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# USE OF CONTROLLED RELEASE BACTERICIDES FOR RECLAMATION AND ABATEMENT OF ACID MINE DRAINAGE

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## ABSTRACT

Oxidation of pyritic materials in mine tailings, refuse piles and spoil is catalyzed by the bacteria Thiobacillus ferrooxidans which, below a pH of 3, accelerate oxidation kinetics by a factor of five to ten. Several chemical agents have been demonstrated to inhibit T. ferrooxidans. However, the effectiveness of these bactericides is material specific. Laboratory techniques were developed to determine which bactericide would provide the greatest economic benefit for an individual site.

Spray applications of bactericides can be used for short term acid abatement in active operations. For reclamation, a dispersed monolithic controlled release system was developed. This system provides active agent in required concentrations for periods of three to five years to permit growth of vegetation using minimal quantities of topsoiling materials.

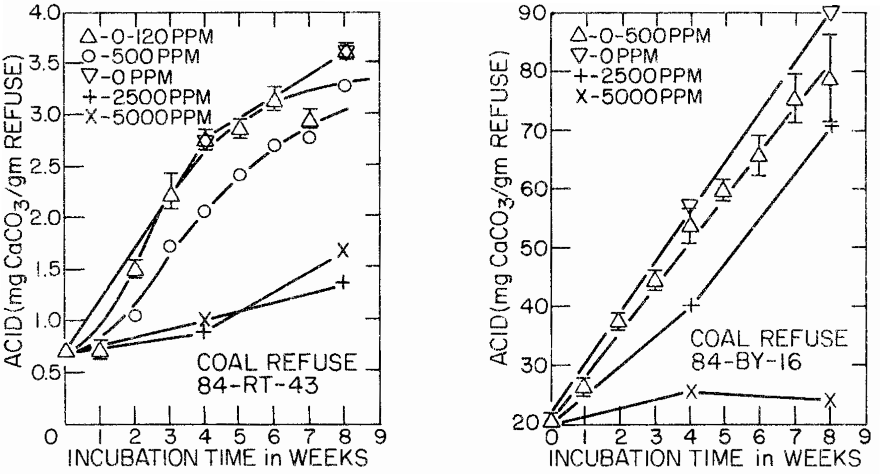
Bactericide release rate is controlled by the polymer matrix and by the size of the monolithic pellets. The pellets are applied by a hydroseeder in a one-step operation which distributes pellets and sprays a bactericide solution. Spray solutions initiate rapid bacteria inhibition and overcome overburden adsorption capacity, while pellets provide long-term control. The system is applied after rough grading of disturbed materials and then covered by topsoiling material.

Four refuse piles in the Appalachian region of the United States were reclaimed in 1984. Water quality improvement of 82% to 95% over control were obtained for acidity, iron, aluminum, manganese and sulfates. Significant loss of vegetation due to acid burnout occurred on the control areas while treated areas support a vigorous vegetation.

## INTRODUCTION

Acid mine drainage occurs as a result of the oxidation of iron sulfides. This oxidation process is catalyzed by the bacteria Thiobacillus ferrooxidans. A pH dependent three-stage mechanism of acid generation has been proposed (Kleinmann, Crerar and Pacelli, 1981).

Inhibiting or destroying these bacteria can significantly slow the rate



| Identification Number | Carbon | Sulfate Sulfur | Pyritic Sulfur | Organic Sulfur | Total Sulfur |
|---|---|---|---|---|---|
| 84-BY-16 | 55.40% | 0.62% | 4.56% | 1.21% | 6.39% |
| 84-RT-43 | 50.30 | 0.11 | 0.43 | 0.78 | 1.32 |

Figure 1. Effect of bactericide concentration on acid generation. Error bars are for ±1 standard deviation based on eight measurements each week.

