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Control of Acid Drainage From Coal Refuse Using Anionic Surfactants

By Robert L. P. Kleinmann and Patricia M. Erickson



UNITED STATES DEPARTMENT OF THE INTERIOR

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	UNIT OF MEASURE ABBREV	VIATIONS USED IN THIS	S REPORT
acre ft	acre foot	mg	milligram
ft	foot	mg/L	milligram per liter
gal	gallon	mL	milliliter
gal/acre	gallon per acre	mL/h	milliliter per hour
in	inch	pct	percent
kg	kg kilogram		part per million
1b	pound		

CONTROL OF ACID DRAINAGE FROM COAL REFUSE USING ANIONIC SURFACTANTS

By Robert L. P. Kleinmann¹ and Patricia M. Erickson²

ABSTRACT

To control the formation of acid drainage at its source, the Bureau of Mines has investigated the role of iron-oxidizing bacteria in the oxidation of pyrite. In laboratory tests, it was determined that <u>Thiobacillus ferrooxidans</u> could be controlled in coal refuse using anionic surfactants, with an associated decrease in acid production of about 75 pct. Based on these results, large-scale tests were conducted at an 8-acre active coal refuse area in northern West Virginia and an ll-acre inactive refuse pile in southern West Virginia. Acid production was decreased 60 to 95 pct for 4 to 5 months after application of 55 gal/ acre of 30-pct sodium lauryl sulfate solution. To date, effluent surfactant concentrations have been extremely low.

Either a hydroseeder or a road-watering truck can be used to apply the surfactant. Since the surfactant solution must reach the pyritic material to be effective, sites that have been reclaimed are generally not amenable to these procedures. A simple laboratory test is described that provides an estimate of adsorption potential; this can be used to calculate a safe application rate.

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The exposure and subsequent oxidation of iron sulfide minerals causes the acidic drainage associated with many coal mines and refuse piles. To meet State and Federal discharge regulations, mining companies spend millions of dollars annually to treat acid water. The Bureau of Mines has investigated possible methods of lowering these costs by slowing the rate of pyrite oxidation, thereby controlling the problem at its source.

The kinetics of acid formation are dependent on the availability of oxygen, the surface area of pyrite exposed, the activity of iron-oxidizing bacteria, and the chemical characteristics of the influent water. Thiobacillus ferrooxidans is the principal iron-oxidizing bacterium involved in pyrite oxidation (29, 35).³ Acidification progresses in a three-stage sequence dependent upon the activity of T. ferrooxidans and solution Eh and pH (30).

One potential method of slowing pyrite oxidation is by inhibition of T. ferrooxidans. Certain anionic surfactants (cleansing detergents) can be used to kill T. ferrooxidans at low pH (13, 30) in an economical and environmentally safe manner, thus reducing acid formation. This report presents the results of treating coal refuse with an anionic surfactant. It also includes a procedural guide for determining if the surfactant treatment is appropriate for a specific site and a method of calculating application rates. Future reports will discuss the treatment of pyritic mine spoil and incorporation of the surfactant into slow-release formulations for long-term control of the problem.

ACKNOWLEDGMENT

The laboratory work described on pages 4-5 was conducted by R. Kleinmann as part of his graduate studies at Princeton University. The financial support contributed by Princeton University, technical assistance provided by E. Mohring, graduate student, University of Minnesota, and geochemical advice provided by D. Crerar, associate professor, during that period are gratefully acknowledged. We also thank Westmoreland Coal Co., Raleigh County, WV, and Kingwood Mining Co., Preston County, WV, for their cooperation.

BACKGROUND INFORMATION

THE PYRITE OXIDATION SYSTEM

The possible involvement of bacteria in the formation of acid drainage was first reported in 1919 by Parr and Powell, who determined that coal inoculated with an unsterilized ferrous sulfate solution produced drainage with higher concentrations of sulfate than did sterile controls (37). The isolation of the bacteria responsible did not take place until 1947 (10-11), at which time it was prothat Thiobacillus thiooxidans posed accelerated pyrite oxidation, whereas

³Underlined numbers in parentheses refer to items in the list of references at the end of this report. T. ferrooxidans (47) merely accelerated iron oxidation. Later studies revealed that T. ferrooxidans could also significantly accelerate pyrite oxidation (48) and that in fact T. thiooxidans could not (35). Other bacteria similar to T. ferrooxidans and capable of accelerating pyrite oxidations were isolated and named Ferrobacillus ferrooxidans (36) and Ferrobacillus sulfooxidans (26). However, these were later judged to be strains of T. ferrooxidans (9, 51).

