Quantifying Mineral Precipitation Processes during Dilution, Mixing, and Neutralization of Acid Rock Drainage

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Abstract

Mineral precipitation from ARD can be identified or indicated by (1) visual inspection (including remote sensing), (2) computations of mineral saturation indices (SIs), (3) ion ratios, or (4) mass flux (mass loading) computations. A visual precipitate represents the integration of water chemistry over time and computations of SIs for a water composition give quantitative tendencies for that water to dissolve or precipitate minerals. The advantages and disadvantages of these methods are demonstrated with carefully collected field data from (I) drainage from Iron Mountain Mines, California, and (II) natural ARD from the Red River Valley, New Mexico.

Keywords: Geochemical Modelling, Element Ratios, Saturation Indices

Introduction

The loss of an aqueous solute from solution occurs through sorption and precipitation. Under controlled laboratory conditions, these processes are readily measured and quantified. For surface waters under natural conditions, these processes are not so readily quantified. The complexities and heterogeneities in natural systems make quantification of this process challenging. Four approaches for identifying and quantifying mass transfer of aqueous solutes to solid phases are described in this paper for contaminants found in acid mine drainage and demonstrated with data from three field sites. These approaches are visual observation, computation of saturation indices, solute ratios, and mass fluxes.

Methods

Visual observation

Once dissolved iron in AMD is oxidized to ferric iron, the solution takes on a reddish colour if the pH is low enough to keep the iron in solution. Because of the very low solubility of ferric iron, precipitation rapidly occurs for pH values generally above 2.2. The precipitate begins as a dull yellow colour and turns orange, red orange, and red brown to dark brown with ageing. Consequently, AMD is readily identified by its visual mark on streambed sediments from iron-staining precipitates.

Iron-stained bed sediment does not necessarily reflect the current chemical compositions of the water flowing over it. Once an insoluble hydrous ferric oxide precipitate has formed, it can take a long time to redissolve when the water composition changes. The precipitate is also the accumulation of many water volumes that have passed over it. It integrates the result of varying water chemistries over some period of time, providing a qualitative time signature of identification, but not necessarily today's water chemistry unless it is actively precipitating in the stream. Ferricretes that have been dated can provide valuable information on the time period of formation.

Saturation indices

Saturation indices (SIs) are one of the geochemical tools to characterize the tendency of a water to dissolve or precipitate a mineral given a fairly complete water analysis. For an AMD sample, it means determining the dissolved major ions, including Fe(II) and

Fe(III) and using a geochemical code, such as PHREEQC (used in this study) to calculate the speciation according to the standard equation

$$SI = \frac{\log[IAP]}{\log K_{sp}}$$

where IAP = ion activity product and K_{sp} = solubility product constant for a specified mineral. When the SI = 0, it indicates the mineral is at solubility equilibrium, if SI > 0 it would indicate supersaturation and possibly precipitating, and if SI < 0 it would indicate undersaturation and the mineral is dissolving if present. Saturation indices are very useful parameters, especially when used in conjunction with mass balances or mass transfer for reactive transport calculations. Their limitations are that they depend on reliable thermodynamic data and they do not tell us the kinetics of the precipitation/dissolution processes.

Ion ratios

If a "conservative" ion can be identified in a surface water or groundwater, other ions can be compared to it by using ratios to see if they indicate mineral precipitation or dissolution. The ratios may also change from mixing with tributaries that have very different ratios, however, if a contaminant source has high concentrations, ratios are not affected by dilution or other tributaries with different ratios.

Mass fluxes

Mass fluxes refer to the solute load by multiplying the discharges by the solute concentrations. The units would be mass per unit time (or moles per unit time). If the mass flux is constant during downstream transport then there is no addition or subtraction of solutes from tributaries even though there may be changes in water flux. Mineral dissolution or contaminating tributaries will increase the mass flux and mineral precipitation will decrease it. There is an important caveat. Streams and rivers can gain or lose water from the subsurface. For losing streams, both mass flux and the discharge will decrease and to account for that a careful tracer injection study with stream gaging is needed. Quantification of mass fluxes are particularly useful for comparing different sources of contaminants in a catchment and predicting the improvement in water quality if selected waste sources are removed (Ball *et al.* 2004).