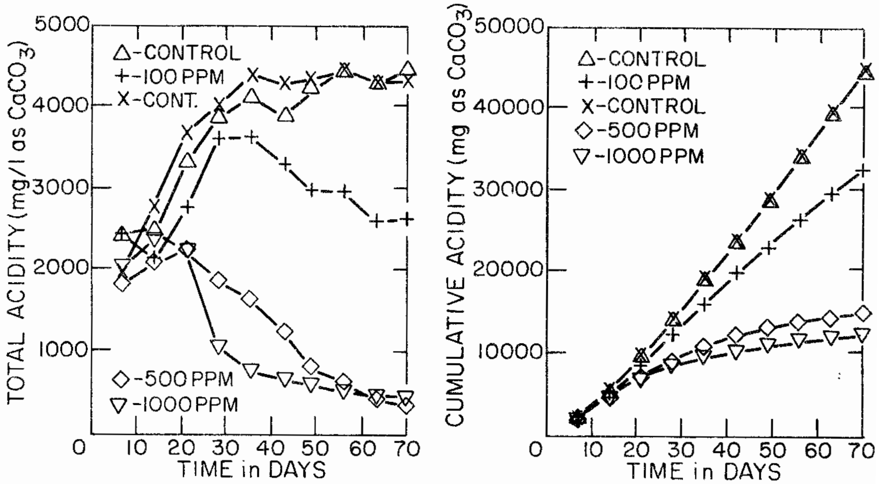


Figure 2. Reduction in acidity over time with increasing concentration of bactericide.

of acid production. Anionic surfactants, organic acids and food preservatives (Onysko, Kleinmann and Erickson, 1984) act as bactericides and inhibit these bacteria. Bactericides can be sprayed on active coal and refuse piles in adequate concentration; however, the bactericide degrades with time and is lost due to runoff resulting in bacterial repopulation and renewed acidification. To overcome this inherent short duration effectiveness of spray applications, controlled release systems were developed.

Bacterial inhibition by controlled release of a bactericide is required for a period of several years to insure successful reclamation. If acid is generated in the early phases of reclamation it can percolate to the surface and destroy vegetation. However, maintaining a strong vegetative cover for three years or more, can break the acid production cycle due to three natural biological processes. (1) As a healthy root system is established, it competes for both oxygen and moisture with acid-producing bacteria. (2) Populations of beneficial heterotrophic soil bacteria and fungi are reestablished resulting in the formation of organic acids which are inhibitory to T. ferrooxidans (Tuttle, Dugan and Apel, 1977). (3) The action of plant root respiration and these heterotrophic bacteria increases $CO_2$ levels in the spoil, resulting in an unfavorable microenvironment for growth of T. ferrooxidans.

## SCREENING TESTS

Control of bacteria through the use of chemical agents requires the evaluation of their effectiveness on different toxic mine wastes. The geochemistry, hydrology, acid generation potential, and neutralization potential of a specific site determine the bactericide that will function most effectively. Suitable laboratory tests that provide good reliable information about site characteristics in a reasonable period of time were developed. These are the Batch Incubation Test and the Column Leach Test (Shellhorn and Rastogi, 1984).

Figures 1 shows results of an eight-week incubation test on two refuse samples, along with their respective sulfur form analyses. Shown are the ensuing reductions in acidity as a function of time with different concentrations of the bactericide. Using the anionic surfactant sodium lauryl sulfate (SLS) as the bactericide, acid reductions of over 65% and 95% were obtained for the low and high acid-producing refuse, respectively. Corresponding changes in pH, Eh, specific conductance and metal ions were seen with time with increasing bactericide concentration.

Figures 2 shows the results from the column leaching test on a high acid-producing refuse using different concentrations of SLS as the bactericide. Acid reduction of over 90% is seen at the higher concentration.

## CONTROLLED RELEASE TECHNOLOGY

Spray applications of bactericides effectively inhibit mine acid formation for three or four months and have to be repeated several times a year to get effective control on active refuse and coal piles. Controlled release systems offer a solution to this costly and time consuming practice. Figure 3 shows a hypothetical scenario for the combination spray and controlled release application.

