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Hydro-Geochemical Behavior of Bicarbonate and Sulfate Ions Leaching from a Sulfide-Poor Silver Mine in Central Mexico: Potential Indicator of Acid Mine Drainage

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Acid mine drainage (AMD) and high heavy metal concentrations in surface and groundwater have been reported as a major problem in and around sulfide-rich mineralized zones worldwide. In fact, there are national and international programs for prevention and monitoring AMD in several countries (Breahut, 2000; Hoglund, 2000; Shea, 2000; Tremblay, 2000). Most of the reported environmental evaluations of AMD in the literature have been done in sulfide-rich mines located at medium latitudes and temperate climate (Banwart and Malmström, 2001; Simms et al., 2000; Younger, 2000; Kim and Chon, 1991). Several efforts have been made for predicting potential for AMD by static and kinetic tests (Sobek et al., 1978, White et al, 1999), and by field experiments (Bencala and Ortiz, 1994). Another line of research in environmental geochemistry has focused on hydrogeochemical modeling of AMD, especially forward or predictive mathematical modeling (Banwart and Malmström, 2001; Brown et al., 2000).

Central Mexico mineralized districts offer good opportunities to explore natural and anthropogenic AMD processes at a variety of climates (from arid, to semi-arid and to humid semi-tropical environments), and in sulfide-rich and sulfide-poor mineralized areas. On the other hand, the hydrogeochemical behavior of the bicarbonate and sulfate ions from different environments: (a) recharge area (mountain springs); (b) mine water; (c) leachates from the tailing impoundments, (d) groundwater; and (e) surface water beyond the mineralizing zone (downstream), are important indicators of the pH balance in the natural system (acid producing and acid consuming reactions).

The historical mine of Zacualpan (exploited since late 1500´s), located some 250 km southwest of Mexico City was selected for analysis of the bicarbonate-sulfate balance, and other geochemical controls in the natural environment and mine tailings impoundments. The main ore from which the mine has been producing silver and lead is sphalerite, galena, stephanite, polybasite, argentite, proustite, pyrargyrite, chalcocite, chalcopyrite and pyrite. Calcite and quartz are present in variable quantities, and are the most important gangue minerals (Villaseñor et al.,

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1993). Currently, there are two tailing impoundments in a low-latitude, humid, semi-tropical to temperate climate at the site. The mining works are done through several adits (La Llave, La Cuchara and Mexico) with a potential risk for AMD. The tailing impoundments have a combined volume of some 400,000 tons and are located on a mountainside at 1,810 m above sea level at the northern slope of the Balsas basin, the Balsas River being a major river in south central Mexico (Figure 1). In this work, we present hydrogeochemical data from near-recharge area water (mountain springs), mine water, leachates from tailing impoundments, and surface creeks downstream from the mine. We also discuss the importance of bicarbonate and sulfate variations in the aqueous system as potential indicators of acid-producing and acid-consuming reactions (interaction water-host minerals) and long term AMD potential in the zone.

MATERIALS AND METHODS

A total of 34 water samples were collected in and around the sulfide-poor silver and lead mine of Zacualpan. Twelve of the samples are from near-recharge-mountain springs; twelve samples are from mine water from different levels inside the mine; 5 samples are from the leachates of the mine tailing impoundments, and the other 5 samples were collected at surface creeks downstream from the tailing impoundments (Figure 1). Sampling was done during the dry seasons (April-May) of 1998 and 2001, and during the peak of the rainy season (September) of 2000. The samples were collected in acid washed, high-density polypropylene 100 ml bottles using 0.45 microns membrane filtration syringes. Two samples were collected at each site, one for sulfate and other anions analyses, and other acidified to pH=2 with concentrated HNO_3 for cation analysis. Temperature, electric conductivity, pH, and alkalinity were measured directly in the field immediately after taking the sample. Alkalinity was determined using digital titration (Hach titration) with 1.6 N H_2SO_4 to pH 3.5. The pH probe was calibrated with commercial standard buffers at pH 4, 7 and 10 after each alkalinity measurement. Samples were transported in a cooler chest at 4°C for analyses of anions with HPLC and cation analyses with AA and ICP-MS at the Geochemistry Laboratory at the University of Wyoming.

