Production of Acid Water in a Lead–Zinc Mine, Coeur d'Alene, Idaho

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ABSTRACT / The Bunker Hill Mine in Idaho's Coeur d'Alene mining district produces approximately 10 m^3/minute of acid water containing high concentrations of heavy metals. Field and laboratory studies indicate that much of the acid water is produced in a single ore body in the upper part of the mine. The ore of this body contains mainly sphalerite, galena, and pyrite in a siderite–quartz gangue. Ground water recharges this ore body through a near-vertical zone of high permeability, which is the result of mining by the caving technique. Ore samples from the caving area contained oxidized forms of iron and produced acid in a laboratory leaching test. Leaching experiments with several ore samples from the mine also indicated that the ratio of pyrite to calcite in the samples strongly controlled the resultant pH values. Oxidation of pyrite to sulfuric acid and compounds of iron is apparently responsible for the production of acid water in the mine. In contrast, dissolution of calcite in water results in a basic solution, with pH around 8.3, that can neutralize the acid produced by the oxidation process. Methods for prevention of acid mine drainage in this and other similar mines are noted.

Introduction

Mining is the main industry in the basin of the South Fork of the Coeur d'Alene River in northern Idaho. This mining district is one of the major silver-, lead-, and zinc-producing areas in the United States. The area also encompasses some of the foremost pollution problems in Idaho (Davis 1978). Most of the pollution of the Coeur d'Alene River occurred before the construction and operation of mine tailings ponds in 1968 (Mink and others 1971; Reece and others 1978). The settling ponds have greatly reduced the discharge of suspended solids into the river. In the past decade, state and federal agencies have enforced more stringent water quality standards that include requiring the reduction of dissolved heavy metal concentrations in waste discharges.

Mink and others (1971) identified the discharge from the Bunker Hill tailings pond as a major source of pollutants. This effluent is constituted by a number of waste discharge streams from the industrial operation. One source of discharge is the low-pH drainage from the Bunker Hill Mine. The mine extends to a depth of nearly 1.6 km and includes more than 250 km of underground workings within a highly faulted block of massive quartzites interbedded with argillites and argillaceous quartzites. Drainage from the Kellogg Tunnel of the Bunker Hill Mine (Fig. 1) averages about 10 m^3/minute of acid water containing high concentrations of heavy metals. This study investigated sources of the acid mine drainage in the Bunker Hill Mine and methods for preventing pollution from this and other similar mines.

Distribution of Acid Water in the Bunker Hill Mine

Samples of water collected from various sites throughout the mine were used to delineate areas containing acid water. A portable Sargent–Welch pH meter was used to measure pH of water samples in the mine immediately after their collection. The pH values are shown on a generalized two-dimensional diagram of the mine in Fig. 1. Low-pH waters are typical in the upper levels of the mine (levels 4–19). The vertical pattern of the low-pH water is influenced by a series of interconnected stops between these levels. Water draining downward follows workings in two major ore bodies, the March ore body and the Flood–Stanley zinc ore body (Fig. 1). The low-pH water follows the Flood–Stanley ore body from level 4 to level 12. On level 12, water from the workings of the Flood–Stanley ore body drains into the workings of the March ore body and continues down to level 19. Downward movement of the low-pH water is enhanced by the interconnected workings and by the fractures induced by mining.

Some of the water moves through ore-rich waste fill in the older stopes as it drains downward. This water becomes more acidic and dissolves heavy metals as it passes through the waste ore. Data from the upper part of the mine indicate that the decrease in pH depends on the type of ore body and the length of time water is in contact with the rock. Water collected from the Flood–Stanley zinc ore body shows a decrease in pH from about 3 at level 4 to less than 2.5 at level 11. Samples from the March ore body show much higher pH values (most

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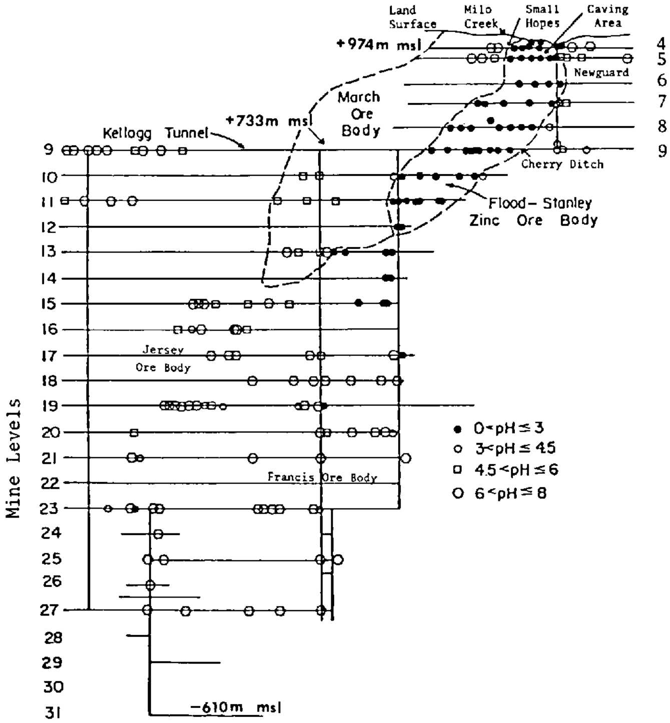

