non-As bearing phases that include gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$], hydrobasaluminite [$\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot n\text{H}_2\text{O}$, $n = 2\text{--}3$], ferrihydrite [a Fe(III) hydroxide] and theophrastrite [$\text{Ni}(\text{OH})_2$]. Precipitated phases that contain important amounts of As include the poorly crystalline arsenate minerals. In the tailings these phases are non-stoichiometric solid solutions that also contain Al (scorodite: $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and Mg and Fe(II) (annabergite: $(\text{Ni}_3\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$), an oxyhydroxide coprecipitate with a variable Fe/As ratio, and As that may be surface precipitated or adsorbed onto ferrihydrite and other mineral surfaces (cf. Li and Stanforth, 2000; Ler and Stanforth, 2003). Preceding formulas are for the pure, end-member mineral phases.

Solids in the neutralized tailings slurry are typically comprised of 50–70% leach residue minerals with the remainder as precipitated solids. The tailings slurry is pumped into the JEB Tailings Management Facility (TMF) for final disposal using a subaqueous emplacement process. Underdrains allow for the removal of the pore water expelled by settling and compaction of the tailings, which is pumped to a water treatment facility.

At the McClean Lake Operation, a comprehensive research program, known as the Tailings Optimization and Validation Program (TOVP) has been under way since 1997. The TOVP has consisted of a series of studies designed to: (1) understand reaction controls on As behavior in the tailings neutralization process in the McClean Lake mill; (2) examine, and optimize the tailings neutralization process in order to reduce As concentrations in JEB TMF pore waters and (3) to evaluate the long-term behavior of As in the TMF.

Several TOVP studies have demonstrated the importance of arsenate mineral dissolution/precipitation reactions as the chief control on As concentrations in tailings pore waters in the TMF. Based on laboratory experiments and modeling, Langmuir et al. (1999a,b) predicted that As concentrations in TMF pore waters over the long-term (thousands of years) would not exceed 1–2 mg/L. This conclusion has been supported by further laboratory tests involving the neutralization of mill raffinates and tailings with Fe/As = 3 (Mahoney et al., 2005), which indicate that pore water As concentrations are less than 1 mg/L in neutralized raffinates. Mill tailings have been continuously emplaced in the TMF since July 1999, and tailings pore waters have been

sampled for chemical analysis each year since then (COGEMA, 2002, 2003). Measurements show that As concentrations in TMF pore waters have decreased from a high of about 5–7 to 1–2 mg/L after 2–3 a of burial (COGEMA, 2003). A substantial amount of work has been performed to assess the distribution of As species in the tailings and pore waters. Redox conditions in the tailings are oxidizing, with E_h values in the TMF typically around 350 to 400 mV (COGEMA, 2002). Additional details about changes in redox related species will be provided in Mahoney et al. (2005). Geochemical modeling of the laboratory and TMF results using PHREEQC (Parkhurst and Appelo, 1999) show that As concentrations are close to chemical equilibrium with respect to a poorly crystalline aluminous scorodite phase ($\text{Fe}_{0.9}\text{Al}_{0.1}\text{AsO}_4 \cdot 2\text{H}_2\text{O}$) (Log K_{sp} for this aluminous scorodite is -25.69), which has been identified in both the experimental studies (Mahoney et al., 2005) and the TMF (COGEMA, 2003). This suggests that over the long-term, the solubility product of scorodite influences the maximum As concentrations in tailings pore waters.

Canadian federal and provincial regulators have expressed concern that significant concentrations of adsorbed As might be released with time from the tailings to TMF pore waters. This study, which was a part of the TOVP, was performed to determine the amount of As that could be readily released from the tailings to pore waters in the TMF.

2. Predicting arsenic releases to TMF pore waters

Published studies and work performed as part of the TOVP indicate that As releases to pore water could be derived from: (1) dissolution of arsenate minerals which in general contain more than 95% of the total As in the tailings; (2) dissolution of Fe/As oxyhydroxide coprecipitates; (3) dissolution of surface precipitated As and (4) desorption of As, probably chiefly associated with ferrihydrite or hydrous ferric oxides (HFO).

In principle, there are two fundamental approaches one could take to estimate or predict As releases to TMF pore waters from potential sources (1) through (4). The first approach, which may be described as the in-depth basic science approach, is to thoroughly characterize the aqueous phase and all of the solid phases in the tailings, and to predict As releases based on an understanding of all reactions and processes in the tailings that potentially affect As concentrations. Theoretically, this approach would allow one to both extrapolate and interpolate from known data using models to predict As releases from any complex tailings, soil or sediment system to pore waters.

The second approach, which is used in this paper, is to measure As releases from solids under conditions as

similar as possible to those observed in the disposal site. The results of such a study will only be applicable to the site and system being investigated.

The in-depth basic science approach requires a full characterization of the solids and solutions involved in reactions that affect As. Solid characterization in complex systems containing As can involve detailed chemical analysis, X-ray diffraction, scanning electron microscopy, electron microprobe, and petrography (cf. Langmuir et al., 1999a), X-ray absorption spectroscopy (XAS) and extended X-ray absorption fine structure (EXAFS) spectroscopy (cf. Waychunas et al., 1996; Manning et al., 1998; Sherman and Randall, 2003; Paktunc et al., 2003, 2004; Cutler et al., 2003). Selective or sequential chemical extractions have also been employed to determine the nature and extent of As associations with different solids in complex systems (cf. Gruebel et al., 1988; Shiwatana et al., 2001; Kim et al., 2003).

