

BENCH-SCALE TEST TO SELECTIVELY RECOVER METALS FROM METAL MINE DRAINAGE USING BIOGENIC H₂S¹

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Abstract: Hydrogen sulfide generated by the anaerobic respiration of sulfate-reducing bacteria was used to treat samples of pH 2.2 water from the abandoned Rio Tinto copper mine in Nevada. The untreated water contained 550 mg/L Fe, 140 mg/L Al, 92 mg/L Cu, 76 mg/L Mn, 60 mg/L Zn, 4 mg/L Co, and 2 mg/L Ni. H₂S was generated in a bench-scale bioreactor and bubbled into the mine water in three precipitator-clarifier units, where metal sulfide precipitation and recovery took place. The treatment system reduced the concentrations of all metals except Mn to less than 0.1 mg/L. Manganese concentrations were reduced by 96% to 3.3 mg/L. A CuS-S⁰ concentrate (33% Cu) and a ZnS-S⁰ concentrate (28% Zn) were produced that may be suitable for metal recovery at existing smelters.

Introduction

Certain anaerobic bacteria are capable of reducing SO₄²⁻ and other sulfur oxyanions to H₂S when provided with a suitable carbon source (Postgate 1984). This reaction can be expressed as



where CH₂O represents labile organic matter. This naturally occurring biological process can potentially remediate acidic, metal-contaminated waste waters by producing H₂S, which reacts with many dissolved metals to form insoluble metal sulfides; by adding alkalinity in the form of HCO₃⁻; and by lowering dissolved SO₄²⁻ concentrations. However, to obtain these benefits, an environment must be created and sustained that is conducive to the growth and activity of the sulfate-reducing bacteria.

Many investigators have proposed the use of bacterial sulfate reduction to treat metal-contaminated mine waters (Tuttle et al. 1969, Wakao et al. 1979, Pugsley et al. 1970), but few field demonstrations have been documented in the literature. Artificial wetlands built to treat coal mine drainage in the Eastern United States have sometimes made use of biological sulfate reduction, although at first this application was inadvertent. Constructed wetlands were often built with a thick layer of organic compost to foster plant growth. Once the compost became saturated with sulfate-rich mine water, it became an ideal environment for a community of anaerobic organisms, including sulfate-reducing bacteria. Biological sulfate reduction occurring in the compost was found to contribute significantly to water treatment, primarily because of the bicarbonate alkalinity generated (Kleinmann et al. 1991). Bacterial sulfate reduction-based treatment systems have also been constructed using compost-filled containers (Dvorak et al. 1992, Hammack and Edenborn 1992), and mine entries filled with organic compost. Other low-cost organic materials, such as composted municipal and yard waste, hay, corn meal, and chicken manure, have also been used to fuel biological sulfate reduction in similar passive treatment systems.

In May 1992, a commercial-scale, bacterial sulfate reduction treatment plant began treating zinc-contaminated ground water at the Budelco Smelter site in the Netherlands using ethanol as the carbon source

¹Paper presented at the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage, Pittsburgh, PA, April 24-29, 1994.

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Proceedings America Society of Mining and Reclamation, 1993 pp 214-222

DOI: 10.21000/JASMR94010214

for the sulfate-reducing bacteria (Scheeren et al. 1992). This plant uses a sludge blanket bioreactor to treat 3,000 L/h of water with a 4-to-6 h residence time. The ZnS sludge that settles to the bottom of the bioreactor is sent to a nearby smelter for zinc recovery.

Sulfate reduction-based treatment systems have generally used a single bioreactor for both the generation of H₂S and the precipitation of metal sulfides (Dvorak et al. 1992, Scheeren et al. 1992, Barnes et al. 1991). These simple systems may be suitable if all components in a waste stream are nontoxic to the bacterial population, and if the production of a mixed-metal sludge or a sludge that contains organics as well as metals is acceptable. However, metal concentrations in mining or mineral processing waste streams often exceed the tolerance levels of anaerobic bacteria (Mueller and Steiner 1992), and mixed-metal precipitates are of less value to potential smelters. An approach that avoids these problems is the use of an inert carrier gas to sparge H₂S from the bioreactor and transport it to one or more separate precipitation reactors (Marchant and Lawrence 1989, Hammack et al. 1993). In the precipitation reactors, H₂S reacts with the waste water to form insoluble metal sulfides. The advantages of this approach are that

1. Potentially inhibitory or toxic metals in the wastewater do not contact the sulfate reducing bacteria,
2. Metal sulfide precipitation reactions can be carried out under conditions that are not conducive to the growth of sulfate-reducing bacteria,
3. Individual metal sulfides can sometimes be selectively precipitated by controlling the pH of the wastewater within the precipitators,
4. Metal sulfides that are processed for metal recovery are not contaminated or diluted with biomass or organic substrate.