Figure 1. Generalized diagram of the Bunker Hill Mine showing location of sampling stations and the respective pH values. msl, mean sea level.

values are in the range of 5.0–6.5) on the same upp levels of the mine. The only low-pH water in the Marc ore body is on level 12 where the Flood–Stanley zinc o body joins the March ore body by a common stope. Mil Creek, above the mine, recharges both ore bodies. The surface waters have a pH of approximately 6.5.

The chemistry of the combined water from the Marc and Flood–Stanley zinc ore bodies was compared with th chemistry of water collected from the lower levels of th mine and from drill holes that intercept country rock an faults (Table 1). In general, the pH of water from th faults and the country rock is greater than 6.5. Wat from the upper levels that passes through the waste-fille stopes has a lower pH, generally less than 3.0. Drainag from the lower levels of the mine has a higher pH of 4– Concentrations of certain elements in waters fro various locations within the mine are also presented i Table 1. Most of the water with high concentrations o heavy metals moves through the older workings in th upper levels of the mine. Samples of ground water from freshly opened area in the lower part of the mine sho low concentrations of heavy metals.

Chemistry and Mineralogy of Acid Water Production

Twenty-one ore samples collected from the mine we analyzed by X-ray diffraction, atomic absorption, an

Table 1. Selected quality data of water from different sources of the Bunker Hill Mine

Water source	pH	Parts per million[a]				Number of samples
		Pb	Zn	Ca	Fe	
Milo Creek (surface)	6.5	<0.1	0.1	1.68	<0.1	15
Diamond drill holes (country rocks and faults)	6.5	0.1	0.1	28.2	<0.1	96
Flood–Stanley zinc ore body	2.4	1.0	5460	21	6380	75
Upper level drainage (represented by Cherry Ditch)	3.0	0.55	460	22.7	297	28
Lower level drainage (represented by levels 9–12)	4.1	0.66	34.3	86.6	1.4	23
Kellogg Tunnel drainage	4.7	2.1	102	97.6	26	203
March ore body	6.5	<0.1	10.9	49	< 0.1	83

[a] Contents of metal in water were analyzed by a PE-303 model atomic absorption spectrophotometer.

Table 2. Location, mineralogy and metal content of representative ore samples from the Bunker Hill Mine

Ore samples	Location	Mineralogy	Range of metal concentrations (wt. %)			
			Pb	Zn	Ca	Fe
Group I (7 samples)	Newguard ore body, level 5; J ore body, level 17; Francis ore body, level 22; exploratory diamond drilling area, level 25	Mostly quartz with galena, sphalerite, siderite, some calcite, ankerite, sericite, and a small amount of chlorite	12.9–0.15	5.21–0.03	8.1–0.2	16.8–2.1
Group II (7 samples)	March ore body; J ore body, levels 20–22; Francis ore body, level 22	Mostly quartz with galena, siderite, sericite, some sphalerite, and traces of pyrite	52.5–0.3	0.88–0.03	0.25–0.02	15.2–0.96
Group III (3 samples)	Flood–Stanley caving area; beneath caving area, level 4	Quartz, oxidized forms of iron, pyrite, sphalerite, galena, siderite, and sericite	2.5–0.6	7.1–0.2	0.1–0.02	10.6–7.9
Group IV (4 samples)	Composite of Small Hopes upper and lower ore bodies, Blue Bird ore type[a]; Francis ore body, levels 17 and 22	Quartz, pyrite, sphalerite, galena, siderite, sericite, and traces of calcite	11.7–1.8	27.8–2.3	0.72–0.07	18.1–8.2

[a] At level 4, similar to Flood–Stanley ore body.

scanning electron microprobe. X-Ray diffraction and electron microprobe analyses were carried out using a Philips Norelco X-ray diffractometer and an ARL-EMX electron microprobe, respectively. In the atomic absorption analysis, samples were digested by nitric acid and hydrochloric acid following the methods for analyzing carbonates and sulfides in *Atomic Absorption Spectrometry in Geology* (Angino and Billings 1972).