3. Determination of adsorbed and desorbed arsenic

3.1. Adsorbed arsenic determination via selective extraction methods

Selective or sequential extraction techniques have been used to distinguish amounts of the different forms of As in complex materials such as soils and tailings (cf. Gruebel et al., 1988; Shiwatana et al., 2001; Linge and Oldham, 2003; Kim et al., 2003). However, there is no consensus on which methods to use for different purposes. For example, Shiwatana et al. (2001) leached soils with 0.5 M NaHCO₃ to desorb surface adsorbed As. In contrast, Kim et al. (2003) treated mine tailings with 0.1 M Na₂HPO₄ solution at pH 8 to release adsorbed As (see also Tokunaga et al., 1991). Although not specific to As, Loux et al. (1989) used hydroxylamine hydrochloride to dissolve amorphous Fe(OH)₃ in soils. The adsorbed metals were believed to report to the leachate solution. The use of a leaching agent demonstrates a problem inherent to all of the methods that employ reagents. Mainly, that to some degree these methods tend to dissolve amorphous phases, which can cause an artificial increase in the amount of so-called readily releasable As.

3.2. Direct measurement of arsenate desorption

Several studies have measured arsenate desorption. Darland and Inskip (1997) report adsorption and desorption rate constants for arsenate onto poorly crystalline Fe(III) oxides at pH 4.0–4.5. Their rate constant for desorption is 30 times larger than the constant for adsorption, indicating hysteresis in the desorption process. O'Reilly et al. (2001) and Fuller et al. (1988) measured arsenate desorption resulting from the addition

of phosphate, from goethite and from precipitated HFO, respectively. O'Reilly et al. (2001) found that about 35% of adsorbed arsenate was desorbed from goethite in 24 h, but that further desorption after longer times was relatively minor. In their study of adsorption by HFO, Fuller et al. (1988) reported that after times ranging from 144 to 188 h, the amount of arsenate desorbed ranged from 0.01% to 13% of adsorbed arsenate. In separate experiments in which SO₄ was added to cause arsenate desorption from goethite, O'Reilly et al. (2001), found that only 2.5% of adsorbed arsenate was desorbed after 5 months.

There is no consensus explanation for the observation that arsenate desorption is usually a small fraction of total adsorbed As. In their study of phosphate adsorption by goethite, Strauss et al. (1997) proposed that the initial, rapid adsorption is onto goethite surfaces, with subsequent uptake through diffusion into the goethite particles. Darland and Inskip (1997) proposed that slow sorption and desorption rates of arsenate by HFO are controlled by slow intra-particle and film diffusion rates. It seems possible that stronger arsenate–Fe surface bonds are formed with time following arsenate adsorption (e.g., bidentate bonds formed from monodentate bonds), accounting for both slower desorption rates and the incompleteness of arsenate desorption.

In a study relevant to the present one, Paktunc et al. (2003) examined As mobilization from Au mine tailings. They employed column leaching tests, mineralogical characterization and EXAFS spectral analysis. Unfortunately, the composition of their leaching solutions was not reported. Paktunc et al. concluded that As in the tailings (about 4% by weight) was present in Fe(III) and Ca–Fe arsenates (43–76%), and bonded to Fe oxyhydroxides (24–50%). In experiments involving tailings and standing water at pH 6.5–7 (roughly comparable to conditions in the JEB TMF), they measured As concentrations of between 0.3 and 2.6 mg/L. No explanation is given for these concentrations, which may have resulted chiefly from the breakdown of the Ca-bearing arsenate phases, as these phases are only stable under alkaline conditions (Bothe and Brown, 1999). Because the authors do not report final solution compositions, it is not possible to determine the state of saturation of those solutions with respect to scorodite or other arsenate phases. Thus, insufficient information is provided to distinguish As concentrations that might have been desorbed from the tailings from those that might have resulted from arsenate mineral dissolution. A notable difference in the present study and that of Paktunc et al. (2003) is that the tailings solids contain abundant gypsum, whereas those of Paktunc et al. (2003) lacked gypsum. The gypsum buffers high pore-water SO₄ concentrations, which stabilize HFO. This prevents the HFO from crystallizing with age and releasing its adsorbed As (Langmuir et al., 1999a).

4. EPICS method and model

4.1. General approach

The studies of Fuller et al. (1988) and Darland and Inskip (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 this study, the As that could be readily desorbed from tailings solids 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 of measuring desorbable As is obviously less aggressive than those suggested by Shiowatana et al. (2001) and Kim et al. (2003), and probably avoids significant dissolution of abundant, relatively amorphous arsenate phases and the release of their associated As. In this study it is assumed that desorbable As does not include As from the dissolution of arsenate minerals, or from the dissolution of Fe/As oxyhydroxide precipitates or As surface precipitates.

4.2. 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 water and solid (tailings) mixture, while keeping the amount of desorbable As plus dissolved As constant, and the total solids constant, the total amount of initially desorbable As can be calculated based upon changes in the dissolved As concentration.

The following example explains the method. A sample consisting 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, however, a supply of releasable As is available to the solution, some of it will be released and dissolved As concentrations will exceed 0.5 mg/L. When the system undergoes further dilution, dissolved 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 the As is in the solution, but the dissolved As concentrations become too low to measure. For this reason, in this study the authors extrapolate from measurable concentrations to infinite dilution.

