FROM RESEARCH TO REMEDIATION – 42 YEARS OF AMD HYDROGEOCHEMISTRY

D. Kirk Nordstrom
U.S. Geological Survey, Boulder, CO 80303

With my retirement approaching, Dr. Skousen asked if I would provide an overview of my contributions to the field of acid mine drainage. This flattering request was so challenging that I couldn't resist. I also wondered if he knew what he was asking for.

Phase I – Introduction to Iron Mountain, California (1974-76)

In 1974, I began pursuing Ph.D. research while a student at Stanford University on what later became the Iron Mountain Mines superfund site in northern California. At the time, the U.S. Geological Survey (USGS) had a funded agreement with the California State Water Resources Board to study the acid mine drainage (AMD) problems of Shasta County. Superfund was not born until 1980. I knew nothing about AMD but I could tell that this site was extraordinary and allowed me the opportunity to do field work, lab work, and theoretical calculations for my thesis. Working in the field, collecting water samples, completing most of the analyses, and interpreting the results by myself was both challenging and exhilarating. I developed a method for measuring Fe(II/III) using FerroZine (similar to, but more sensitive than, the older phenanthroline method, Lee and Stumm, 1960), we used direct-current plasma atomic emission spectroscopy (DCP-AES) and atomic absorption (AA) spectrophotometry (flame and graphite furnace), and I analyzed nearly 100 samples from pH 0.8 to 7.5 mostly by myself. These were likely the most complete AMD analyses at the time, or at least competitive with those from Pennsylvania and Ohio coal mine drainage. Water chemistry speciation codes were just beginning to appear and I needed one to help interpret my analyses. Jim Ball and I took the existing WATEQ code (Truesdell and Jones, 1974) and modified it to include Cu, Zn, and Cd complexes of sulfate, Fe(II/III) species, and modified or added the thermodynamic data for minerals typically found in AMD such as jarosite, melanterite, and forms of ferric hydroxide (Ball et al., 1979; Nordstrom et al., 1979). Improving the thermodynamic data in geochemical codes has continued to be a project of mine to this day. Adding the Fe(II/III) species allowed the calculation of the redox potential for the iron redox couple and led to the first comparison of measured with calculated Eh (Nordstrom et al., 1979). The latest comparison of this type (Fig. 1 A, B) can be found in Nordstrom (2011a) and can be used to corroborate the reliability of speciation calculations (Nordstrom and Campbell, 2014). This last point is important to emphasize. It shows that not only does the Nernst equilibrium equation work for this system but that all our assumptions regarding activity coefficients and the reliability of stability constants are corroborated. It is not often that we have an independent means of checking the accuracy and precision of our speciation computations. The other important insight that this comparison showed was that the orders of magnitude supersaturation with respect to freshly precipitating ferric hydroxide was a filtering artifact; i.e. even with a filter pore size of 0.1 micrometers ferric hydroxide colloids were getting through the filter, dissolving in the sample acidification, and appearing in the results as dissolved Fe(III). The comparison of Eh values before and after removing non-detects also shows the improvement in the correlation and shows the improvement in equilibrium saturation indices for hydrated ferric oxide minerals (Nordstrom, 2011a).

