PREVENTION OF WATER POLLUTION PROBLEMS IN MINING: THE BACTERICIDE TECHNOLOGY

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ABSTRACT

In pyritic environments, the bacteria *Thiobacillus ferrooxidans* catalyze acid formation by increasing the oxidation rate of pyrite by a factor of one million. This acid solubilizes metals and pollutes adjacent streams and lands. Bactericide sprays during mining and waste disposal operations attack the source of the problem by preventing acid formation and metals solubilization. Used in conjunction with current water treatment systems, bactericides can dramatically reduce operating costs. Controlled release bactericides contribute to successful reclamation by providing assurance against revegetation failure and post-reclamation water quality problems that can necessitate perpetual water treatment. While inhibiting *T. ferrooxidans*, these organic compounds aid in the establishment of beneficial heterotrophic bacteria which support vegetation. These conditions continue to persist after the bactericide is depleted from the controlled release system. Case Studies I and II show that bactericides inhibit acid generation during hard rock and coal mining operations and they are cost effective. Case Studies III and IV illustrate the improvement in water quality and vegetation after reclamation when controlled release bactericides were used. Economic analyses show cost benefits are achieved when controlled-release bactericides are part of the reclamation plan.

INTRODUCTION

Bacterial catalysis of sulfide oxidation in coal, coal waste, waste rock, mine tailings and sulfide ores has been well documented [Beck et al., 1968 and Schnaitman et al., 1969]. Anionic surfactants, organic acids, and food preservatives have been extensively used [Onysko et al., 1984 and Tuttle et al., 1977] to control the activity of the iron and sulfur oxidizing bacteria, *T. ferrooxidans*. Kleinmann and others [1981] showed that anionic surfactants are the most economical inhibitors of *T. ferrooxidans* activity. They are extremely effective bactericides at low concentrations and low pH values and are themselves biodegradable [Dychdala, 1968]. The four case studies of commercial applications show that bactericides can be effectively and economically integrated into mining operations, waste disposal procedures, and site reclamation.

SITE EVALUATION

All sites are evaluated to determine if bactericide treatment is needed and if the proposed treatment is an economical option. Diagnostic information includes topography, hydrology, geology, mineralogy and microbiology data. Sulfur forms and acid-base account data determine acid-producing potential [Sobek et al., 1978] and provide a basis to determine cost of conventional treatments for comparison. Lime requirement measurements [Sobek et al., 1978] are needed to determine the amount of neutralizers required to handle existing acid conditions at reclamation sites. No large quantities of lime are required to neutralize potential acidity because the bactericides prevent further acid formation.

Microbiological enumeration tests of the site material are determined using a 9K media [Horowitz et al., 1988]. Incubation and column leach tests [Shellhorn and Rastogi, 1984] are used to assess the bactericide's effectiveness in controlling acid production in the particular site material, and to set the dosage requirements. Table 1 and Figure 1 show site qualification data generated during the site evaluation of a silver waste rock dump. Table 2 and Figure 2 illustrate pre-qualification data from a coal refuse disposal site.

Table 1. Pre-Qualification Data from a Silver Mine

Paste	Sulfur Forms (%)				$CaCO_3$ Equivalent (Tonnes/ 1000 Tonnes of Material	
pH	Total	Sulfate	Sulfide	Organic	Acid Potential	Neutralization Potential
5.0	0.486	0.119	0.365	0.002	11.4	0.91

Lime Requirement = 5 tonnes/hectare
Bacterial Populations = 30,000-300,000/mL of Extract

Table 2. Pre-Qualification Data from a Coal Refuse Disposal Site

Paste	Sulfur Forms (%)				$CaCO_3$ Equivalent (Tonnes/ 1000 Tonnes of Material	
pH	Total	Sulfate	Sulfide	Organic	Acid Potential	Neutralization Potential
7.4	7.000	0.390	6.200	0.410	193.75	12.56

Lime Requirement = 1 tonne/hectare
Bacterial Populations = Tested after Inoculation