RESULTS AND DISCUSSION

Stiff diagrams (Figure 2) for all the samples show that the mountain spring-water (a), mine water from the shallowest level (140; b); and some creeks downstream from mine tailings (e) are bicarbonate-rich type of water. In contrast, samples from the tailings impoundments (d); and mine-water from the deepest level (245; c) belong to sulfate-rich type of water. Dissolution of sulfide minerals should be occurring between levels 140 and 245 because the transition from bicarbonate (calcite dissolution controlled system) to sulfate (sulfide dissolution controlled system) types of water occurs between these two levels. The sulfate ion for all the samples shows an evolution towards increasing concentration from the mountain

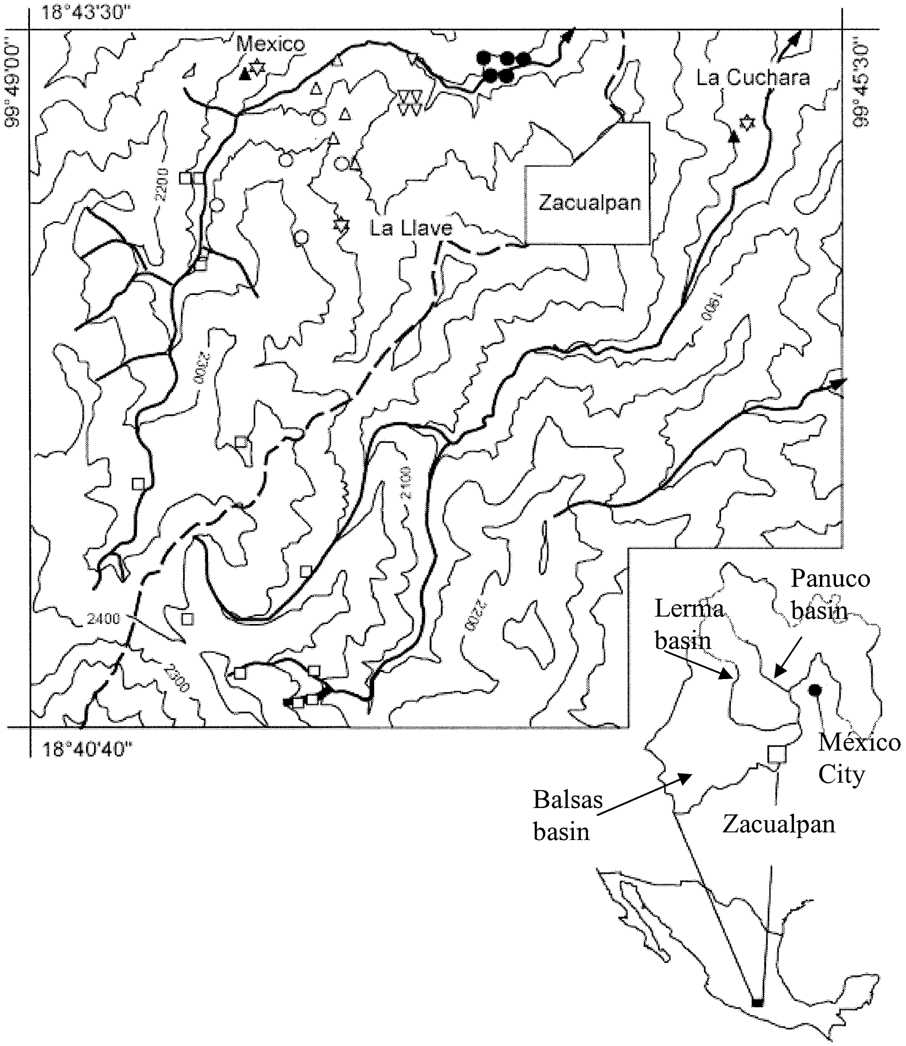

Figure 1. Location map of the Zacualpan Mine and location of water samples.

