Coupling PHREEQC with GoldSim for a More Dynamic Water Modeling Experience

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Abstract

Mining operators strive to improve their tools for decision-making about water management to minimize risks and costs related to water quantity and quality issues. These issues are typically interrelated and complex such that interpretation and prediction of system dynamics requires implementation of innovative approaches that make use of observed data and fundamental hydrochemical concepts. We have developed an approach that couples the dynamic systems modelling framework of GoldSim with the geochemical reaction simulation capabilities of PHREEQC as described by Eary (2007). The approach utilizes a dynamic link library (DLL) code to handshake and transfer data between the two programs at every model timestep.

The coupled GoldSim-PHREEQC approach simulates mixing and reactions taking place at key mixing points along flow paths and at key water storage locations (e.g., ponds, tanks, pit lakes). Empirical factors affecting chemical loads can be calibrated to observed flows and chemistry at multiple locations and then used for predicting future water quality as operating and environmental conditions change.

Including geochemical reactions at each model time-step provides an efficient approach for applying a thermodynamic framework for understanding important geochemical processes that affect water chemistry. The approach also identifies the subset of reaction processes that may not be well explained by thermodynamic-based calculations and require empirical adjustment and time periods in response to events such as facility shut downs, climate events, and closure and remediation. The resulting calibrated model can be used to challenge our understanding of the reactions that are attenuating or not attenuating solutes at various site locations and to help understand, predict, and manage water quality going forward.

This modelling approach was applied to a proposed mine site in the northern Michigan (U.S.A.) to simulate various stages of operational and closure conditions to predict the quality of water that will require treatment. The model provided an efficient approach for making robust predictions of treatment requirements in terms of both water quality and quantity as a function of mine operations and closure.

Keywords: water balance, GoldSim, geochemical modelling, PHREEQC, water management, closure

Introduction

Effective mine water management and closure planning require a system-wide understanding of both the water balance and chemical balance. They also require modeling tools that can be used to answer specific questions important for planning, such as:

- How reliable is our water source (quality and quantity) and how much storage will we need?
- What treatment methods will be required to meet discharge standards?
- What is the most efficient way to reduce the water inventory when nearing closure?
- Will the pit lake require treatment and, if so, how can costs be minimized?
- Are there opportunities to blend or segregate waste streams to reduce operational and closure cost and risk?

The foremost requirement for answering these types of questions is an accurate water and solute conceptual model, upon which, predictive models can be constructed using representative hydrologic, geochemical, and water chemistry data.

Mine water flows and chemistry are strongly interdependent and while they can be managed separately, there are significant advantages to integrating flow and chemistry evaluations. Historically, the common approach has been to evaluate flow and reactive chemistry separately and then integrate the results through approximation of system dynamics. The most common simulation platform used for site-wide mine water and chemical balances with true temporal dynamics is GoldSim (GTG, 2017). Coupling GoldSim with more advanced, reactive chemistry has typically involved manually porting output from the flow model, as input to the reactive chemistry model. This method necessarily required the user to extract a few timesteps over the life of the model period and set up the reactive chemistry model to simulate and predict the chemistry for these few timesteps. This method is effective at predicting the general trends and overall chemistry at selected locations; however, it is not effective at evaluating short term trends (e.g., climatic effects and kinetically controlled reactions) without the time-consuming effort of exporting high-resolution timesteps. In addition, simulating even shorter-duration trends or events, such as upset conditions, or particular storm events was not practical. Recent advances; however, have made it possible to couple these types of models using a linking program to simulate the reactive chemistry at every timestep, e.g., monthly, daily, or hourly, thereby facilitating the simulation of short-term trends and episodic events.

In this paper, we present a description of the approach for linking GoldSim to PHREEQC using a Dynamic Linking Library (DLL). This approach provides a seamless link between GoldSim and PHREEQC to allow programs to handshake and transfer flow and chemistry data between the two programs during each timestep. We also present a case study where this approach was used to predict the chemistry of various site sources and support water treatment plant design.

Methodology

A variety of water balance and geochemical modeling platforms can be run in batch environments and/or link to other programs to share data. The authors have successfully linked GoldSim with PHREEQC and with Geochemists Workbench (Bethke, 2018) in a variety of ways via an external dynamic link library (DLL) file.