Spray applications have the advantage of delivering an effective dose of the active agent quickly, but the level falls rapidly due to runoff and biodegradation. To maximize the duration of effectiveness using a spray application, it is necessary to use large amounts of the agent, resulting in waste and in potential environmental problems (Figure 3a). Decreasing the dosage increases the application frequency required (Figure 3b). The controlled release system takes time to deliver the minimum effective concentration. The primary advantage, however, is that once an effective concentration is attained, it can be maintained for extended periods using less total active agent. The removal processes (biodegradation, degradation, hydrolysis, photolysis, leaching, etc.) following spray application follow first order kinetics (Kydonieus, 1980);

$$t_e = \frac{t}{k_r} \ln \frac{M_\infty}{M_e} \qquad (1)$$

where $t_e$ is the time an effective level is maintained, $k_r$ is the rate constant for removal, $M_\infty$ is the initial amount of agent applied and $M_e$ is the minimum effective amount. Thus, increasing the duration of effectiveness requires an exponential increase in the initial application. Maintaining an effective concentration using a controlled release system results in a greatly enhanced duration of effectiveness as follows (Kydonieus, 1980):

$$t_e = \frac{M_\infty - M_e}{k_D\ M_e} \qquad (2)$$

where $k_D$ is the rate constant for delivery from the controlled release device.

Figure 4 shows how combined initial bactericide spray applications and controlled release systems can be utilized to get an immediate effective dose and long-term effectiveness without overapplication or the need for frequent reapplication. The initial spray application required is dependent not only on the concentration required to inhibit acid producing bacteria, but on the capacity of the overburden to adsorb the bactericide.

Among the various factors which must be considered in the design of a controlled release system are the choice of the polymer system and its interaction with the active agent. The polymer must be capable of incorporating the agent either by solution or as a heterogeneous blend in which particles of the active agent are contained within the polymer matrix. Further, the polymer - bactericide system should not chemically alter the bactericide, but rather should act as safe harbor for the active agent until release occurs. The polymer system and any additives present must be harmless to the environment and be biodegradable after the useful life. The chemical and physical environment must be considered when developing controlled release systems. The system must be functional in the environment for which its use was intended. The controlled release system must be designed to be applicable in the field providing uniform coverage over affected areas with the ability to remain active at the site for the desired time period. Some specific factors which were taken into account in the development of a controlled release system for acid mine drainage are reviewed in Table I.

Numerous concepts have been employed for controlled release and have been extensively discussed (Kydonieus, 1980). The concept employed here for acid mine drainage treatment is the dispersed substance monolithic system

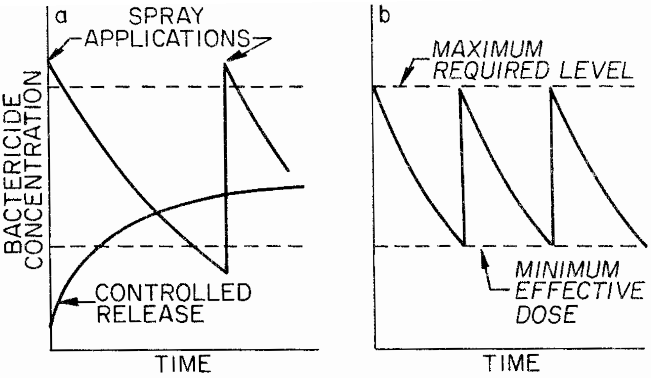


Figure 3. a. Short-term spray application duration vs. long-term controlled release duration.

b. Spray application system required for effective control.

