

Thermodynamic clues for acidic and neutral mine drainage

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Mine drainage is a common environmental problem accompanying mining, ore processing, and waste disposal. There are many ways of dealing with the problem, with specific approaches depending on the elements released, acidic or neutral nature of the solutions, disposal forms, and local conditions. The ultimate goal, however, is to minimize the concentration of unwanted elements, a notion that has its rooting in thermodynamics. It provides clues and hints even though we know that much in these systems is also controlled by disequilibrium processes and kinetics of transformation from the metastable to stable states.

Most mine drainage systems, at least in the earlier stages of operation, produce copious poorly crystalline materials which are iron-, aluminum-, or manganese-based. Are they produced as the most metastable compounds, only to dwindle as the time goes on? Studies on such systems, considering the many polymorphs, compositions, but also the role of the surfaces have shown that these mineraloids, for example ferrihydrite, are in a state of thermodynamic equilibrium with other phases of similar composition, such as goethite or hematite, if particle size of all these materials is kept very small. Only if they grow, they become metastable. Additionally, they can be stabilized by other elements such as calcium, phosphate, arsenate, or sulfate. Thermodynamically, such materials can be understood in terms of ion adsorption onto the surface or as single solid phases, although without crystalline order.

One of the components of mine drainage that sparks interest and fear in the public is arsenic. Many minerals are known from oxidation zones and mine drainage sites, but only a few of them are of greater abundance and importance. Scorodite is common and seems to be, at least at low pH, the phase of choice for disposal of arsenical waste. Other minerals in acidic or neutral systems can be found and their thermodynamic properties have been systematically measured. Although phases with lower solubility than that of scorodite can be found, their use is compromised by their incongruent dissolution and production of the poorly crystalline iron oxides, such as ferrihydrite. There are also phases that do not suffer from such unwanted effects in a certain pH range, such as $\text{FeAsO}_4 \cdot 0.75\text{H}_2\text{O}$, but its synthesis requires high temperatures. Our results also show that arsenic can be incorporated into common iron oxides, such as hematite, *via* epitaxial intergrowth. True solid solutions carry potential for lower solubilities but must be characterized and tested.

Antimony, a common and commonly overseen contaminant in neutral mine drainage systems, has been reported as “mobile as an Sb(V) species under common environmental conditions” by some authors, but as “geochemically immobile in solution and in soils” by others. The reconciliation of these conflicting statements can be done if thermodynamics and kinetics of the antimony-containing systems are considered. Unfortunately, time is needed to reach the immobile state, desired by the environmental regulations. The very insoluble tripuhyite (FeSbO_4) forms very slowly, as nanoparticles that tend to agglomerate but not fuse into larger crystals.

The study of oxidation zones as long-term natural experiments on metal-rich systems, together with thermodynamic and kinetic research, can provide valuable clues for the

improvement of the waste management. Mineralogists can thus contribute significantly and deliver much needed input for mine engineers, technologists, and environmental regulators.