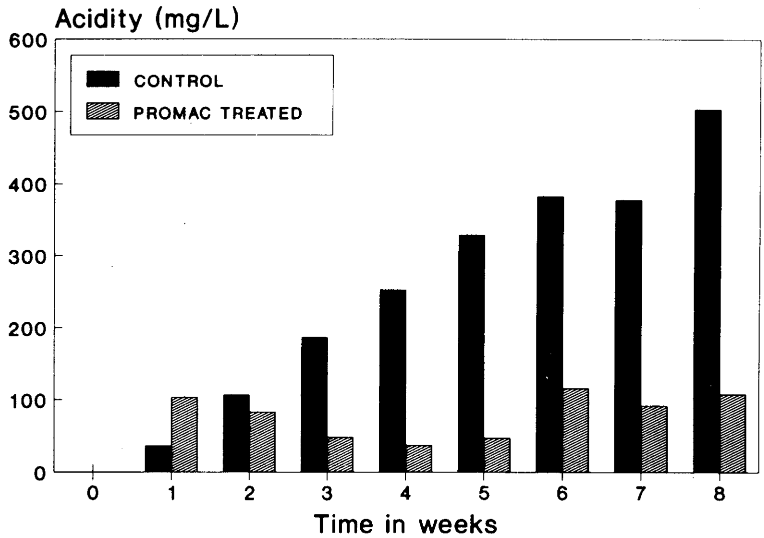

Figure 1. Acidity Data from Silver Mine Waste Rock Column Leaching

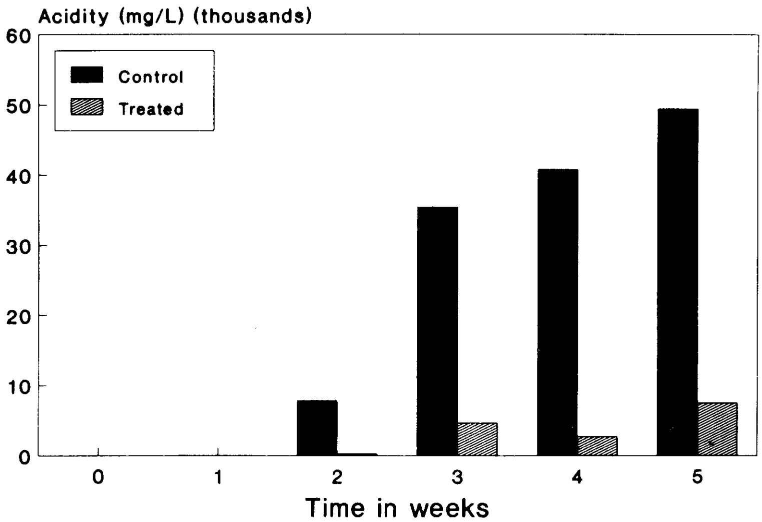

Figure 2. Acidity Data from Coal Refuse Incubation Study

ACTIVE OPERATIONS

The use of bactericides during mining and waste disposal operations can minimize acidity, sulfates and metals in runoff water. This improvement in water quality leads to reduction in the costs of neutralization chemicals, sludge removal and disposal, equipment maintenance, energy, and personnel [Benedetti et al., 1990]. If the decision to use bactericides as an integral part of water quality control is made during the design and permitting phases of mining, the total capacity of a water treatment system can be reduced, resulting in considerable savings in up-front capital expenditures.

The most common use of bactericides in active operations is a periodic surface spray of the coal refuse pile, coal stockpile, waste rock dump, etc., using a hydroseeder. Another method used at coal preparation plants is an automated spray bar system to apply the bactericide directly to the coal or coal waste as it leaves the processing plant via the conveyor belt system. The first method is the most flexible and requires a hydroseeder with a crew of two that costs U.S. $600-$900 per day. The second method carries an up-front cost of U.S. $4,000-$7,000 for equipment and installation. The second method is easy to maintain but lacks flexibility. The hydroseeder method was used in both situations because of its flexibility and low cost.

Case I: A Silver Mine Operation

Current U.S.A. open-pit silver mining generates large quantities of waste rock that must be properly handled and disposed. All waste rock is placed into a previously mined pit as backfill. The pit is usually backfilled to the top, graded, and revegetated.

Pre-qualification testing showed that the waste rock contained metal sulfides (mostly pyrite) capable of a long acid generation period. The waste rock had a sulfide-sulfur content that ranged from 0.1% to 1.7% and tested positive for *T. ferrooxidans* populations. Water quality data for the outflow at an older refuse disposal area in late 1988 was pH = 3.6 to 4.8, acidity = not measured, and sulfates = 1780 to 2170 mg/L.