Experiments with these ore samples provided a controlled examination of variables controlling acid production. Ore samples used in this experiment were ground first. The ground samples (less than − 10 mesh size) were then stirred with distilled water in beakers at room temperature under atmospheric pressure. A ratio of 10 g of ore to 250 ml of water was used in the leaching experiment. Water samples were taken periodically and filtered for chemical analysis. The solution pH was monitored and recorded continuously using a strip chart recorder.

The experiments in which ore was exposed to water showed that the effect of the ore sample on water was consistent with the minerals present in the samples. Most of the samples experienced a rapid drop in pH at the start of the reaction, followed by a gradual increase in pH, which eventually reached a stable pH. Other parameters, such as content of metals and sulfate, continued to increase for longer periods of time. The extent of the initial change in pH and the later stable pH varied considerably from sample to sample.

The ore samples can be classified into four groups based on their mineralogy and capacities for producing acid as shown in Table 2 and Fig. 2.

1. Group I produces a basic solution. These samples contain little or no pyrite and have a high concentration of calcium.
2. Group II produces little effect on the solution; both acidity and alkalinity are low as is sulfate. These samples contain little or no pyrite and are low in calcium concentration.
3. Group III produces a strongly acidic solution. These ore samples are oxidized; they contain significant amounts of oxidized iron, some pyrite, and only very low concentration of calcium and magnesium.
4. Group IV produces acid (as evidenced by sulfate concentration) initially but then consumes it to give a solution that is neutral or basic. These ores contain pyrite and varying amounts of carbonates.

Production of acid water in the Bunker Hill Mine is obviously related to the oxidation of pyrite and pyrite to calcite ratio in the rock. Discussions on the mechanisms of transformation of pyrite to sulfuric acid and compounds of iron (Smith and Schumate 1970) and on the neutralization of acid mine drainage with limestone are available in the literature (Appalachian Regional Commission 1969). Readers are referred to those references for details.

Conclusion and Recommendations

The measurements of water chemistry suggest that the major acid-producing area of the Bunker Hill Mine is the

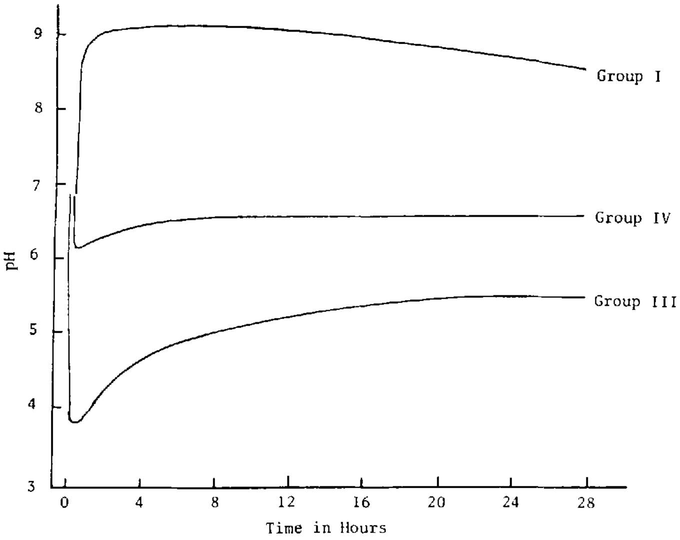

Figure 2. Variation of pH of solution during leaching of some representative ore samples from the Bunker Hill Mine. Descriptions of ore sample groups are given in the text.

Flood–Stanley zinc ore body. The upper levels (4, 5, and 6) of this ore body produce most of the acid. This part of the mine is the caving area that was opened to mining in the late 1940s. Here, caving has extended to the land surface, leaving a crater about 60 m across and 12 m deep. The caving area crater, as shown in Fig. 1, is at the intersection of three small valleys tributary to Milo Creek. Samples of ore from this caving area generally are oxidized and contain significant amounts of pyrite. Laboratory leaching experiments have demonstrated that this type of rock is capable of producing acid. The large flow of water in the Flood–Stanley area is the result of ground water recharging through the surface depression formed by caving.

A mining company can reduce the problems of acid water in future mining activities and can control some of the problems from past mining. In theory, 2 moles of calcite are required to neutralize the acidity produced by each mole of pyrite. Therefore, any weight ratio of pyrite to calcite in excess of 0.6 should eventually produce acid. Core samples taken before mining can be evaluated for pyrite and carbonates to determine the acid-making potential of the ore. The information may then be used along with other factors to determine the mining methods to be used for a given area. Block caving would be precluded unless the savings inherent in this technique offset the costs of treating the acid water produced. It may also be possible to mine a deposit in a manner that by-passes the most troublesome rocks. Introducing lime or limestone into lower drainage ways of an acid-producing area is also a possible way of minimizing the acid water problem.

The choice of a mining technique or the manner of its application will be determined by considering a number of factors in addition to the production of acid water. However, the potential of producing acid water is an important input in planning future mining activities.

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