<u>T</u>. <u>ferrooxidans</u> actually accelerates pyrite oxidation by two mechanisms: by direct oxidation and by oxidizing Fe^{2+} to Fe^{3+} , which in turn oxidizes the sulfide minerals (6, 15, 21, 43). Direct bacterial oxidation of pyrite is generally slower than the indirect process (52), although some strains and adapted cultures display the opposite tendency (18). Direct oxidation is probably most important during initial acidification, when complete hydrolysis of Fe³⁺ and the resultant precipitation of Fe(OH)₃ are too rapid to allow ferric iron to act as an important oxidant.

During the first stage of this process, fine-grained pyrite is oxidized either by <u>T</u>. <u>ferrooxidans</u> or by air with equal amounts of acidity produced by the oxidation of sulfide to sulfate (reaction A) and by the oxidation and hydrolysis of iron (reaction B) (5):

$$FeS_{2} + \frac{7}{2}O_{2} + H_{2}O$$

$$\longrightarrow Fe^{2+} + 2SO_{4}^{2-} + 2H^{+}; \quad (A)$$

$$Fe^{2+} + \frac{5}{2} H_2 O + \frac{1}{4} O_2$$

 $\longrightarrow Fe(OH)_3(s) + 2H^+.$ (B)

The ability of <u>T</u>. ferrooxidans to accelerate the rate of pH decline is important, for each rainfall potentially interferes with the initial buildup of acid. As long as alkalinity exceeds acidity, the only major downstream effect is an increase in sulfate concentration. Once acidity significantly exceeds alkalinity, it becomes difficult to return the acid-producing system to stage l.

As the pH decreases, abiotic oxidation of Fe^{2+} slows down dramatically, according to the rate law:

$$\frac{-d (Fe^{2+})}{dt} = k \frac{(0_2 (aq)) (Fe^{2+})}{(H^+)^2}, \quad (1)$$

where (Fe^{2+}) , $(O_2(aq))$, and (H^+) are activities, k is the rate constant, and t is time $(\underline{46})$.

As the abiotic rate decreases, T. ferrooxidans assumes its primary role of oxidizing Fe^{2+} , thereby allowing reaction B to continue producing acidity and ferric hydroxide. Although the reaction stoichiometry remains the same, this step is defined herein as a transition point from the primarily abiotic stage 1 to the bacterial catalysis-controlled stage 2. Eliminate <u>T. ferrooxidans</u> and the pyritic system will stabilize. Otherwise, the pH decline typically continues to stage 3, where the reaction chemistry changes to a biologically mediated cycle of reactions C and D (30, 48):

$$Fe^{2+} + \frac{1}{4} O_2 + H^+$$

 $\longrightarrow Fe^{3+} + \frac{1}{2} H_2O;$ (C)

FeS₂ + 14Fe³⁺ + 8H₂O

$$\longrightarrow$$
 15Fe²⁺ + 2SO₄²⁻ + 16H⁺. (D)

As acidification proceeds and the pH in the immediate vicinity of the pyrite falls to less than 3, the increased solubility of iron and the decreased rate of $Fe(OH)_3$ precipitation result in increased Fe^{3+} activity (43). At an interstitial pH of approximately 2.5 (corresponding to a drainage pH of 3.5 to 4.0), bacterial oxidation of Fe^{2+} and reduction of Fe^{3+} by the pyrite (reactions C and D) combine to cause a dramatic increase in acidity and iron concentrations, as can be seen in figure 1. Eliminating the bacteria halts this third stage and thus reduces acid production.