In the following derivation, As that occurs in precipitated forms in the neutralized tailings slurry (as arsenate minerals such as scorodite and annabergite, Fe/As oxyhydroxide precipitates or surface precipitates)

is defined as $As_{(ppt)}$. Adsorbed As that is not readily desorbed is also considered part of $As_{(ppt)}$. Desorbable As is termed $As_{(desorb)}$. Sorbent phases include ferrihydrite, hydroxysulfate minerals, clays and possibly precipitated gypsum. The third form of As is that dissolved in the solution ($As_{(aq)}$). These 3 forms make up the total As ($As_{(total)}$).

$$As_{(total)} = As_{(ppt)} + As_{(desorb)} + As_{(aq)} \quad (1)$$

Total and aqueous As concentrations can be readily determined using standard analytical methods. The desorbable As plus dissolved As in Eq. (1) may be defined as the readily released As ($As_{(rr)}$),

$$As_{(rr)} = As_{(desorb)} + As_{(aq)} \quad (2)$$

Desorbable As responds rapidly to slight 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. The authors 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 Eq. (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 Eq. (4) into Eq. (3)

$$As_{(rr)} = As_{(aq)}[V_{(aq)} + K_d^{rr}M_{(solid)}] \quad (6)$$

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

$$\begin{aligned} As_{(aq1)}[V_{(aq1)} + K_d^{rr}M_{(solid)}] \\ = As_{(aq2)}[V_{(aq2)} + K_d^{rr}M_{(solid)}] = As_{(rr)}, \end{aligned} \quad (7)$$

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 ($1/As_{(aq)}$) vs. the volume of solution for two or more experiments. As shown by the derivation given in Appendix A, K_d^{rr} then equals the intercept (b) of the line connecting the data, divided by the slope (m) of that line times the mass of solid, or

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

The most direct method to estimate the amount of readily released As is to first calculate $F_{(desorb)}$, the fraction of As that is readily desorbed. This is defined by,

$$F_{(desorb)} = \frac{As_{(desorb)}M_{(solid)}}{As_{(desorb)}M_{(solid)} + As_{(aq)}V_{(aq)}} \quad (10)$$

Introducing K_d^{rr} , and rearranging Eq. (10) becomes:

$$F_{(desorb)} = \frac{\left[\frac{K_d^{rr}}{V_{(aq)}/M_{(solid)}} \right]}{\left[1 + \frac{K_d^{rr}}{V_{(aq)}/M_{(solid)}} \right]} \quad (11)$$

The desorbable concentration can be calculated with the equation:

$$As_{(desorb)} = \frac{F_{(desorb)}(As_{(aq)}V_{(aq)})}{(1 - F_{(desorb)})M_{(solid)}} \quad (12)$$

The total amount of readily released As ($As_{(rr)}$) can then be calculated by summing the As mass in the liquid phase [$As_{(aq)}V_{(aq)}$] and $As_{(desorb)}$. The total readily released As can also be calculated using the equation:

$$As_{(rr)} = \frac{[As_{(aq)}V_{(aq)}]}{[1 - F_{(desorb)}]} \quad (13)$$

4.3. Model simulations

The EPICS methodology was originally designed to measure concentrations in simple systems where the distribution coefficient behaves in a linear fashion. A series of model simulations were performed here to verify that the assumptions and the computational method could be applied to the more complicated system of As desorption from ferrihydrite.

The desorption reactions were modeled using the program PHREEQC (Parkhurst and Appelo, 1999), and the diffuse layer model (Dzombak and Morel, 1990). Table 1 lists the species and surface complexes used in the modeling. The PHREEQC model was used because the distribution of the different forms of As can be readily determined at each modeling step. Therefore, the amount of readily released As measured using

Table 1
Summary of data used in PHREEQC simulations for As aqueous species and diffuse layer adsorption reactions^a

Aqueous species	Reaction	Log K
H ₂ AsO ₄ ⁻	H ₃ AsO ₄ = H ₂ AsO ₄ ⁻ + H ⁺	-2.24
HAsO ₄ ⁻²	H ₃ AsO ₄ = HAsO ₄ ⁻² + 2H ⁺	-9.2
AsO ₄ ⁻³	H ₃ AsO ₄ = AsO ₄ ⁻³ + 3H ⁺	-20.7
CaHAsO ₄ ⁰	Ca ⁺² + H ₃ AsO ₄ = CaHAsO ₄ + 2H ⁺	-6.51
CaAsO ₄ ⁻	Ca ⁺² + H ₃ AsO ₄ = CaAsO ₄ ⁻ + 3H ⁺	-14.48
CaH ₂ AsO ₄ ⁺	Ca ⁺² + H ₃ AsO ₄ = CaH ₂ AsO ₄ ⁺ + H ⁺	-1.18
MgAsO ₄ ⁻	Mg ⁺² + H ₃ AsO ₄ = MgAsO ₄ ⁻ + 3H ⁺	-14.36
MgHAsO ₄ ⁰	Mg ⁺² + H ₃ AsO ₄ = MgHAsO ₄ + 2H ⁺	-6.34
MgH ₂ AsO ₄ ⁺	Mg ⁺² + H ₃ AsO ₄ = MgH ₂ AsO ₄ ⁺ + 1H ⁺	-0.72
Surface complex		
Hfo_wOH ₂ ⁺	Hfo_wOH + H ⁺ = Hfo_wOH ₂ ⁺	7.29
Hfo_wO ⁻	Hfo_wOH = Hfo_wO ⁻ + H ⁺	-8.93
Hfo_wH ₂ AsO ₄	Hfo_wOH + AsO ₄ ⁻³ + 3H ⁺ = Hfo_wH ₂ AsO ₄ + H ₂ O	29.31
Hfo_wHAsO ₄ ⁻	Hfo_wOH + AsO ₄ ⁻³ + 2H ⁺ = Hfo_wHAsO ₄ ⁻ + H ₂ O	23.51
Hfo_wOHAsO ₄ ⁻³	Hfo_wOH + AsO ₄ ⁻³ = Hfo_wOHAsO ₄ ⁻³	10.58
Hfo_wOCa ⁺	Hfo_wOH + Ca ⁺² = Hfo_wOCa ⁺ + H ⁺	-5.85
Hfo_wOMg ⁺	Hfo_wOH + Mg ⁺² = Hfo_wOMg ⁺ + H ⁺	-4.6
Hfo_wOHSO ₄ ⁻²	Hfo_wOH + SO ₄ ⁻² = Hfo_wOHSO ₄ ⁻²	0.79
Hfo_wSO ₄ ⁻	Hfo_wOH + SO ₄ ⁻² + H ⁺ = Hfo_wSO ₄ ⁻ + H ₂ O	7.78

^a Data for arsenic solution species from Langmuir et al. (1999a). Data for surface complexation reactions from Dzombak and Morel (1990).

the EPICS calculation could be directly compared to the amount estimated using PHREEQC. A potential problem was expected if the distribution coefficients did not follow linear isotherms as assumed in the EPICS model. A non-linear isotherm could be expected if the surface charge of sorbing solids were to change during the experiments, which would change the surface potential.