In this study, we evaluated a bench-scale bacterial sulfate reduction treatment system for the treatment of a low-pH mine drainage that contained Fe, Al, Cu, Mn, Zn, Co, and Ni. The performance goals for the treatment system were to produce an effluent having a circumneutral pH and containing less than 0.1 mg/L of any heavy metal. In addition, the treatment system was expected to recover both a copper and a zinc concentrate that could be processed at existing smelters for metal recovery.

Experimental Work

The water treated in this study was obtained from the Rio Tinto Mine, an abandoned copper mine located about 80 miles north of Elko, NV, near Mountain City. Active mining was conducted at the site between 1932 and 1947, and in situ leaching operations were carried out in the early 1970s. A chemical analysis of the water (as received) is shown in table 1.

System Design

The bench-scale treatment system consisted of a bioreactor and three precipitator-clarifier units (fig. 1). H₂S generated by sulfate-reducing bacteria was sparged from the bioreactor by an inert N₂ carrier gas and bubbled through untreated mine water in precipitator 1. Here, the H₂S reacted with copper and ferric iron in the mine water to form copper sulfide (equation 2) and elemental sulfur (equation 3):



The combined gas-liquid effluent from precipitator 1 flowed into clarifier 1 (C-1), from which a CuS-S⁰ concentrate was recovered. The gas-liquid effluent from C-1 then flowed into precipitator 2, where the pH of the solution was maintained between 2.2 and 4.0 by the addition of NH₄OH (aqueous solution containing 3%

Table 1. Chemical analysis of Rio Tinto Mine water.

Parameter	Concentration (mg/L)
Fe	550
Al	140
Cu	92
Mn	76
Zn	60
Co	4
Ni	2
pH ¹	2.2

¹ pH in standard units

parts was used to pump mine water through the treatment system at a rate of 2.5 mL/min. The carrier gas was recirculated at a rate of 150 to 250 mL/min using a single-piston, vacuum-pressure pump.

Bioreactor

The sulfate reduction bioreactor was a 15.4-cm-ID by 162-cm-long, translucent PVC column packed with crushed steel mill slag (2 cm by 2 cm). The slag was added to provide additional surface area for bacterial attachment (Maree et al. 1987, 1990). With the slag in place, the void volume of the bioreactor was 15 L. The liquid-gas effluent from clarifier 3 was combined with a nutrient solution (described in the following section) and was pumped into the base of the bioreactor. The recirculated carrier gas, the metal depleted but sulfate-rich mine water, and the nutrient solution then flowed up through the bioreactor and exited at the top in a combined liquid-gas stream that flowed into a liquid-gas separator (fig. 1).

The bioreactor was initially inoculated with a mixed culture of anaerobic microorganisms that had been obtained from composted manure and maintained on Postgate's "B" medium (Postgate 1984) for more than 1 yr. A nutrient solution containing 2 g/L beet molasses (specific gravity = 1.3), 4 g/L CaCl₂•2H₂O, 6 g/L MgCl₂•6H₂O, 2 g/L FeSO₄•7H₂O, 2 g/L KH₂PO₄, and 2 g/L yeast extract was added at a rate of 1.6 mL/min using an FMI piston pump. There is no evidence in the literature that suggests that sucrose, which comprises about 50% of beet molasses, can be used directly by sulfate-reducing bacteria. However, bacteria present in the mixed anaerobic culture would be expected to hydrolyze sucrose and ferment it further to simpler organic acids, such as lactate and pyruvate (Maree et al. 1987). These simpler organic compounds can be directly used as carbon sources by sulfate-reducing bacteria (Postgate 1984, Fauque et al. 1991). The sulfate needed for cell respiration and the NH₃-N needed for cell growth were provided by the mine water that flowed into the bioreactor from clarifier 3.

Table 2. Void volumes and residence times for reactors used in this study.