The possibility of reducing acid drainage by bacterial inhibition was first considered in 1953 but was rejected as impractical due to probable rapid repopulation (<u>34</u>). Later attempts to inhibit <u>T. ferrooxidans</u> in the field or in largescale laboratory experiments were unsuccessful (<u>5</u>, <u>42</u>), which supported this viewpoint. Despite the results of these early attempts, it was felt that the crucial role played by <u>T. ferrooxidans</u> in pyrite oxidation warranted a reexamination of the potential use of bactericidal methods in mining environments.

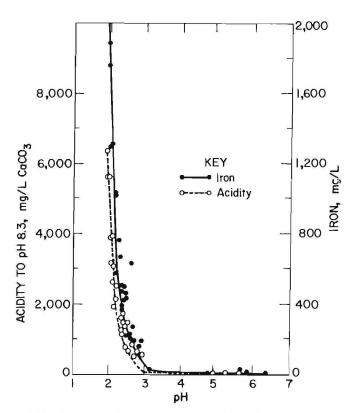


FIGURE 1. - Acidity and total dissolved iron versus pH for a series of experiments conducted in laboratory simulations of a coal refuse pile (28).

The biological literature contains numerous laboratory inhibition studies of T. ferrooxidans conducted in attempts to understand the unusual biochemistry of its metabolism. These studies demonstrated the vulnerability of T. ferrooxidans to certain metals (such as mercury, tellurium, and molybdenum), organic acids, and some anionic surfactants (13, 25, 41, 49-50). After eliminating substances that were environmentally unsafe or too expensive for large-scale use, it was decided to test anionic surfactants. These surfactants, used as cleansers in laundry detergent and shampoos, fill <u>T</u>. <u>ferrooxidans</u> in culture medium at concentrations as low as 2 to 5 mg/L (<u>13-14</u>, 28).

INHIBITORY EFFECTS OF ANIONIC SURFACTANTS

Anionic surfactants are generally regarded as good cleansers but poor bactericides (54). However, it has been shown that their ability to inhibit bacterial activity increases markedly at low pH The various means by which surfac-(16).affect microorganisms have been tants summarized by Hugo (24), who concluded that alteration of the semipermeable properties of the cytoplasmic membrane is the most typical mode of inhibitory action. This view is supported by demonstrated disaggregation of cell walls of other bacteria by the interaction of sodium lauryl sulfate (SLS) with the lipid, lipoprotein, and lipopolysaccharide fractions of the cell wall (40). T. ferrooxidans possesses a multilayered cell wall, which allows it to maintain an approximately neutral internal pH despite the extremely acid environment in which it lives (3, 7, 12, 23, 33). At low concentrations, it appears that anionic surfactants induce seepage of H⁺ into the cell, which slows Fe²⁺ oxidation by decreasing the activity of pH-sensitive enzymes. Higher concentrations of the surfactant kill the bacteria, presumably by causing permanent damage to these enzymes and the membrane material (13, 22, 28, 38).

LABORATORY TESTS

Inhibitory effects of anionic surfactants were monitored in the laboratory under humid conditions simulating the intermediate belt of the zone of aeration as described in Kleinmann and (29), using 50-g Crerar samples of crushed, rinsed, and sterilized highsulfur coal. To simulate the presence of T. ferrooxidans in natural mine infiltration, a 0.1-mL inoculum of a pure culture of the bacteria, in 9K medium (44), was trickled onto the samples every 3 days. Immediately following this, 0.6 mL of water with varying concentrations of surfactant was applied. Sterile controls received no inoculum.

effect of four of Figure 2 shows the the anionic detergents on acidity and dissolved iron. The inhibitory effect SLS, which was especially marked for was also the most effective in limiting bacterial population. Samples containing SLS at concentrations from 5 to 20 ppm showed proportionally delayed growth when transferred to 9K culture medium; at 25 ppm SLS was bactericidal, with acidity and iron concentrations reduced to about those of sterile controls. Other anionic detergents required somewhat higher concentrations to obtain the same effects (fig. 2). Generally, about 10 times more surfactant was required to kill T. ferrooxidans in coal refuse than in 9K culture media (28).

