# Geochemical Modeling for Mine Site Characterization and Remediation

D. Kirk Nordstrom[1]

[1]*University of Colorado, Boulder, CO 80303 USA, dkirknordstrom@comcast.net*

## Abstract

Geochemical codes are routinely used throughout the world for investigating a wide variety of water-rock interactions including mine site characterization and remediation. Unfortunately, there is an underappreciation for the knowledge that a code user must bring to bear on the interpretation of code output, the limitations of popular codes, and their reliability. Examples of code testing are shown through comparison of calculated and measured Eh, comparison of simulated pyrite oxidation with actual field samples, and mineral saturation indices consistent with field conditions for calcite. Hydrous ferric oxides can appear to be supersaturated because colloids pass through 0.1 and 0.45 µm filter pore sizes. The colloid effect on ferrix oxide satuation indices was demonstrated by comparing measured vs. calculated redox potentials, removing non-detects for Fe(III), and recalculating saturation indices. The results show no supersaturation for freshly precipitating iron oxides. Aluminum precipitates occur at the pH where the first hydrolysis constant is reached, making it an easily predictable phenomenon. Other minerals such as barite and anglesite may appear supersaturated because of grain size effects or the lack of disulfato-metal stability constants in the code. Modeling of mass balances is often overlooked and even more important because of its role in the conceptual model of a site. This paper highlights important points of geochemical modeling for mine site characterization and remediation from Nordstrom and Nicholson (2017).

**Keywords:** geochemical modeling, mine site remediation, code reliability, mineral saturaton, redox

## Introduction

From the beginning of computerized geochemical modelling in the late 1960s and early 1970s, substantial progress has been made with code development and application. This improvement in code sophistication has led to misunderstandings about the uncertainties and limitations of code application. Models have been confused with codes; model and code assumptions have not been fully understood; "model validaton" has been a routine and incorrect phrase for scientific studies; and modelling with proprietary and non-proprietary codes have been used for mine permitting without adequate review (Nordstrom, 2012). In more general terms, modelling of all kinds and consequential failures of predictions have led some researchers to point out that quantitative models cannot be trusted (Pilkey and Pilkey-Jarvis, 2007) and why so many predictions often fail (Silver, 2012). It appears that science and computerized modelling has far outpaced our actual understanding of environmental systems such as the geochemistry of mine sites. In this paper I summarize the main points from our recent publication on Geochemical Modeling for Mine Site Characterization and Remediation (Nordstrom and Nicholson, 2017). This handbook is the 4th in a series of 6 that cover management technologies for metal mining influenced water. The handbook covers hydrogeochemical process such as speciation, mass balances, redox chemistry, hydrologic modelling and reactive-transport modelling.

## Main Hydrogeochemical Processes

The main geochemical processes that occur at sulphide-rich metal mine sites are: (1)

sulphide mineral oxidation, (2) carbonate mineral dissolution, (3) gypsum dissolution and precipitation, oxidation and reduction (redox) of several metals, metalloids, and sulfur, (4) iron precipitation, (5) aluminium precipitation, (6) silica precipitation, (7) efflorescent salt formation and dissolution, (8) mixing of waters, and (9) evaporation. Most of these reactions are described by stoichiometric equations found in Plumlee (1999), Lottermoser (2010), Blowes et al. (2014), and Nordstrom and Nicholson (2017). Geochemical modelling of some of these reactions are described below.

## Pyrite oxidation and iron precipitation

Simulating pyrite oxidation and iron precipitation is a good test for any geochemical code because of its complexity, especially with regard to redox processes. It is also the primary reaction that causes acid mine drainage from sulphide mines. Fig. 1 shows a graphical model of the change in pH with the amount of pyrite oxidized. The calculations were obtained with the PHREEQC code (Parkhurst and Appelo, 2013) and replotted from Nordstrom and Campbell, 2014).