The following methods have been utilized for integrating PHREEQC calculations with the GoldSim model:

Manual Method – This method involves exporting GoldSim mass/volume results to a spreadsheet for post-processing at selected GoldSim time steps into values that can be manually entered into the PHREEQC input file. This "hands-on" approach allows as much flexibility as needed to customize the PHREEQC model to suit the geochemical conditions. This approach also provides an opportunity for modelers to provide a "common sense" check on both the GoldSim and PHREEQC outputs for each simulation. Some automation of this process can be built into the post-processing spreadsheet to speed up the process for multiple, similar runs.

Pre-Modeling Method – This involves running a large number of PHREEQC models to create a database of various combinations of mixing waters of different types and different ratios. Results are compiled as a set of mixing/reaction "type curves" and are used in GoldSim as multi-dimensional Lookup Table elements. Programming can be written into GoldSim to select the appropriate water chemistry from the Lookup Table. This approach results in fast run-times for GoldSim (because it will not have to call PHREEQC during the model run) but is limiting because with more than one or two waters, the number of pre-modeling runs can be excessive. Also, if there are any changes in water chemistry or reaction conditions, pre-modeling would have to be re-done and re-submitted into the GoldSim Lookup Tables.

DLL (automated) Method – This method involves setting up GoldSim to communicate with PHREEQC via a DLL file. Figure 1 shows the overall concept. It involves setting up two approximately parallel models: one for the water balance and a second for the chemical balance. The water balance keeps

track of flows and storage. Flows are typically input as time series data. Storage is simulated through the use of reservoirs or pool modeling elements. In parallel, GoldSims tracks the chemical balance as masses of solute transferred in flows over time. Typically, water chemistry data are input as time series, which when multiplied by flow rates gives mass transfer rates. A modeling element called a cell pathway links the two parallel calculation sequences of the water balance and chemical

balance together to produce concentrations for the storage reservoir. This is not the only sequence of calculations that can occur but is perhaps the most common.

The bulk concentrations yielded by the cell pathway in GoldSim represent the result of conservative mixing, that is, no reactions are included. The purpose of the DLL is to account for the effects of reactions on the bulk concentrations. To achieve this purpose, the DLL performs the following functions: re-
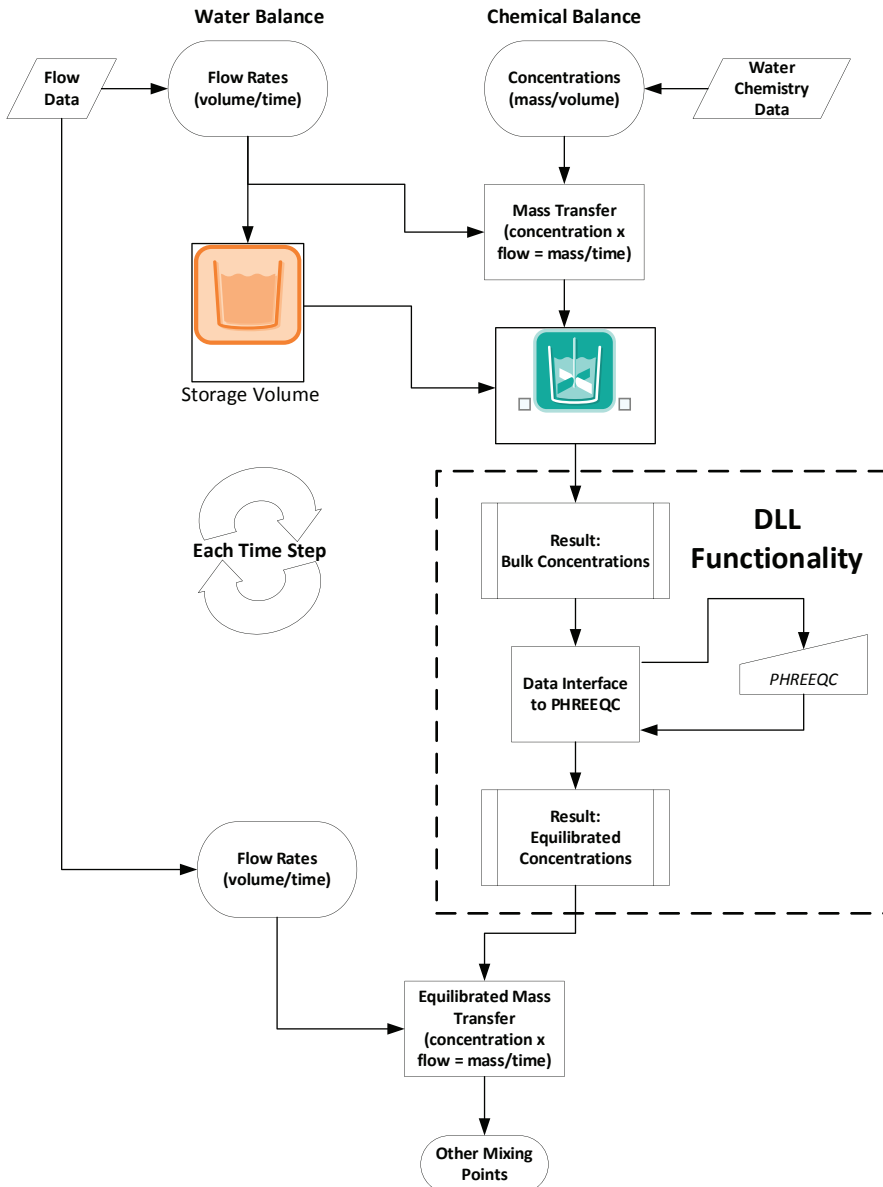