Possible inhibition of inorganic pyrite oxidation by anionic detergents was also investigated (28). Table 1 presents the results of a 22-day experiment using the crushed, sterilized pyritic coal refuse and SLS concentrations up to 50 mg/L applied at 5-day intervals. In addition, one experimental pair received 50 mg/L FeCl₃ with each application, as a test for inhibition of ferric oxidation of pyrite. At the end of the experiment, the coal was filtered and rinsed with 100 mL of deionized, distilled water. Acidity

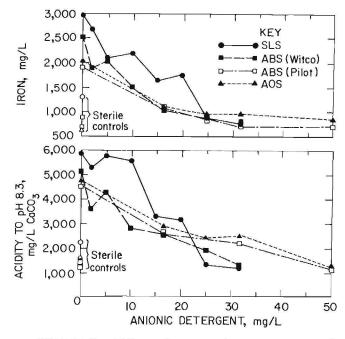


FIGURE 2. - Effect of anionic detergents on acid production from pyritic coal. SLS = sodium laury sulfate, ABS = alkyl benzene sulfonate, AOS = alpha olefin sulfonate (28).

and iron analysis of the filtrate and the drainage collected during the experiment indicated that the SLS did not significantly affect direct (air) oxidation or abiotic ferric oxidation of pyrite.

TABLE 1. - Effects of sodium lauryl sulfate on crushed sterilized pyritic coal in a laboratory simulation of the intermediate belt of the zone of aeration

Composi	tion of	each rain-	SLS	Acidity to	Total iron,
fall infiltration, mL			concentration, pH 8.3		mg/L
GW ¹	SLS ²	FeCl ₃ ²	mg/L	$CaCO_3$ as mg/L	
6	0	0	0	2,380	695
6	0	0	0	2,280	800
3	0	3	0	3,375	765
5	1	0	16.7	2,280	741
4.5	1.5	0	25	2,630	604
4	2	0	33	2,000	645
3	3	0	50	2,875	820
0	3	3	50	3,420	735

Synthetic groundwater (53).

²Concentration = 100 mg/L.

INITIAL CONSIDERATIONS

Laboratory and pilot-scale tests (28-30) indicated that anionic surfactants had the potential to slow down pyrite oxidation by inhibiting T. ferrooxidans. Full-scale tests were needed to determine the effectiveness of the method under field conditions, Of particular interest were the degree to which water quality could be improved and the application frequency needed to control pyrite oxidation.

An immediate problem was determining an application rate for the field sites. Application at the inhibitory concentration determined in the laboratory (25 mg/L SLS) was clearly too low: Infiltration from the next rainfall would dilute the surfactant and allow repopulation. Adsorption of SLS on the spoil or refuse also had to be considered since relative adsorption and desorption rates would control pore water SLS concentration and the rate of SLS migration. The application frequency would also depend on the rate of SLS loss by hydrolysis in the acid environment and by biodegradation.

It was decided that initial application rates would be based on the amount of SLS that could be adsorbed within the top 1 ft of refuse. A procedure for estimating this adsorption capacity is described on pages 10-11. The l-ft-thick treatment zone was selected for several reasons: (1) Oxidation was assumed to occur largely in a near-surface oxygenated zone (17, 20), (2) desorption would subsequently allow downward migration, and (3) it was preferred to undertreat rather than overtreat, to prevent significant SLS concentration off the site. Although SLS is generally regarded as safe for household use, it can have deleterious effects on aquatic life at relatively low concentrations (1-2, 8).

The surfactant is generally shipped as a 30-pct solution and must be diluted on-site. Site-specific factors, such as availability of water and infiltrationrunoff characteristics, determine how much the surfactant is diluted.

INACTIVE REFUSE AREA TEST

The first site chosen was an ll-acre inactive coal refuse pile in Raleigh County, WV. The pile was formed of Beckley Seam refuse during the late 19th century by dumping from an aerial tramway. It is 1,500 ft long, 450 ft wide, and approximately 130 ft high at its crest. Quality of the drainage from the pile has been monitored by Westmoreland Coal Co. for over a decade, thus providing a good baseline against which the effectiveness of the method could be judged.

The adsorptive capacity of the coal refuse was determined to be about 45 mg SLS/kg of material, using the procedure described on pages 10-11. This is approximately equivalent to 150 lb SLS/acre ft, or 1 drum (55 gal) of 30-pct SLS per acre. The site was treated during late September 1981 with 10 drums of 30-pct SLS, diluted 175:1 (fig. 3). Water samples were collected at least once a week thereafter and routinely analyzed for sulfate, acidity, pH, iron, and anionic surfactants (4).