Figure 2 demonstrates the change in pH of field samples before (initial) and after (final) dissolved ferrous iron oxidized compared to the simulation (Nordstrom and Campbell, 2014). This particular fit only works well if the $\log K_{sp}$ = ≈3 for hydrous ferric oxide (or ferrihydrite) because the crossover point is very sensitive to the $\log K_{sp}$ of the precipitating phase. If the iron phase precipitating is changed, the crossover point changes substantially (Fig. 1). The fact that there are crossover points reflects inflection points in the curves and indicates a buffering reaction. More details can be found in Nordstrom and Campbell (2014).

Supersaturation has frequently been observed for waters precipitating hydrous ferric oxides. This effect seems to be caused by nanocolloids passing through the field filtering system, resulting in Fe(III) concentrations that are higher than those truly dissolved. This effect was discovered by comparing measured with calculated Eh (based on Fe (II/III) determinations and speciation computations). Fig. 3A shows the comparison for more than 1,000 acid mine water samples from the western USA. Many samples agree quite well and others not well. When samples that were below detection limits for Fe(III) ($10^{-5.5}$ molar) were removed, Fig. 3B shows that nearly all the samples remaining now show good agreement (Nordstrom, 2011).

Using only the selected values from Fig. 3B to calculate the ferrihydrite saturation indices (SIs), I have demonstrated that supersaturation no longer occurs (Fig. 4B) compared to using all the samples (Fig. 4A).

Hence, supersaturation for hydrous ferric oxides are an artifact of filtration because the colloid concentration is so high compared to the dissolved Fe(III) concentration, it only takes a small amount of colloids to give apparent supersaturated conditions.