Unit	Void volume, L	Flow rate mL/min	Residence Time h
Precipitator 1	0.9	2.5	6
Precipitator 2	1.6	2.5	11
Precipitator 3	1.8	2.5	12
Clarifiers	.24	2.5	1.6
Bioreactor	15	4.1	60
Entire system	20	--	94

NH₃). Zinc sulfide formed in precipitator 2, and a ZnS concentrate was recovered from clarifier 2 (C-2). From C-2, the combined gas-liquid effluent flowed into precipitator 3, which was maintained at pH 7.6 to 8.0, again with NH₄OH. The precipitator-clarifier 3 (PC-3) was installed to remove any remaining heavy metals before the combined gas-liquid stream flowed into the bioreactor.

Precipitators and clarifiers were constructed from 5-cm-ID translucent polyvinyl chloride (PVC) pipe. Details of the precipitators and the single-baffle clarifiers used in this treatment system are shown in figure 2. The volume and hydraulic residence time for these units are given in table 2. A diaphragm pump with Teflon-wetted

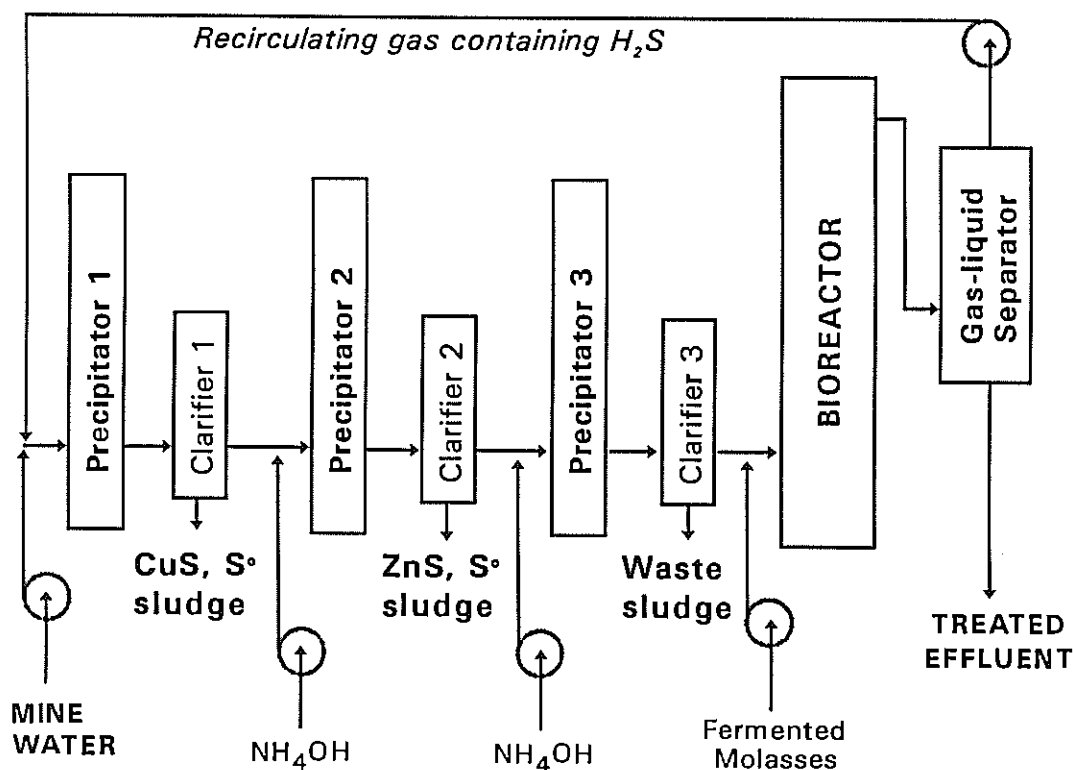


Figure 1. Schematic for bench scale biogenic H_2S treatment system.

Analytical Methods

Influent, effluent, and samples from each clarifier were collected 2 to 3 times a week during the continuous operation of the treatment system. All samples were filtered using $0.45\text{-}\mu\text{m}$ acetate filters. The filtrate was analyzed for Fe, Cu, Zn, Mn, Al, Co, Ni, Cd, and Pb using inductively coupled argon plasma emission spectrometry (ICP). Precipitates from the clarifiers were dried at 102°C for 12 h, weighed, and digested with aqua regia. The aqua regia solution was filtered, diluted to a known volume, and submitted for ICP analysis as above. All chemical analyses were carried out according to U.S. Environmental Protection Agency guidelines (1979).

