Calibration of a PHREEQC Based Geochemical Model to Predict Surface Water Discharge Compositions from an Operating Uranium Mill in the Athabasca Basin

J. J. Mahoney\textsuperscript{a}, R. A. Frey\textsuperscript{b}

\textsuperscript{a}Mahoney Geochemical Consulting LLC
Lakewood, Colorado USA

\textsuperscript{b}AREVA Resources Canada, Inc.
Saskatoon, Saskatchewan CA

Abstract. AREVA Resources Canada, Inc. has developed a predictive geochemical model of the surface water discharge system for their McClean Lake Operation. The Sink Vulture Treated Effluent Management System discharges treated waters through Sink Reservoir, followed by flow into Vulture Lake and finally into McClean Lake. Waters from two treatment plants, the dewatering of the JEB Tailings Management Facility, surface runoff, and rain and snow that falls onto the lakes make up the overall water balance. The source fluxes are converted into mixing proportions for use in the geochemical modeling program PHREEQC, which performs mixing calculations followed by evapoconcentration, equilibration with the atmospheric gases, mineral precipitation and surface complexation reactions. Strong agreement between observed and modelled concentrations was noted for many elements including sodium, potassium, chloride and magnesium. For these parameters simple mixing and dilution explain the downstream concentrations. Calcium and sulphate are generally conserved. However, discharges oversaturated with gypsum appear to rapidly precipitate gypsum. Similarly powellite precipitation may lower molybdenum concentrations in some cases. Arsenic and uranium undergo attenuation due to surface complexation onto ferricydrite. The agreement between observed and modelled concentrations demonstrates that this approach will provide robust predictions for the range of conditions expected at the McClean Lake Mill.

1. Introduction

AREVA Resources Canada, Inc. operates the McClean Lake Mill in northern Saskatchewan, Canada. The mill processes a wide variety of uranium ores; of which treated tailings are disposed in the JEB tailings management facility (TMF) [1]. The Tailings Preparation process was designed to treat arsenic and other metal concentrations in mill waste streams, resulting in trace concentrations in the tailings pore water. Water from the TMF is collected through an underdrain system. It is mixed with additional waters from the TMF surface pond and processed through a three stage water treatment plant to meet surface water discharge standards. The water treatment plant provides secondary treatment to the entirety of milling wastes treated through the tailings preparation process. Ground water from the dewatering of the JEB TMF perimeter and treated effluent from the SUE mining operation provide additional sources that are discharged to the Sink Vulture Treated Management Effluent System.
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(SVTEMS) (Figure 1). These waters are first discharged to Sink Reservoir then into Vulture Lake and finally to McClean Lake.

Figure 1. Site layout of the SVTEMS with Stiff diagrams for the major water sources and total dissolved solids concentrations.

Figure 1 shows the average total dissolved solids (TDS) concentrations and Stiff diagrams for these source term waters. The figure indicates that the JEB Water Treatment Plant (JWTP) has the highest TDS concentration at more than 2000 mg/L. The JWTP also provides the greatest load of dissolved constituents to the SVTEMS. The JWTP discharge normally makes up about 30 percent of the annual water balance to Sink Reservoir. The JEB water is classified as a calcium sulphate dominated solution. The same fingerprint, albeit more diluted, is still observed as the water migrates to Sink Reservoir and then to Vulture Lake. Another water source that primarily enters Vulture and McClean Lakes is surface runoff. The model also includes a contribution of precipitation (rain and snow) that falls directly on the lake surfaces.

Throughout the last 15 years, the McClean Lake Mill has processed various uranium ores. The mill has also upgraded the water treatment system. System upgrades and ore process optimizations have produced a wide range of source term concentrations. Given the variability of the source waters it was decided that a model that relied primarily upon geochemical processes would be an improvement over one that used statistical analyses of previously reported lake data. A model that uses the site water balance and measured concentrations from the major sources, coupled with the various geochemical processes of equilibration with gases, mineral precipitation, evapoconcentration and surface complexation provides a robust predictive model that can evaluate changes in ores, processing operations, changes in water sources and water balance, and changes to the water treatment operations. PHREEQC version 3 [2] was selected because it is a public domain program that can perform all the required model calculations. The program is supported through the US Geological Survey. The SVTEMS model is primarily a batch mixing model, with mineral precipitation and surface complexation reactions that attenuate trace metals. Each set of calculations represents a single year, there is no year-to-year carry over in the annual models. Measured concentrations were generally based upon the average of 11 or 12 samples per year.