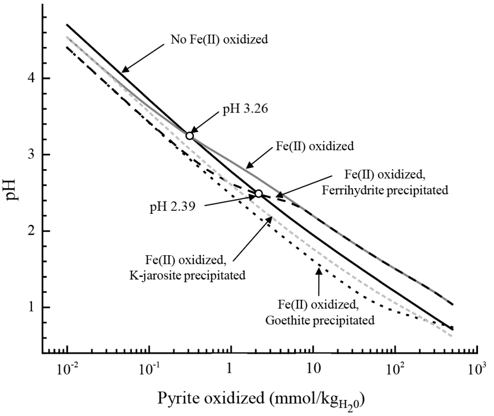

*Figure 1. Simulation of pH from pyrite oxidation.*

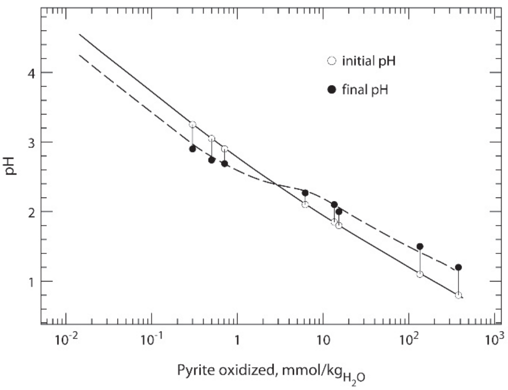

*Figure 2. Comparison of field samples*

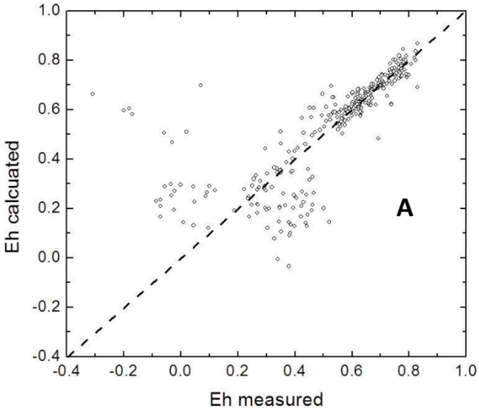

***Figure 3A.*** *Measured vs. calculated Eh for mine waters*

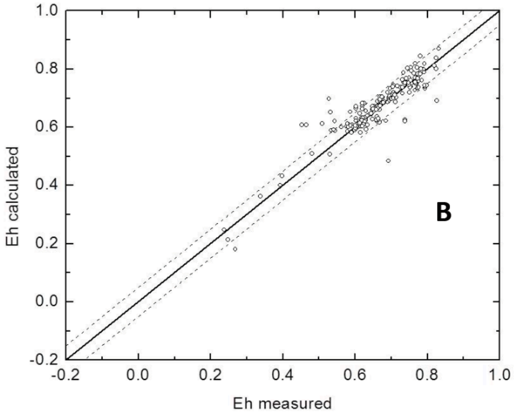

***Figure 3B.*** *Fig. 3A with points removed that were below detection for Fe(III).*

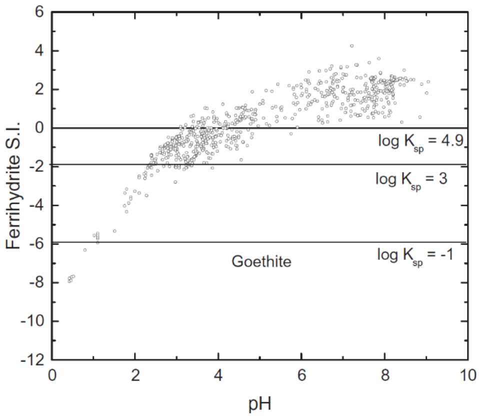

**Figure 4A.** *Ferrihydrite saturation indices for all samples.*

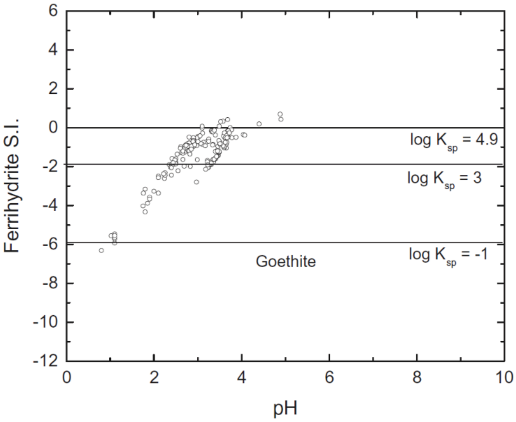

**Figure 4B.** *Saturation indices after removal of samples with Fe(III) below detection.*

## Aluminum Precipitation

Aluminum has been shown to precipitate when acid mine waters are diluted through mixing or neutralized by buffering up to a pH near the pK1 for Al hydrolysis (5.0). This condition was first reported by Nordstrom and Ball (1986) and has been further confirmed for 1,500 mine water samples across the wester USA (Nordstrom, 2011). The key diagram is reproduced in Fig. 5.

The samples plotted in Fig. 5 show undersaturation up to a pH of about 5 and then a limit is reached between 5 and about 7.5. For pH values above 7.5 a downward trend in SI values is very likely related to organic complexing which maintains a constant Al concentration in solution, but the hydrolysis in the code speciation is not accounting for that and causes the SI values to decrease because of increasing activity of $Al(OH)_4^-$ which decreases the activity of $Al^{3+}$ in the SI.

## Calcite solubility equilibrium

One of the earliest examples of mineral solubility equilibrium being reached in a groundwater was that of Langmuir (1971) for a shallow limestone aquifer in Pennsylvania. His analytical data were rerun through PHREEQC using the data of Plummer and Busenberg (1982) and the SI values plotted as a function of pH as shown

