A Hydrogeochemist's Mindful Toolkit: Conceptualization, Characterization, And Modeling Of Mine Sites Producing Acid Mine Drainage

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Abstract

After 50 years of studying acid mine drainage, three themes need improvement for more effective and cost-efficient mine-waste remediation: conceptualization, characterization, and modeling.

Conceptualization depends on one's background and experience with geology, hydrology, chemistry, hydrogeochemistry, microbiology, mining, and mineral processing.

Characterization builds on conceptualization using detailed knowledge of best practices.

Modeling always contains assumptions and misconceptions that become clearer through hypothesis testing and further data collection.

Two important skill sets stand out the most: a solid knowledge of the field of hydrogeochemistry, and humility when facing complexity. Then many of the costly mistakes of the past can likely be avoided.

Keywords: Remediation, conceptualization, characterization, modeling

Introduction

Acid metal-rich discharges from mining activities are one of the largest and most difficult problems to prevent and remediate. Nriagu and Pacyna (1988) estimated that 6,000 metric tons of Zn, 2,500 metric tons of Pb, and 900 metric tons of Cu per year were discharged to worldwide surface waters from metal mining activities. Berner and Berner (1996) estimated that 48% of the annual global sulfate flux of the world's rivers to the oceans was man-made pollution (acid rain, fertilizers, and acid mine drainage) and amounts to 77 x 1012 metric tons. Of that, a substantial portion is from mining and smelting activities. To date we still do not know approximately how much global sulfate flux is from metal mining compared to other anthropogenic activities or natural sources. Nieto *et al.* (2013) reported that 35,682 metric tons/a of sulfate out of an anthropogenic global 1.24 x 108 metric tons/a (Meybeck, 2003), or 0.03%, is discharging from the combined Tinto and Odiel Rivers when rainfall flush-out events are included. They also reported 649 metric tons/a of Zn, or nearly 3% of the global flux came from these rivers alone. Galvan *et al.* (2012) evaluated the mass flux of metals and sulfate in the Meca subbasin of the Odiel River Basin, SW Spain and for the water year 2000–2001, the sulfate flux was 18,645 metric tons/a, more than half of the two much larger basins. More recent studies indicate that sulfate flux from pyrite weathering and from pollution sources may be seriously underestimated (Burke *et al.*, 2018).

The number of disasters resulting from failed waste impoundments that have been addressed by several experts such as Davies (2002) and appear to be on the rise. The resulting spills can have both physical and chemical detrimental effects down gradient. Kossoff *et al.* (2014) list a dozen examples of well-known impoundment failures and a list of toxic chemical substance concentrations for eight of these. More spills have occurred since their paper was published. The pore water in sulfidic tailings waste can contain very high concentrations of sulfuric acid and metals. Mine portals can discharge water with pH values below 1.0 and underground massive sulfide mines have produced waters of negative pH (Nordstrom, 2011).

The purpose of this paper is to review the general approach to remediation of complex mine waste sites which generate acid mine drainage and, from my own experience, make a few suggestions. My suggestions fall into the categories of conceptualization, characterization and modeling.

Conceptualization

How one conceives of mine waste material, especially acid mine drainage, depends on several factors. There is documentation available on site-specific properties, visual observations from site inspections and maps and photographs, etc. Each person also brings their own perspective obtained through education and experience that shape how one conceives of the problem at hand and interprets the documentation. Every expert tends to understand things from a particular viewpoint that could be as much deleterious as helpful. A microbiologist tends to think of waste processes as always catalyzed by microbes. A geologist considers the rocks, rock structure, and mineralogy but not so much the microbes. A hydrogeologist looks at the rocks as a bounding structure to flowpaths but not so much as reactive material. The chemist sees chemical composition in both rocks and waters but might not see the importance of flowpaths or microbes. The mining engineer understands the operations of mining and mineral processing but not the need for additional expertise. Remediation of complex mine sites typically requires expertise from all of these areas – geology, hydrology, chemistry, hydrogeochemistry, microbiology, mining and mineral processing. The conceptual model addresses what is known, what is unknown and needs to be known, what sources and sinks of contaminants exist and what actions should be on the priority list.

A mine waste site can be a hydrogeochemical mess and although many books and papers have addressed the subject, these publications can be limited in terms of the authors' perspectives. For a single book, Lottermoser (2010) integrates quite well most all these important factors. Because these subjects are typically not courses covered by civil engineering curricula — consulting companies, mining companies, and regulatory agencies must either hire this expertise or learn these skills through training. Progress has been slow in recognizing the importance of conceptualization.

