

**FATE OF HEAVY METALS IN COLORADO WATERS AND
RIVERS**

by

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ABSTRACT

Reclamation of contaminated wetlands polluted by acid mine drainage will require a greater understanding of the interaction between contaminated waters and sediments. In high altitude meadows, continual flooding can maintain an anaerobic condition. Oxidized sediments showed an increase in Zn and total S concentration, compared to sediment-solution at initially taken from the site. The addition of acid mine water to sediments in a reducing environment had a significant effect on Zn concentrations. The addition of electrons from organic substrates lowered the concentration of Zn by approximately 10 fold. As expected, the reduction process also lowered redox (p_e and $p_e + pH$) and decreased total sulfur in solution. Zn sulfide precipitation was verified with the chemical speciation program, MINTEQA2.

INTRODUCTION

Mountain meadow wetlands in Colorado often intercepts acid mine water as it flows towards larger stream and rivers. If these wetlands are drained, a contamination threat to downstream waters exists. If these wetlands are continually submerged, existing contamination risks are lowered and incoming acid mine waters are detoxified. This detoxification can be separated into two components: 1) adsorption of heavy metals by the organic material present in the sediments, and 2) precipitation of heavy metals by reduction processes. Considerable work has been done

on the adsorption process but only sparse research has been done on the reduction process. The purpose of this study was to provide an in depth examination of reduction as a detoxification process for reclaiming acid mine waters.

We investigated the reduction-precipitation of Zn in the mountain meadows near Leadville, Colorado. Zinc was chosen since it is the major heavy metal pollutant in this area and it is usually the first heavy metal to precipitate as a sulfide. Reduction processes have a great potential for lowering inputs from acid mine drainage. We initiated a study to further understand the potential for reduction to detoxify acid mine drainage in Colorado's mountain meadows. This remediation approach requires a minimal cost compared to soil removal.

OBJECTIVES

When mining ores and waste containing sulfides are allowed to oxidize the solubility of metals contained in the ores and sediments greatly increase. Reversing this process through microbial reduction precipitates many heavy metals as sulfides (Machel, 1989) and at the same time increases pH (Lundin, 1990). Our objective was to investigate the oxidation and reduction process in sediments previously contaminated by acid mine water. The effect of oxidation on fresh sediments was followed by a study contaminated water effects in reducing and oxidizing environments.

BACKGROUND INFORMATION

In geologic terms, Leadville, Colorado is an ideal area to study redox transformations of heavy metals. The primary geologic materials is a metal sulfide deposition including lead, gold, zinc, silver, iron and arsenic. In addition to the sulfide deposits, dolomitic limestone containing zinc silicates, copper carbonates, lead oxides are often present (Levy, 1989). The mining boom of the 1800's removed large amounts of these ores for extraction silver and gold. Tailings from the mining activity were removed to outlying areas or stored in situ. Tailings containing metal sulfides oxidized slowly under contact with atmospheric oxygen. This oxidation process transforms sulfides to sulfates and releases protons, thus acidifying the system. The acidification process solubilizes metals associated with the resultant sulfides. Ultimately, water in contact with these tailings move downslope and flow across mountain meadows until discharged into the Arkansas river. These meadows consist of highly reduced bog areas. With time these metals interact with the bog soils and re-precipitate as metal sulfides or they are absorbed by the organic matter. The precipitation of heavy metals in reduced environment of mountain meadows is a potentially important decontamination process.

METHODS AND MATERIALS

Sites near the confluence of California Gulch and the

Arkansas River meadows of the Edith Seppi ranch were chosen for this study. This area has a history of heavy metal contamination originating from acid mine waters of the Leadville mining area to the east. Historically, contaminated wastes from California gulch flowed across these meadows. We selected 10 sites to sample water currently used for irrigation (Fig. 1). Water currently diverted from the Arkansas river upstream from California gulch flows from the Arkansas river (site 10), across the meadows (sites 9 through 2) and ultimately into the Arkansas river (site 1). Sediments and water flowing over the sediments was collected during irrigation in the mid-summer of 1991. Water and sediments were immediately placed into 1 L containers, purged with argon gas to inhibit oxidation, and the samples were sealed. Water samples were filtered through 0.2 μ filters, then measured for pH, E.C. and pe. Within one week of collection, this water was measured for important cations using ICP (inductively coupled plasma) and important anions by ion chromatography. We predicted that if Zn sulfides were present in these samples, Zn and S concentrations would increase during a long term oxidation experiment. We predicted that long term reducing conditions would decrease the total concentration of Zn, increase pH, and lower total S in solution.