Although the units for K_d^{tr} as shown in Eq. (8) are volume/mass (V/M), the modeling calculations do not require that K_d^{tr} be reported in V/M units. This is because the sorbed concentration is expressed in terms of a concentration of adsorbed As/L. In the diffuse layer model in PHREEQC, surface sorption sites have no mass. The substrate, which is typically HFO, has a mass, but the model does not require that the adsorption sites have a mass. In the model, the units for K_d^{tr} in this application are (moles/L of $As_{\text{sorbed}}/(\text{moles/L of } As_{\text{in solution}})$). In the experiments the mass of the sorbent is not required, because all concentrations are referenced to the aqueous phase. The authors calculate a dimensionless distribution coefficient in the same fashion that a dimensionless Henry's law constant is calculated. In the experimental measurements that use actual tailings, the mass of solid is a constant for each test, so that likewise it is eliminated from subsequent calculations.

For the primary leaching solution, which was As-free, the assumed major ion concentrations were 400 mg/L Ca, 230 mg/L Na, 243 mg/L Mg and 2400 mg/L SO_4 . Arsenic was added to the primary solution in various initial concentrations to produce the starting solution for each model. One liter of the primary solution was allowed to react with the adsorption sites. To further simplify the calculations, only one type of adsorption site was used. The weak sites (Hfo_wOH), as defined by Dzombak and Morel (1990) were assumed at a concentration of 0.001 mol/L, for all of the simulations.

To obtain the data required for the EPICS calculation, additional leach 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 mixes two or more solutions. The increase in volume as the solutions are added together is included as part of the MIX keyword calculations. This makes the PHREEQC program ideally suited to verifying the EPICS method. A portion of a PHREEQC input file is shown in Appendix B. For each step in the process, the 1 L of As bearing solution was mixed with a volume (0.2 to 4.0 L) of the "As-free" leaching solution, and the new mixture equilibrated with the adsorption sites. This is not exactly the same process that occurs in the experimental measurements, but the models do provide data that can be used to verify the computational methods.

The simulations of As adsorption on HFO were run at various As concentrations, and pH values adjusted with $Ca(OH)_2$. Table 2 summarizes the verification calculations at concentrations of 0.1, 1, and 10 mg/L total As. The amount of readily releasable As is calculated using Eq. (12) to first estimate the EPICS calculated sites and then Eq. (13) to calculate the total amount of readily released As. Table 2 provides a comparison of EPICS and PHREEQC calculated site concentrations. The model, and subsequent calculations, show that readily released As concentrations, calculated using the EPICS methodology, and the total initial values used in PHREEQC are in close agreement. The model simulations demonstrate that the EPICS method is computationally sound.

Fig. 1 shows As concentrations for two PHREEQC simulations. The theoretical dilution lines in Fig. 1 show As concentrations if simple dilution is the only process operating on the system. Departures of model-simulated lines from the dilution lines indicate that a significant solid reservoir of As buffers dissolved As concentrations. The data are replotted in Fig. 2 as inverse concentrations, which linearizes both the data and the dilution

Table 2
Verification of the EPICS procedure by comparison with PHREEQC modeling results

Initial As concentration (mg/L)	pH	$As_{(aq)}$ (moles/L)	K_d^{tr}	$F_{(desorb)}$	EPICS Calculated sites (moles)	PHREEQC Calculated sites (moles)	Readily released As (moles/L)		Percent agreement EPICS vs. PHREEQC
							EPICS	PHREEQC	
0.1	6	1.22×10^{-8}	155	0.99	1.32×10^{-6}	1.33×10^{-6}	1.35×10^{-6}	1.34×10^{-6}	100.6
	7	9.14×10^{-10}	5725	1.00	1.34×10^{-6}	1.34×10^{-6}	1.34×10^{-6}	1.34×10^{-6}	100
	8	8.64×10^{-11}	506	0.99	1.33×10^{-6}	1.34×10^{-6}	1.33×10^{-6}	1.34×10^{-6}	99.4
1	6	1.31×10^{-7}	469	0.98	1.32×10^{-5}	1.33×10^{-5}	1.35×10^{-5}	1.34×10^{-5}	100
	7	1.03×10^{-8}	123	0.99	1.34×10^{-5}	1.34×10^{-5}	1.34×10^{-5}	1.34×10^{-5}	100
	8	9.61×10^{-10}	448	0.99	1.33×10^{-5}	1.34×10^{-5}	1.33×10^{-5}	1.34×10^{-5}	99.3
10	6	2.69×10^{-6}	28.4	0.93	1.25×10^{-4}	1.31×10^{-4}	1.30×10^{-4}	1.34×10^{-4}	97.3
	7	6.45×10^{-7}	53.5	0.96	1.29×10^{-4}	1.33×10^{-4}	1.30×10^{-4}	1.34×10^{-4}	97.4
	8	4.87×10^{-8}	130	0.98	1.31×10^{-4}	1.34×10^{-4}	1.31×10^{-4}	1.34×10^{-4}	98.2

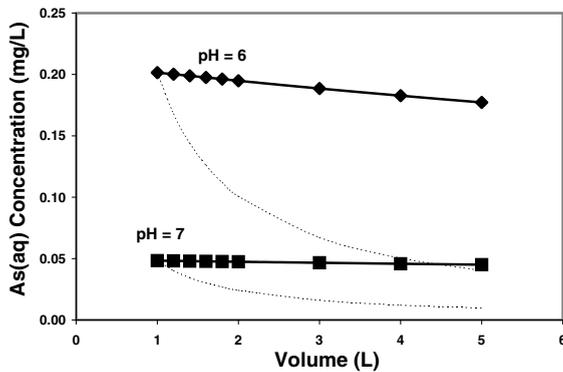


Fig. 1. Model derived $As_{(aq)}$ values computed from PHREEQC simulation of the EPICS procedure at pH 6 and 7, assuming As adsorption on ferrihydrite (HFO), and total readily released As = 10 mg/L. Theoretical dilution lines are dashed.