2. Update of Thermodynamic Database

The thermodynamic database included with PHREEQC [2] was updated and corrected. The original database was the WATEQ4F.dat database included with PHREEQC version 2. Updates included:
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- For Uranium - Replaced constants in WATEQ4f.dat with the OECD NEA [3] selected complexes and values to define uranyl complexes. Replaced the two diffuse layer model constants for uranyl surface complexation onto hydrous ferric oxide (HFO) estimated by Dzombak and Morel [4] with the four surface complexes reported by Mahoney et al. [5]. Added the divalent uranyl carbonate complexes as reported by Dong and Brook [6]. Removed the $\text{UO}_2(\text{HPO}_4)_2^-$ and $\text{UO}_2(\text{H}_2\text{PO}_4)_3^-$ complexes per discussions in Grenthe et al. [7].

- For Arsenic - Included the metal arsenic complexes reported in Langmuir et al. [8] and additional complexes reported by Marini and Accornero [9,10]. Replaced the diffuse layer surface complexation constants for arsenic onto HFO reported by Dzombak and Morel [4] with revised reactions and constants by Gustafsson and Bhattacharya [11].

- For Molybdenum - Replaced the surface complexation reactions reported by Dzombak and Morel for HFO with the reactions and constants reported by Gustafsson [12].

3. Model Setup

Water balance information (Table 1) and water compositions for the source terms and compliance points were provided by AREVA Resources Canada. The water balances were recalculated in EXCEL to provide the mixing proportions required by PHREEQC. Precipitation rates were based upon annual measured rainfall/snow amounts at the site and the surface area of each water body.

Table 1. Summary of water balance, calculations in 1000m$^3$/year. No surface runoff was noted for Sink Reservoir for the 12 years listed below.

<table>
<thead>
<tr>
<th>Year</th>
<th>Direct Sources</th>
<th>Precipitation</th>
<th>Surface Runoff</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dewatering Wells</td>
<td>CM01B</td>
<td>SC01</td>
</tr>
<tr>
<td>2000</td>
<td>2110</td>
<td>1548</td>
<td>1075</td>
</tr>
<tr>
<td>2001</td>
<td>2329</td>
<td>1477</td>
<td>1303</td>
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<td>2002</td>
<td>1315</td>
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<tr>
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<td>2007</td>
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<td>1335</td>
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<td>2008</td>
<td>1026</td>
<td>1672</td>
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<tr>
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<td>837</td>
<td>1592</td>
<td>291</td>
</tr>
<tr>
<td>2010</td>
<td>636</td>
<td>1447</td>
<td>0</td>
</tr>
<tr>
<td>2011</td>
<td>521</td>
<td>958</td>
<td>170</td>
</tr>
</tbody>
</table>
Evaporation rates were based upon the surface area of each lake. Rates were determined from environmental monitoring programs conducted at the time of facility licensing. Another contribution to the mixing calculations, not listed in Table 1, was residual water in each lake. These volumes were determined from topographical surveys at the time of initial facility licensing.

The steps of the annual PHREEQC models were:

1) The CM01B (JWTP) solution composition is printed out for reference, and user defined equilibrium phases were allowed to precipitate, these phases may include gypsum, powellite, or ferrihydrite. Surface complexation reactions can be included based upon the amount of ferrihydrite that precipitates, final models did not include surface complexation at this step.

2) The Sink Reservoir mixing process is the next step. The CM01B, TMF dewatering waters, SUE treated water, direct rain/snow precipitation and any residual water in Sink Reservoir are mixed. Evaporation is included in the next step, and a correction term is included to bring the volume of water back to 1 liter for use in later mixtures. Equilibrium phases are allowed to precipitate. These phases may include ferrihydrite. Surface complexation reactions can be included based upon the amount of ferrihydrite that precipitates in the mixed water.

3) The Vulture Lake composition is defined by mixing the Sink Reservoir water with surface water runoff, as well as an initial volume of water in the lake and additional rain/snow precipitation. Evaporation, equilibration with minerals and surface complexation reactions are allowed; in general the solutions are too dilute for mineral precipitation reactions to proceed.

4) The McClean Lake composition is estimated by mixing the previously estimated Vulture Lake water with added runoff, rain/snow precipitation and any water in the lake. Evaporation, equilibration with minerals and surface complexation reactions are allowed; in general the waters in McClean Lake are too dilute for mineral precipitation reactions to proceed.

Each subsequent annual model repeats the same sequence.