LABORATORY METHODS

Three experiments were conducted: long term oxidation, long-term oxidation with added acid mine water, and long-term

reduction with acid mine water. In all experiments, 35 g of sediment was added to a 60 ml total volume of solution defined below. These experiments were continued for 85 d. In both the reduced and oxidized experiments containing acid mine water, 15 g of organic material from the surface of a non-contaminated bog from the nearby vicinity was added. This treatment was included in the reduction study as an organic microbe substrate to supply electrons for reduction. It was also included in the oxidized study to equalize any Zn adsorption resulting from this material.

To the oxidized experiment without mine water, 60 ml of distilled-deionized water was added. In the oxidized experiment containing mine water, 40 ml of distilled-deionized water was added to 20 ml of acid mine water. This ratio was chosen to approximate dilutions resulting irrigation history. The acid mine water was collected from the headwaters of California Gulch, simulating a water composition similar to that which was originally applied. The mixture had the following composition;

Zn = 83.5 μ M

Fe = 25.6 μ M

Mn = 116.2 μ M

S = 773.8 μ M

pH = 5.3

The sediment and solution in all experiments was placed in a 125 ml erlenmeyer flask then placed on an orbital shaker at 60 orbital min⁻¹. For the reduction experiment, the headspace within

the flasks was purged with a gas mixture of 95% argon to insure anoxic conditions and 5% CO₂ to simulate the elevated wetland carbon dioxide concentrations. This gas mixture was pulsed for 15 sec at 5 min intervals throughout the experiment by means of a timed solenoid valve connected to the compressed gas source. Flasks were connected in a series of three in the aeration stream. In the oxidizing experiments, compressed air was added continuously instead of pulsed.

After 85 d, the flasks from the reducing experiment were removed from the shaker and measurements of Eh and pH was made. This was accomplished by removing a 30 ml aliquot of the sediment-solution and placing it into a 50 ml centrifuge tube fitted with two septums purged with a 5% CO₂ and 95% gas mixture. At this time a cap fitted with a combination pH electrode and platinum electrode and gas inlet and outlet were fitted to the centrifuge tube. The electrodes were connected to a electrode switching unit and pH/Eh meter. The centrifuge tube was then fitted with a septum fitted cap and gas inlet and outlet septum. After purging with the gas mixture, the sample was centrifuged at 18,000 rpm for 12 min. An aliquot of 10 ml was passed through a 0.2 u filter. These precautions were used to avoid oxidation of the sediment solution sample. For cations a 5 ml aliquot of this solution of this aliquot was acidified with 15 μ L of concentrated HCl to prevent precipitation of metal oxides. The second 5 ml was used to measure E.C. and all anions. For the oxidizing experiments, samples for analysis were taken by

centrifuging and filtering the supernatant through a 0.2 μ filter.

RESULTS

OXIDATION EXPERIMENT

Our first objective was to determine the effect of oxidation of the sediments on Zn and S concentrations. We hypothesized that the anoxic nature of the meadow area would maintain a low concentration of Zn in surface waters. Since surface waters are in constant contact with atmospheric oxygen, their redox measurement will not be representative of the actual subsurface redox conditions. If subsurface waters are oxidized, high concentrations of Zn resulting from ZnS oxidation would be measured. Thus if Zn sulfides were present, the concentration of Zn would be increased during a long term oxidation experiment.

The effect of the long term oxidation is seen in Fig 2. The mean Zn concentration was 20.81 μ M for the oxidized samples, while the initial sampling was 1.79 μ M, a 12-fold increase in Zn concentration. If Zn levels are elevated, it follows that total S concentrations should also increase. This was verified as seen from Fig.3, indicating an increase in total S concentration from 417 μ M to 617 μ M during oxidation. These results strongly suggest that with time Zn sulfides precipitate within these meadows. Drainage and subsequent oxidation of these meadows on the other hand are expected to increase Zn levels within these sediments.

REDUCTION EXPERIMENT

Since organic matter additions were equal for both the oxidized and reduced experiments containing acid mine water, it is assumed that any changes in solution chemistry were due to microbial reduction. The following results indicate several important differences that resulted from reduction. As mentioned previously, important indicators for Zn sulfide precipitation are: increased pH, decreased redox (pe and pe + pH) and decreased total Zn and S concentrations. From Fig. 4, it is shown that redox levels, reported as pe, are dramatically lower in the reduced sediments, a mean of -2.57 compared to 6.17. Since zinc sulfide precipitation consumes hydrogen ions, it follows that pH should increase. Figure 5 shows at least a whole unit increase in pH with reduction. The redox parameter (pe + pH) showed a considerable mean difference (Fig. 6) with the reduced sediments 8 pe + pH units below the oxidized sediments. Finally, zinc levels shown in Fig. 7 to be dramatically reduced (from mean μM of 19.81 to 2.89) for the reduced sediments. The total S data in Fig. 8, show a similar reduction with an average of 615 μM S decrease.