Water quality improved after a 3-month lag period, with a 60-pct decrease in acidity, sulfate, and manganese and a 90pct decrease in iron (figs. 4-7). The lag period was presumably caused by the time required for infiltration to flow through the old pile, but stored acidity in the form of sulfate salts may also have been a factor. Seasonal effects can be discounted since in previous years the contaminant concentrations peaked in win-The magnitude of the improvement ter. was greater than any change observed over the past 10 years. The obvious correlation between sulfate, acidity, and manganese indicates that as acid production was reduced, leaching of trace metals such as manganese also decreased. The disproportionately greater decrease in



FIGURE 3. - Hydroseeder being used to spray sodium lauryl sulfate on 11-acre refuse area in southern West Virginia. Application rate: 55 gal/acre of 30-pct solution, diluted 175:1.

iron appears to indicate that at least some of the refuse reached a pH high enough to precipitate ferric hydroxide within the pile.

Before application of the SLS, Westmoreland Coal Co. was spending about \$7,500 per month to treat the drainage from this pile. Based on the observed improvement in water quality and the costs of the SLS application, reduced water treatment costs paid for the SLS application in about 3 weeks.

ACTIVE REFUSE AREA TEST

The second field test was at an active coal refuse area in Preston County, WV. The pile is primarily Freeport Seam refuse from a preparation plant operated by Kingwood Mining Co. Inactive sections of the refuse pile are down gradient of the 8-acre active section and are revegetated; treatment of the drainage from the entire refuse area costs Kingwood Mining about \$1,000 per month.

One problem with the Kingwood refuse site was the lack of background data for the active section being treated. A pond was therefore constructed by Kingwood Mining Co. to collect surface runoff from much of the treated area, thus providing some indication of whether the application of the surfactant improved water quality.

Adsorption tests indicated that an application rate of 1 drum per acre was again appropriate. The area was treated in early November 1981, using a hydroseeder, with a dilution factor of 50:1 (due to a shortage of good-quality water).

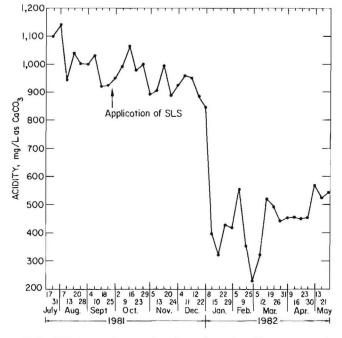


FIGURE 4. - Effect of sodium lauryl sulfate on acidity of drainage from 11-acre inactive coal refuse pile in southern West Virginia.

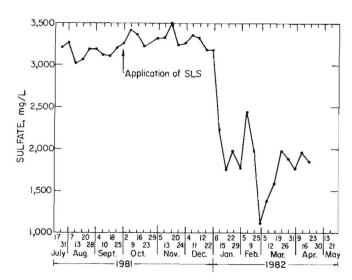


FIGURE 5. - Effect of sodium lauryl sulfate on sulfate concentrations at the southern West Virginia site. Lowered sulfate concentrations demonstrate that the acid production is being controlled at the source.

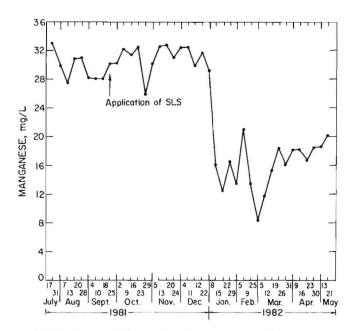


FIGURE 6. - Effect of sodium lauryl sulfate on manganese concentrations at the southern West Virginia site. By reducing acid production, dissolution of trace metals is decreased.