□ **Water samples from Mountain Creeks**
▲ **Mine-water samples (level 50)**
△ **Mine-water samples (level 140)**
○ **Mine-water samples (level 245)**
∇ **Water from tailings impoundments**
● **Water samples of surface downstream creeks from the tailings**
☆ **Mine adit entrance**

spring water to the mine-water and leachates from the mine tailing impoundments. These sulfate increases could result from depletion of calcite and continuing dissolution of sulfide minerals along the path of groundwater flow. Figure 3 shows a plot of total dissolved solids (TDS) vs. concentration of sulfate.

The regression line (Fig. 3) indicates a clear direct relationship between the TDS and sulfate. Therefore, it is suggested that the major process controlling water chemistry is dissolution of metal sulfides. The sulfate concentration ranges between 8 and 56 mg/l in the samples from the mountain springs and creeks, and between 755 and 949 mg/l in the leachates from the tailing impoundments. For the metallurgical process (flotation) to concentrate the metal ore, the processing plant at the mine site uses mine-water from the level 245, which is pumped to the surface. This mine-water (level 245) has a sulfate concentration ranging from 181 to 586 mg/l. The water from this level inside the mine shows a significant increase of sulfate with respect to the mountain springs and some surface water (creeks). This increase could be explained by a longer reaction time of the groundwater with the metal sulfide bearing host rock. At all the sampling sites, the leachates from the mine tailings increased in sulfate concentration. This fact makes the sulfate a conservative ion because it is the ion with the greatest impact on the TDS. Bencala and Ortiz (1999) did a successive mass balance comparison on the sulfate data collected during an environmental characterization at the inactive mine site at Summitville, Colorado. They conclude that the sulfate may likely precipitate to some degree in the coatings of the streambed, but the high concentrations of sulfate indicate a relatively low loss in precipitates. Thus, while not ideally conservative, sulfate may act as a useful ambient tracer.

Calcium presents a similar behavior to the sulfate. Calcium increases its concentration as the water increases its time of contact with the sulfide bearing rock. The samples with lower Ca concentrations correspond to the mountain springs and surface creeks, whereas the highest Ca concentrations belong to the deepest level water-mine samples (level 245) and leachates from the tailing impoundments. Figure 4 shows two evolution lines for Ca. The first line (continuous line) corresponds to increase of Ca concentration without the influence of mining activities (natural water-rock interaction). The second line (dotted line) corresponds to increase of Ca by the interaction of water with mine tailings.

The bicarbonate concentrations from all the samples of the Zacualpan mining district point to a hydro-chemical evolution dominated by mixing of waters from the different environments as the main controlling process. The bicarbonate concentrations in the creeks and mountain spring waters range from 23 to 95 mg/l, whereas the concentration of bicarbonate in the leachates from tailing impoundments range from 131 to 300 mg/l. This evolution trend includes the mine water from different levels (depths). The concentration of bicarbonate increases rapidly from the mountain creeks and springs (reference baseline),

