From research to remediation: Application of hydrogeochemical research for effective mine site remediation

D. Kirk Nordstrom

U.S. Geological Survey.
3215 Marine St., Suite E-127.
Boulder, CO 80303 USA.
Tel: (01) 303-541-3037 Fax: (01) 303-447-2505
e-mail address: dkn@usgs.gov

Abstract

The remediation of environments contaminated by acid mine drainage and solid wastes from large metal mines in mountainous areas of the western USA is complex and does not lend itself to simple engineered solutions. The quantity of disturbed earth and contaminated waterways and the complexities of site geology, hydrology, geochemistry, and mineral processing often defy detailed characterization. Consequences of remediation are not easily predictable or quantifiable: indeed, remediation is experimental and can benefit from hydrogeochemical research. Four applications of hydrogeochemical research developed at the US Geological Survey are demonstrated: (1) measurement of negative pH waters at Iron Mountain, CA, (2) mass balance calculations at Iron Mountain to show whether a flowpath existed or not, (3) mass loading profiles from synoptic/tracer studies at Questa, NM, and (4) reactive-transport modeling, based on synoptic/tracer data at the Summitville mine and the affected drainage basin to provide remediation scenarios of water quality downstream.

At Iron Mountain, California, an application of the Pitzer model using the PHRQPITZ code allowed measurements of negative pH waters found in underground workings. These waters were actively precipitating soluble efflorescent salts such as melanterite, coquimbite, römerite, and rhomboclase. A mine plugging scenario was simulated with the PHREEQE code to demonstrate that plugging the Richmond mine would lead to deleterious consequences. A mass balance calculation with the BALANCE code demonstrated that plugging the Richmond Mine would

not prevent ground waters from entering the nearby Hornet mine so that it would also have to be plugged. Mass balance calculations, when combined with detailed mineralogy and mineral chemistry, can provide a much more reliable accounting of the water-rock interactions for site characterization and baseline, pre-remediation conditions.

Continuous-flow tracer-injection studies as developed in the USGS, with proper synoptic sampling, are the most reliable means of identifying the magnitude of inflows from surface and ground waters. Once they have been identified, the relative benefits of remediating multiple sources can be quantified and can lead to improved cost-benefit analyses. Synoptic/tracer studies can also quantify the degree of remediation success when done after remediation has been completed. When synoptic/tracer studies are combined with reactive-transport modeling it becomes possible to construct remediation scenarios to weigh the relative merits and costs of remedial alternatives. The Summitville mine study is a good example of this approach.

1 Introduction

Mineral extraction, processing, and metal and non-metal production has been the backbone of modern society. It has also led to the disturbance and contamination of huge quantities of air, water, and soil. Attempts have been made and are continuing to be made to restore these degraded resources. However, the scale and complexity of restoring or remediating mine sites does not lend itself to simple engineered solutions. The complexities include the geologic framework, the hydrologic conditions, the geochemical processes including microbial catalysis, and the overprint of mining extraction and mineral processing. These aspects are frequently ignored or inadequately addressed in the hurried attempt to “engineer” the solution and, consequently, well-intentioned remedial attempts can fail (Nordstrom, 1999, 2000). Heterogeneities such as discontinuities or strong gradients in lithology, rock integrity, permeability, and ground-water chemistry or flow can also foul attempts at remediation. Proper application of available research on hydrogeochemical processes can often reduce these types of uncertainties, thereby reducing costs of remediation. Unfortunately, the engineering mentality is often too presumptuous and proud to accept advice from the earth science community on remediation planning. These are the seeds from which future mistakes are born.

The purpose of this paper is to present four examples of hydrogeochemical research developed at the US Geological Survey that have effectively improved mine site characterization and remediation.

2 Negative pH, efflorescent salts, and why *not* to plug a mine

During remedial investigations on the Iron Mountain Superfund mine site in northern California, the issue of whether or not to plug the Richmond Mine portal to prevent acid effluent from discharging was strongly debated. Iron Mountain, once the largest copper mine in California, became the largest discharger of acid and dissolved metals. A considerable amount of historical data exist for effluent composition and discharge from the Richmond Mine because it is the largest single source of dissolved metals (both in terms of concentration and in terms of flux) in the Iron Mountain district. A summary of the data for discharge, pH, Cu and Zn concentrations for 1983-91 are shown in Table 1.