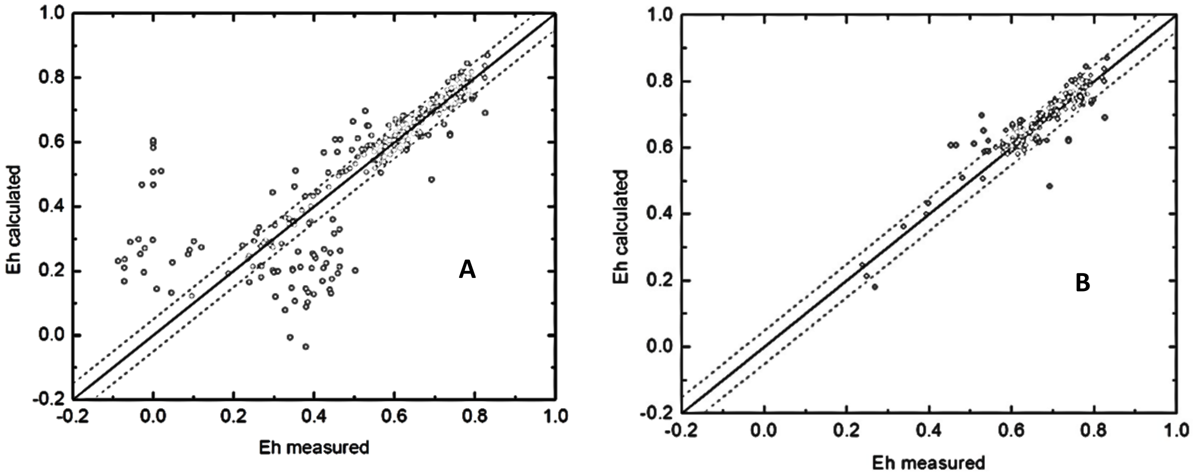

Figure 1. Comparison of Eh calculated from Fe(II/III) determinations and speciation compared to Eh measured with a Pt electrode. **A.** Results from more than 1300 water analyses from the western U.S. **B.** Results from A after eliminating values where Fe(III) or measured Eh were less than detection (Nordstrom, 2011a).

The analyses from my Ph.D. thesis were used as evidence in legal proceedings brought against the mine owner at Iron Mountain before superfund began. During the EPA superfund legal proceedings, I was deposed as an expert witness. A settlement was reached in December of 2000 (Jacobs et al., 2016) which was the largest superfund amount at the time ($862 million).

While beginning field work in 1974, I discovered that no one had properly documented the temperature-dependence of ZoBell's solution (Nordstrom, 1977; ZoBell, 1946), a standard solution to check the poising of redox potential measurements. So I utilized available equipment at the USGS, measured it, and fully interpreted the data in terms of an ion association model. Dr. Claude ZoBell (marine microbiologist at Scripps Oceanographic Institute) saw my published paper, wrote me a most complimentary letter, and requested 2 reprints. He published nearly 300 papers and discovered 65 species of ocean bacteria. I also made the first determination of ferrous iron oxidation rate in a moving stream at pH 2.5, building on the earlier work of Singer and Stumm (1968). The results showed that the rate was driven by iron-oxidizing bacteria and were comparable to optimized lab studies of microbial ferrous iron catalysis (Nordstrom, 1985; Nordstrom and Southam, 1997; Nordstrom, 2003). I am particularly pleased that one of our young USGS colleagues, Dr. Kate Campbell, has continued studies of the ferrous iron oxidation, hydrolysis, and precipitation rates that include kinetic modeling with PHREEQC and an application to troublesome scale formation in an AMD pipeline at Iron Mountain (Campbell et al., 2013).

Phase II – Detour to University of Virginia (1976-80)

Unable to obtain a National Research Council post-doc at the USGS because of a trivial oversight, I was hired as an Assistant Professor at the University of Virginia where I already had a master's student waiting to work with me, Thomas Dagenhart, Jr. He did the first study to document the efflorescent mineralogy of salts at mine tailings sites along Contrary Creek, VA and to show the effect of rainstorms when these salts dissolved and caused a spiked increase in metal concentrations and a decrease in pH in the creek just prior to entering Lake Anna (see Nordstrom, 2011a). Younger (2000) coined the term "first-flush" for these phenomena (more references in Nordstrom, 2011a). The Soil Science Society of America invited me to review pyrite oxidation and efflorescent salt formation at a Soil Chemistry session in Ft. Collins (Nordstrom, 1982a) for a special publication on Acid Sulfate Weathering (one of my most cited articles). This invitation gave me the opportunity to update and improve my geochemical and microbiological understanding of pyrite oxidation that I had sketched out in my Ph.D. thesis. During this time I encouraged Dr. Bruce Taylor to work on oxygen and sulfur stable isotopes of sulfate (Taylor et al., 1984a, b) to see if this approach could give us a better understanding of the mechanisms of pyrite oxidation. Later, I helped with a more thorough USGS field investigation of the stable isotopes of water and sulfate in 90 samples from mine drainage and natural acidic drainage in the San Juan Mountains (Nordstrom et al., 2007). The conclusions from this last study showed two major interferences with interpreting both stable isotopes of sulfur and oxygen in dissolved sulfate. First, the contributions of gypsum and anhydrite dissolution and their isotopic composition had to be discerned as suggested by Dr. Krouse. Second, varying residence times of AMD underground with the opportunity to evaporate make it difficult, if not impossible, to relate the water isotopes to the oxygen isotope composition in sulfate. One of the unexpected consequences of that study was the graphical depiction of the three main geochemical processes dominating the water chemistry, pyrite oxidation, gypsum dissolution and calcite dissolution, shown in Fig. 2. The domination of pyrite oxidation is observed in acidic drainage with low Ca/SO_4 ratio and $\delta^{34}S$ values typical of hydrothermal pyrite (-5 to +3; very little sulfur isotope fractionation occurs during oxidation dissolution of the pyrite). When gypsum dissolution dominates, Ca/SO_4 molar ratios are close to unity and the $\delta^{34}S$ in the dissolved sulfate is high (+7 to +11) because it is derived from hydrothermal anhydrite which typically contains heavy isotopic compositions. When Ca/SO_4 ratios are high (>1), the waters are carbonate-buffered with neutral pH because of the dominance of calcite dissolution. Nearly all the waters sampled fit within this triangular distribution, suggesting either they are mixtures of the end-member waters or they are intermediate in the degree of the end-member processes.