At the Iron Mountain mines superfund site, the potentially responsible parties advocated mine plugging for a legacy mine actively producing large quantities of acid mine drainage. The concept, still promoted today, was that the mine pool created by plugging would cover the remaining massive sulfide and block the access of oxygen and prevent the formation of acid mine drainage. The site was the worst possible site for mine plugging for a host of reasons (Nordstrom and Alpers, 1999). Mining had excavated a complex array of mines leaving numerous adits and drillholes that would allow strongly acidic water ($pH<1$) from a mine pool to leak out in all different directions into two different catchments and not easily contained. The mine pool would be well above the groundwater table. An active landslide existed above the main workings and several steam vents can be seen in winter, allowing easy entrance for water and oxygen. The country rock has no helpful buffering capacity against this acid water. After considerable deliberation, the mine was not plugged. Instead, a lime treatment facility was set up to neutralize the acid mine drainage which primarily discharged from two portals, and it was relatively easy to capture and treat. Many other mines in the western US having similar hydrogeochemical characteristics were plugged, the mine pool backed up and became enriched in acid and metal concentrations, was not contained and the consequent pollution of receiving streams and rivers became worse. Alternative treatment had to be installed for these sites, usually a lime neutralization plant, while the mine pool was dewatered. The predicted Iron Mountain mine plugging scenario was done and confirmed for other sites; it is often not a preferred option.

One disturbing aspect of neutralization plants is that they cost millions of dollars to build and maintain. At Iron Mountain, the amount of time it would take to exhaust the production of acid mine drainage at current weathering rates is approximately 3,000 years. Neutralization will not be supported in perpetuity because the cost is far greater than what can be supported by society and orders of magnitude higher than the value of the metals mined. A practical long-term remedial solution has yet to be determined for this site and many others.

Another example of mistaken conceptualization was on the Questa project (2001–2007) when the US Geological Survey was asked to determine the pre-mining groundwater quality of an active mine site. The Questa mine produced molybdenum ore concentrate. A proximal analog catchment that had not been mined was used to understand the pre-mining groundwater composition. Prior to the USGS participation a consultant was estimating the pre-mining groundwater quality by gathering surface sediments over a large area of mineralized ground and using analyses of quick water leach tests as a proxy for groundwater compositions. These test results bore little resemblance to actual groundwater compositions, and it points out the importance of informed conceptualization. Of course, one can change the water composition of leach tests by simply changing the ratio of solids to water, but it still did not mimic actual groundwater compositions.

Conceptualization should include a source-sink-receptor or flux-reservoir schematic of contaminant sources and pathways of mobility. The first schematic will be primitive, and as more and more site data are gathered it can be refined and improved. Examples of these schematics can be found in Nordstrom and Nicholson (2017).

Characterization

Characterization builds on conceptualization to formulate a plan with high and low priorities for what is needed to best quantify contaminant reactivity and mobility. In other words, to put numbers on amounts, reactivities and transport for the conceptualization. Characterization fills in the gaps and makes a strong case for the importance of remediation. Decisions must be made on what samples to collect, how to collect the samples, from what locations should the samples be collected, and for what purposes. Even though plenty of information is available on protocols for sampling, preservation, and analysis, protocols are not always followed and sometimes the protocols themselves are deficient. For example, EPA holding times for chloride and sulfate in water samples has been 28 days. If the sample has been filtered and kept in a cool or refrigerated space, those water samples can be held for many months without any change in concentration. I tried to find out why there were such restrictive holding times and discovered that there was no documentation. Even the EPA QA/QC director did not know where the holding time numbers came from. The USGS holding time on the same constituents is 6 months and the only reason they have a time limit is because there is not enough storage space to hold the bottles longer than that. I resolved my particular issue by taking a small sample set and analyzing them for sulfate within the holding time period and months after. The results were exactly the same within analytical error. I then explained why certain major ions are conservative in the sense that they will not change over time if the water is collected properly. Those results were found acceptable to both regulators and industry representatives. The last time I checked, chloride and sulfate holding times were still 28 days without explanation or reference.

When water samples are being collected from a site, certain field parameters must be obtained such as pH, temperature, specific conductance, and often dissolved oxygen. I experienced a situation where a non-USGS person was asked to collect a groundwater sample from a well and measure field parameters. The person reported a pH of 4. Several subsequent samples were collected by USGS personnel in which there was no discernible difference in water composition except that personnel following protocols always reported a pH slightly above 6. That much difference in pH is unacceptable when the procedures have been spelled out for decades (Bates, 1973). Another explanation is that in this example the well was not adequately purged before sampling.

Regulators do not usually require routine Fe(2/3) determinations on acid mine water samples. Consequently, charge balances on acid water samples might not be adequately balanced and the behavior of one of the most important cations in the water will not be characterized sufficiently. Ferrous iron, Fe(II), is highly soluble and mobile at any pH, whereas ferric iron, Fe(III), is highly insoluble at moderately acid to neutral pH values. Charge balance on a water sample is a simple QA/QC (quality assurance/quality control) procedure that helps to confirm the reliability of the analysis for major ions. Because of the control of trace metal sorption by freshly precipitating ferric oxides and hydroxides, analytically determining and understanding iron redox chemistry is a critical requirement for characterizing acid mine drainage. The analytical procedure for this requirement is both simple and robust. There is every reason to collect and preserve (with HCl) samples for Fe(2/3) redox determinations.