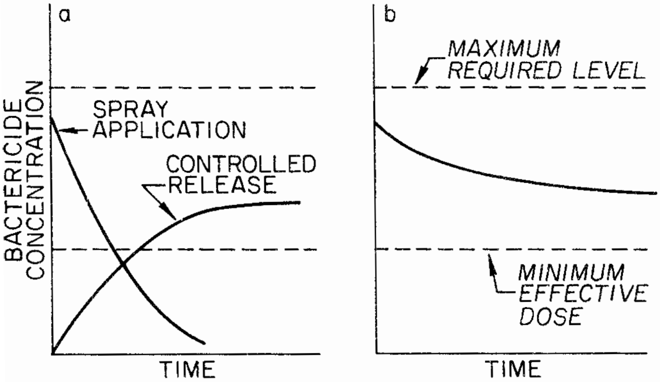


Figure 4. a. Delivery of bactericide from single spray application vs. controlled release device.

b. Bactericide controlled release system with tailored spray and controlled release delivery.

a fixed total volume of material, the release rate will be greater where the surface to volume ratio is large. The release kinetics will be profoundly affected by geometry where the active surface area from which release occurs changes with time due to extraction of material from the outer layers. Certain shapes such as spheres and cylinders favor rapid extraction rates at early times and lower rates later as the effective surface area decreases (Roseman and Carderelli, 1980).

## Materials and Methods

The dispersed monolithic pellets are made by extruding and chopping a blended stock of polymer, active agent and other chemicals. These chemicals serve two purposes, first, as porosigens or hydrophobes, they affect rate of release and second, as lubricants or polymer alloys, they serve as processing aids. To rapidly screen materials for relative release characteristics, a quick extraction procedure was developed.

A number of pellets based on their size and active agent content are selected and placed in a large volume of water in a wide-mouth jar. The ratio of the volume of water to active agent is chosen such that the amount of active agent released is easily detectable and the concentration of the agent in the water is insufficient to materially alter the rate of release. The jars are constantly rolled and the active agent concentration in the water is periodically measured. Figure 5 shows the rates of release obtained in the rapid extraction tests for four different systems. The slower rates of release offer considerable advantages. Not only can the system sustain bacterial inhibition for a longer time period, but it can be used in smaller size pellets, or conversely, the active agent content can be increased while maintaining a usable life. Pellets generally range in size to a maximum of about 6 mm diameter and 12 mm long. A mix of pellets of different size and active agent content is used to obtain the desired effect on a site.

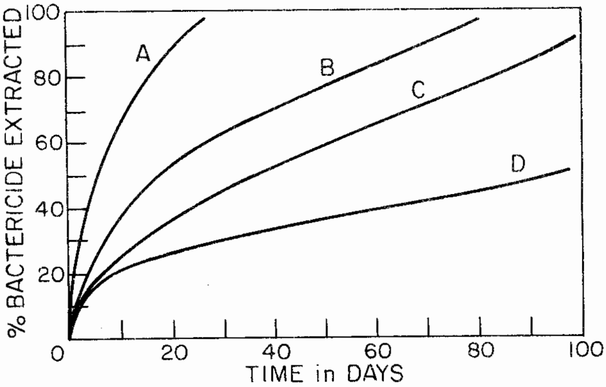


Figure 5. Bactericide release rates from monolithic systems. A. Natural Rubber. B. Ethylene vinyl acetate. C and D. Polyethelene.

Table I. Specific factors considered in developing a controlled release system for acid mine drainage.

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- Chemical Environment
    - pH, acidity
    - Moisture content
    - Pyrite content

- Physical Environment
    - Particle size distribution
    - Soil cover
    - Slope
    - Accessibility (application)
    - Degree of vegetation
    - Type of overburden material
    - Age of material - stage of acid production

- Climate
    - Precipitation (average and events)
    - Temperature - (average and extremes)

- Hydrology
    - Percolation rates
    - Runoff rates

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(Fox and Rastogi, 1983). In such a system, when the soluble and the dispersed component are in equilibrium within the polymer matrix and the concentration of dispersed particles is sufficiently low so as not to be interconnected, release rate follows $t^{1/2}$ order kinetics such that

$$M_t = kt^{1/2} \tag{3}$$

where $M_t$ is the amount of the agent released, t is time and k is the release rate. This type of release kinetics holds for almost the entire release curve. Where the solubility of the active agent is sufficiently low, and where the concentration is high, a porous network of interconnecting capillaries or pores exists. Release from such systems is not due to diffusion of the active substance through the polymer matrix but through the elution media. These systems also follow $t^{1/2}$ kinetics. The release rate is directly proportional to the porosity $\varepsilon$ and the tortuosity $\tau$ of the matrix such that

$$Q_t = \left[SD \frac{\varepsilon}{\tau} \; (2A - \varepsilon \cdot S)t\right]^{1/2} \tag{4}$$

where $Q_t$ is the amount extracted at time t per unit surface area, S and D are solubility and diffusion coefficients and A is the total concentration of dispersed agent within the polymer matrix.