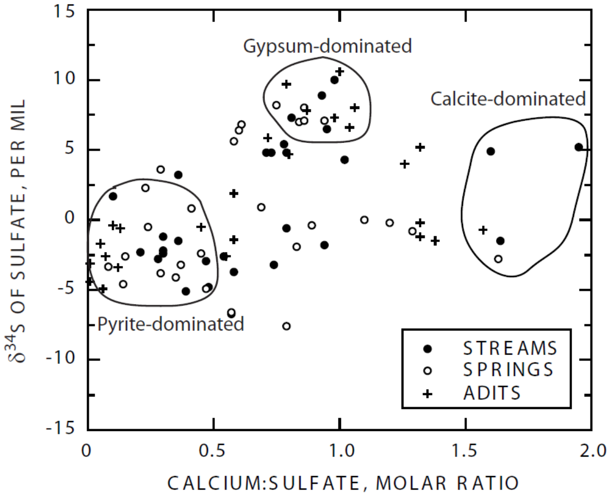

Figure 2. $\delta^{34}S$ of dissolved sulfate in streams, springs, and mine adits plotted against the Ca/SO_4 ratios. Data based on samples from the San Juan Mountains (Nordstrom et al., 2007).

I had an outstanding Ph.D. candidate, Carl Moses, who obtained the first complete analyses of intermediate sulfoxyanions (thiosulfate, polythionate, and sulfite; Moses et al., 1984) occurring during pyrite oxidation that built on the earlier work by Goldhaber (1983). It was also the first careful examination of the effect of sample preparation on initial oxidation rates. The effects of dissolved oxygen versus Fe(III) at different pH values were also compared. Unfortunately, I left Virginia before Carl finished but our often cited paper did get published under the able guidance of Janet Herman and Aaron Mills (Moses et al., 1987).

I had the good fortune of having an office next to Dr. Gene Likens who took a sabbatical at Virginia. I had some ideas about the solubilities and phase relations among aluminum minerals that might control dissolved aluminum concentrations and he and Dr. Bruce Hanshaw (USGS) strongly encouraged me to write a paper on that subject. That paper began to take shape before I left Virginia and was finished and published after I joined the USGS in Menlo Park, CA (Nordstrom, 1982b). Although I had found evidence in the literature for a mineral, jurbanite, that fit the description of van Breemen's hypothesized mineral ($AlOHSO_4$) which might control Al concentrations at low pH, it turned out to be a false lead because jurbanite is an efflorescent salt that only forms at very low pH and its estimated solubility was done without the benefit of recent Pitzer data for highly soluble salts (Bigham and Nordstrom, 2000). The paper did provide an integrating framework for considering aluminum mineral solubilities as controls on aluminum concentrations.

Phase III – USGS activities in Menlo Park, CA (1980-91)

In 1981-82 we collected drainage water and downstream samples from the Leviathan Mine in Alpine County, CA and noticed a most distinct trend with aluminum concentrations and free ion activities with pH and sulfate concentrations (Fig. 2A,B). Our samples ranged in pH from 1.8 issuing from the mine to 8.2 in the receiving waters farthest downstream. It was an opportune site because the AMD issued near the headwaters of Leviathan Creek and were gradually neutralized by tributaries and the East Fork of the Carson River without any other acid drainage complicating the mixing. When the activity of the free Al ion was plotted against pH (Fig. 2A), two distinct slopes can be recognized, a shallow slope for pH values less than about 4.5 and a steep slope at higher pH values. Going from low pH values the aluminum concentrations correlate well with sulfate concentrations (Fig. 2B) indicating simple dilution from tributary mixing. At higher pH values than 4.5 a distinct non-correlation with sulfate concentrations occurs (Fig. 2B) that does correlate with a freshly precipitating form of $Al(OH)_3$ shown in Fig. 2A (Nordstrom and Ball, 1986). The precipitation of this aluminous material can be seen quite well below the confluence of Leviathan Creek with Mountaineer Creek where the pH jumps from 3.5 to 5.5. Massive amounts of white precipitation were observed at this juncture.