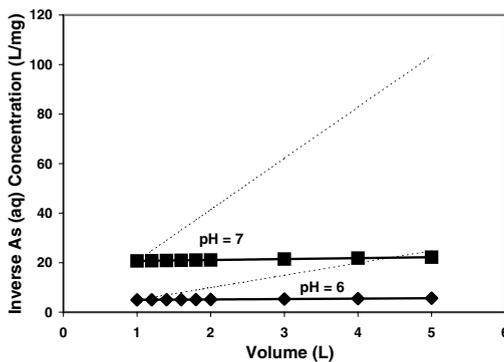


Fig. 2. Inverse concentrations of model derived $As_{(aq)}$ values computed from PHREEQC simulation of the EPICS procedure at pH 6 and 7, assuming As adsorption on HFO, and total readily released As = 10 mg/L. Theoretical dilution lines are dashed.

lines. By definition, the dilution lines correspond to a K_d^{TR} of 0.0. As shown by Fig. 2 these lines have an intercept of zero, and a slope that equals the inverse concentration at the first data point.

For the pH 7.0 data, a regression calculation gives a slope of 0.38, an intercept of 20.3, and a K_d^{TR} of 53. Similar calculations for the pH 6.0 data lead to $K_d^{TR} = 28$. The K_d^{TR} for the pH 7.0 data is greater than that for pH 6.0 because both solutions contain large SO_4 concentrations. Desorption of the SO_4 with increasing pH increases the number of sites available for As adsorption, which increases K_d^{TR} .

5. 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 of the slurry was measured. The mass of the slurry was measured by reweighing the container. The initial volume was defined as V_1 . For most measurements, the slurries contained 400–600 g of solids. The remainder of the slurry consisted of neutralized raffinate. Slurry solids were allowed to settle and an aliquot of supernatant solution was carefully drawn off. This and subsequent aliquot volumes were kept as small as possible, and were always less than 25 mL. The collection of small aliquots was necessary to keep the overall system ‘closed’ with respect to total As. This was also the primary reason for using large initial volumes. The aliquot was filtered (0.45 μm) and analyzed for total As. After each aliquot was drawn off, the container was reweighed to estimate the mass of solution removed.

The leaching procedure required waters with two different As concentrations. 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. Approximately 3 to 4 L were required for each desorption experiment.

Earlier verification calculations using PHREEQC demonstrated the need to maintain a constant ferrihydrite surface charge as the two solutions were mixed. Consequently, leaching solutions had to have the same pH and major ion composition as the starting solutions. The ‘‘As-free’’ leaching solution was prepared as follows. A 9% ferric sulfate solution, made up by diluting a stock ferric sulfate solution, was neutralized with added lime to pH 5, yielding a precipitate that consisted primarily of gypsum and an amorphous ferric hydroxide. This precipitate was rinsed and pressure filtered to remove unreacted ferric sulfate solution and unreacted lime. The tailings discharge water was then added to the rinsed filter residue and pressure filtered. The filtrate was collected and analyzed for As and major ions including SO_4 , Ca, Na, Mg and Ni. This produced an ‘‘As-free’’ water with an As concentration of less than 0.01 mg/L. The composition of the leaching solution was compared to the composition of the starting solution to assure that As removal did not change the major ion concentrations. If the dissolved As concentration in the leaching solution was less than 1.0% of its value in the neutralized raffinate/tailings slurry, and if concentrations of the other major species were within 15 relative percent difference (RPD) of their values in the neutralized raffinate, then that composition was considered suitable for use as the leaching solution. Because the usual concentration of As in the tailings thickener underflow water is approximately 1 mg/L, the maximum acceptable As in the leaching solution was less than 0.01 mg/L. Table 3 shows the As and other species concentrations in the starting solution, leaching solution and final solution from a typical set of desorption measurements. The results indicate RPDs of less than 10% for SO_4 , 12% or less for Ca, and zero for Mg and Na.

Table 3
Summary of analytical results for a typical desorption experiment

Solution	pH	As	Ca	Mg	Na	SO ₄	Fe	Ni
Starting solution	7.67	0.98	590	100	100	2100	0.24	0.87
Leaching solution	7.14	0.004	670	100	100	2310	0.02	0.59
Final solution	7.7	0.32	650	100	100	2260	0.1	1.04

All concentrations are in mg/L.

Because of the large volumes required by the experimental 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 total volume added was determined after reweighing the container and correcting for the density of the leachate solution. The new volume was defined as V_2 . The slurry was mixed for approximately 10 min and the pH was measured. If the pH had changed by more than 0.1 pH units, it was adjusted by adding either Ca(OH)₂ or concentrated H₂SO₄. The reaction bottle was mixed again and the solids allowed to settle. In most experiments settling times were limited to approximately 1 h. The pH was rechecked, and if it had not changed by more than 0.1 units from the starting solution value, a sample was withdrawn for chemical analysis. Because dissolved As concentrations are a strong function of pH, the pH was kept constant throughout all the dilution steps.

The process of adding leaching solution, measuring the weight and volume of solution after the addition, adjusting pH, and extracting an aliquot for chemical analysis was repeated two more times (V_3 and V_4). Finally, the remaining water in the slurry was removed by filtration and the solids weighed. The filtered solution and solids were then analyzed for their As concentrations. For the liquid aliquots, total As was measured using inductively coupled Ar plasma spectrometry.