Table 1. Mean and range of values for discharge, pH, zinc, and copper in the Richmond effluent water.

	Mean	**Range**
Discharge (L/s)	4.4	0.5 - 50
pH	0.8	0.02 - 1.5
zinc (mg/L)	1,600	700 - 2,600
copper (mg/L)	250	120 - 650

Conditions at Iron Mountain are nearly optimal for the production of acid mine waters, and this mine drainage is some of the most acidic and metal-rich reported anywhere in the world (Nordstrom and Alpers 2000; Nordstrom et al. 2000). Prior to the late 1980's when major remediation efforts began, approximately 2,500 tons of pyrite weathered every year from the Richmond Mine and water containing about 300 tons per year of dissolved Cd, Cu, and Zn drained from the site into the Sacramento River. During periods of high runoff, sudden surges of acid mine waters into the Sacramento River have caused massive fish kills that state and federal agencies have investigated since 1939. In the Richmond Mine, about 8 millions tons of massive sulfide remain. At current weathering rates it would take about 3,200 years for the pyrite in the Richmond ore body to fully oxidize. The massive sulfide deposit is about 95% pyrite excavated by tunnels, shafts, raises, and stopes which allow rapid transport of oxygen by air advection. The sulfides are at or above the water table so that moisture and oxygen have ready access.

Plugging the Richmond Mine portal seemed like a simple solution but no one knew the consequences of this action. I was specifically asked by the USEPA what the water quality of the mine pool would be in a mine plugging scenario. I couldn't provide any idea without some knowledge of the underground conditions. The USEPA renovated a portion of the Richmond workings so that the underground conditions could be examined and samples of minerals and water could be obtained for examination and analysis. In September 10-12, 1990, the first field trip for geochemical sampling revealed extremely acidic seeps with pH values as low as -3.6 and total dissolved solids concentration of more than 900 g/L and huge quantities of soluble iron sulfate salts. Three of the most acidic water samples taken from the Richmond Mine are shown in Table 2 below along with the main soluble salt found associated with the water sample. In addition to melanterite, rhomboclase, and römerite, large quantities of coquimbite and voltaite were also identified. The PHRQPITZ code, containing the Pitzer model for activity coefficients (Pitzer 1991), was used as a basis for defining the pH and calibrating the electrodes. Details of the procedure can be found in Nordstrom et al. (2000).

With this information, a chemical scenario could be estimated for the composition of the mine pool that would form upon plugging. The assumption was made that the salts would dissolve but the amount of extremely acidic waters could not be quantified and was ignored. The exact amount of salts was also not quantifiable but the identification of the dominant salts was possible. Hence, assuming a proportion of salts that reflected those observed underground, the chemical composition of water was calculated as a function of the volume of dissolved salts with the computer code PHREEQE (Parkhurst et al. 1980). The

Table 2. Three examples of extremely acidic waters from Iron Mountain.

Sample	**90WA109**	**90WA110A**	**90WA110C**
Temperature, ^{o}C	38	42	46
PH	-0.7	-2.5	-3.6
Element, mg/L			
Aluminum	6,680	1,420	--
Antimony	16	29	--
Arsenic (III)	38	32	--
Arsenic (total)	154	340	--
Barium	0.1	0.2	--
Beryllium	0.1	0.2	--
Boron	2.5	17	--

Cadmium	48.3	211	--
Calcium	330	279	--
Chromium	0.75	0.6	--
Cobalt	15.5	5.3	--
Copper	2,340	4,760	--
Iron (II)	79,700	34,500	9,790
Iron (total)	86,200	111,000	16,300
Lead	3.8	11.9	--
Magnesium	1,450	437	--
Manganese	42	23	--
Molybdenum	1.0	4.2	--
Nickel	2.9	3.7	--
Potassium	1,170	194	--
Selenium	2.1	4.2	--
Silicon (as SiO_2)	34	35	--
Silver	0.65	2.4	--
Sodium	939	416	--
Strontium	0.49	0.90	--
Sulfur (as SO_4)	360,000	760,000	--
Thallium	0.15	0.39	--
Tin	15	41	--
Titanium	125	1.0	--
Vanadium	11	15	--
Zinc	7,650	23,500	--
Associated Mineral(s)	melanterite	rhomboclase römerite	rhomboclase