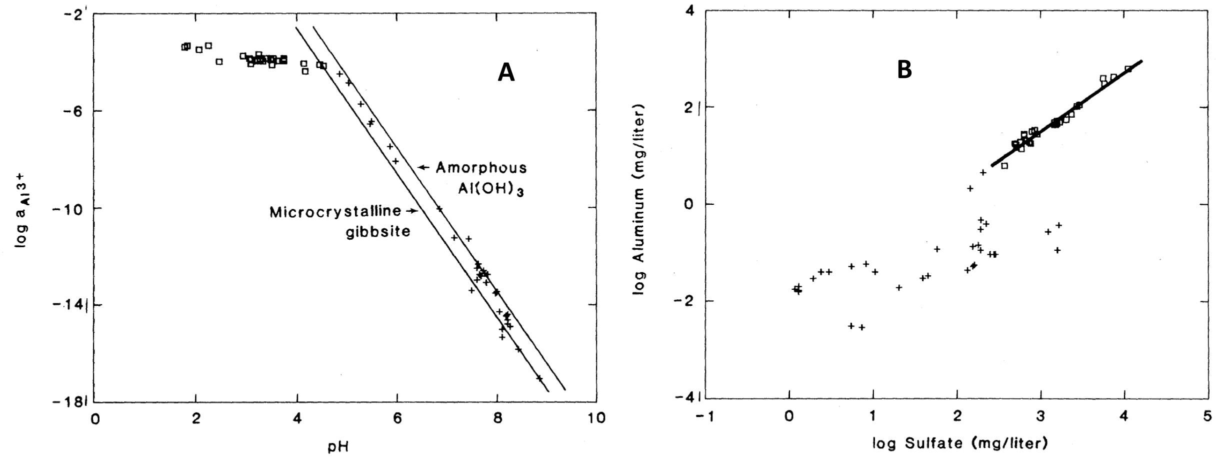

Figure 3. Water samples from Leviathan Creek and the Leviathan Mine downstream to the East Fork Carson River (Nordstrom and Ball, 1982). **A.** Logarithm of the free aluminum ion activity, $a_{Al}{}^{3+}$, plotted against pH. **B.** Logarithm of the dissolved aluminum concentrations plotted against logarithm of the sulfate concentrations, both in mg/L.

The break in slopes at pH near 4.5 is the effect of incipient aluminum hydrolysis for which the $pK_1 = 5.0$. Aluminum hydroxide precipitation cannot occur without hydrolysis taking place and this is pH dependent. My analysis of this phenomenon was also confirmed when I plotted 1300+ analyses from the western U.S. (Nordstrom, 2011a). Our best site for aluminum precipitate was later found in the San Juan Mountains at a place variously called "Paradise Portal" and "White Death." It was another example of how the proper application of relatively simple chemistry, the pH of hydrolysis, can be generalized to explain a common phenomenon seen in a wide variety of waters (e.g. Adams et al., 2000). I have often told students that just knowing the pK_1 for any metal cation is a powerful predictive tool for not only estimating the onset of precipitation with increasing pH, but also the relative sorption properties with pH. Our knowledge of aqueous aluminum thermodynamic properties was well established through two review papers we published on this subject (Nordstrom and May, 1989, 1996).

During this time the Iron Mountain superfund debates between the EPA and the potentially responsible parties (PRPs) were heating up and the PRPs were pushing hard for plugging the main drainage tunnel. I was asked by the EPA what would be the consequences of such action, specifically what would be the chemistry of the consequent mine pool. I couldn't answer that question without some data and other information. I suggested that if we could go underground, we might be able to obtain the necessary data. I was joined by my first post-doc, Dr. Charles Alpers, and in September of 1990 we were allowed underground and found huge quantities of efflorescent salts and waters with negative pH. Over the next 9 years we carefully went through our data and finally published some of it in an invited National Academy Press paper (Nordstrom and Alpers, 1999). We measured pH values from -0.7 to as low as -3.6. We collaborated with Drs. Blowes and Ptacek at the University of Waterloo and submitted our main paper on negative pH to Environmental Science and Technology (Nordstrom et al., 2000). As we suspected, it was rather controversial (Science and Nature had rejected our paper earlier because a senior editor said was not interesting enough to their readers). The highlight of this work came when I presented our answer to the question of what the mine pool chemistry would be under a mine plugging scenario. It would create about 600,000 m^3 of $pH \leq 1$ water with grams per liter of dissolved metals encased in a rock with no neutralization capacity and full of holes sitting on top of the groundwater table and ready to leak out in numerous unpredictable localities at unpredictable discharge rates. The EPA decided against the mine plugging option. Many other mines have been plugged with similar results to what we had predicted.