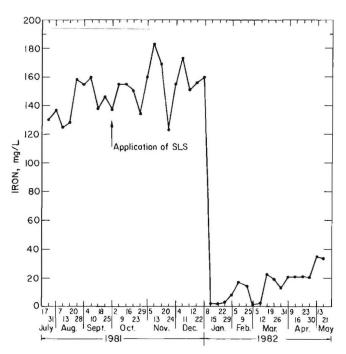


FIGURE 7. - Effect of sodium lauryl sulfate on iron concentrations at the southern West Virginia site. The disproportionate decrease in iron probably indicates that areas of the refuse pile are alkaline enough to result in iron hydrolysis and precipitation.

Water quality improved dramatically within a month of the SLS application. Acidity, sulfate, and iron were reduced by more than 95 pct and remained low for about 4 months after treatment (fig. 8). A complicating factor at the site is untreated material which was added during that interval; it is impossible to separate out the effects of the acidification of the new untreated refuse from the diminishing effects of SLS.

Effluent concentrations of surfactant have been extremely low at both sites. Except for one measurement of 0.6 mg/L shortly after application of the SLS to the inactive pile, SLS concentrations have been consistently less than 0.1 mg/L; no SLS has been detected in the stream at the discharge point of either treatment plant.

PROCEDURAL RECOMMENDATIONS

As a result of previously published articles by the authors (27, 31-32), the mining industry has started using anionic surfactants on coal refuse, coal stockpile areas, unreclaimed mine spoil, and waste sulfide rock. At present, more than 50 mining companies are using the technique with varied success. One coal company has applied an anionic surfactant two or three times a year to a developing coal refuse area for 4 years. The drainage is still showing net alkalinity, despite the fact that the coal refuse typically produces acidic drainage within 6 months. At the other extreme are sites where the technique produced no apparent effect or only a short-term improvement in water quality. Some of these failures can be explained simply, such as when the dosage rate or site conditions were obviinappropriate. At other sites it ously may never be known why the technique failed to reduce acid production, a1though possible reasons are discussed

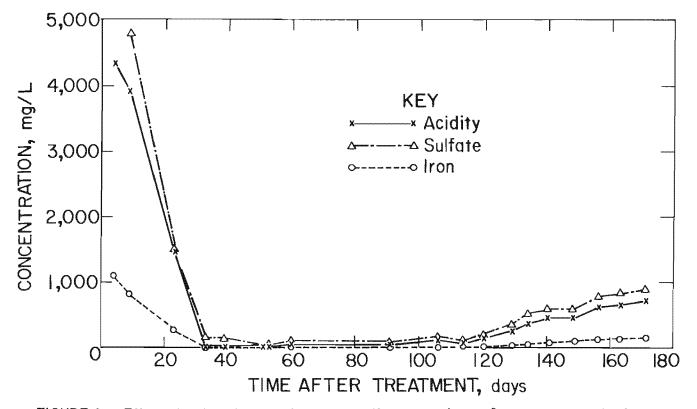


FIGURE 8. - Effect of sodium lauryl sulfate on runoff water quality at 8-acre active coal refuse pile in northern West Virginia. Application rate: 55 gal/acre of 30-pct solution, diluted 50:1.

below. Generally however, the technique has been successful. To improve the success rate, the following procedure is recommended.

PRELIMINARY CONSIDERATIONS

The first step in deciding if the surfactant technique is appropriate for a specific site is determining if it is potentially cost effective. Assume for the moment an approximate annual material cost for surfactant of \$600 per acre. Add to that the cost of three applications, the expense of which will vary from site to site. One should consider, for example, whether the surfactant will be applied with equipment already on-site and using available personnel time or with contracted equipment and manpower. For potential savings, assume a 60-pct decrease in acidity; this will reduce neutralization costs by about the same amount. If a 90-pct decrease in sludge accumulation is further assumed, one can estimate an associated annual savings based on the frequency with which the pond is normally cleaned. Other treatment costs, such as equipment and operator expenses, will generally not decrease significantly since the volume of water to be treated stays the same.

Since the surfactant must reach the pyritic material to be effective, the presence of intervening overburden or topsoil will clearly reduce the effectiveness of the treatment. If the cover is highly permeable, treating with somewhat higher levels of surfactant will compensate; if not, the surfactant will probably all be adsorbed by the nonpyritic material or will be washed away in surface runoff. Several mine operators have recently tried to solve this problem by applying the anionic surfactant solution through shallow wells; it is too early to judge if they have been successful.