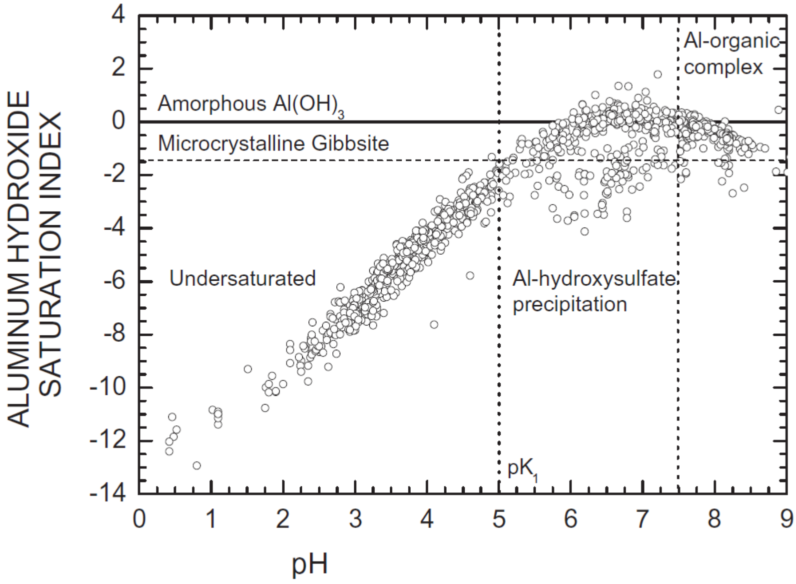

***Figure 5.*** *Al(OH)$_3$ saturation indices relative to pH for the same samples shown in Fig. 4A.*

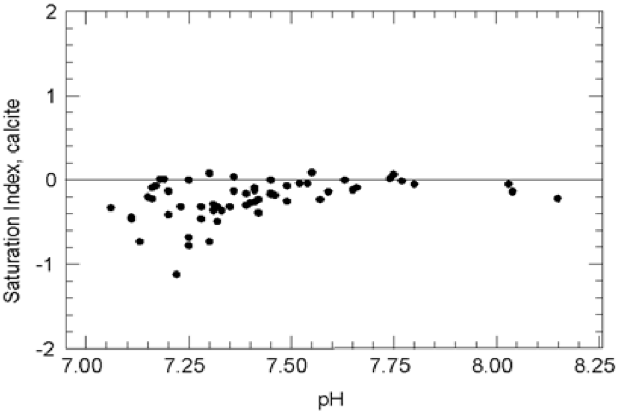

***Figure 6.*** *Saturation indices for calcite plotted relative to pH for groundwaters obtained from a limestone aquifer using field data of Langmuir (1971) and thermodynamic data of Plummer and Busenberg (1982).*

in Fig. 6. This is one of the best examples of mineral solubility equilibrium for field data, but it is common for saturation indices to be supersaturated. Reasons can include inadequate thermodynamic data, kinetic inhibitions, lack of metal-organic complexing data, and insufficient analytical quality.

## Barite and Anglesite Mineral Saturation

It is common to find that the SI values for barite and anglesite are supersaturated by about 0.5 or more. If these minerals are freshly precipitating from the water column, then the supersaturation could easily be a grain size effect on solubility. The other possibility is that these waters contain very high sulfate concentrations which could form double sulfate-metal complexes with barium and lead. These are occasionally suggested in the literature but usually not included in speciation codes. Their exclusion could also cause apparent supersaturation which is not really there.

## Mass Balances

Mass balances simply convert the change in water chemistry along some flowpath to an assemblage of minerals that must have dissolved or precipitated to cause the change in water composition. This procedure is adequately explained in many other publications that are cited in Nordstrom and Campbell (2014) and Nordstrom and Nicholson (2017). The main result from studies on acid mine drainage is that no matter what assumptions one makes for the mineral assemblage, iron and silica are always precipitated (Nordstrom, 2011) . The iron precipitation is obvious because of visual staining, the silica precipitation is not obvious, but has been confirmed in mineralogical studies (Jambor, personal communication).

## Geochemical Models, Test Cases, Codes, and Examples

The examples of testing geochemical models and codes shown above are described in Nordstrom and Nicholson (2017) along with hydrologic modelling fundamentals, reactive-transport modelling for mine sites, a listing of codes and databases, and several case studies. The most detailed, advanced, and exhaustive case study using geochemical modelling at a mine site was done by Glynn and Brown (2012) and their 15-year perspective (reproduced in Nordstrom and Nicholson, 2017) should be read by all geochemical modelers working on mine wastes. Not only are the major limitations described, but the optimal approach for modelling is described.

## Conclusions

Geochemical modelling for mine site characterization and remediation is a sophisticated science that requires background and training in chemistry, geology, hydrology, mineralogy, microbiology, mining, and mineral processing. Large uncertainties abound and it is still an area of active research, not a finished routine product. Major advances have been made and there are applications that are worth pursuing, but only for modelers who have sufficient experience with field work as well as with the codes.