4. Model Results

4.1. Conservative Species

The agreement between the measured and modelled concentrations shows that many of the major ions are conserved, and the concentration changes along the flowpath are due solely to mixing with other waters and evaporation. Elements that display this behavior include sodium, chloride, (Figures 2 and 3), potassium, and magnesium. The downstream samples in Sink Reservoir, as well as Vulture and McClean Lakes show good agreement between the measured and modelled concentrations. Figure 2 shows some elevated concentrations of sodium in the JWTP water in 2008 and 2009. This is related to regeneration of the solvent used in the ore recovery process. This spike is readily seen in the model in the Sink Reservoir and Vulture Lake samples. Chloride also shows good agreement in the downstream lakes. There is a slight positive bias in the Sink Reservoir samples, but the modelled concentrations in Vulture Lake show better agreement. A similar pattern was observed in the potassium data, where modelled concentrations tended to be greater than observed values in Sink Reservoir, but showed near concurrence in Vulture Lake. The modelled magnesium concentrations provide good matches to the observed concentrations. Aluminum also appears to be conserved. Models that allowed for the precipitation of gibbsite \([\text{Al(OH)}_3]\) or boehmite \((\text{AlOOH})\) showed significantly poorer fits. Intra-year variations in pH may have some influence on this parameter.

The agreement between the measured and model predicted concentrations of these species indicates that the water balances for the twelve years of sampling provide reasonable fits. Further adjustments to the water balances are not required. Differences between observed and modelled concentrations may be caused by mineral precipitation or surface complexation.
Figure 2. Comparison of measured and modelled sodium concentrations in the SVTEMS. The vertical lines represent the annual concentrations for years 2000 to 2011 for the JWTP discharge and the downstream Sink Reservoir followed by Vulture and McClean Lakes.

Figure 3. Comparison of measured and modelled chloride concentrations in the SVTEMS.

For most years, calcium and sulphate (Figures 4 and 5) act as conservative elements. But in the years where the JWTP samples are oversaturated with respect to gypsum (CaSO$_4$·2H$_2$O) a slightly better fit is noted if gypsum is allowed to precipitate. The figures show two different models, the first model did not allow for the precipitation of gypsum (open triangles). The second model (filled squares) did allow for precipitation, and samples from the years 2007, 2008, and 2009 were determined by PHREEQC to be oversaturated. The removal of calcium and sulfate from these these three samples improved the overall fit of the model. The solubility product constant had a log $K_{sp}$ value of -4.58, and it was not adjusted to improve the fit.
4.2. Arsenic and Uranium - Attenuated Species

The behaviour of arsenic is one of the most interesting processes identified. Arsenic concentrations are significantly lower than would be calculated if arsenic was solely retained (conserved) in the aqueous phase (Figure 6). Concentrations in the source waters are too low to suggest the precipitation of solids such as ferric arsenate or scorodite [8]. Surface complexation onto the iron from the JWTP and dewatering wells discharges appears to be the most reasonable process. Iron precipitates as ferrihydrite [Fe(OH)₃], also known as HFO. To better quantify the surface reactions, a series of calculations were
run using PhreePlot [13]. This program uses all the features of PHREEQC, but it allows for adjustment of parameters to optimize the fit between observed and modelled concentrations. PhreePlot calculates the weighted residual sum of squares (WRSS) between the observed and modelled concentrations. The optimization routine changes user defined parameters to minimize the WRSS. In these models the surface site density function changes as the program optimizes the fit between the measured and modelled concentrations for the 36 arsenic data points in the three water bodies. Arsenic was selected for calculations because in many pit lake models [14] it tends to show the greatest amount of surface complexation for models that use default site densities per mole of ferrihydrite formed. The resultant concentrations tend to be unrealistically low. However, most pit lake models do not have the detailed observational data that is available from the McClean Lake operation so for most models the default, rather than fitted surface site density values are used.

The PhreePlot fitting calculations were set up in the following manner. After mixing the source waters in Sink Reservoir, the model is allowed to precipitate ferrihydrite. The amount precipitated is based upon the amount of iron in the JWTP and the TMF dewatering discharges. The concentration of sorption sites is proportional to the amount of ferrihydrite formed. Dzombak and Morel [4] defined the weak site (Hfo_wOH) concentration to be 0.2 moles of surface sites per mole of ferrihydrite available and strong sites (Hfo_sOH) are 0.005 moles/mole. These are the default values used in many geochemical models. Arsenic only forms surface complexes with weak sites, simplifying the fitting calculations. For our discharge model, PhreePlot estimated a value of 0.09 moles/mole for the first six years and 0.129 moles/mole for the final six years. The strong site density was calculated as the fitted weak site density divided by 40, this maintains the proportion of weak to strong sites reported by Dzombak and Morel. These modelled values are conservative as the fitted site densities are lower than the laboratory estimated values. Surface complexation reactions were not identified in Vulture or McClean Lake as all the excess iron is precipitated in the upper mixing region of Sink Reservoir.

