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Natural clean-up of a stream contaminated by mine and mill wastes: A reaction analogous to liming in water treatment

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ABSTRACT: Boulder Creek is a small stream in an arid region of the U.S.A. The non-contaminated water of the stream has a high pH and high alkalinity. Metal-rich, acidic mine-water seeps into the creek at two locations. Contaminants are rapidly precipitated below the points of mixing, in reactions that are similar to liming in water treatment. Computer modeling with PHREEQE generally verifies the precipitation mechanism.

1 INTRODUCTION

Boulder Creek comprises one of the major watercourses in an otherwise arid region of western Arizona, U.S.A. The stream supports a rich diversity of wildlife. Areas of the drainage of Boulder Creek are highly mineralized with a variety of metals. The abandoned Hillside mine-mill complex, on the banks of the creek, includes tailings, waste piles, and collapsed adits and shafts. The mine, which operated from the 1880's to the 1950's, extracted chiefly gold and silver, with arsenopyrite and pyrite as major gangue minerals. A variety of other precious-metal and base-metal ores from the surrounding region were also processed at the mill.

The creek and seepage waters were studied over a period of about three years. Systematic sampling was conducted over one entire year to measure seasonal changes.

Seepage of metal-rich waters from tailings and a collapsed mine adit enter the stream at two distinct points. At seasonal low water, heavy precipitates of Fe, As, Al, Cu, and other metals form almost instantaneously below the points at which contaminated waters mix with creek water. Virtually complete devastation of stream biota occurs below the points of mixing, but recovery is very rapid downstream. During periods of high-water, dilution and mixing of the water and sediment quickly disperse the precipitated metals.

2 COMPOSITIONS OF WATERS

Water in the upstream non-polluted portions of Boulder Creek has a pH as high as 8.5, alkalinity up to 282 mg/L as $CaCO_3$, and is rich in dissolved oxygen. The water is predominantly Na-Ca-HCO_3 in composition. A maximum concentration of 515 mg/L TDS was measured in the upstream portions of the stream at low water in August. Below the mine and mill complex the alkalinity, bicarbonate, and pH decrease, with increases in sulfate, TDS, and dissolved and particulate metals. Two distinct seepages from the mine and mill wastes into the stream can be recognized. The first and most important is an acidic seepage from the base of the uppermost tailings pile. This water has a pH of 2.4 and concentrations (in mg/L) up to 8550 TDS, 5240 SO_4, 260 Al, 34 As, 100 Cu, 610 Fe, 52 Mn, and 92 Si. The tailings seepage appears to be oxygenated, with iron in the Fe(III) state. Filtration using a 0.45 um membrane filter shows that from 30% to 95% of the metal in the seepage water is in dissolved form, depending on the metal.

The second seepage comes from a collapsed mine adit downstream an additional 1250 meters. The water from the collapsed adit has a pH of 5.4 and contains (in mg/L) up to 2640 TDS, 1480 SO_4, 21 As, 68 Fe, 45 Mn, 9.5 Zn, 19 Si, but non-detectable concentrations of Al and Cu. The adit water is lower in oxygen than the tailings seepage, with iron largely in the Fe(II) form.

Upon entry of the seepage waters, iron and As are the first metals to precipitate, followed by Al and Cu, with Mn, Zn, and Cd being the most mobile.

As the seepage waters mix with stream water, heavy precipitation occurs. Immediately downstream from the tailings seepage, a heavy floc of reddish-brown material forms, and during low-water it quickly settles to the bottom of the stream. Chemical analysis shows that this material is mainly iron oxyhydroxide, enriched in As and SO_4. About 20 meters farther downstream a heavy greenish-white precipitate forms and is rich in Al and Cu. Stream biota are sparse to absent at the locations of heavy precipitation of metals, especially during periods of low water. However, at a distance of approximately 1100 meters downstream, the water is clear, the pH has again risen to 8.4, and most of the metals have precipitated. At this downstream location the stream is again rich in aquatic plants, insects, and fish. It is obvious that the alkaline, oxygenated water of the stream is very effective in causing the precipitation and removal of the most toxic metals and thus allowing a rapid recovery of the stream. Such a rapid recovery would certainly not be the case for less alkaline, more dilute streams in a more temperate climate. For example, in the mountains of Colorado, severe contamination of streams may extend for tens of kilometers below point sources of acid-mine drainage.

Depending on the season and the metal, as much as 90% of the metal in the stream water is in particulate form.

The removal of dissolved metals from the water is very clearly reflected by increases in the metals in the stream sediments at the corresponding locations. Computer modeling (WATEQF - Plummer et al., 1976) suggests that the Fe-rich precipitate is probably a jarosite and that the Al-rich precipitate is probably jurbanite, in agreement with similar studies by Nordstrom (1982), Chapman et al. (1983), Filipek et al. (1987), and Karathanasis et al. (1988).

3 TITRATION MODELING

In the field, the flow of contaminating seepage waters into Boulder Creek appears to be similar to a titration that might be performed in the laboratory. That is, the water of the creek is essentially titrated by metal-rich waters at two seepage locations, the upstream tailings pile and the downstream collapsed adit.

To test the concept that the mixing simulates a titration, the "titration mode" of the computer model PHREEQE (Parkhurst et al., 1980) was used, in which adit seepage water was added in 5 mL increments, up to a total of 50 mL, to a hypothetical initial volume of 50 mL of creek water. The volumes of water to be used in the model titration were estimated by calculating a mass balance for the analyzed concentrations of Cl and SO_4 in the creek water above and below the point at which the adit seepage enters and mixes with the creek water. Chloride and SO_4 were chosen for the mass balance because they are probably the most conservative of the dissolved species. The mixed value of Cl below the point at which the adit water enters the creek yields a calculated volume of 50 mL of seepage water added to 50 mL of creek water, and SO_4 in the mixed water yields a calculated mixture of 42 mL of seepage water and 58 mL of creek water. The adit seepage was chosen for this exercise because the point of mixing is easily observed and sampled in the field; in contrast, the flow of seepage water from the upstream tailings into the creek is diffuse and difficult to observe. Table 1 summarizes the chemical compositions of adit water and creek water that were used to calculate the volumes of water in the model titration.