Phase IV – USGS activities in Boulder, CO (1991-present)

From our inventory of chemical analyses on Iron Mountain effluent water we noticed seasonal trends in the Zn/Cu ratios which we could relate to the formation and dissolution of zincian cuprian melanterite (Alpers et al., 1994), again showing the importance of soluble salts in controlling the chemistry of strongly acidic mine drainage. Further work on the natural attenuation of metal contaminants in Leviathan Creek was possible when Dr. Jenny Webster came to work with me for 9 months (Webster et al., 1994). We continued to improve our analytical expertise with AMD with better instrumentation and showed that colorimetric iron determinations were often more precise than those from inductively-coupled plasma atomic emission spectroscopy (ICP-AES) and that DCP-AES was better for a few elements than ICP-AES (Ball and Nordstrom, 1994). Since that time, inductively-couple plasma mass spectrometry (ICP-MS) has largely taken over but every method has some interferences and having multiple techniques available can improve the accuracy and precision for all contaminants determined.

The effect of microbial growth on water chemistry, especially the formation of AMD, has always interested me. Our first microbiological review of AMD (Nordstrom and Southam, 1997) has often been cited as it gives the basic framework of much our knowledge of this subject. It was later followed by Nordstrom (2000, 2003) and a wider biological review by Robbins et al. (2000) for Iron Mountain.

Two important and comprehensive reviews on sulfate minerals (both soluble and insoluble) summarized what we knew about this subject and its relation to AMD (Jambor et al., 2000; Bigham and Nordstrom, 2000) in a Mineralogical Society of America book on sulfate minerals. Our collaboration with Dr. Jamieson (Queen's University) was instrumental in revealing the water chemistry co-existing with the minerals copiapite and jarosite (Jamieson et al., 2005a,b) found at Iron Mountain. Such studies help us to show the pH and water composition range that produces a particular mineral.

The short course on environmental geochemistry of mineral deposits produced one of our best review papers on the subject (Nordstrom and Alpers, 1999) along with another chapter on geochemical modeling for mining environments (Alpers and Nordstrom, 1999).

The subject of rare-earth element (REE) geochemistry in AMD had rarely been addressed, other than the excellent thesis of Dr. Maria Gimeno (1999) who documented evidence for the tetrad effect. Hence, Dr. Philip Verplanck, another post-doc, took on this challenge and showed that partitioning of REE into precipitating solids occurred at higher pH values (>5) where aluminum precipitated and not during iron precipitation at lower pH values (Verplanck et al., 2004). Hence, no fractionation of REEs takes place during acid dissolution of REE-bearing minerals and the REE pattern can be assumed to be that of the dominant mineral source of the REEs.

The question of what the water quality was like before mining is not only interesting from a scientific viewpoint but also from a regulatory viewpoint because pre-mining water quality was often more contaminated than drinking water standards. Such “background” concentrations should be the goal of environmental restoration, not a standard that never existed in a particular area. From 2000 to 2007, I led a group of 30 USGS researchers to determine the pre-mining groundwater quality at an active mine site in northern New Mexico. Twenty-seven reports were published and summarized in Nordstrom (2008). These studies included groundwater hydrology and geochemistry; surface water hydrology and geochemistry; airborne and surface mapping of mineralogy; reactive-transport modeling; environmental geology and debris flow hazards; geomorphology and its effect on hydrology and water chemistry; structural geology and its effect on groundwater flow patterns; local and regional water balances; and geophysical studies of depth to bedrock and to groundwater. A detailed study of a proximal analogue provided the information necessary to estimate groundwater concentrations of 14 constituents of concern for a dozen small catchments on the mine site (Nordstrom, 2008). The conclusion was that several constituents were likely greater than the New Mexico groundwater standards, the largest anomaly being manganese which was as much as 250 times the standard. The study was the first of its kind and provided a better cleanup goal for the mining company and a scientifically justified goal for the regulators. More recently, I published a review of natural acidic drainage and what generalizations can be drawn. One aspect is clear, that mining can increase the flux and concentrations of acid, metals, and sulfate by one to three orders of magnitude over natural conditions (Nordstrom, 2015).

Overviews of AMD continue to be requested (Nordstrom, 2011b; Nordstrom et al., 2015) and the need for alternative remedial options to lime neutralization plants and mine plugging will continue. The potential effects of climate change on receiving waters downstream from AMD deserves serious consideration (Nordstrom, 2009). Better approaches to remediation planning is possible but not commonly used (e.g. Ball et al., 1997; Runkel and Kimball, 2002). The best method of preventing AMD is to plan for it at the time of mine planning instead of later when the damage is too great to remediate easily or inexpensively.

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