DISCUSSION

We have shown that reduction of sediments in the presence of acid mine water significantly reduced the Zn concentration in solution. This disappearance of zinc is the result of the addition of electrons to the solution environment. This

conclusion is based on the decrease in both S and Zn in solution, the lower redox levels and increased pH in the reduction experiment. Comparison of the initial waters to the same sediments under long term oxidization, indicate Zn sulfides were present in the meadows as Zn and S both increased upon oxidation.

Metal sulfides precipitation depend in part on the solubility the mineral source of the metal to be precipitated and the availability of electrons. In our study, we supplied electrons via the oxidation of organic material by microbes. Solubility characteristics of the source mineral was provided by comparing the important solution measurements to known solubility data. This was accomplished by the use of the EPA chemical speciation model, MINTEQA2. Lindsay (1979) suggested that the mineral sphalerite ZnS , is the most probable zinc sulfide to form under surface sediment environments. The saturation indices based on ion activity products (IAP) of all ten sites are shown in Table 1. A negative number indicates under saturation while a positive number indicates precipitation or oversaturation. For seven soils, the solution composition suggests this mineral has precipitated while three samples are undersaturated. These results confirm our hypothesis that Zn sulfides have formed and are responsible for the reduction of Zn in solution.

SUMMARY

We have found that microbial reduction in mountain meadow sediments has a significant effect on decreasing soluble zinc in

associated waters. Although organic complexation has been shown to be important heavy metal sink, we have shown that in the case of zinc, reduction and the subsequent formation of sulfides is also an important decontamination process. These findings have two important implications for wetland management. First, mountain meadows have a potential for detoxifying large amounts of heavy metals. Secondly, meadows previously contaminated naturally or through mining activities have a high potential for downstream pollution if these meadows are drained. The methodology used in this study suggest an economical approach for management of wetlands in helping to reduce heavy metal pollution in Colorado streams.

REFERENCES

Levy, D.B., Barbarick, K.A., Siemer E.G. and L.E. Summers. 1989. Heavy Metal Contamination of Soils and Plant Species of the Arkansas Valley Near Leadville, Colorado. Technical report TR89-7. Colorado Agricultural Experiment Station.

Lindsay, W.L. 1979. Chemical Equilibria in Soils. John Wiley & Sons. New York.

Lundin, L., and B. Bergquist. 1990. Effects On Water Chemistry After Drainage of a Bog for Forestry. *Hydrobiologia* 196:167-181.

Machel, H.G. 1989. Relationships Between Sulphate Reduction and Oxidation of Organic Copounds to Carbonate Diagenesis, Hydrocarbon Accumulations, Salt Domes, and Metal Supleide Deposits. *Carbonates and Evaporites*. 4:137-151.

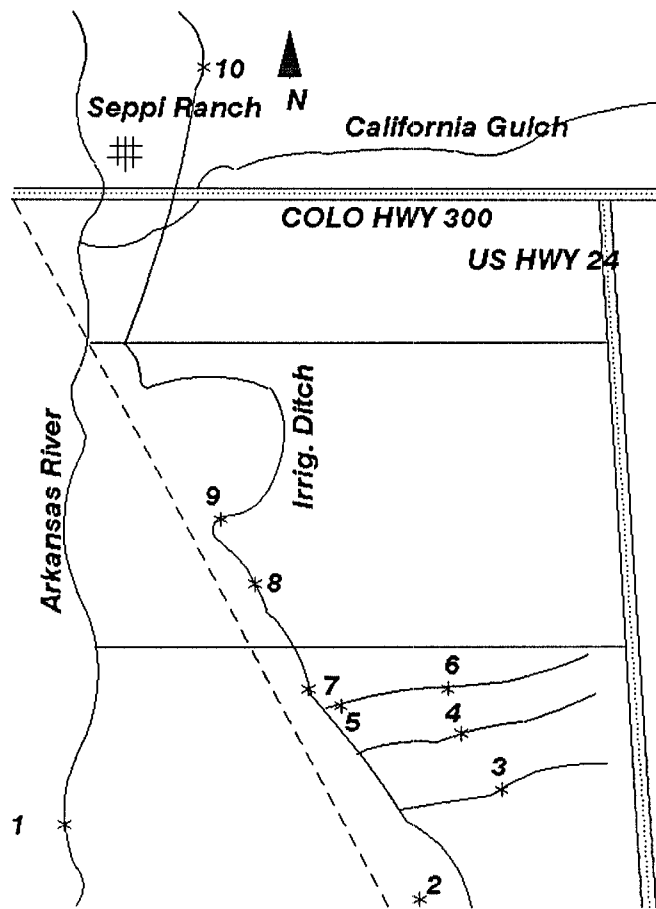


Figure 1. Map of collection site near Leadville, Colorado.