If quick results are required, two other factors must be considered: hydrologic flow-through time and ground water pools. Flow-through time is the time it takes for rainwater to infiltrate through the mine material and emerge in a spring or seep. In mine spoil, flow-through times of over a year have been measured (19). In such a case, improvement in water quality at the discharge point cannot occur faster than water flows through the material.

Ponding of acid water on the old mine floor or in a refuse area also retards or masks the effect of reduced acid production. The presence of such a pool can sometimes be surmised by a steady acid load in the base flow during dry periods and only slight changes in the acid load during higher flows. If the pool volume is significant, it could be years before a decrease in acid production is reflected by more than a gradual improvement in water quality. If faster results are desired, alkalinity must be added to the pool in sufficient quantities to neutralize all of the acidity present.

APPLICATION PROCEDURES

If, based on the above considerations, the site appears appropriate for the surfactant treatment, the obvious question is how much surfactant is required. As described earlier, the concentrations needed to kill T. ferrooxidans in small volumes of coal refuse are quite low (25 to 40 mg/L). Such an application would be ineffective at an actual mine site because it would fail to reach most of the oxidizing pyrite. It is necessary to determine the adsorption capacity of the material being treated and to compensate for that adsorption with extra surfactant.

A simple laboratory procedure has been developed to provide an estimate of adsorption potential for overburden and coal refuse. A representative sample of the material to be treated is placed in a large, tared Buchner funnel, tamped to a uniform depth of 2 in, and weighed. A surfactant, such as SLS, is applied evenly over the material at approximate loads of 60 mg SLS/kg of coal refuse. Typical SLS concentrations range from 300 to 30,000 mg/L and are selected on the basis of the anticipated infiltration rate.

After the surfactant application, the top section of a second funnel or a perforated plate is fitted onto the packed funnel to allow even distribution of a distilled water rinse. The rinse solution is continuously applied through plastic tubing from a distilled water reservoir. The height of the reservoir is adjusted to balance influent and effluent flow rates; in relatively impermeable samples inundation is unavoidable and effluent flow rates can be as slow as 100 mL/h. Rinse effluent is collected in 100-mL fractions until no sudsing is observed on shaking.

The stock SLS solution and rinse fractions are analyzed for anionic surfactants by the methylene blue technique or a comparable standard method (4). Adsorption is calculated as the difference between the mass of SLS applied and that eluted and is recorded as milligrams of SLS adsorbed per kilogram of sample. Alternatively, adsorption can be reported as pounds SLS per acre inch, calculated from the known funnel area and sample thickness.

The laboratory test provides only a relative measure of adsorption capacity, since field conditions are not duplicated. On coal refuse, we base our application rate on the adsorptive capacity of the top l ft, since the most active zone of oxidation is typically shallow, and since surfactant, at reduced concentrations, will penetrate beyond this surface layer. We have been deliberately conservative to avoid the risk of significant surfactant concentrations in the effluent; we will test the effect of higher dosage rates in the future.

At sites where the pyritic material is not exposed, excess surfactant must be applied to compensate for that which will be adsorbed by the overburden. The adsorption rate can be determined using the procedures described and by assuming that the adsorptive capacity of the entire column must be accounted for. The extent of oxidation in buried pyritic spoil and refuse has not been determined, making it difficult to determine how much surfactant should be allotted for the actual acid source. Research is underway to determine oxygen concentrations at depth in coal refuse and mine spoil, which should help answer this question.

Based on adsorption tests conducted to date, application rates generally range from 1/4 to 1 drum of 30-pct SLS per acre. It is necessary to dilute the surfactant solution both to provide sufficient coverage and to allow for infiltration; the optimal dilution ratio is site specific. At low dilution rates (less than 125:1), application rates should be increased slightly to compensate for higher adsorption rates; also, excessive foaming can be a problem. Ideally, a dilution of 500:1 or even greater would be best, but in practice this would result in surfactant solution flowing over land as runoff, and in significantly higher labor costs.