Figure 1 *Conceptual depiction of the DLL operation*

ceives the bulk concentrations via GoldSim's DLL interface and formats them for input to PHREEQC, runs PHREEQC, reads the PHREEQC outputs, and returns the results to GoldSim (Figure 1). The returned concentrations represent the effects of chemical processes defined in the PHREEQC model on the bulk concentrations. The equilibrated concentrations can then be used in subsequent modeling calculations. The power of this approach is that these operations can be done at each time step of the model. The

negative aspect of this approach is that the run time can be very long, depending on the number of times PHREEQC is called for calculations, timestep, and simulation period.

Validation

One of the most common types of calculation needed in GoldSim models of water chemistry is mixing two or more waters with different chemical compositions. A typical scenario is an acidic water mixing with an alkaline water. Under these circumstances, conserva-

Table 1 Validation Model Input Chemistry and Equilibrium Phases

| Species	Acidic Chemistry	Alkaline Chemistry	Species	Acidic Chemistry	Alkaline Chemistry	Equilibrim Phases	SI	Initial amount (mol)
Al	124.03	0.009	Mn	33.1	0.831	$O_2(g)$	-0.7	1
As	0.0103	0.0348	Mo	0.0186	0.009	$CO_2(g)$	-3.5	1
Ba	0.041	0.048	NO_3-N	0.827	2.02	Gypsum	0	0
Ca	616	722	Na	17.9	52	$Fe(OH)_3(a)$	0	0
Cd	0.01034	0.0002	Ni	0.041	0.0014	$Al(OH)_3(a)$	0	0
Cl	14.5	15.9	Pb	0.186	0.022			
Co	0.08243	0.00055	SO_4	2512	1855			
Cu	0.454	0.0033	Sb	0.001	0.164			
HCO_3	0	60.9	Si	0.0047	0.0019			
Fe	66.2	0.007	Sr	0.299	0.738			
K	10.6	85.471	Zn	7.97	0.58			
Mg	36	6.8	pH	3.68	8.86			
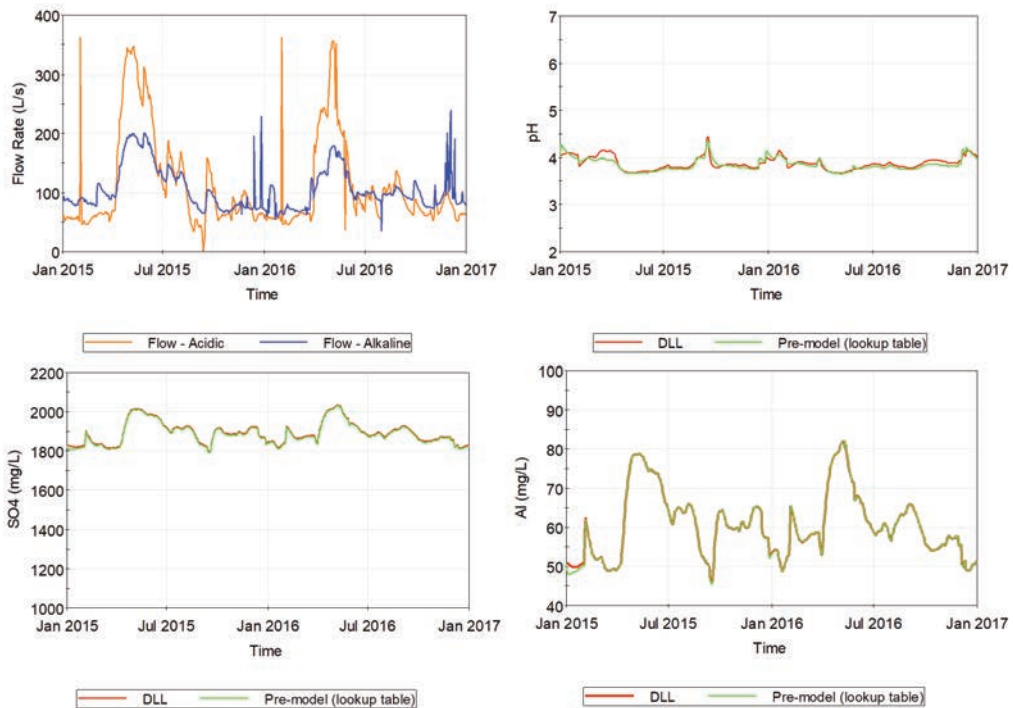
Figure 2 Comparison of the DLL (automated) method to the pre-modelling (lookup table) method