Other routine QA/QC procedures for water and sediment samples should be readily available in submitted reports, such as field and lab blank determinations, detection limits, methods of field and lab analyses, spiked recoveries, and, most importantly, results from standard reference samples (for both waters and solids). When the full suite of major ion determinations have been completed for a water sample, the conductance can be calculated and compared with the measured value as an accuracy check in addition to the charge balance assessment (McCleskey *et al.*, 2012) in addition to the charge balance.

I have seen examples of the dissolved concentration of potentially toxic metals and metalloids greater than the "total" concentration, i.e. the concentration on an acidified unfiltered sample. This result reflects problems with sample collection or preservation or analytical procedures and should be resolved. As a footnote, US Geological Survey field and lab teams rarely observe this difference. It seems to be more apparent when the contractor who collects the samples is different from the contractor who analyses the samples and different from the QA/QC auditor who screens the samples. When there are serious disconnects in communication between field teams and lab teams, it is easier for mistakes to occur in analytical results. One or two people who are responsible for data interpretation should accompany the field team and visit the analytical lab to follow the chain of custody for confirmation of protocols and to understand if there were any unexpected field or lab issues that could have caused unacceptable analytical determinations.

As the data is compiled it should be incorporated into a site model that addresses flux/reservoir (or stocks/flows) and identifies the dominant sources, pathways, and receptors. Seasonal trends and storm events should be sampled to determine the effects of weather and climate change.

The next level above sampling and analysis is interpretation of the data in a fashion that allows a manager, regulator, or non-technical person to understand the meaning of the results. At this point, the schematic conceptualization of the data is revisited and any serious knowledge gaps reported. Interpretation involves being intimately familiar with the analytical data, the field site, and what plots and diagrams are most useful. Hence, the characterization phase may include hydrogeochemical modelling for interpretation and it certainly does include modeling when considering scenarios for planning remediation or answering site specific questions about hydrogeochemical site behavior.

Modeling

Modeling is a complex subject that begins with the development of conceptual models, analogous to the conceptualization described above. It is essential to remember that (1) a model is not a computer code, (2) models are not unique, (3) models, if not tested, lack meaning, (4) if models are tested and predictions agree with independent observations, this result is not "validation", and if they don't agree, the models are not invalidated, (5) models and scenarios should not be confused with each other, (6) poor model predictions usually result from poor conceptual models, and (7) models are inherently "incorrect" but can be useful (Nordstrom, 2012; Nordstrom and Campbell, 2014; Nordstrom and Nicholson, 2017).

The importance of the conceptual model cannot be overemphasized. I can do no better than to quote (Bredehoeft, 2005).

"Every model has as its foundation a conceptual model."

"The conceptual model is based on the subjective judgment of the analyst."

"A numerical model provides a tool by which to test the appropriateness of the prevailing concept."

"One can expect the conceptual model to be continuously updated as new information is acquired."

To these I would simply add that all models are incomplete, and deficiencies are addressed with implicit or explicit assumptions. These assumptions can be unimportant or seriously deleterious to the calculations or unknown as to their effect on the result. What matters most is that they are transparent and better to be made explicit. Uncertainty analysis can help to identify what are the most sensitive variables which might point to more field and analytical data to better constrain the model.

A strong or reliable model is one that has been well tested for a wide range of conditions. If we are interested in an environmental model, it must field tested. For how long? Some have suggested around 25 years to make sure that extreme weather events and changing climate conditions are monitored and understood. I tend to agree. A better approach is to recycle and reuse these waste materials in ways that are safe for human health and the environment. Modeling is well-educated guesswork, and too many modelers view their models as immutable. I prefer the wisdom of Erica Thompson (2022) who stated:

"Model Land provides us with maps of the future, but they are not always the maps that we need. Some are plain and simple; some are elaborate and embellished; most are in some ways misleading; all were drawn by someone fallible; all have limits beyond which we can only write 'Here Be Dragons.' The terrain outside Model Land is bumpy and disputed. While our models can predict, warn, motivate or inspire, we must ourselves navigate the real-world territory and live up to the challenge of making the best of our imperfect knowledge to create a future worth living in."

I have reviewed reports where an elaborate scheme of transport equations, combined with rate and equilibrium equations for geochemical reactions and other equations for physical processes to predict metal and/or acid concentrations, present a remediation scenario that gives a highly optimistic viewpoint. But when the question is asked: Has there been a demonstration project to show the feasibility of such a scheme? It doesn't exist. There has been no testing of the complex model to find out if it works as planned, if the assumptions are adequate, and what are the major limitations and weaknesses. Hence, it is only a possible scenario or thought experiment and not even a scenario to which you can assign a vague uncertainty. There are models and scenarios that can be tested because they are short-term experiments and there are others that can never be tested in a human lifetime of 70 or 80 years, such as a high-level radioactive waste repository because it must last a few hundred thousand years without harming the biosphere. If they cannot be tested, they cannot be confirmed, and they certainly cannot be validated.

If we don't plan for on site reuse and recycling of mine wastes as the mine plan is developed before any extraction begins, it is a missed opportunity and will likely lead to an environment that is more expensive to manage at and following mine closure.

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