The initial bactericide application took place on October 18, 1988 using a 37,800 liter water truck with wing spray bars. Subsequent applications were identical to the initial application. Because of the climate, all exposed waste rock was sprayed after the snow melted in the spring and before the snow accumulated in the fall. Between these two dates, the disposed waste rock was treated at the completion of each 18.3-30.5 meter lift.

Two "nests" of lysimeters were established in an area of untreated waste rock and in an area of ProMac treated waste rock. Water samples were obtained when a sufficient quantity of soil moisture has been collected in each lysimeter. There has been improvement in water quality parameters in the bactericide treated waste rock after the first treatment.

Analysis of water samples obtained from lysimeters in the untreated area showed the pH = 4.2, acidity = 2541 mg/L, and sulfates = 1001 mg/L. This water quality in the plant root zone would have a deleterious effect on site vegetation and the returning groundwater table. Water quality data from the treated area showed pH = 5.6, acidity = 182 mg/L, and sulfates = 297 mg/L. This type of water quality would not kill vegetation and would not be as polluting to the groundwater table as the water from the untreated area.

Costs and Economics: The cost (U.S. dollars) of five bactericide applications over a 15-month period to the active waste rock disposal area (10.2 ha and 1,484,000 tonnes of waste rock) is: (1) Bactericide = \$19,950, (2) Water Truck = \$500, (3) Operator = \$240, (4) Water = \$100, giving a total cost of U.S. \$20,790.

Table 3. Cost Savings (U.S. dollars) at Silver Mine Operation

Reagent	Cost/Day With Bactericide	Cost/Day Without Bactericide	Extrapolated Chemical Cost Savings/Year With Bactericide
Caustic Soda	\$40	\$554	\$167,660
Soda Ash	26	363	103,050
Hydrated Lime	10	136	26,050

The data (Table 3) illustrate the daily and yearly cost savings in chemical costs based on this water quality improvement and an estimated flow of 6.3 L/s for the three most common neutralizing chemicals. The cost savings are much greater when associated savings are added. Associated savings include manpower to monitor and maintain the treatment system; electric power necessary to drive the pumps and chemical-feed machinery; and maintenance costs of sedimentation and treatment ponds including sludge removal and disposal. As bactericide treatment continues, the cost savings can be expected to increase.

Case II: A Coal Refuse and Ash Disposal Area

This site receives fly ash and bottom ash from an electric power generation station and coal refuse from the coal preparation plant that supplies coal to the generating station. The site is being built in two stages, with Stage I previously completed and Stage II now in use. As the disposal site grows in size, more pyritic materials are exposed to surface water infiltration and runoff.

The pre-qualification testing showed that both ash and refuse contained sufficient pyrite (ranging between 0.2 to 6.2%) to generate acid. Stage I of this site had been constructed at an earlier date and left untreated; therefore, acid sulfate salts had been generated and stored in the refuse. Over time, infiltrating surface water solubilizes the acid salts and leaches them from the refuse. Analysis of the leachate from the disposal area showed the water had a pH of 2.2, acidity equal to 12,038 mg/L, and a total iron content of 3,500 mg/L. The leachate from the disposal area is collected at a central treatment point where it combines with drainage from the entire station before the water is treated and discharged offsite. The initial bactericide application was made in December 1988 using a hydroseeder. Subsequent treatments were identical to the initial one and are applied at three-month intervals to all exposed refuse.

Water quality data are collected routinely by the utility from the central treatment point before the water is treated. The change in acidity and iron concentrated in the leachate from the disposal area shows that acidity has dropped to 2,700 mg/L and iron to 710 mg/L (Figure 3).