6. Results and discussion

Series 1 desorption experiments were run with 1 h between extractions (Table 4). Results of 4 of these experi-

ments, plotted as inverse concentrations, along with theoretical dilution lines are shown in Figs. 3(a) and (b). Table 4 also gives the ratio V_4/V_1 , which represents the overall dilution during the tests. Values for K_d^{tr} were estimated using the linear 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^{tr} are relatively small and range from 0.44 to 2.77 (Table 4). With the exception of the first set of measurements (Set 1.1), correlation coefficients (R^2) range from 0.92 to nearly 1.0. Table 4 also includes the initial and final pH values measured for each step during the process. In spite of an up to 5-fold dilution in some experiments, only slight changes in pH were noted during the tests and so corrections to the pH of the slurries were not required. It is believed that the solids helped buffer the pH.

The results of the first series of tests indicated that little As was released from the solids. In the Series 1 tests extraction times were limited to approximately 1 h. The complete procedure for the 3 steps took less than 4 h. A short time for the extractions was originally used because of concerns that other processes such as mineral dissolution could release additional As into the solution. The generally low amounts of As released from the Series 1 measurements demonstrated that releases from other phases were not an issue. To determine if a slow release process needed to be considered, additional tests were run using a longer time between dilutions. Table 5 summarizes the measurement results for the Series 2 tests. The first test was run as a control with the usual 1 h between measurements. The second two tests were run with 12 h between measurements. During these tests, samples were gently mixed every 2 h.

Table 4
Summary of As desorption measurement results for Test 1 experiments, with 1 h between extractions

Test number	Initial pH	Final pH	Initial As _(aq) (mg/L) (C_1)	Final As _(aq) (mg/L) (C_4)	V_4/V_1	Inverse slope	Inverse intercept	R^2	K_d^{tr}
1.1	7.65	7.68	0.62	0.14	5.8	2.01	0.89	0.64	0.44
1.2	7.7	7.67	0.32	0.12	4.4	1.83	1.1	0.95	0.6
1.3	8.1	8.04	0.81	0.31	4.5	0.63	0.79	0.96	1.25
1.4	8.03	7.94	0.95	0.49	4.2	0.31	0.86	0.92	2.77
1.5	7.57	7.7	0.98	0.32	5.1	0.68	0.6	0.99	0.88

V_4/V_1 is the overall dilution for the tests.

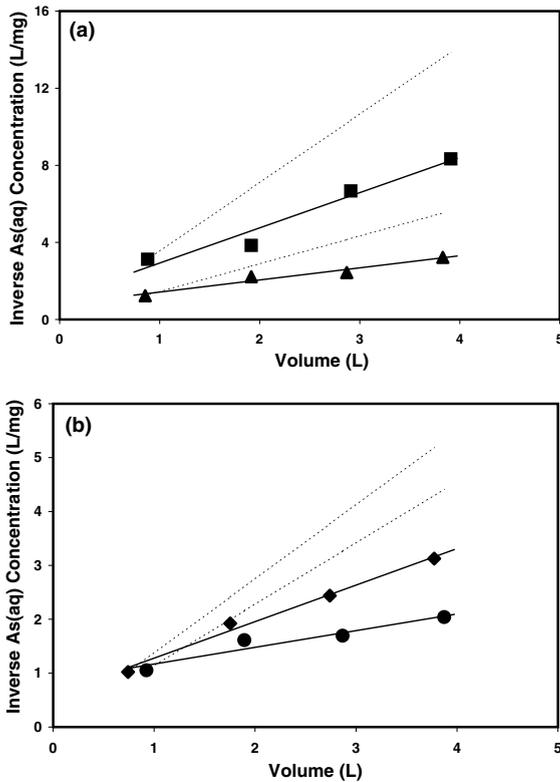


Fig. 3. (a) Test 1 (1 h between extractions): inverse concentrations of EPICS experimental results (Sets 1.2 (filled squares) and 1.3 (filled triangles)) showing experimental data (symbols), linear regressions of the data (solid lines), and theoretical dilution lines (dashed). (b) Test 1 (1 h between extractions): inverse concentrations of EPICS experimental results (Sets 1.4 (filled circles) and 1.5 (filled diamonds)) showing experimental data (symbols), linear regressions of the data (solid lines), and theoretical dilution lines (dashed).

Fig. 4 demonstrates that there was no difference between the Series 2 experiments that used 12 h between leaching/sampling times and the experiment with 1 h between leaching steps. The similarity of results supports the assumption that readily released As is rapidly desorbed in response to changes in the dissolved As concentration. The fact that additional As was not released over time also demonstrates that the remaining As (most

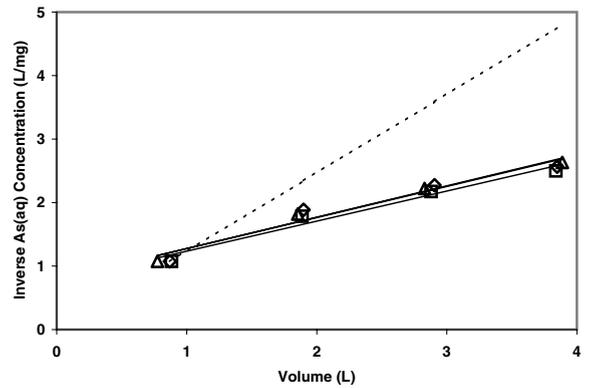


Fig. 4. Test 2 inverse concentrations of EPICS experimental results showing experimental data (Test 2.1, 1 h, open triangle; Test 2.2, 12 h, open diamond; Test 2.3, 12 h, open square), linear regressions of the data (solid lines), and a single theoretical dilution line (dashed).

of the As) associated with the solid phases is practically immobile.