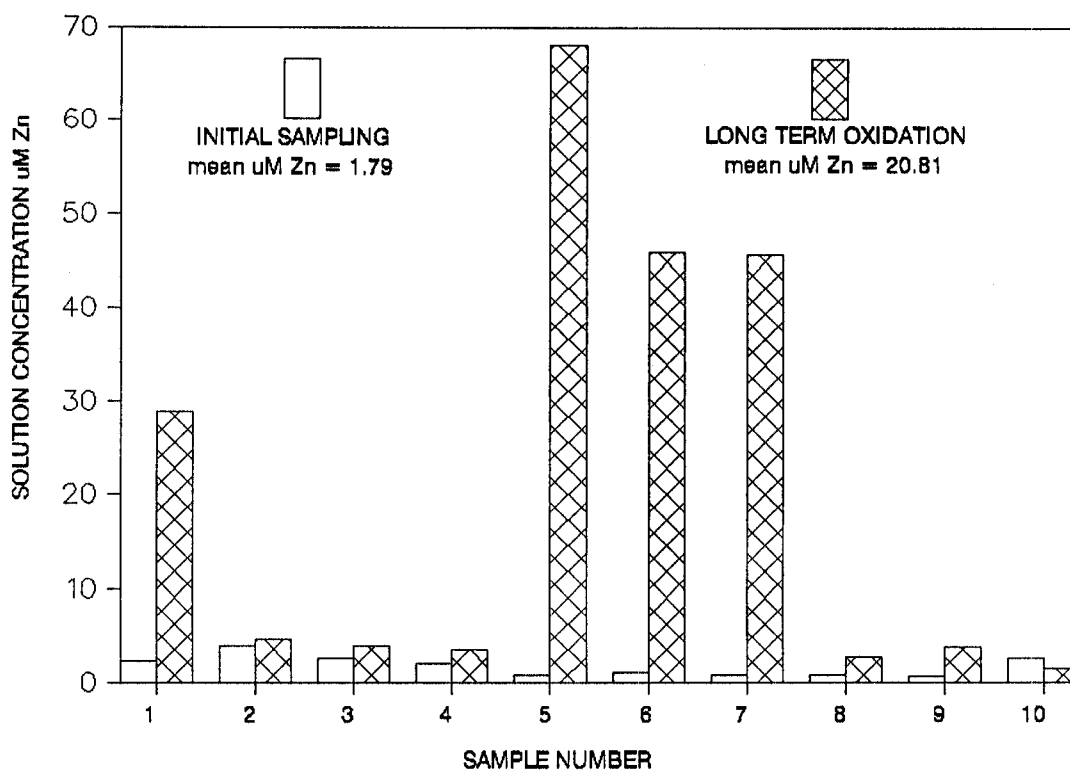


Figure 2. Zn concentrations from initial sampling and long-term oxidation experiment.