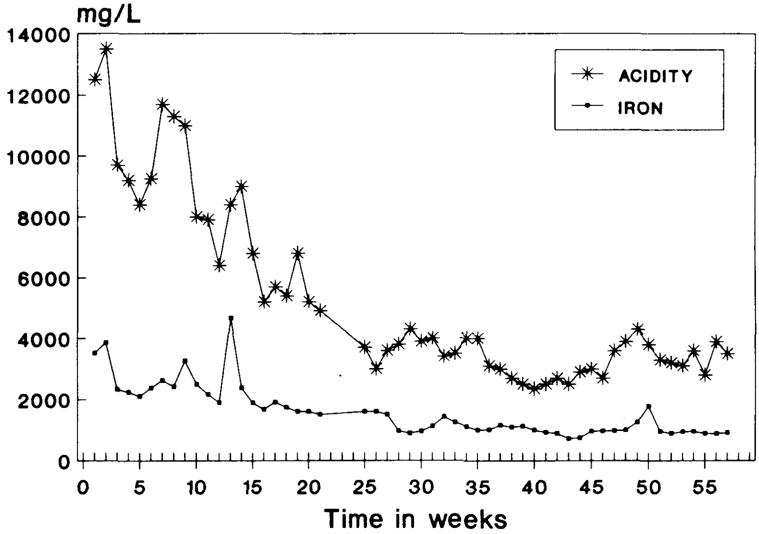

Figure 3. Water Quality Improvement After Bactericide Treatment

<u>Costs and Economics</u>: The cost (U.S. dollars) of a single application to the 8.1 ha refuse and ash disposal area totals $20,000 with bactericide ($18,400), hydroseeder ($1,000), operator ($480) and water ($120) included. The yearly total cost of bactericide treatments is $80,000 for improving the quality of the average daily flow (3.5 L/s) of drainage from the refuse and ash disposal site.

Table 4. Cost Savings (U.S. dollars) at Coal Refuse and Ash Site

Reagent	Cost/Day With Bactericide	Cost/Day Without Bactericide	Extrapolated Chemical Cost Savings/Year With Bactericide
Caustic Soda	$641	$2,850	$730,150
Soda Ash	460	2,040	496,820
Hydrated Lime	70	310	7,890

The daily and yearly cost savings (Table 4) in neutralization chemical costs are based on the improvement in water quality. The client currently treats all wastewater in a hydrated lime treatment system before it is discharged offsite. The cost savings are much greater when reduction in personnel, electric power, sludge removal and disposal, and maintenance costs are taken into consideration.

RECLAMATION

Bactericides provide assurance against post-reclamation problems of vegetation failure and acid discharges. These problems can result in postponement of bond release, yearly site maintenance, and perpetual water treatment. Bactericides have worked effectively with less than 30 cm of soil cover and only enough lime to neutralize existing refuse acidity [Sobek et al., 1990].

The pre-qualification tests are used to determine a site-specific bactericide dosage consisting of an instantly available spray and controlled release pellets. The entire treatment is normally applied in a single step using a hydroseeder. After the site has been graded but before the soil cover is applied, the appropriate product mix is applied. The bactericides are, therefore, placed in direct contact with the acid-producing material that contains the large population of *T. ferrooxidans*.

Case studies III and IV are two reclamation projects which have been closely monitored for several years. Each of these sites has "control" areas that are identical to the bactericide-treated areas in all respects of site material, lime, soil cover, seeding, fertilizing, etc., except for the bactericide treatment itself.

Monitoring of these sites included periodic water collection from soil moisture samplers (pressure-vacuum lysimeters) that were installed at different locations in all treated and control areas. Site inspections, biomass measurements, recording of precipitation and periodic enumeration of bacterial populations in the refuse pile were other parameters monitored.

Case III: Rt. 43 Reclamation Project, East Springfield, Ohio

This 2.02 ha triangular site was divided into two parts with one part receiving the bactericide spray and controlled release pellets of Generation I configuration. These were rubber pellets with a release life of two years. The entire site was covered with 15-20 cm of soil followed by standard Ohio Department of Natural Resources reclamation recommendations for lime, seed, fertilizer, and mulch. The site was reclaimed in 1984.

Pre-qualification tests showed the refuse to have a paste pH less than 3, pyritic-sulfur = 0.43%, sulfate-sulfur = 0.11%, and organic-sulfur = 0.78%. Pre-reclamation seep water had a pH of 2.7 and acidity of 1,034 mg/L.