The results in Fig. 4 show little scatter in the calculated concentrations of readily released As. This demonstrates that the method has a high degree of precision. Unlike the Series 1 tests, which were performed separately over several weeks using different feeds from the tailings neutralization circuit, the slurry used in the Series 2 tests was collected and composited over a few hours. The slight variability of K_d^{rr} values for the Series 1 tests in Table 4 probably results from either variations in the composition of the raffinate and leach residue sent to the tailings neutralization circuit, or from variations within the tailings neutralization circuit during several weeks of mill operation.

Table 6 summarizes results of subsequent EPICS calculations, including the values of K_d^{rr} and $F_{(desorb)}$. The table compares initial $As_{(aq)}$ concentrations to the concentration of desorbed As, and to the total amount of readily released As. In these tests, initial As concentrations constitute from 38% to 70% of the total readily released As in the slurry.

The percentage of readily released As in the tailings slurry is compared to the total As content of the slurry in Table 7. Clearly, only a very small % of the total As

Table 5
Summary of As desorption measurement results for Test 2 experiments with 12 h between extractions

Test number	Initial pH	Final pH	Initial concentration of As (C_1) (mg/L)	Final concentration of As (C_4) (mg/L)	V_4/V_1	Inverse slope	Inverse intercept	R^2	K_d^{exch}
2.1–1 h	7.82	7.76	0.93	0.38	5.0	0.49	0.79	0.98	1.6
2.2–12 h	7.89	7.88	0.93	0.39	4.4	0.49	0.78	0.95	1.6
2.3–12 h	7.89	7.88	0.93	0.4	4.3	0.47	0.76	0.97	1.6

V_4/V_1 is the overall dilution for the tests.

Table 6
Calculation of readily released As in JEB mill tailings using the EPICS method

Test	K_d^{rr}	$F_{(desorb)}$	Initial As _(aq) (mg/L)	As desorbed (mg/L)	Readily released As (mg/L)
1.1	0.44	0.31	0.62	0.27	0.89
1.2	0.6	0.38	0.32	0.19	0.51
1.3	1.25	0.56	0.81	1.01	1.82
1.4	2.77	0.73	0.95	2.63	3.58
1.5	0.88	0.47	0.98	0.86	1.84
2.1–1 h	1.6	0.62	0.93	1.49	2.42
2.2–12 h	1.6	0.62	0.93	1.49	2.42
2.3–12 h	1.6	0.62	0.93	1.49	2.42

Table 7
Percentage of readily released As in mill tailings

Test	Initial volume of solution (L)	Readily released As (moles)	Mass solids (g)	% As in solids	Total As in solids (g)	Total As in solids (moles)	Total As in solution (moles)	Readily released As %
1.1	1.07	1.28E-05	464.7	0.158	0.734	0.010	8.85E-06	0.130
1.2	0.88	6.01E-06	298.2	0.126	0.376	0.005	3.76E-06	0.120
1.3	0.85	2.07E-05	277.9	0.149	0.414	0.006	9.19E-06	0.374
1.4	0.92	4.40E-05	470.46	0.25	1.176	0.016	1.17E-05	0.280
1.5	0.74	1.82E-05	337.8	0.26	0.878	0.012	9.68E-06	0.155
2.1–1 h	0.78	2.52E-05	575.4	0.177	1.018	0.014	9.68E-06	0.185
2.2–12 h	0.87	2.81E-05	575.1	0.167	0.960	0.013	1.08E-05	0.219
2.3–12 h	0.88	2.84E-05	561.7	0.199	1.118	0.015	1.09E-05	0.190
							Average	0.21
							SD	0.08

is dissolved in solution or readily desorbed from the solids. An average of only $0.21 \pm 0.08\%$ of the total As is readily released. The low percentage of readily released As in the neutralized tailings slurry, demonstrates that processing of the acid tailings slurry in the JEB mill to immobilize As has been optimized. However, this only applies to the tailings slurry before it is discharged into the JEB TMF. The discharged slurry typically contains 200 to 400 g/L of solids. In the TMF the tailings are dewatered and become compacted so that the ratio of solids to liquids increases. This suggests all other factors remaining constant, that the percent of total As present in the tailings as readily released As may decrease further with compaction of the tailings.

7. Conclusions

Of major concern to Canadian provincial and federal regulators has been the possibility that As releases from buried U mill tailings in the JEB TMF at McClean Lake, Saskatchewan, might significantly contaminate adjacent ground waters and surface waters. The authors developed and tested a method to address this issue, which included laboratory measurement and modeling of As desorption from neutralized mill tailings slurries. Based on the EPICS method of Gossett (1987), experi-

ments involved the addition of successive volumes of an As-free leaching solution to the neutralized tailings slurry. This resulted in As desorption from the slurry. Both the slurry solution and the leaching solution were chemically identical, except for their dissolved As content, which was about 1 mg/L in the initial slurry solution. In the experiments and modeling, readily released As was defined as the sum of the As initially dissolved in the neutralized slurry plus the As desorbed to solution following addition of the As-free leaching solution. The EPICS approach for measuring As desorption was selected: (1) because it is relatively gentle and avoids the leaching of As associated with poorly crystalline arsenate solids and strongly adsorbed by hydrous Fe(III) oxides and (2) because it closely matches the conditions in JEB TMF pore waters. Prior to performing the desorption experiments, the validity of the mathematical derivation of the EPICS method was checked by comparing EPICS-predicted desorption results to the same results predicted using the diffuse layer adsorption model (Dzombak and Morel, 1990) in the geochemical code PHREEQC (Parkhurst and Appelo, 1999). Excellent agreement between the modeling results demonstrated that the EPICS method was computationally sound.