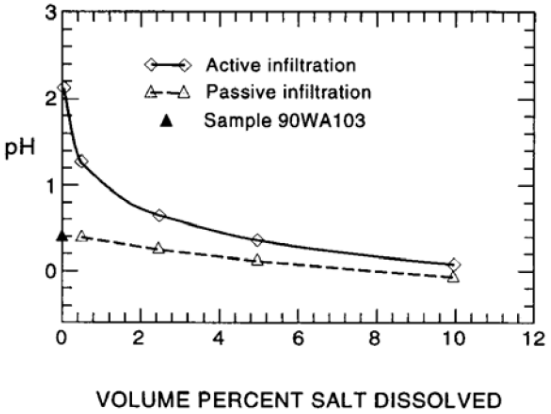

Figure 1. Decrease in pH of mine pool as a function of dissolved salts.

result was calculated and appears in figure 1 above. The conclusion was that about 600,000 m^3 of water with pH equal to or less than 1 and with many grams per liter of dissolved metals would be produced above the existing water table, in a rock with little or no neutralization capacity and in which ground-water flow would be governed by fractures, faults, tunnels, adits, and drillholes. In other words, water flow paths would be unpredictable and probably not easily controllable. The conclusion was that mine plugging at Iron Mountain could be a dangerous, high-risk, and ineffective alternative. Partly for this reason, mine plugging was never attempted.

3 Study of hydrologic connections with mass balances

The Hornet Mine at Iron Mountain, California is located in close proximity to the Richmond Mine and at a lower elevation. The Hornet effluent is the second worst quality mine discharge at Iron Mountain. It was thought that the Hornet effluent originated in the Richmond and if the Richmond were plugged, flow from the Hornet would cease. The access of water to the openings that connected the Richmond to the Hornet, however, was questioned because much of the underground workings had caved in and the passageways may be blocked to water flow. To determine if there was hydrologic connection between the two mines, 5 independent methods were used (Alpers et al. 1992). Of these methods, the mass balance method was the most definitive. Using the BALANCE program (Parkhurst et al. 1982), the effluent composition from the Richmond was characterized in terms of the mineral reactions that would produce it. The mineralogy was well characterized and 11 minerals could account for the water chemistry of the Richmond discharge: albite, sericite, kaolinite, epidote, chlorite, silica, calcite, pyrite, chalcopyrite, sphalerite, and melanterite. The gases oxygen and carbon dioxide also had to be included in the mass balance. For the evolution of water from rain water (pure water was used) to Richmond effluent, all the above minerals had to dissolve except silica and melanterite which had to precipitate. Oxygen gas reacted and carbon dioxide produced. The same analysis was done for the Hornet effluent. Then mixing was applied to see if it were possible to begin with Richmond water and mix it with clean ground water to produce the Hornet effluent. The result was that the only models that satisfied the constraints were ones that allowed a maximum of 2% of the Richmond water in the Hornet effluent. The remaining chemistry of the Hornet had to be produced by reaction within the Hornet mineral deposit. The other 4 methods also confirmed that there had to be little or no hydrologic connection between the Richmond and Hornet workings.

4 Synoptic/tracer studies and reactive-transport modeling

Two methods, stream tracer studies with synoptic sampling and reactive-transport modeling, are powerful tools that can quantify discharge in mountainous streams, determine surface and subsurface inflow discharges and loads, identify the major loading sources from mineralized areas, and identify the major in-stream processes affecting stream chemistry (Kimball et al. 2002). They have been frequently used not only for quantifying source loadings and in-stream processes but also to evaluate remediation alternatives (Kimball et al. 2003; Ball et al. 2004). These methods provide a much clearer picture of sources of acid-rock or acid-mine drainage and the potential improvement of site-specific remediation on the receiving stream or river. Consequently they have been in considerable demand during the planning and execution of environmental restoration of lands affected by acid-rock drainage.