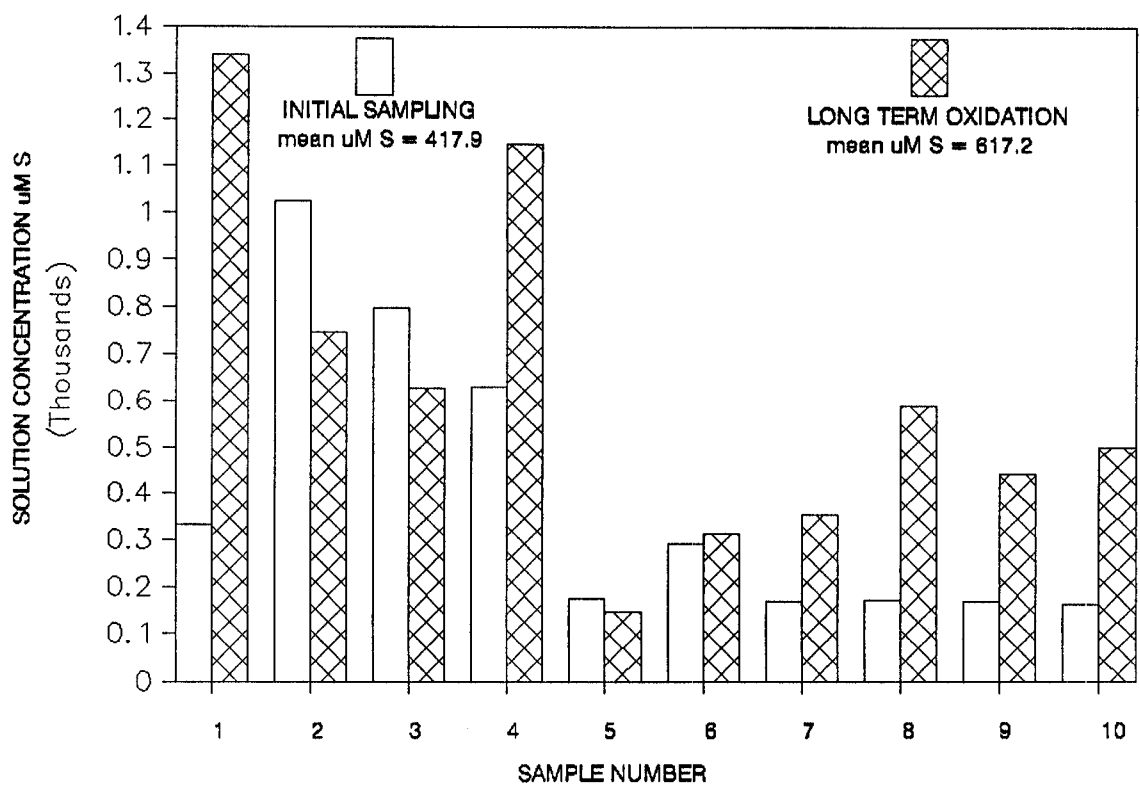


Figure 3. Total S concentrations from initial sampling and long-term oxidation experiment

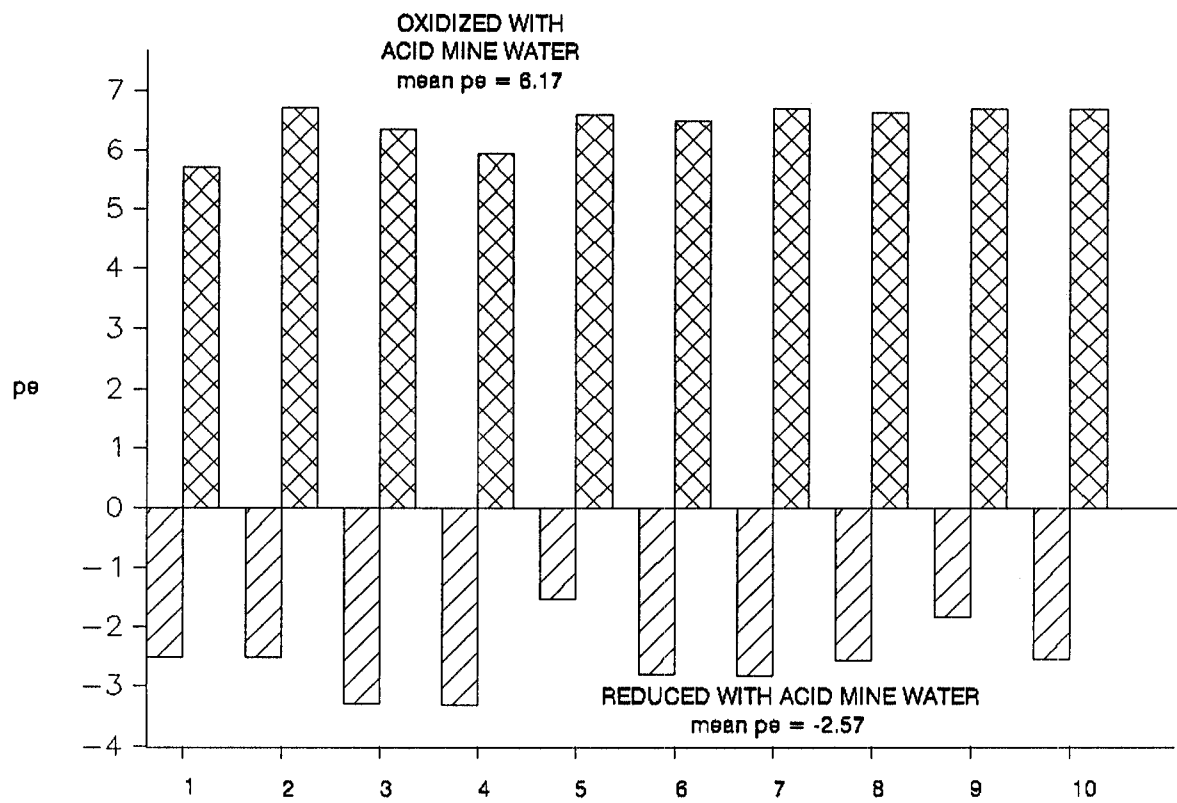


Figure 4. pe measurements for oxidized and reduced experiments.