The experimental results indicated that the amount of As readily released from the tailings is small. In all cases, the As desorbed by dilution was less than 3

mg/L. Distribution coefficients for readily released As ranged from 0.44 to 2.77. With K_d^{rr} values this small, the total amount of desorbed As was similar in magnitude to the concentration of As in the initial tailings solution. In fact, the initial slurry concentration of As comprised from 38% to 70% of the total readily releasable As.

Total As comprised from 0.13% to 0.26% of the total weight of tailings solids. Previous work (Langmuir et al., 1999a,b) indicates that the vast majority of the As in the tailings is strongly bound in solids, either as arsenate mineral precipitates 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 being used for As immobilization in the JEB mill and tailings management facility. These involve the addition of ferric sulfate, if necessary to produce a molar Fe/As ratio of 3 or more in acid tailings raffinates, followed by the addition of lime to pH 4 to optimize precipitation of scorodite. The slurry is retained in the pH 4 tank for approximately 90 min and then transferred to another tank for further liming to pH 7–8 before tailings disposal in the JEB TMF.

Separately, this study shows that distribution coefficients for the desorption of contaminants from complex solids can be determined using the EPICS method when dilution effects are the chief cause of desorption as expected in the JEB TMF. The method is applicable to desorption measurements not only from tailings, but also from other complex solids including soils and sediments.

Appendix A. Derivation of the relationship between inverse concentration slope and intercept with K_d^{rr}

For solutions 1 and 2, the slope m equals

$$m = \frac{\frac{1}{As_{(aq2)}} - \frac{1}{As_{(aq1)}}}{V_{(aq2)} - V_{(aq1)}} \tag{A.1}$$

Rearranging gives

$$m = \frac{As_{(aq1)} - As_{(aq2)}}{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]} \tag{A.2}$$

The intercept b can be estimated from

$$\frac{\frac{1}{As_{(aq2)}} - b}{V_{(aq2)} - 0} = \frac{As_{(aq1)} - As_{(aq2)}}{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]} \tag{A.3}$$

Solving for b , this becomes

$$b = \frac{1}{As_{(aq2)}} - \frac{[As_{(aq1)} - As_{(aq2)}]V_{(aq2)}}{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]} \tag{A.4}$$

Combining terms produces

$$b = \frac{As_{(aq1)}[V_{(aq2)} - V_{(aq1)}] - [As_{(aq1)} - As_{(aq2)}]V_{(aq2)}}{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]} \tag{A.5}$$

which is equivalent to

$$b = \frac{As_{(aq2)}V_{(aq2)} - As_{(aq1)}V_{(aq1)}}{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]} \tag{A.6}$$

The intercept divided by the slope is

$$b/m = \frac{[As_{(aq2)}V_{(aq2)} - As_{(aq1)} \times V_{(aq1)}]}{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]} \times \frac{As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]}{[As_{(aq1)} - As_{(aq2)}]} \tag{A.7}$$

The $As_{(aq1)}As_{(aq2)}[V_{(aq2)} - V_{(aq1)}]$ terms cancel to give

$$b/m = \frac{As_{(aq2)}V_{(aq2)} - As_{(aq1)}V_{(aq1)}}{[As_{(aq1)} - As_{(aq2)}]} \tag{A.8}$$

Multiplying both the top and bottom by -1 produces

$$b/m = \frac{As_{(aq1)}V_{(aq1)} - As_{(aq2)}V_{(aq2)}}{[As_{(aq2)} - As_{(aq1)}]} \tag{A.9}$$

This equation is similar in form to Eq. (8). Dividing by the mass of solid ($M_{(solid)}$) gives K_d^{rr} .

$$K_d^{rr} = \frac{As_{(aq1)}V_{(aq1)} - As_{(aq2)}V_{(aq2)}}{[As_{(aq2)} - As_{(aq1)}]M_{(solid)}} \tag{A.10}$$

Accordingly, the slope and intercept can be obtained from a linear regression of the inverse concentration data.

Appendix B. Portions of a PHREEQC input file used in testing EPICS calculations

TITLE: MODEL OF As ADSORPTION FOR EPICS CALCULATIONS 1 mg/L pH 7.0

```

SOLUTION 1 Raffinate for first experiments
pH 7.0
temp 25
units mg/L
As 1.0
Ca 400
Na 230
S 2400
Mg 243.0

SAVE solution 1

PHASES
Fix_H+
H+ = H+
log_k 0.0
    
```

(continued on next page)

Appendix B (continued)

SELECTED_OUTPUT

```
-file EPICS sorb one ppm As.sel
      -reset true
      -totals As
      -molalities Hfo_wOHAsO4-3
      Hfo_wHAsO4- Hfo_wH2AsO4
```

END

USE Solution 1

EQUILIBRIUM_PHASES 2

```
O2(g)          -30.0
Fix_H+         -7.0 Ca(OH)2 10.0
```

SAVE Solution 2

END

SOLUTION 3

```
pH             7.0
temp           25
units          mg/L
Ca             400
Na            230
S             2400
Mg            243.0
```

END

EQUILIBRIUM_PHASES

```
O2(g)          -30.0
Fix_0H+        -7.0 Ca(OH)2 10.0
```

USE SOLUTION 2

SURFACE 1

```
      Hfo_wOH 1.e-3 600. .52
# surface site density 0.2 moles/mole
```

END

MIX

```
2          1
3          .2
```

EQUILIBRIUM_PHASES

```
O2(g)          -30.0
Fix_H+         -7.0 Ca(OH)2 10.0
```

SURFACE 1

```
      Hfo_wOH 1.e-3 600. .52
# surface site density 0.2 moles/mole
```

END

MIX

```
2          1
3          .4
```

EQUILIBRIUM_PHASES

```
O2(g)          -30.0
```

Appendix B (continued)

```
Fix_H+         -7.0 Ca(OH)2 10.0
```

SURFACE 1

```
      Hfo_wOH 1.e-3 600. .52
```

END

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