Results

Iron Mountain – visual

Figure 1 shows the typical red colour of dissolved ferric iron in Boulder Creek near Iron Mountain, California with pH of about 2.0 making a confluence with Spring Creek with a pH of about 2.4 after mixing. Figure 2 is an example of hydrous iron oxide precipitates on a boulder downstream in

Figure 1 Acid mine drainage from Iron Mountain where Boulder Creek makes confluence with Spring Creek (air photo by D.K. Nordstrom, 1985).
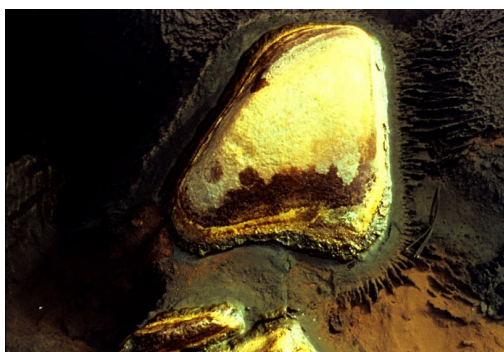

Figure 2 Boulder in Boulder Creek showing recent precipitates in yellow (schwertmannite) and aged precipitates in dark brown (goethite) (photo by D.K. Nordstrom, 1976).

Spring Creek showing the recent precipitate in yellow (schwertmannite) and older brown precipitates (goethite) that have aged.

Iron Mountain – Saturation indices

Saturation indices for $Fe(OH)_3$(am), which are very similar to those for freshly precipitating hydrous ferric oxide (ferrihydrite or schwertmannite), have often shown supersaturation by orders of magnitude in AMD. (Nordstrom 2011) This effect results from colloidal particles passing through the filter unit when the colloid concentration is substantially higher than the dissolved concentration of ferric iron (Nordstrom 2011).

For the downstream section from Boulder to Spring Creek (Fig. 1) and further downstream to Spring Creek Reservoir, a set

of data was selected from (Nordstrom 1977) collected on the same day. Most saturation indices were strongly undersaturated with the exception of $Fe(OH)_3$(am) which was approaching saturation (Fig. 3). The main reason for nearly ubiquitous undersaturation is the low pH (2-2.4).

Iron Mountain – Ion ratios

For the same set of data in Fig. 3, ion ratios for Fe/SO_4, Mg/SO_4, Al/SO_4, and Zn/SO_4 are plotted against decreasing sulfate concentration in Fig. 4, the direction of downstream flow. The source is Boulder Creek which has such a high sulfate concentration that it cannot be plotted on the same graph but the ratios for it are shown along the Y-axis. The ratios are all constant, reflecting
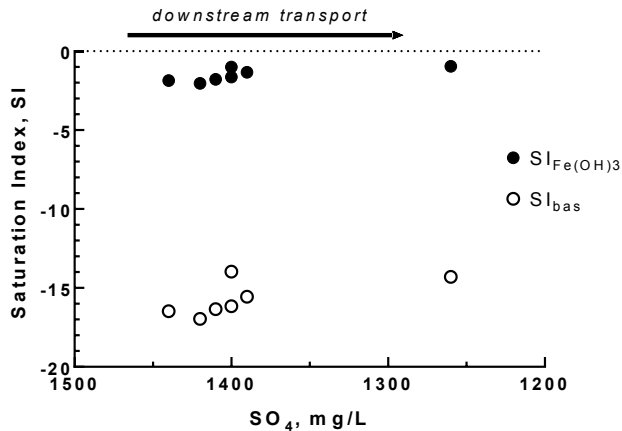

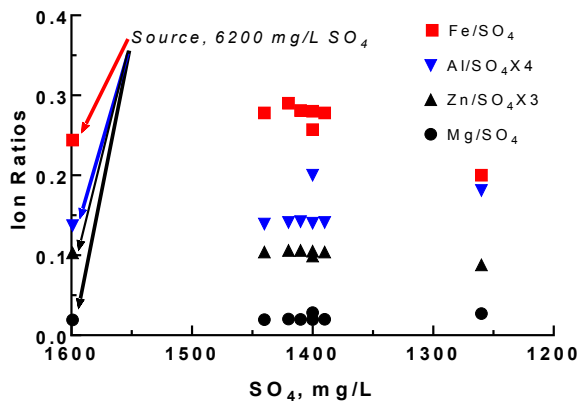Figure 3 Saturation indices for freshly precipitating hydrous ferric oxide, Fe(OH)3, and for basaluminite.