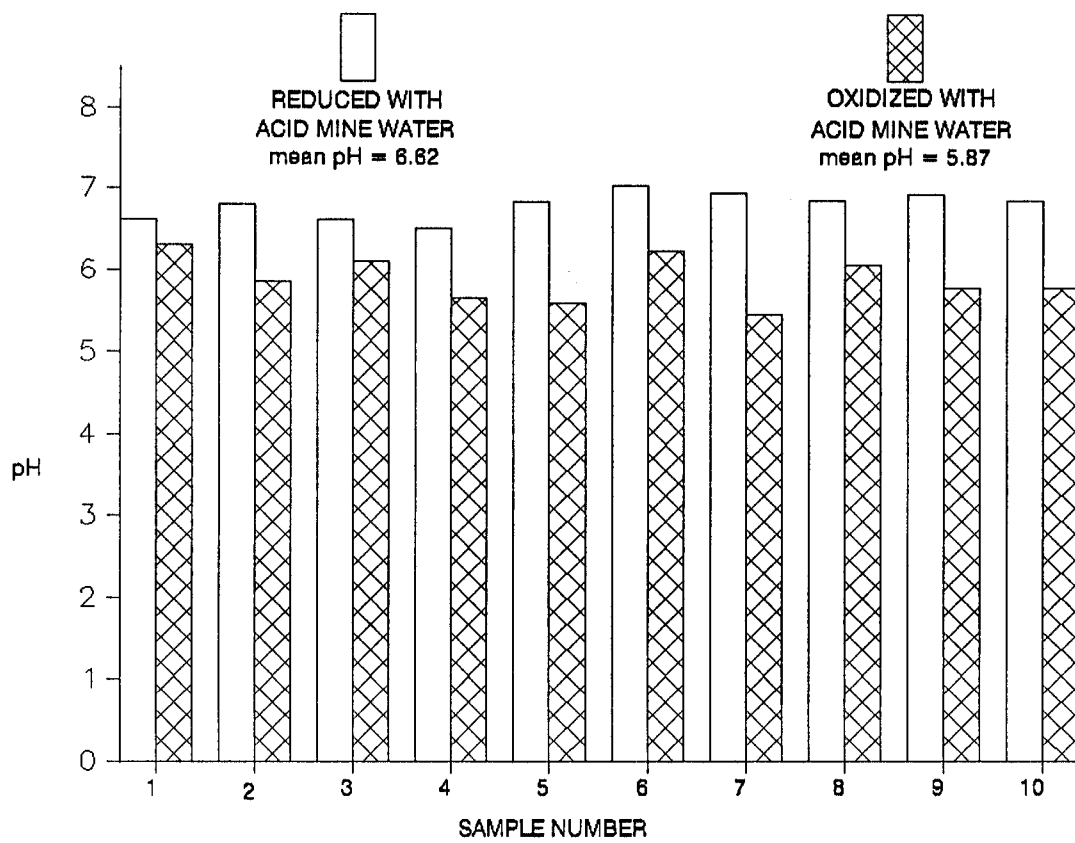


Figure 5. pH measurements for oxidized and reduced experiments.