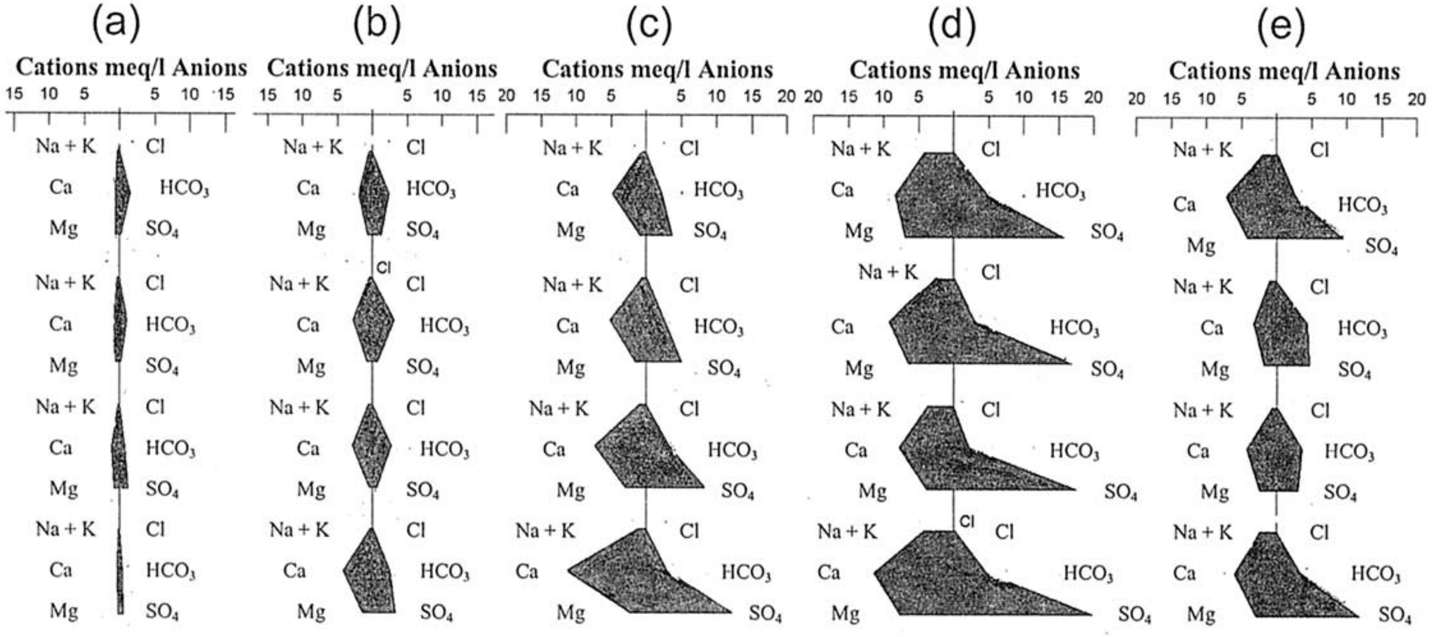

Figure 2. Stiff diagram of representative water samples from Zacualpan mine district: (a) Mountain springs; (b) Mine water (level 140); (c) Mine water (level 245); (d) Leachates from tailings impoundments; (e) Downstream from tailing impoundments. The trend (a)-(b)-(c) indicates a natural hydrogeochemical evolution (from HCO$_3$-rich water to SO$_4$-rich water); (d) is an anthropogenic sulfate enriched water [(c) + metallurgical reagents]; and (e) is the result of the mixing between (a) and (d), with dilution as the main process.

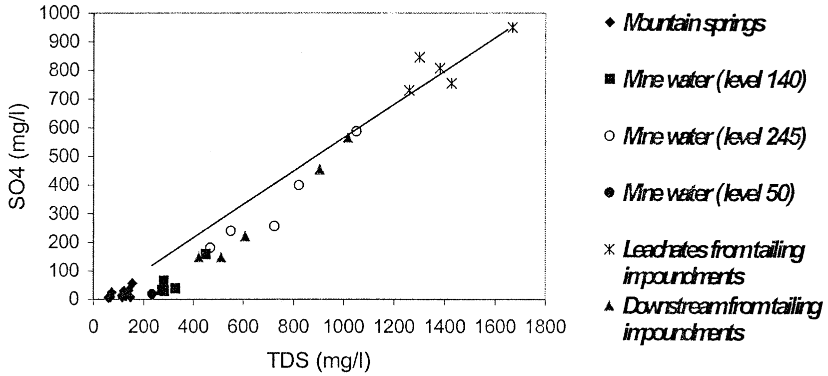

Figure 3. Relationship between TDS and SO_4. The straight line shows SO_4 as major ion influencing TDS.