Uranium (Figure 7) also appears to be attenuated through surface complexation processes. Preliminary models confirmed this, but if site concentrations were adjusted to optimize the uranium data, then the modelled arsenic concentrations would be lowered significantly. Current models show only slight amounts of uranium attenuation due to surface complexation. It was decided that overestimating the modelled uranium concentrations and not underestimateing arsenic concentration was the more reasonable approach and it produced a model that used conservative assumptions (that tend to increase modelled concentrations so are more protective of the environment) in its predictions.

Figure 6. Comparison of measured and modelled arsenic concentrations in the SVTEMS. The figure shows two different models. The open triangles assumed no surface complexation, the filled squares assumed surface complexation onto hydrous ferric oxide.
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Figure 7. Comparison of measured and modelled uranium concentrations in the SVTEMS. The figure shows two different models. Open triangles assumed no surface complexation. The filled squares assumed surface complexation onto hydrous ferric oxide based upon PhreePlot fitting of the arsenic data to estimate the surface site density function.

4.3. Molybdenum

Molybdenum (Figure 8) behaved somewhat similarly to calcium and sulphate. Figure 8 shows the results of three models. The first model did not allow for the precipitation of powellite (CaMoO₄), and those models overestimate molybdenum concentrations in Sink Reservoir and Vulture Lake for years 2001, 2002 and 2003. The second model allowed for powellite precipitation if the solution was oversaturated with respect to that solid. The results of those calculations under estimate molybdenum

Figure 8. Comparison of measured and modelled molybdenum concentrations in the SVTEMS.
concentrations during those three years. Finally models were prepared that adjusted the solubility product constant of powellite. A trial and error model increased the log $K_{sp}$ to -7.65 and it produced an intermediate fit (not shown on Figure 8).

The final model used PhreePlot and the optimized log $K_{sp}$ value was -7.67 (X’s in Figure 8). The final model log $K_{sp}$ value is close to the trial and error value. The greater solubility of this phase may reflect a less stable amorphous solid with a greater solubility or more likely it reflects incomplete precipitation caused by a combination of slow precipitation kinetics and short residence time during transit to Sink Reservoir. It is unlikely that molybdenum concentrations at values high enough to allow for powellite formation will be observed in future JWTP discharges. In 2004, additional treatment efforts were implemented to lower molybdenum concentrations in the JWTP discharge to levels that are significantly below the solubility limit ($\log K_{sp} = -7.95$). The current model allows for surface complexation, but the amount of surface complexation for these later samples is slight and not readily visible on the figures.

4.4. Other Parameters

Several other parameters also demonstrate attenuation along the discharge flowpath. Modelled ammonia concentrations tend to be consistently greater than observed values suggesting that ammonia is apparently undergoing partial nitrification. In the initial models because the model assumes oxygenated conditions the modelled ammonia converts to nitrate and the pH drops significantly. This great a pH change is not observed, therefore ammonia was decoupled with nitrate. This is a common practice and PHREEQC has a special database for this eventuality.

Modelled selenium is also lower than measured selenium and a possible redox process is under consideration. Surface complexation reactions of selenate onto HFO are too small to have any significant impact.

Iron requires additional evaluation. Poor fits are observed in Sink Reservoir. However, better agreements are noted in Vulture Lake. Additional samples that should show seasonal effects are being evaluated and it is hoped that a better understanding of redox processes will be developed.

5. Conclusions

The PHREEQC based model of the SVTEMS has provided numerous insights into the geochemical conditions within the Sink Reservoir and the downstream lakes. Dilution plays an important role in the attenuation of all components. But simple geochemical processes can, depending upon initial concentrations, attenuate calcium, sulfate, arsenic, uranium, molybdenum, selenium and ammonia. The deeper understanding of the processes demonstrates that for arsenic and uranium, much of the attenuation capacity can be provided by the residual iron released from the JWTP and dewatering discharges.

The inclusion of PhreePlot as part of the modeling protocol provides an additional tool to develop rigourously fitted parameters for surface complexation and solubility product calculations. Additional evaluations of more seasonal (three samples per year) and/or monthly data are underway and it is expected that future models will incorporate at least one redox based process.

The goal of preparing a simple model that includes pertinent geochemical processes has been achieved. This model provides a valuable methodology to assist in evaluating the downstream impacts caused by possible changes to the mill and water treatment operations over the short and long term. This quantitative model will also help in further evaluations of the detailed geochemical processes throughout the SVTEMS.
REFERENCES


J. J. Mahoney and R.A. Frey

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