Results and Discussion

In the bench-scale treatment system tested in this study, the recirculated carrier gas contained about 0.3% H_2S when it exited the bioreactor. Assuming this concentration to be constant throughout the system, the pH ranges for metal sulfide formation were calculated based on the pH-dependent dissociation of H_2S and the solubility of each metal sulfide. Figure 3 shows the pH range where each metal present in Rio Tinto Mine water would theoretically form metal sulfides when reacted with the H_2S -containing carrier gas. The low-pH boundary for each metal indicates the lowest pH at which a sulfide of that metal would form, given the concentration of the metal in the mine water and the H_2S concentration of the carrier gas. The right boundary indicates the minimum pH that must be maintained to reduce the concentration of that metal to less than 0.1 mg/L. In reality, the H_2S concentration of the carrier gas is depleted as it flows through the treatment system, and the solubility of the newly formed metal sulfide is often significantly higher than the published values for the sulfide mineral (Peters et al. 1984). Therefore, we expected the experimentally determined pH ranges to be shifted towards the higher pH.

Precipitator-Clarifier 1

CuS was expected to form in precipitator-clarifier 1 (PC-1) because the pH of Rio Tinto Mine water (pH 2.2) was higher than the theoretical minimum pH for CuS precipitation (fig 3). However, because the mine water pH was near the low-pH boundary for ZnS formation, it was uncertain if ZnS would also form. Experimental results (fig. 4) indicated that all Cu was removed from the Rio Tinto Mine water in PC-1. The concentrations of Fe and Ni increased slightly in PC-1 owing to corrosion of stainless steel fittings. The metal content of PC-1 sludge averaged 33% Cu and 0.3% Zn, with no other detectable metals. Sulfur comprised the bulk of the sample and was present as both S^{2-} and S^0 , formed by the reduction of ferric iron (equation 3).

Precipitator-Clarifier 2

During the study, the pH in precipitator-clarifier 2 (PC-2) was maintained between 2.2 and 4.0, the predicted pH range for ZnS formation (fig. 3). This pH range seemed appropriate for the precipitation of a relatively pure ZnS concentrate because Cu should have been completely removed in PC-1, and CoS, NiS, FeS, and MnS should not theoretically form below pH 4.5 (fig. 3). However, our initial attempts to operate at pH 3.8 to 4.0, where Zn removal was maximized, resulted in significant precipitation of $Al(OH)_3$. In addition, operation at pH greater than 3 resulted in the precipitation of $Fe(OH)_3$, since Fe^{3+} was not completely reduced in PC-1. In consideration of these constraints, the potential operating range was then limited to pH 2.2 to 3.0. Figure 5 shows the Zn concentration of PC-2 effluents when operated at selected pH's between 2.2 and 3.8. The performance of PC-2 was optimal at pH 2.8, where more than 99% of the Zn was recovered, but Fe and Al remained in solution. The PC-2 sludge formed at pH 2.8 contained 28% Zn, 0.7% Fe, 0.4% Ni, 0.3% Co, and no detectable Al or Mn. As in the PC-1 sludge, S^0 and S^{2-} comprised most of the PC-2 sludge. The presence of Co and Ni in this sludge was unexpected because these elements should not precipitate as sulfides at pH 2.8 (fig. 3). However, Co and Ni may have adsorbed to precipitating ZnS particles. This possibility was not investigated further.

Precipitator-Clarifier 3

Precipitator-clarifier 3 (PC-3) was included in this treatment system to provide a metal-depleted but sulfate-rich feed to the bioreactor by removing Zn, Co, Ni, Fe, and Al from the effluent of PC-2. Therefore, PC-3 was operated at pH 7.6, a pH where the effluent concentration of all remaining metals, except Mn, should be less than 0.1 mg/L. We did not expect to be able to remove Mn because of the high solubility of MnS ($K_{sp} = 5.6 \times 10^{-16}$). As expected, the effluent concentrations of all metals except Mn were less than 0.1 mg/L. Surprisingly, Mn concentrations were reduced from 71 mg/L to 3.3 mg/L, presumably due to rhodochrosite ($MnCO_3$) precipitation. Because anaerobic fermentation reactions produce HCO_3^- or CO_2 as products, the P_{CO_2}