Water Quality: Water quality data from lysimeters for four years following reclamation (Figure 4) show moisture quality in the refuse

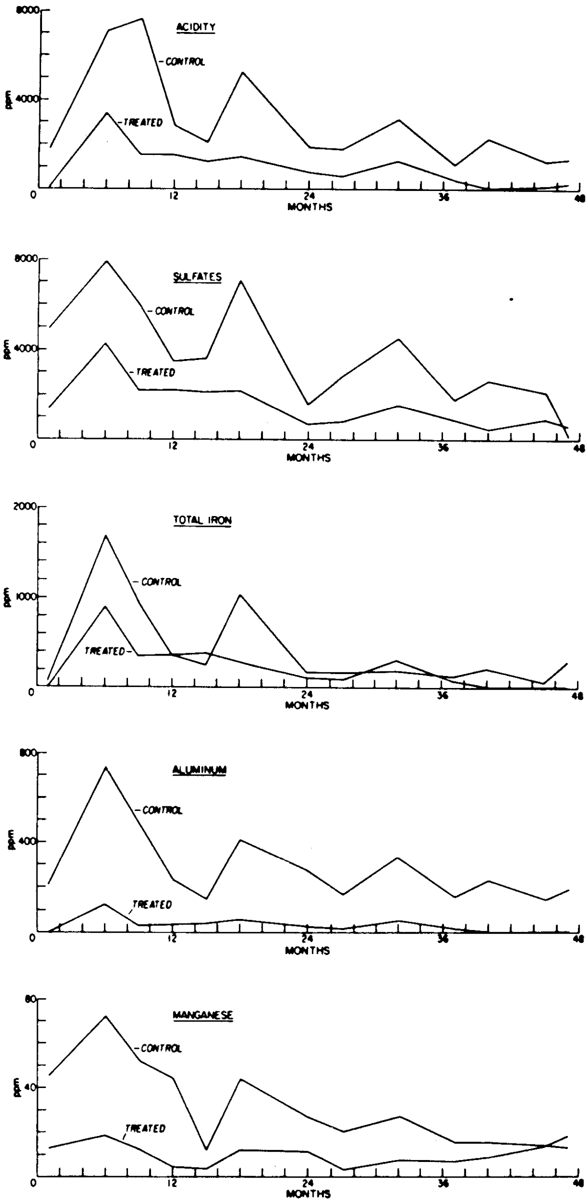

Figure 4. Refuse Water Quality Data from the Rt. 43 Site

about 60 cm below the soil cover. The differences in the individual parameters (acidity, total iron, sulfates, manganese, and aluminum) between the treated and control (untreated) areas are indicative of bactericide effectiveness and its continued longevity beyond the life of the pellets. The treated area maintains consistently improved conditions and stability.

The data summarized in Table 5 are the percent reduction in each parameter when the average of all water quality measurements from samples taken out of the four lysimeters in the treated portion of the site are compared with the average of all water quality measurements from samples taken out of the four lysimeters in the untreated portion of the site. The data (Table 5) indicate that ProMac treatment has been very successful in reducing all parameters, except for manganese in 1987 and 1988. In the second year, except for total iron, the reductions are not as large as in year one.

Table 5. Reduction in Specific Parameters When Comparing Treated to Untreated Areas at Route 43 Site

Parameter	Year 1985	1986	1987	1988
Acidity	72%	58%	97.2%	89.0%
Specific Conductivity	35%	32%	67.2%	86.0%
Total Iron	52%	73%	92.1%	99.6%
Manganese	94%	91%	44.0%	15.6%
Aluminum	93%	89%	99.5%	98.9%
Sulfates	68%	58%	81.4%	57.0%

Total iron shows a 21% increase in reduction in 1986 and a 40.1% increase in reduction in 1987 when compared to 1985.

Microbiology: Heterotrophic microorganisms aid revegetation; therefore, their populations were studied in the bactericide treated area "topsoil" versus the untreated area "topsoil" on an annual basis. The results of the study indicate that the treated area clearly has more heterotrophic bacteria than the untreated control area, and that the heterotrophic population in the treated area is growing more rapidly. A count of *T. ferrooxidans* populations in the refuse indicate that the treated area has a smaller population and that this difference has been maintained. Figure 5 shows the *T. ferrooxidans* and heterotroph populations in 1989, five years after completion of reclamation.