Geochemical models (like most models) are not unique, they are not "final," they do not give exact answers, only approximations. they are helpful tools to understand reactions and processes. Don't let the sophistication of the model outpace the available field data. A combination of inverse modelling and forward modelling can lead to the most insightful understanding of complex processes at mine sites, as shown most clearly by Glynn and Brown (2012). The core of modelling is the conceptual model and mass balances. Nothing improves our conceptual model of a site more than better field data, which best constrains our modelling conclusions.

## Acknowledgements

The author thanks the U.S. Geological Survey for the opportunity to pursue research on acid mine drainage for more than 40 years, the EPA for their support of some of my research, and the supportive collaboration of many of my fine colleagues at the USGS and elsewhere.

## References

Blowes DW, Ptacek CJ, Jambor JL, Weisener CG, Paktunc D, Gould WD, Johnson DB (2014) The Geochemistry of Acid Mine Drainage, In: Sherwood-Lollar B (Ed.) Environmental Geochemistry, Vol 11.5, Treatise on Geochemistry, 2nd edition, Elsevier Science, NY, p 131-190, doi.org/10.1016/B978-0-095975-7.00905-0

Glynn P, Brown J (2012) Integrating field observations and inverse and forward modelling: Application at a site with sparse spatial information, In: Bundschuh J and Zilberbrand M (Eds.) Geochemical Modleing of Groundwater, Vadose and Geothermal Systems, CRC Press, Boca Raton, FL/Balkema, p 181—233

Langmuir D (1971) The geochemistry of some carbonate ground waters in central Pennsylvania, Geochim Cosmochim Acta 35:1023—1045

Lottermoser BG (2010) Mine Wastes – Characterization, Treatment and Environmental Impacts, Springer, New York, NY, 400 pp, doi: 10.1007/978-3-642-12419-8

Nordstrom DK (2011) Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters. Appl Geochem 26:1777—1791, doi:10.1016/j.apgeochem.2011.06.002

Nordstrom DK (2012) Models, validation, and applied geochemistry: Issues in science, communication, and philosophy. Appl Geochem 27:1899—1919, doi:10.1016/j.apgeochem.2012.07.007

Nordstrom DK, Ball JW (1986) The geochemical behaviour of aluminium in surface waters. Science 232:54-56

Nordstrom DK, Campbell KM (2014) Modeling low-temperature geochemical processes, In: Drever JI (Ed.) Surface and Ground Water, Weathering, and Soils, Vol 7.2, Treatise on Geochemistry, 2nd edition, Elsevier Science, NY, p 27-63, doi.org/10.1016/B978-0-08-095975-7.00502-7

Nordstrom DK, Nicholson A (2017) Geochemical Modeling for Mine Site Characterization and Remediation, Soc Mining Metall Explor, Englewood, Colorado, 159 pp,

Parkhurst DL, Appelo CAJ (2013) Description and input and examples for PHREEQC: Version 3 - - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, Techn Meth 6-A-43, US Geol Surv, Denver, Colorado,

Pilkey OH, Pilkey-Jarvis L (2007) Useless Arithmetic – Why Environmental Scientists Can’t Predict the Future, Columbia University Press, New York, NY, 248 pp

Plumlee, GS (1999) The environmental geology of mineral deposits, In: Plumlee GS and Logsdon MJ (Eds.) The Environmental Geochemistry of Mineral Deposits, Part A: Processes, Techniques, and Health Issues, Soc Econ Geol, Littleton, Colorado, p 71-116

Plummer LN, Busenberg E (1982) The solubilities of calcite, aragonite and vaterite in $CO_2$-$H_2O$ solutions between 0 and 90°C, and an evaluation of the aqueous model for the system $CaCO_3$-$CO_2$-$H_2O$. Geochim Cosmochim Acta 46:1011-1040

Silver N (2012) The Signal and the Noise – Why So Many Predictions Fail – but Some Don’t. The Penguin Press, New York, NY, 534 pp