The synoptic/tracer method involves adding a conservative tracer such as LiCl solution to acidic streams and NaBr solution to neutral to basic streams by continuous-flow injection at the upstream end of a given reach. Tracer concentrations are then measured at several downstream locations and the data are used to determine volumetric flow rate. Synoptic sampling is done both in the main stream and for all visible inflows. Mass loadings are calculated and the difference between sampled inflow loadings and increases in main stream loadings are attributed to unsampled ground-water inflows.

An example of manganese mass loadings for a 20 km reach of the Red River Valley in New Mexico is shown in figure 2 for two different water years (2001 and 2002). These are cumulative instream load plots not the actual instream loads. That is, the instream load increases from the accumulated inflows only, they do not decrease. This example is based on two synoptic/tracer studies to determine the location and quantity of inflows from both natural and mined source areas. There are several striking differences between the two water years. First, the loadings during 2001 are greater overall than those in 2002. The reason for this difference is that 2002 was the driest year on record and flows had decreased. Furthermore, during the 2002 tracer the mining company was pumping groundwater from the alluvial aquifer. This pumping helps to explain why there was a big jump in manganese loading at about 14 km in 2001 but not in 2002. The mine site reach is from about 10 km to about 19 km, occupying the lower half of the profile. It is obvious that considerable amounts of manganese are mobilized from the mine site but what is not clear is how much of this manganese loading is from mining activities, i.e.

leaching of waste rock piles, or from natural weathering and transport, because the magnitude of natural manganese mineralization (chiefly rhodocrosite) is known to be greater at the mine site than further upstream and natural acidification of ground waters has occurred at the mine site before any mining took place. The manganese load increases near the beginning of the reach and again at about 7 km are from natural sources.

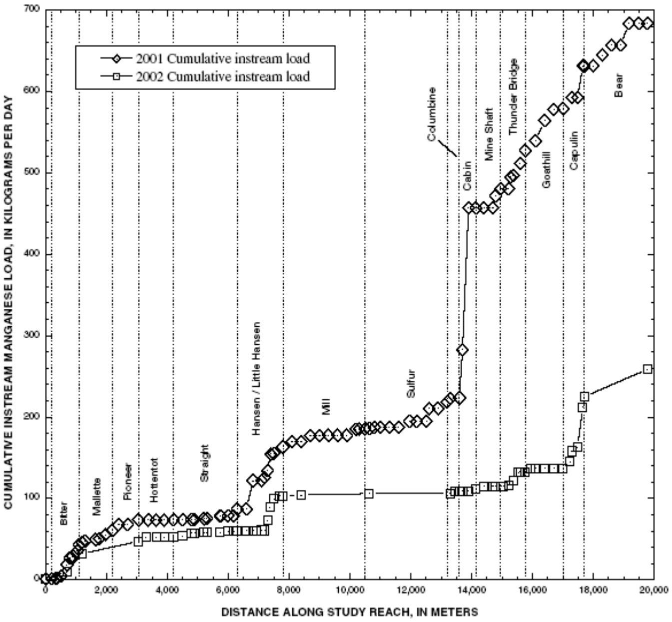

Figure 2. Cumulative mass loading curve for manganese in the Red River, New Mexico for water years 2001 and 2002.

Reactive-transport models use data derived from the synoptic/tracer method to calibrate the model. After calibration, then conservative solutes in the main stream are modeled and compared to actual measurements through the use of the OTIS program (Kimball et al. 1994; Runkel 1998). If the conservative constituents are adequately modeled then reactions are simulated by coupling OTIS with the MINTEQA2 code in the OTEQ code (Runkel et al. 1996). The OTEQ code considers aqueous speciation equilibria, one-dimensional transport with advection, disperison, lateral inflow, transient storage, distribution between mobile and immobile phases, precipitation/dissolution, particle settling, and sorption.