The ratio of thiobacilli to heterotrophs is more important than the actual populations of *T. ferrooxidans* and heterotrophic bacteria which can vary from year to year, depending on environmental conditions. Horowitz and Atlas [1976] and Walker and Colwell [1976] found that specific classes of microorganisms are better presented as a ratio of the total population. Specific classes of bacteria will increase in number as a result of a total increase in the bacterial population. Thus, if the total number of bacteria increases in a specific environment, it is expected that a general increase in every specific group of bacteria will be seen.

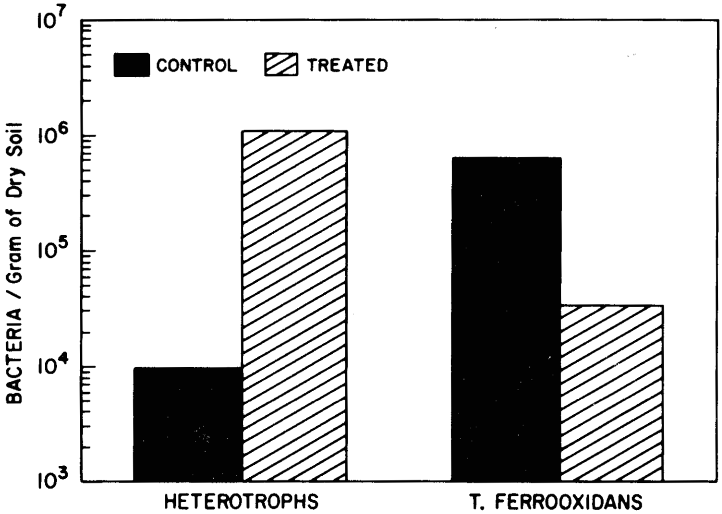

Figure 5. Bacterial Populations at the Rt. 43 Site in 1989

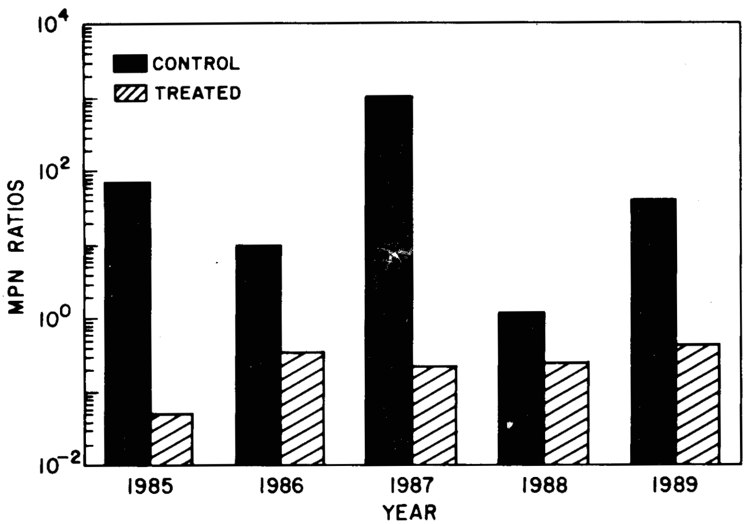

Figure 6. Ratio of *T. ferrooxidans* to Heterotrophs at Rt. 43 Site

The ratios of thiobacilli to heterotrophs for a five-year period (Figure 6) make the differences between the treated and control areas very clear. The data indicate a fairly stable and low ratio of thiobacilli to heterotrophs in the treated area. In the control area, the ratios are much higher. The ratio on the bactericide treated area has always been less than one.

Vegetation: The treated area has a dense vegetative cover along with volunteer legume growth facilitated through nitrogen fixation by the high heterotrophic bacteria population. The control side has lost much vegetation to burnout and soil erosion. Biomass production was measured by running transect lines across the plots. The treated area had a total biomass of 2915 kg/ha in 1989 while the control area only had a total biomass of 315 kg/ha. In 1990, the treated area had a decrease in total biomass to 1,709 kg/ha while the control area increased slightly to 565 kg/ha total biomass.

Case IV: Dawmont Refuse Reclamation Project, Clarksburg, WV

This 14.2 ha site was treated with Generation III plastic pellets with a release life in excess of seven years. The site received 30.5 cm of soil cover after application of the bactericide spray and controlled release pellets. A 0.4 ha area was left as a control. Standard reclamation practices were followed to lime, fertilize, seed, and mulch the site. This site was reclaimed in 1987.