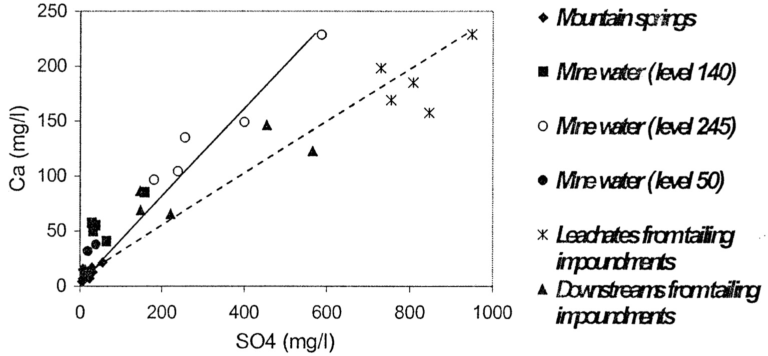

Figure 4. The continuous line shows natural evolution in concentration of Ca ion. Doted line shows evolution in concentration of Ca ion due to mining activity.

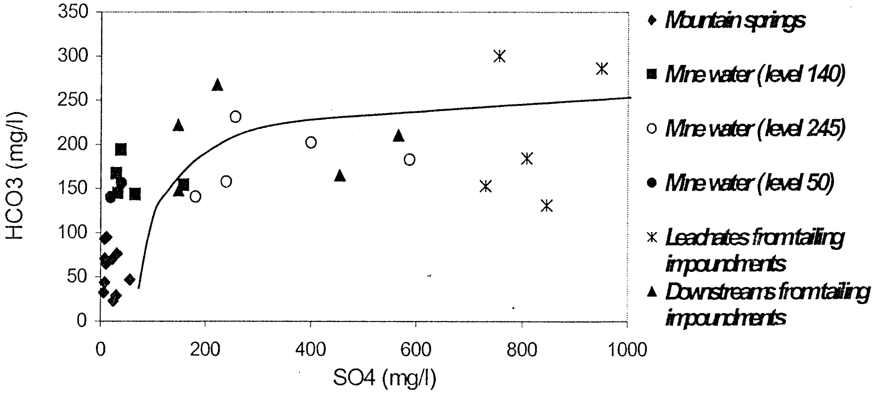

Figure 5. Relationship between HCO_3 and SO_4 in water samples from Zacualpan.

towards the location of samples from mine-water from the level 140, which indicates a water chemistry dominated by calcite dissolution (Figure 5). From that point on, the bicarbonate increases less rapidly (asymptotic) towards the level 245 (deepest mine level), where the sulfide dissolution surpasses calcite dissolution. Figure 5 shows a sulfate vs. bicarbonate plot, demonstrating this hydrogeochemical evolution and the position of the different groups of waters (mountain springs, surface creeks, mine water from different levels and leachates from mine tailings).

There are relatively few major processes controlling natural water chemistry (Nordstrom and Alpers, 1999). One of these is dissolution (oxidation) of pyrite, which is an acid-producing reaction and controls the sulfate concentration in the water. Field experiments at a mine site by Bencala and Ortiz (1999) indicate that sulfate may act as a useful conservative ambient tracer. Another of these processes controlling water chemistry is the dissolution of calcite and other carbonates, which are acid-consuming reactions and control the concentration of bicarbonate in water. The relative concentrations of bicarbonate and sulfate are a good indicator of the natural balance between acid-producing and acid-consuming reactions. At the Zacualpan area, the hydrogeochemical evolution indicates that an increase in sulfate (dissolution of pyrite) coincides with a decrease in bicarbonate (acid consuming reaction). Thus, it is suggested that once the mining operation shuts down at Zacualpan, the sulfate concentration in water could surpass the bicarbonate concentrations when the acid-producing reactions overcome the acid-consuming reactions. Hence, the potential for generation of acid drainage remains latent at the Zacualpan mining site. Future work will focus on continuing the monitoring of surface and groundwater, and experimentally testing the sulfide bearing minerals for AMD. Currently, there are three 2 m long leaching column experiments running for better evaluation of the potential AMD of the mine waste material.

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