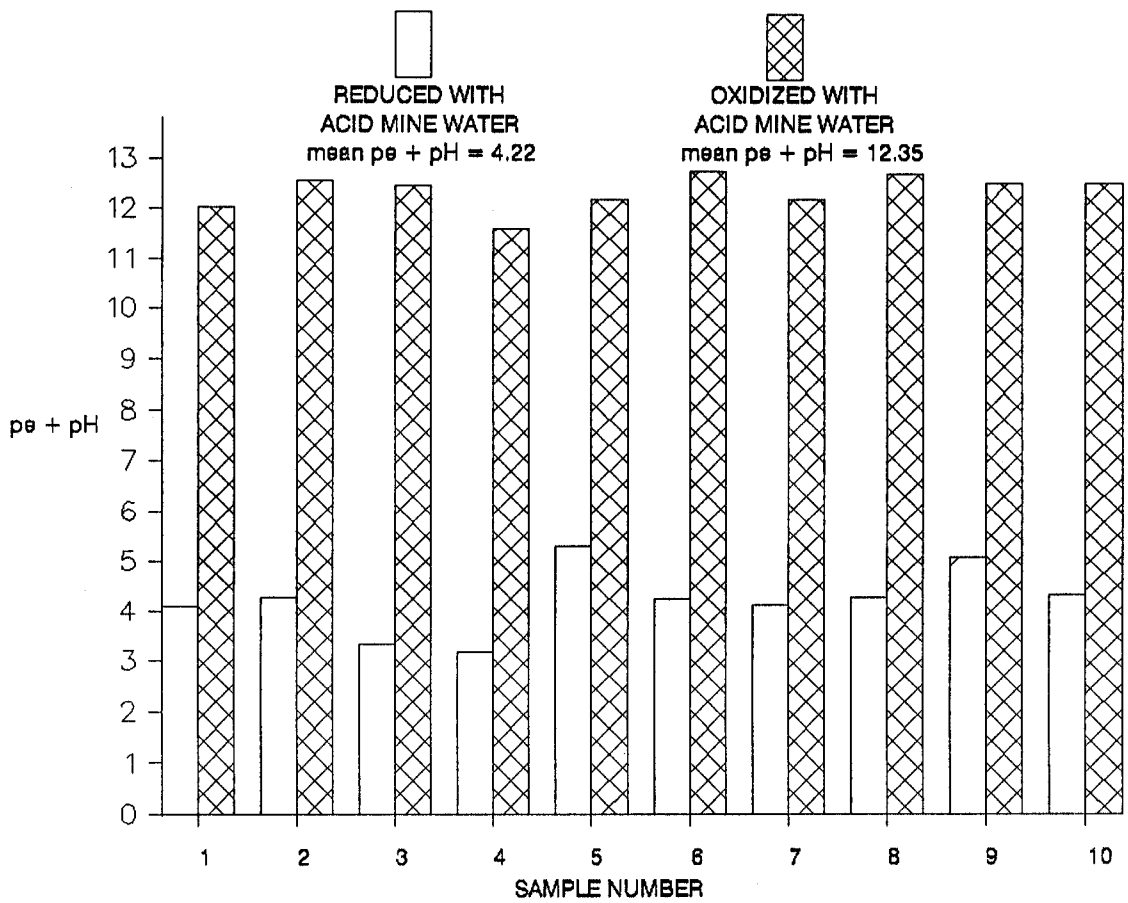


Figure 6. pe + pH measurements for oxidized and reduced experiments.