Figure 4 Ion ratios of iron, aluminium, zinc, and magnesium to sulfate with downstream transport and dilution.
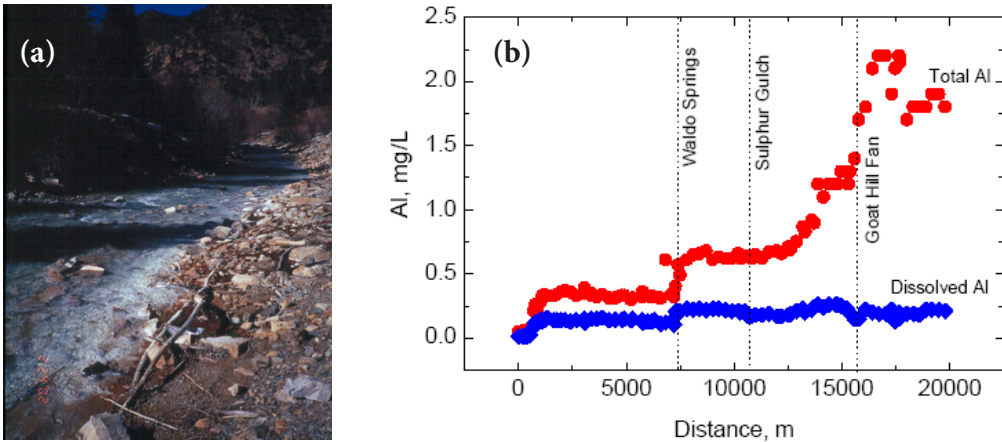
Figure 5(a) *White hydrous aluminium oxides precipitating along the banks of the Red River from acid groundwater seeping into a circumneutral pH river (photo by D.K. Nordstrom).*

Figure 5(b) *Total aluminium (red) and ultrafiltered dissolved aluminium (blue) over 20 km of the Red River (Nordstrom et al. 2008).*
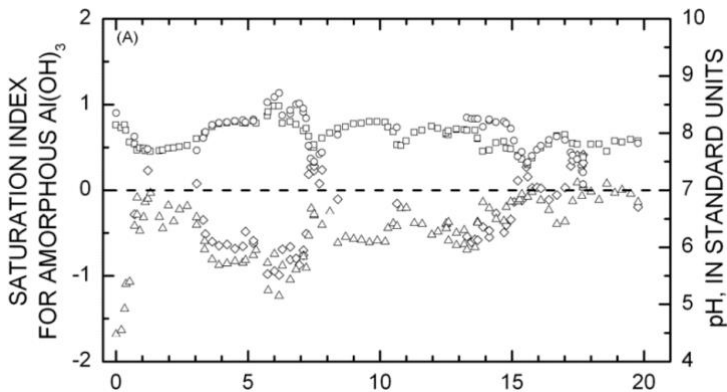

Figure 6 *The pH is shown in open circles and squares (for two profiles done 1 year apart) and the amorphous Al(OH)3 saturation indices are shown as open diamonds and open triangles for the same Red River profile as in Fig. 5b (Ball et al., 2005).*

the source with two exceptions. One sample at about 1400 mg/L SO_4 decreases slightly in the Fe/SO_4 and the Zn/SO_4 ratios and increases in the Mg/SO_4 and Al/SO_4 ratios. This anomaly is caused by a contaminated tributary with less dissolved iron and zinc and more dissolved magnesium and aluminium. The other exception is the last point at the lowest sulfate concentration. This sample has undergone nearly complete oxidation of dissolved iron and some of that iron has precipitated and some zinc and aluminium has been attenuated.