Both hydroseeder and road watering trucks have been used by mine operators for application of the surfactant solu-With either machine, it is importion. tant to add the water to the tank at the bottom (using a hose) to avoid excessive foaming. For the same reason, agitation should be avoided as much as possible. Care should be taken when dealing with the concentrated surfactant; gloves should be worn to avoid "dishpan hands," and contact with the skin and eyes should be avoided. Finally, it is recommended that the tank and hoses be thoroughly rinsed of all surfactant after the application is completed, as the concentrated solution can cause pitting if allowed to remain.

OTHER CONSIDERATIONS

In the field tests and laboratory work, SLS was used rather than other anionic surfactants. There were two reasons for the initial choice: SLS inhibited T. ferrooxidans at lower concentrations than other generally available surfactants tested, and it hydrolyzes and breaks down in an acid environment. It was felt that these two factors would reduce the likelihood of significant contamination in the receiving stream. High adsorption, which was not initially considered, has contributed to the fact that probably effluent surfactant concentrations have been extremely low. We have, however, continued to use SLS in our field tests rather than introduce other variables. Some may wish to test other anionic surfactants, such as linear alkyl benzene sulfonate and alpha olefin sulfonate, which require somewhat higher concentrations to effectively inhibit T. ferrooxidans but which are less expensive and less acid sensitive than SLS. The latter factor may be especially important on refuse areas where the surface pH is very low; it is possible that in such a case SLS may lose its effectiveness by hydrolyzing before it contacts most of the oxidizing pyrite. Experiments are in progress to find acid-resistant surfactants that are equal to or more effective than SLS in inhibiting T. ferrooxidans (39, 45).

Reapplication of the surfactant is normally required to replace what is desorbed or degraded. When material from exposed refuse area was tested 2 an months after treatment, virtually no surfactant was found in the top 1 ft, although some surfactant remained below that level. In contrast, at another site that had been topsoiled and revegetated immediately after application of the surfactant, and from which there was virtually no subsurface drainage for about 18 months, enough surfactant remained to cause visible sudsing when, 2 after months of heavy rainfall, ground water reached the surface.

Potential consequences of using anionic detergents to reduce acid formation must be considered so as to avoid substituting one environmental problem for another. Studies of the chronic and acute effects of anionic detergents on fish and aquatic invertebrates indicate that kidney damage occurs in fish after long exposure to low levels (2 to 15 mg/L) of detergent, and that acute toxicity occurs in some species at concentrations as varied as 0.6 to 40 mg/L (1-2, 8). The World Health recommends that stream Organization concentrations not exceed 1.0 mg/L; other regulatory groups have recommended even lower values (e.g., Pennsylvania's Department of Environmental Resources, 0.25 mg/L). As stated earlier, effluent concentrations of SLS at the Bureau's field sites have been very low, typically below 0.1 mg/L in the effluent and below detectable limits in the receiving stream. The laboratory procedure to determine the application rate is apparently effective in preventing overtreatment; the only remaining concern is surfactant concentrations in the runoff. To minimize this risk, it is recommended that the surfactant be applied only when the ground is unsaturated and when no major rainstorms are expected for several days.

The surfactant solution has been sprayed onto revegetated sites with no apparent adverse effects on vegetation. It is recommended that treatment predate seeding by several weeks. It should similarly be in advance of any lime applications, as that might diminish the effectiveness of the surfactant.

CONCLUSIONS

1. Thiobacillus ferrooxidans plays an important role in determining the rate of pyrite oxidation. Anionic surfactants, applied at concentrations greater than 25 mg/L, reduce this bacterial activity and thereby slow acid production.

2. A laboratory procedure has been developed to determine suitable application rates for a specific site. Based on existing field data, the procedure appears to be effective in preventing overtreatment. Surfactant concentrations have generally been less than 0.1 mg/L in the effluent from the treated areas.

3. Sodium lauryl sulfate was applied to an ll-acre inactive coal refuse pile in southern West Virginia at a material cost of about \$200 per acre. Acid production fell approximately 60 pct, with an associated 90-pct decrease in iron concentration.

4. An 8-acre active coal refuse area in northern West Virginia was similarly treated. Acid production fell approximately 95 pct, with an associated 95-pct decrease in iron concentration. 5. At sites where water treatment costs are high, application of an anionic surfactant should be considered. Surfactant application should be repeated three times a year for maximum benefit.

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