Pre-qualification tests showed samples from this site to have a paste pH of 2.0, a pyritic-sulfur of 15.6%, and no neutralizers. The acid-base account showed that the deficiency of neutralizers was 497.87 tonnes per 1,000 tonnes of refuse. Seeps from the site had pH values ranging from 2.1 to 2.5, acidity from 2,876 mg/L to 20,610 mg/L with iron, manganese and aluminum concentrations as high as 3,600 mg/L, 290 mg/L, and 1,303 mg/L respectively.

Water Quality: Water quality data from lysimeters for 29 months after the site was reclaimed (Figure 7) show the treated area has made significant improvements in acidity, sulfates and metals. The control area appears to be subjected to climatic fluctuations from year to year. Overall, metals and acidity in the treated area's refuse moisture have been improved from 75% to 95%.

Microbiology: The ratio of thiobacilli to heterotrophs at the interface zone serves as a strong indicator for the overall microbial picture of the site. It balances situations such as high or low carbon availability or many other non-specific environmental factors that may affect the overall numbers. In most cases, it can be expected that the ratios of a specific bacterial group to the overall population will stay roughly constant. Total populations of *T. ferrooxidans* and heterotrophs in 1989 at the Dawmont site are found in Figure 8.

The ratios of thiobacilli to heterotrophs (Figure 9) in the control area increased 10-fold from 1987 to 1988, and very slightly in 1989.