Iron Mountain – Mass fluxes

Water discharges from mine portals and major creeks at Iron Mountain were measured along with the water chemistry to determine the flux of hazardous metals from the catchment to the Sacramento River. Overall, some 270 tons of copper, zinc, and cadmium were discharged annually to the Sacramento River before remediation began. The largest single flux of metals was from the Richmond portal where some 209 tons of zinc discharged annually, and pH values were typically 0 to 1.5. The next largest

flux was from the Lawson portal, followed by weathering of waste piles in Slickrock Creek and Boulder Creek. Knowing these mass fluxes, the USEPA could prioritize the different sources for remediation.

Red River Valley – Visual observations

Naturally acidic groundwater seeps into the Red River in northern New Mexico and upon mixing and neutralization, hydrous aluminium oxides precipitate along the riverbanks (Fig. 5a). Total aluminium (unfiltered acidified sample) continually increases downstream, yet dissolved aluminium is maintained at a nearly constant value from solubility equilibrium with this hydrous aluminium oxide (Fig. 5b).

Red River Valley – Saturation indices

Saturation indices are shown (Fig. 6) for amorphous $Al(OH)_3$ with the same set of data shown in Fig. 5b.

There are several points where natural acid groundwaters seep into the Red River, as shown by the dips in the pH data of Fig. 6, and the saturation indices are close to or at the equilibrium value. In this example the saturation indices match the visual observations and suggest aluminium precipitation.

Red River Valley – Ion ratios

In contrast to the suggestion of aluminium precipitation by SI values, a stronger case is made by ion ratios. In Fig. 7 a plot of Al/SO_4 ratios are shown for acid groundwaters from the Straight Creek catchment and continuing downstream in the Red River.

From Figs. 7 (a) and 7 (b) it is clear that aluminium is conservative like sulfate until a pH of about 4 or higher is reached and then substantial amounts of aluminium are precipitated. Aluminium can be conservative or non-conservative which depends primarily on pH. Fig. 7 also shows the amount of aluminium precipitated in a given volume of water. To determine quantitatively the total amount of aluminium precipitated, the discharge of acid water into the Red River must be measured or estimated.

Conclusions

Visual observation, saturation indices, element ratios, and mass fluxes, when combined, give a remarkably clear picture of the processes of iron and aluminium precipitation in both groundwater and surface water from the mixing and neutralization of ARD. Each approach has a role in quantifying contaminant transport and each must be understood to have certain limitations.

References

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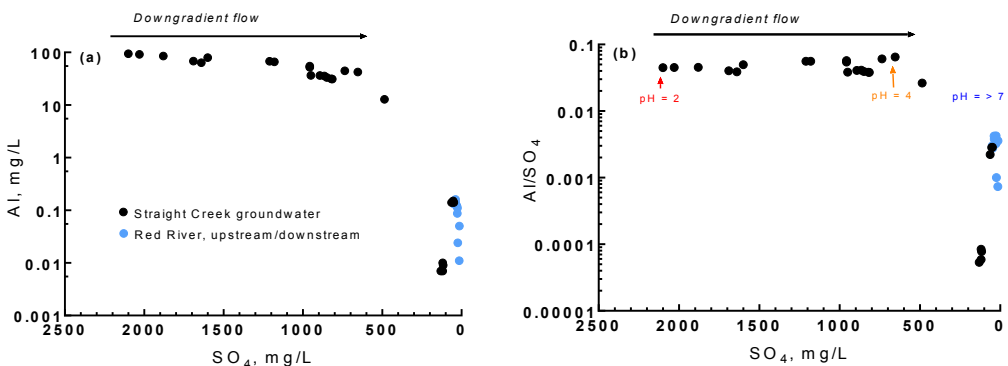

Figure 7(a) Plot of aluminium concentrations with decreasing downgradient sulfate for the Straight Creek drainage, groundwater, and the receiving water of the Red River.

Figure 7(b) Plot of Al/SO_4 ratios against downgradient sulfate for the same data points as in (a).

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