tive mixing calculations will not be representative of the final water chemistry because of the effects of aqueous speciation, mineral/gas solubility, and redox.

Mixing an acidic water with an alkaline water is used here as a test case to compare the DLL (automated) method directly to the pre-modeling method. In this comparison, the pre-modeling was done by mixing the solution chemistries in Table 1 in 1 percent increments to create a table of results representing 100 possible outcomes resulting from mixing. The mixing calculations assumed equilibrium with atmospheric $O_2(g)$ and $CO_2(g)$ and the solubilities of secondary solids of gypsum, ferrihydrite, and $Al(OH)_3(a)$ (Table 1). The results from the calculations were used to construct a lookup table where the index to the resulting water chemistries is the mixing proportion. The flows are dynamic, so the mixing proportions change over time. These calculations were implemented in a GoldSim model.

For comparison, the same solution chemistries were input to a second GoldSim model. In this second model, the DLL functionality was added to allow the calls to PHREEQC to be performed at each time step. The same set of equilibria as specified in Table 1 was also used in this model.

The results from the two approaches are shown in Figure 2. There are small differences at the start of the simulation, but after about 5 to 10 days, the results are very close. There are also small differences in pH at times when the flows are changing rapidly due to the sensitivities of the solubilities of ferrihydrite and $Al(OH)_3(a)$. These differences could be minimized by increase the number of mixing increments for the pre-modeling lookup table.

Case Study – Water Treatment Plant Design at a Proposed Mine in Northern Michigan

The Back Forty Project (Aquila Resources) is a gold-zinc sulfide mine project in the Upper Peninsula of Michigan in the northern United States. Aquila is evaluating future site water quality with respect to water treatment requirements in a strict regulatory environment with highly-sensitive ecological risk issues. The sulfidic ore and waste pose acid-generation risk; however, the groundwater that will enter the pit sump during operations is predicted to carry significant alkalinity load which, based on the current mine plan, will mix with runoff/seepage from waste piles, stockpiles and tailings in engineered seepage collection systems and reservoirs. This design has raised questions about the need for, type, and scale of water treatment that will be required for managing site water quality prior to surface water discharge via a permitted outfall.