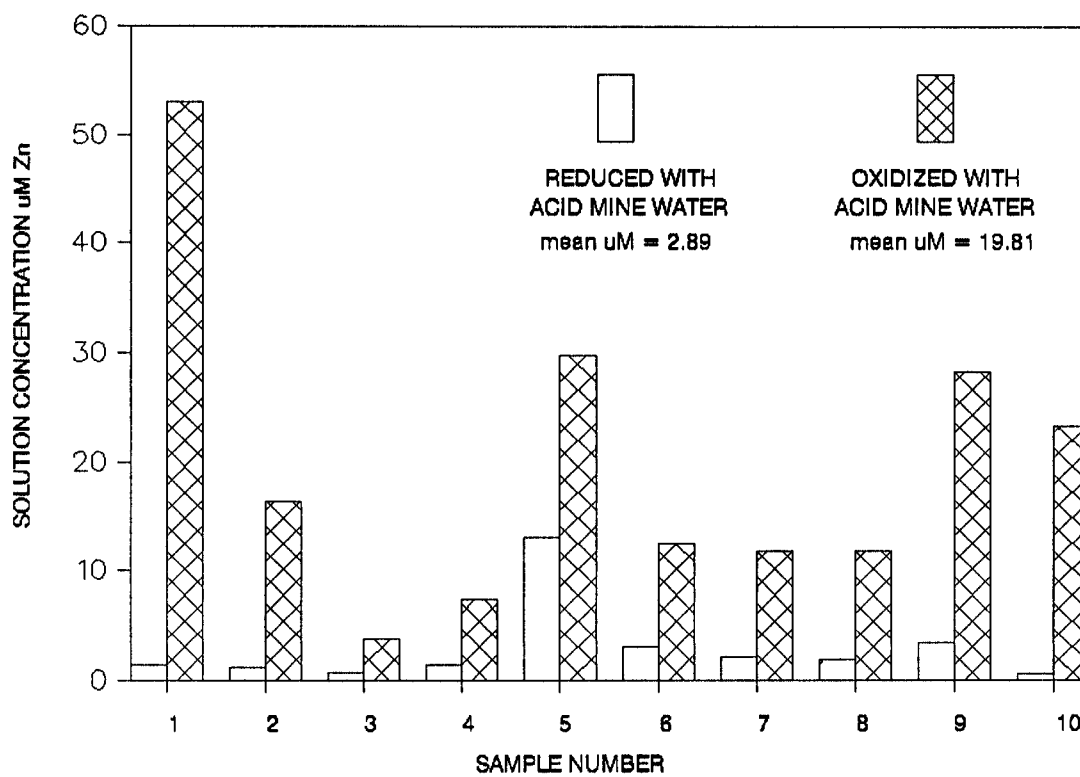


Figure 7. Zn concentrations for oxidized and reduced experiments.

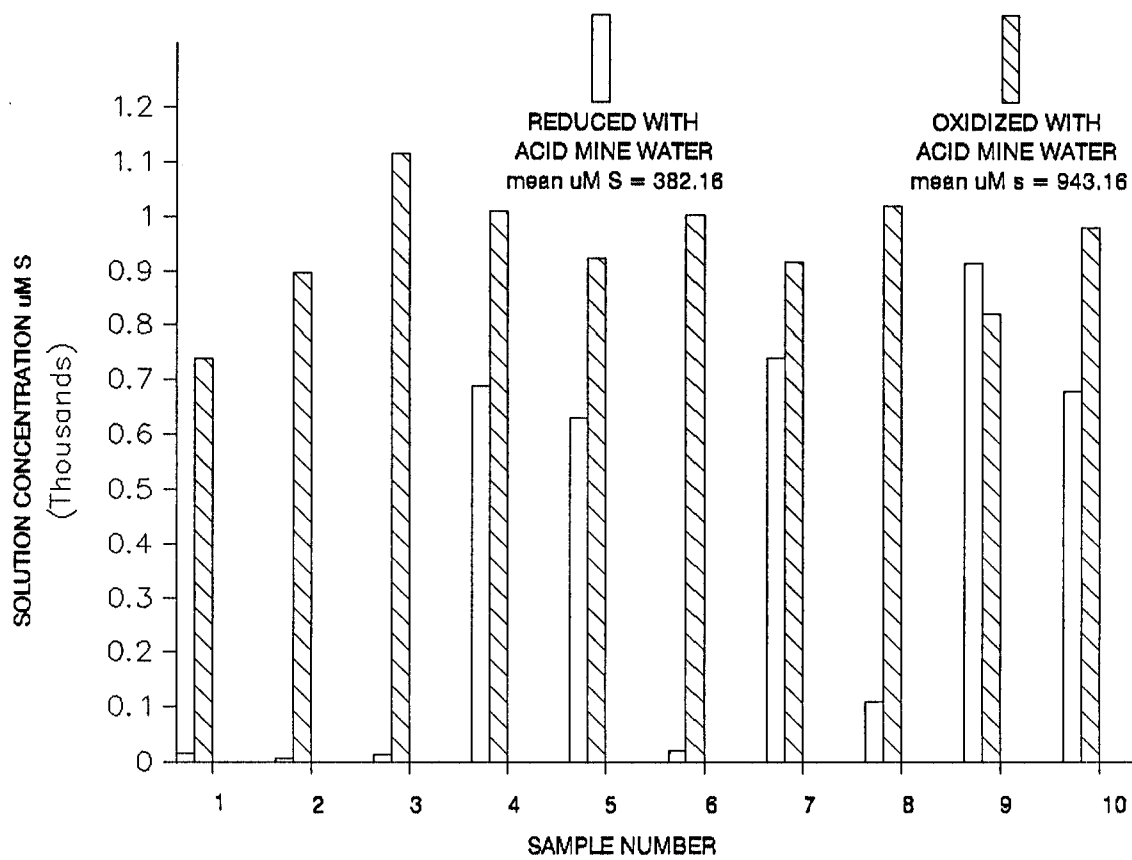


Figure 8. Total S concentrations for oxidized and reduced experiments.

Table 1

SATURATION INDEX FOR MOUNTAIN MEADOW SEDIMENTS

ZnS (sphalerite)

<u>Sample No.</u>	<u>Saturation Index</u>
1	1.0
2	-0.73
3	2.37
4	1.15
5	-5.93
6	0.12
7	0.26
8	0.55
9	-4.73
10	3.27