Table 1. Dissolved components (mg/L) in adit water and in Boulder Creek at points immediately upstream and downstream from mixing with adit water. (0.45 um filter)

Component	creek above	adit seep	creek below
$T^{o}C$	30	22	averaged
pH	6.7	5.4	6.6
Ca	55	332	229
Mg	40	146	101
Na	101	92	115
K	9.8	11	11
Cl	42	24	33
SO_4	335	1430	971
F	4.2	6.2	5.1
Mn	24	36	24
Si	6.6	19	13
alkal. ($CaCO_3$)	158	145	117

A preliminary run with PHREEQE yielded a Pco_2 value of E-1.4 atm. for the mixed pool below the point of mixing, and this value was fixed for the titration. The Eh was estimated to be (+)400 mV for the adit water and was held constant throughout the

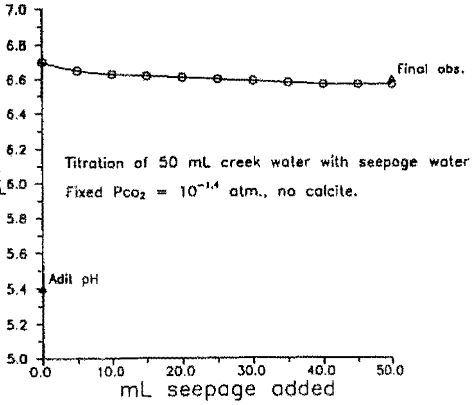

Fig. 1 Calculated pH of a mixture of 50 mL of creek water titrated with 5 mL increments of adit seepage water. Triangles represent measured values. Initial pH value of creek water is shown by first circle (at 0.0 mL adit water added).

titration. The temperature of the mixed water was a linear average between the creek water at 30°C and the adit water at 22°C Figure 1 shows the results of the simulated pH from the titration, compared to the actual pH measured in a pool of mixed water below the entry point of the adit water; the agreement is excellent.

Figure 2 shows the computed alkalinity versus the observed alkalinity; again, the agreement is quite good. The titration was assumed to take place in the absence of calcite; if calcite is assumed to be present, the computed alkalinity in the mixed water rises to very high and unrealistic values.

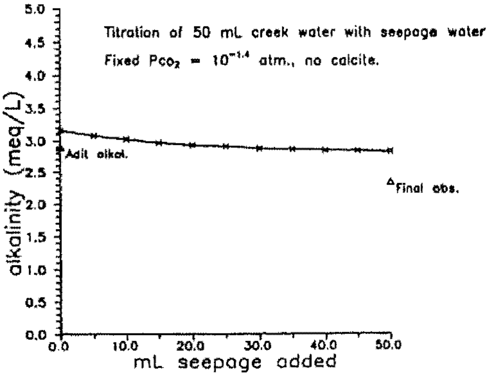

Fig. 2 Calculated alkalinity of a mixture of 50 mL of creek water titrated with 5 mL increments of adit seepage water. Triangles represent measured values. Initial alkalinity of creek water is shown by first circle (at 0.0 mL of adit water added).

Finally, Figure 3 shows the predicted sequence of precipitation and dissolution of solid compounds resulting from the hypothetical titration.

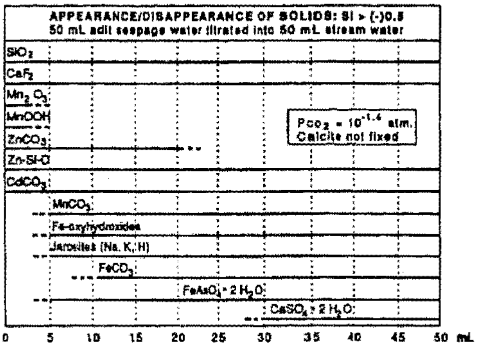

Fig. 3 Predicted sequence of precipitation and dissolution of minerals from mixtures of adit water and creek water, as a function of volume of adit water added to 50 mL of creek water. Plotted according to computed saturation indices; see text for details.

Solids are shown on Figure 3 if the computed saturation index was either positive (representing supersaturation) or, if the saturation index was negative (representing undersaturation), it was more positive than (-) 0.5.

We did not attempt to identify the solid phases present in the stream sediment, but the predictions of Figure 3 seem reasonable. In particular, the early precipitation of Fe (potentially in several forms) and As (as scorodite) is interesting and fits the field observations. The potential for early mobility of Mn and Zn due to undersaturation, followed by later saturation also fits the field observations. Neither Al nor Cu was detectable in the waters involved so that those components could not be modeled.

4 CONCLUSIONS

During the course of this study it was found that dissolved metals and other contaminants are quickly and strongly precipitated by mixing of metal-rich mine waters with normal creek water. This occurs largely because of the alkaline, wellbuffered nature of the stream water in this arid region. In the relatively short distance of about two km downstream from the points of contamination, the stream recovers sufficiently to support an abundant aquatic flora and fauna. The chemical reactions can be modeled as a simple titration of metal-rich seepage water into creek water, in a ratio of about 1:1. In a more temperate climate, the distance of severe contamination downstream would probably be at least tens of kilometers. Based on the field observations and chemical measurements, the regulatory agencies involved in the study concluded that clean-up of this site should be left to nature. A decision was therefore made that the "no-action" alternative would be most protective of the environment.

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