An example of the application of OTEQ to a stream system receiving acid mine drainage is provided by the Summitville mine study (Ball et al. 2004). Two synoptic/tracer studies were done in Wightman Fork and the

Alamosa River, one under high-flow conditions and the other under low-flow conditions. Figure 3 shows the results of OTEQ simulations for pH and concentrations of Al, Fe, and Cu under the high-flow conditions of June, 1999. These constituents are the most reactive in this aqueous system. All other solutes behaved conservatively. Furthermore, there were feedback loops such that any changes in one constituent affected the others. For Fe, Al, and Cu both dissolved and “mobile” (dissolved plus suspended particles) were measured and simulated. The simulation results gave excellent comparisons with the measured data. Next the model was used to calculate 9 remediation scenarios. These scenarios ultimately provided results needed by the State of Colorado to make final decisions on the most effective remedial alternatives for improving water quality (Ball et al. 2004).

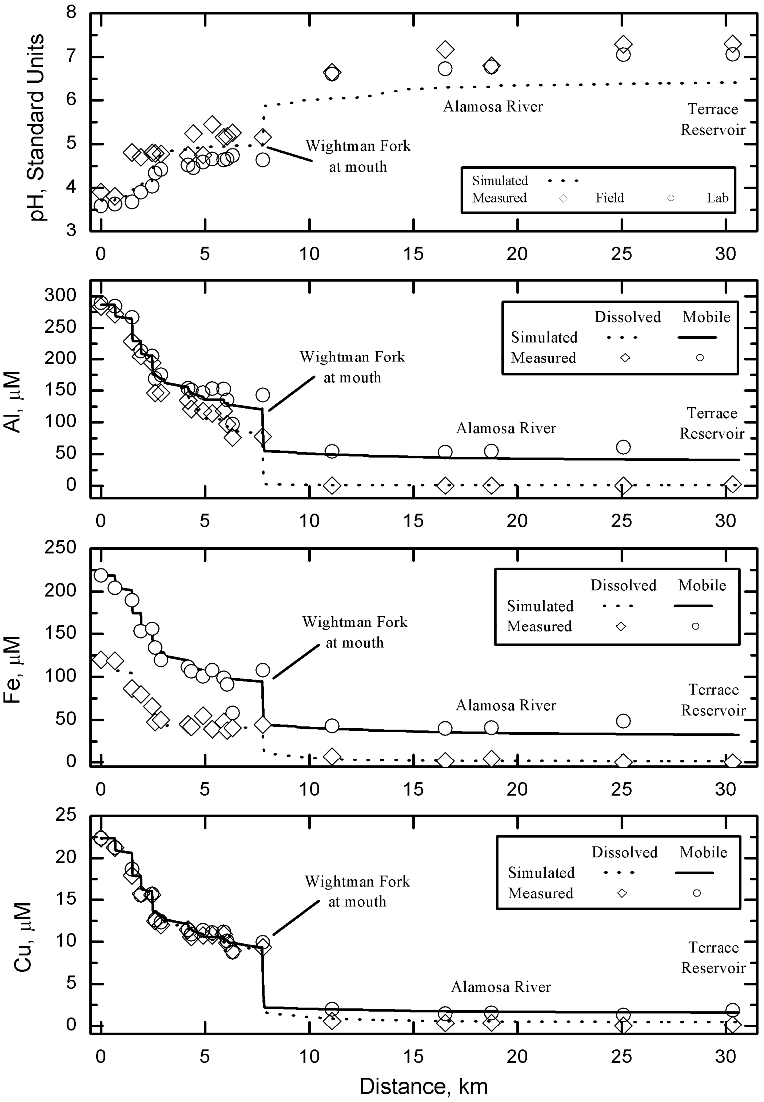

Figure 3. Profiles of pH, and concentrations of dissolved and mobile (dissolved and particulate) aluminum, iron, and copper with distance along the Wightman Fork/Alamosa River system, Colorado.