A predictive, GoldSim-PHREEQC coupled model was built based on the conceptual design of the site water circuit, presented in Figure 3. The model was enabled with a stochastic precipitation data set to support probabilistic simulation to generate stochastic/random precipitation events, when required. The model was developed for the pre-operations construction period of 12 months, the entire life of mine of 78 months, and pre-closure period of 3 months. Contact water and storm water flow rates, associated with each of the facilities, was represented in the water balance portion of the model based on the projected facility size, material characteristics, estimates of runoff coefficients, and unsaturated infiltration rates, as appropriate. Estimates of water chemistry, associated with each of the respective flow components, were derived from either site-specific water quality data, process water chemistry data, or were derived from a significant database of geochemical testing data from static and kinetic testing of site soil, waste rock, ore, and tailings materials. The proposed mine materials balance for the site was used to assign chemical source terms to pit wall runoff and waste rock piles containing a mixture of geologic rock types. As described above, solute mass loading calculations were tracked in GoldSim for 41 chemical constituents (pH, alkalinity, major ions, and dissolved metals and metalloids). The GoldSim model was linked via DLL coding to PHREEQC to apply geochemical speciation, redox, and mineral/gas solubility controls to predict the chemistry of water to be treated that is collected in the Contact Water Basin (CWB) (Figure 3). Results from PHREEQC were imported back into GoldSim at each timestep and used

in subsequent mixing calculations in the CWB. Flow and geochemical model predictions were produced at several locations and through time over the life-of-mine modeling period.

The final product from this phase of work was a user-friendly modeling tool that could be updated and refined for future calibration and predictions of flows and water chemistry at several points in the circuit. A major finding of this phase was the importance of the alkalinity loading for maintaining circumneutral pH conditions in the inflow to the water treatment plant (Figure 3). Identifying this as a risk allowed Aquila Resources to direct efforts toward improving confidence in the pit groundwater inflow rates through advancement of their hydrogeologic modeling in combination with their site groundwater quality dataset. Upcoming work includes updating the water chemistry model with refined site engineering plans, additional water quality and geochemical data, and extending the model into the post-closure period.

Acknowledgements

References

Bethke, C.M., 2018. The Geochemist Workbench Release 12.0, Reaction Modeling Guide, a User's Guide to React and Gplot. Aqueous Solutions, LLC.

Eary, T. (2007) Linking GoldSim with the PHREEQC Geochemical Model with a Dynamic Link Library. 2007 GoldSim User's Conference, San Francisco, CA.

GTG. 2017. Dynamic Monte Carlo Simulation Software. GoldSim Technology Group, LLC (www.goldsim.com)

Parkhurst DL, Appelo CAJ (2013). Description of Input and Examples for PHREEQC Version 3 – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. US Geological Survey Techniques and Methods 6:1-497.
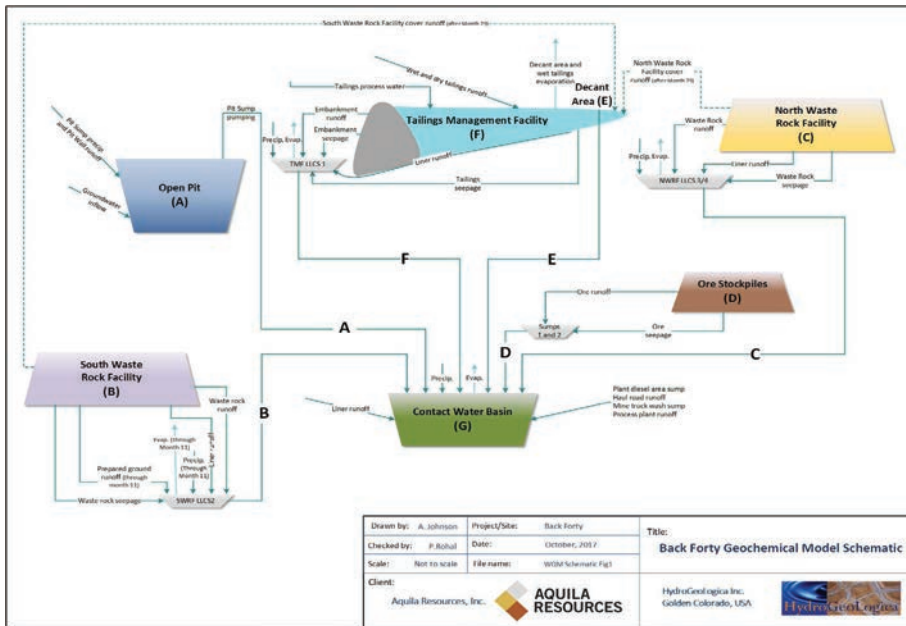

Figure 3 Back Forty Mine Site Water Conceptual Model