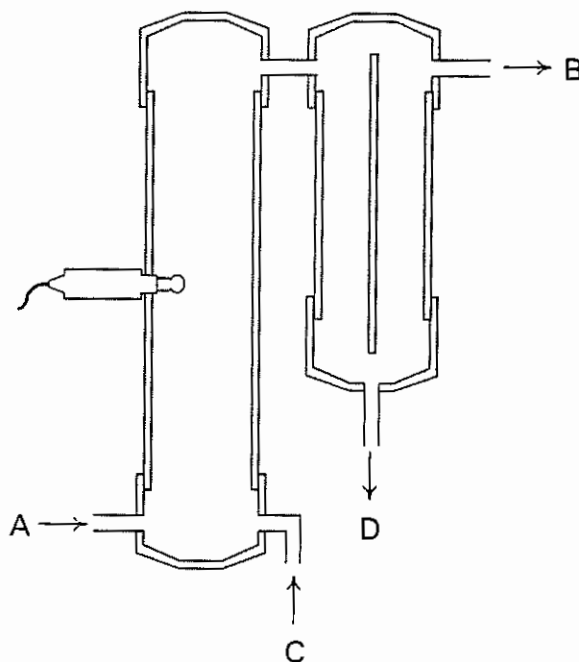


Figure 2. Detailed drawing of a precipitator/clarifier unit showing: A) the liquid/gas inflow; B) the liquid/gas outflow; C) the NH_4OH addition port; and D) the sludge removal port.

in the recirculated carrier gas would be high compared with that in ambient air. Since a significant proportion of the CO_2 dissolved in the pH 7.6 mine water would have been present as CO_3^{2-} , it is likely that MnCO_3 formation ($K_{sp} = 6.31 \times 10^{-11}$) was responsible for most of the observed decrease in Mn concentration.

Conclusions

The bench-scale, biogenic H_2S treatment system tested in this study was effective in the removal of Cu, Zn, Co, Ni, Fe, Mn, and Al from Rio Tinto Mine water. In addition, this treatment system produced a CuS-S° concentrate (33% Cu) and a ZnS-S° concentrate (28% Zn) that may be suitable for metal recovery at existing smelters.

New mine water treatment technologies must ultimately be compared with conventional lime treatment in terms of performance, cost, and reliability. Potential advantages of biogenic H_2S treatment over conventional lime treatment include the ability to achieve lower metal concentrations in treated effluent, the potential for metal recovery, and the production of metal sludges that are faster settling, denser, and more stable.

The operating cost of a biogenic H_2S treatment system will likely vary greatly depending on application and location. Although the beet molasses used as an organic food source for bacterial sulfate reduction in this study cost about \$83 per metric ton, the value of recovered metals may more than offset this cost. In many cases, no-cost or low-cost organic wastes could be used as carbon sources for sulfate-reducing bacteria. For example, anaerobic digestors at existing sewage treatment facilities can be modified for H_2S production (Butlin et al. 1956).

Biogenic H_2S treatment may be the method of choice in applications where there are

1. High concentrations of salable metals,
2. Low-cost carbon sources or existing anaerobic sewage treatment facilities,
3. Concerns about sludge volume and toxicity,
4. Strict discharge standards for heavy metals and sulfate.

The treatment plant at the Budelco Smelter established biogenic H_2S treatment as a technology for treating slightly acidic waste waters containing a single metal on a commercial scale (Scheeren et al. 1992). The present study suggests that the application of biogenic H_2S treatment to acidic waste waters containing several metals, and their selective recovery, is also feasible.