Conclusions

The reults of hydrogeochemical research at the US Geological Survey have proven applicable to the remediation of water quality at mine sites in the western USA. In particular, the application of mass balance models, geochemical reaction models, and reactive-transport models to sites where the geochemistry has been carefully characterized has made science-based remediation decisions possible. Regulatory agencies can make sound management decisions based on best available information. More specifically, mine plugging is not a desirable alternative because the resultant mine pool can be of extremely poor water quality and in a hydrologically unstable situation. When this water does discharge, the location of discharge is not easily predictable and it will be more difficult to treat. Stream tracer studies and the resultant mass loading profiles can provide much more quantitative information on inflow sources and location of inflow. Reactive-transport models can not only simulate instream reactions and mixing processes but they can also provide a framework for remediation scenarios so that the most cost-effective alternatives can be chosen. Recognition of geologic, hydrologic, and geochemical features controlling water flow and composition is essential to wise water quality regulation.

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References

Alpers CN, Nordstrom DK, Burchard JM (1992) Compilaiton and interpretation of water-quality and discharge data for acidic mine waters at Iron Mountain, Shasta County, California, 1940-91. *US Geological SurveyWater-Resources Investigations Report 91-4160.*

Ball JW, Runkel RL, Nordstrom D.K. (2004) Evaluating remedial alternatives for the Alamosa River and Wightman Fork, near the Summitville Mine, Colorado: Application of a reactive-transport model to low- and high-flow simulations. Chap. 3 *In Environmental Sciences and Environmental Computing, Vol. 11.* Zanetti, P. (Edit).The EnviroComp Institute (http://www.envirocomp.org).

Kimball BA, Runkel RL, Walton-Day K (2003) Use of field-scale experiments and reactive solute-transport modelling to evaluate remediation alternatives in streams affected by acid mine drainage. Chap. 13 *In Environmental Aspects of Mine Wastes.* Jambor, J.L., Blowes, D.L., and Richie, A.I.M. (Edits). Mineralogical Association of Canada, Ottawa, 261-282.

Kimball BA, Broshears RE, Bencala KE, McKnight DM (1994) Coupling of hydrologic transport and chemcial reactions in a stream affected by acid mine drainage. *Environ. Sci. Tech.* 28, 2065-2073.

Kimball BA, Runkel RL, Walton-Day K, Bencala KE (2002) Asessment of metal loads in watersheds affected by acid mine drainage by using tracer injection and synoptic sampling: Cement Creek, Colorado. *Appl. Geochem.* 17, 1183-1207.

Nordstrom DK (1999) Consilience and conciliation: the need for less human impact and more humane impact. *In Geochemistry of the Earth's Surface*. Ármannsson, H. (Edit). A.A. Balkema, Rotterdam, 139-142.

Nordstrom DK (2000) Advances in the hydrogeochemistry and microbiology of acid mine waters. *Inter. Geol. Rev.* 42, 499-515.

Nordstrom DK, Alpers CN (1999) Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund sie, California. *Proc. Nat'l. Acad. Sci.* 96, 3455-3462.

Nordstrom DK, Alpers, CN, Ptacek CJ, Blowes DW (2000) Negative pH and extremely acid mine waters from Iron Mountain, California. *Environ. Sci. Tech.* 34, 254-258.

Parkhurst DL, Plummer LN, Thorstenson DC (1980) PHREEQE – A computer program for geochemical calculations. *U.S. Geological Survey Water-Resour. Invest. Report 80-96.*

Parkhurst DL, Plummer LN, and Thorstenson DC (1982) BALANCE – A computer program for calculating mass transfer for geochemical reactions in ground water. *U.S. Geological Survey Water-Resour. Invest. Report* 82-14.

Pitzer KS (1991) Theory: Ion interaction approach. *In Activity Coefficients in Electrolyte Solutions*. Pitzer, K.S. (Edit). CRC Press, Boca Raton, Florida, 75-153.

Runkel RL (1998) One-dimensional transport with inflow and storage (OTIS): A solute transport model for streams and rivers. *U.S. Geological Survey Water-Resour. Invest. Report 94-4018.*

Runkel RL, Bencala KE, Broshears RE, Chapra SC (1996) Reactive solute transport in streams 1. Development of an equilibrium-based model. *Water Resour. Res.* 32, 409-418.