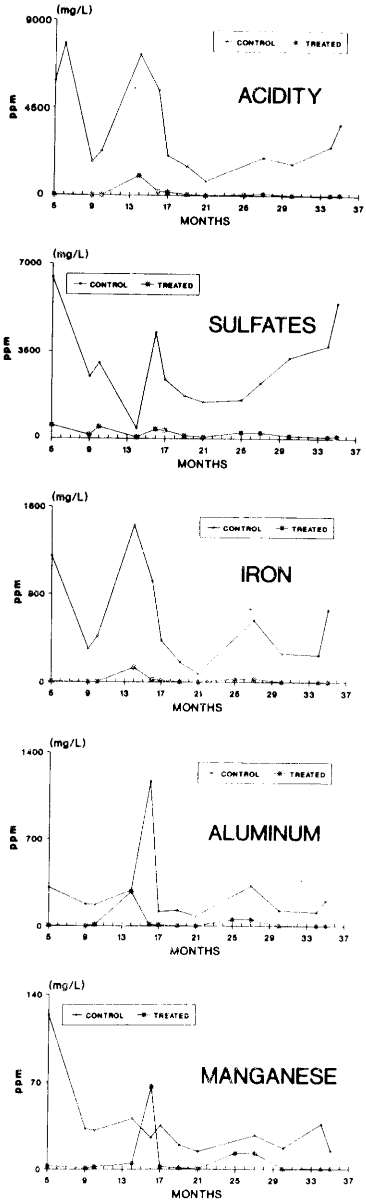

Figure 7. Refuse Water Quality Data from the Dawmont Site

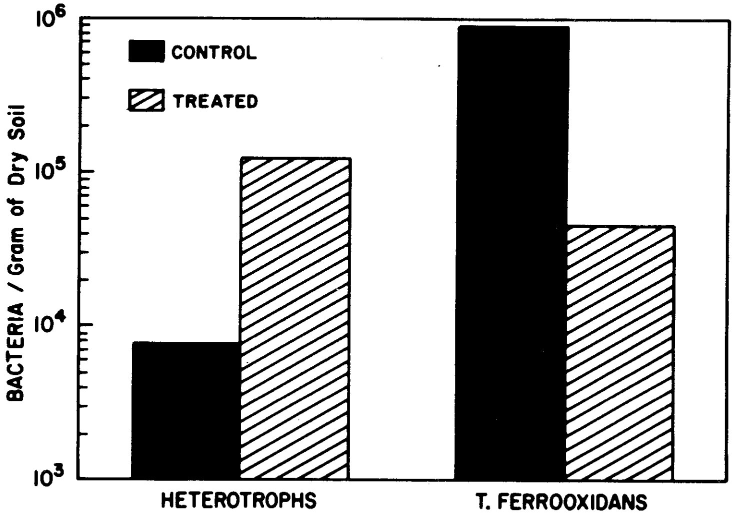

Figure 8. Bacterial Populations at the Dawmont Site in 1989

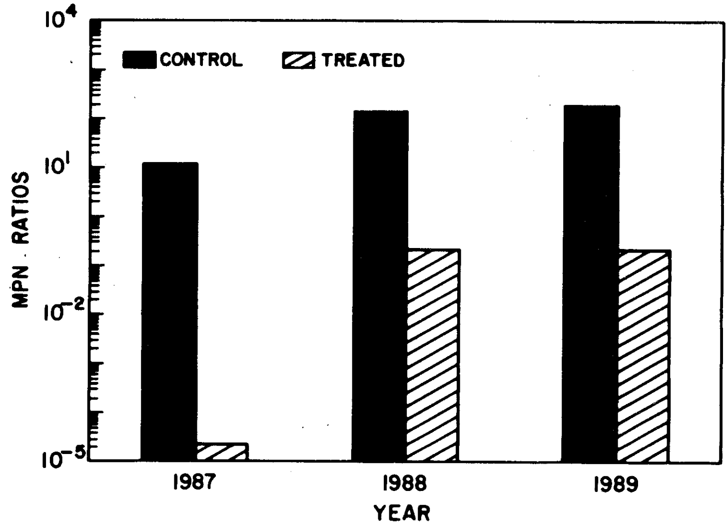

Figure 9. Ratio of *T. ferrooxidans* to Heterotrophs at Dawmont Site

In the treated area, ratios were low in 1987, increased 10,000-fold in 1988 and remained the same in 1989. A much lower ratio was expected to be obtained for the treated area in these years. Climatic conditions could be responsible for these unexpected results.

Vegetation: Qualitatively it is easy to distinguish between the vegetative cover over the entire treated area and the 0.4 ha control. Biomass production in 1989 was 1,604 kg/ha from the treated area while the control area had only 1,033 kg/ha. Considering the continuing deterioration in the control area, the 1990 biomass data showing greater differences in biomass production was not unexpected. In 1990, the total biomass of the treated area was 4,447 kg/ha while the control area only produced 1,325 kg/ha total biomass.

Cost and Economics of Bactericides in Reclamation

The cost of bactericide application is site-specific because the dosage is dependent on numerous factors that are site-specific. Therefore, treatment costs (U.S. dollars) can vary from $3,705 per hectare for a 12.2 hectare spoil area to $5,928 per hectare for a 2.03 hectare site of highly pyritic coal refuse. In most cases, bactericide treatment costs less than 10% of the total reclamation price. Cost offsets are available from the reduction in the amount of soil cover and lime needed.

Liming can be drastically reduced because bactericides limit future acid production. Soil cover depth can be reduced to 30.5 cm, which in turn reduces clearing, grubbing, transportation and reclamation costs associated with borrow areas. Bactericides enhance vegetation growth and protect against acid burnout, thereby minimizing site maintenance costs [Rastogi and Sobek, 1986]. The data (Table 6) show the potential for cost savings with bactericide treatment.

Table 6. Cost per Hectare of Site Reclamation in U.S. Dollars

Item	Standard Practice	With Bactericides
Site Grading	$ 3,700-12,400	$ 3,700-12,400
Lime	99- 3,000	99- 250
Soil Cover	4,950-19,800	2,500- 7,400
Borrow Area	1,750- 7,500	850- 2,000
Seeding	750- 1,000	750- 1,000
Site Maintenance	1,700- 5,000	500- 1,700
Engineering	1,250- 2,500	1,250- 2,500
Bactericides		3,700- 5,950
Bactericide Application		250- 500
Total	$14,199-51,200	$13,599-33,700
COST SAVINGS		4% - 34%

CONCLUSIONS

The following conclusions can be drawn from these cases:

1. Bactericide sprays are effective in controlling water pollution during mining and refuse disposal operations.

2. Bactericides can be the most economical solution during the mining and refuse disposal operations by minimizing water treatment and associated costs.

3. Controlled release bactericide systems are economical and effective in improving reclamation quality and probability of long-term reclamation success, including the improvement of water quality in any post-reclamation seeps.

4. Bactericide treatments change the microbiology of the site and this condition continues to persist after all bactericides are depleted, thereby returning the site to a stable landform.

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