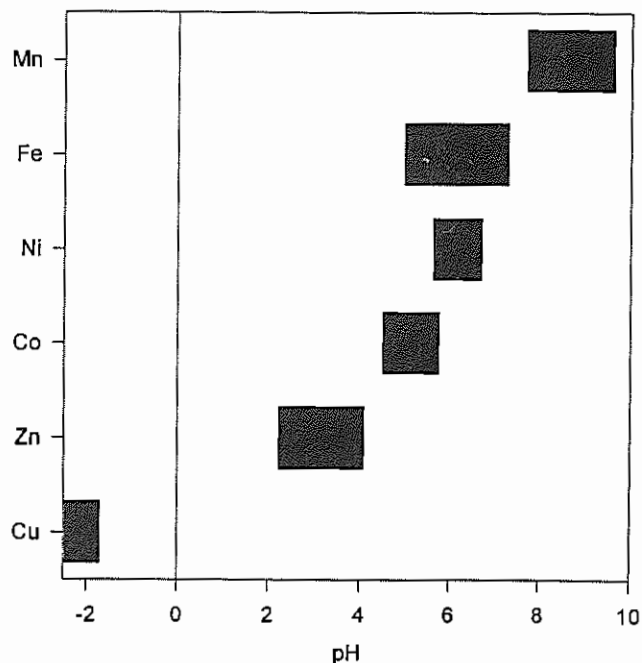


Figure 3. Theoretical pH ranges for the precipitation of different metal sulfides with biogenic H_2S . The low-pH limit is the minimum pH at which a metal sulfide will form given the concentration of that metal in Rio Tinto Mine water. The high-pH limit is the minimum pH that must be maintained to reduce the concentration of that metal to less than 0.1 mg/L.

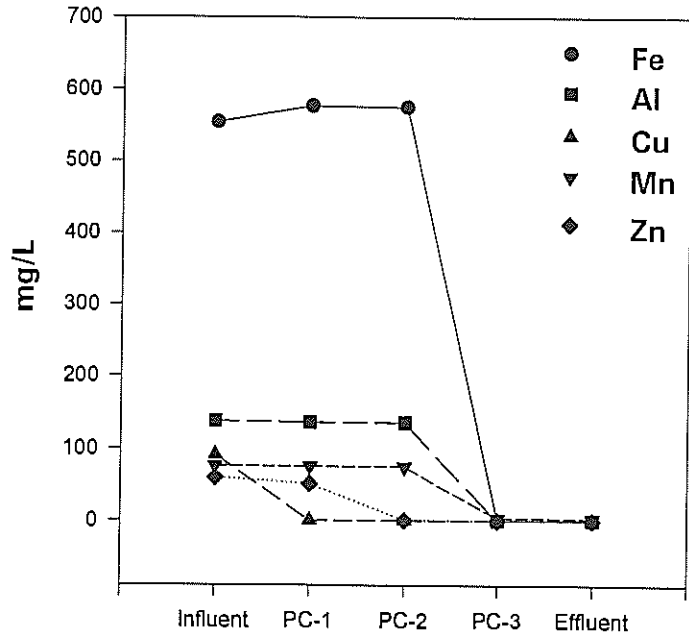


Figure 4. Dissolved metal concentrations at different points in the biogenic H₂S treatment system.

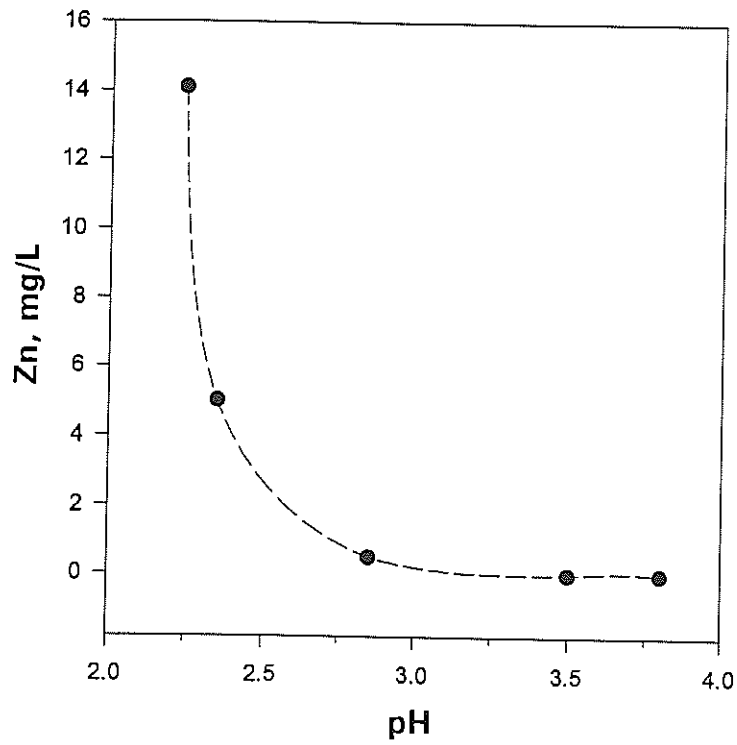


Figure 5. Zinc concentrations remaining in solution in precipitator/clarifier 2 when operated in the pH range 2.2-3.8.

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