## The Effect of Surface Area

The release of active substance is related not only to the type of system employed, but also to the geometry of the controlled release device. Many shapes and sizes are available ranging from large slabs or sheets to microcapsules measured in microns. It is intuitively obvious that given ment. Subsequent to site grading, but prior to the application of soil cover, a hydroseeder is used for a one-step application of bactericide solution and the controlled release pellets. A two-step process can also be used with a hydroseeder for spraying and a lime spreader for application of controlled release materials. Both approaches are followed by standard reclamation practice of soil cover, liming, seeding and fertilizing.

## Field Evaluations

In 1984, four refuse piles were reclaimed in Ohio and West Virginia, where a variety of controlled release systems and bactericide concentrations are being evaluated. Control tracts have been established at each to provide an experimental comparison through two methods of water quality monitoring. Aside from the bactericide applications, normal reclamation practices in grading, liming, soil cover, seeding and fertilizing were used. Topsoil depth was about 200mm.

Core sampling designed to critically and statistically evaluate water quality as a function of depth has been utilized. Core data showed significant improvements in water quality parameters between treated and control areas (Table II). Fifty cores taken 144 days after bactericide application were subdivided each into four sections of 50mm. Each core segment was analyzed using a procedure similar to a standard U.S. Environmental Protection Agency leaching method. The differences in water quality parameters decrease with depth as would be expected.

Table II. Core sample results.

| | Percent Difference - Untreated Over Treated Area | | | | |
|---|---|---|---|---|---|
| Core Depth | Acidity | Total Iron | Aluminum | Manganese | Sulfate |
| 0- 50 mm | 50% | 356% | 94% | 26% | 0% |
| 50-100 mm | 36% | 231% | 50% | 158% | 36% |
| 100-150 mm | 9% | N/A | N/A | N/A | N/A |
| 150-200 mm | 16% | N/A | N/A | N/A | N/A |

*All percentage values are valid at the 99% or higher confidence level.

Larger differences in water quality parameters were seen in more recent data obtained from lysimeter monitoring at 191 days subsequent to bactericide application (Table III). Eight lysimeters, four in each of the treated and control areas, placed approximately 300mm into refuse material were sampled. Comparison of averaged values from the treated section to the control show considerable improvements in acidity, specific conductance, total iron, ferrous iron, sulfate, manganese, and aluminum.

Visual observations during this monitoring period support the results from core sampling and lysimeter monitoring. Significant loss of vegetation due to acid burnout, as well as an acid seep at the base of the con-

## USE OF CONTROLLED RELEASE SYSTEMS IN RECLAMATION

Acid toxic mined lands severely discourage growth of vegetation and are a source of water pollution. To reclaim these lands, often large quantities of lime and soil from borrow areas are used with elaborate water treatment control systems. Controlled release bactericide systems can effectively reduce the cost of both reclamation and water treatment.

The use of controlled release systems in reclamation has been reduced to a practical method (Shellhorn and Rastogi, 1985). Sites under consideration are visited and geologic and hydrologic factors are assessed. Site material is analyzed to determine bactericide effectiveness and acid production capacity using geological factors, chemical composition, and tests described earlier. This information is then used to determine the dosage requirements and the specific mix of pellets.

Figure 6 shows the results of acid inhibition from four different bactericides on refuse samples described earlier. The results illustrate the variability of inhibition and thus the material-specific nature of bactericides. In fact, bactericide X105L actually increased the measured acidity in the high sulfur refuse. These results make a compelling case for site-specific pre-evaluation. Any one bactericide is not universal and cannot be indiscriminately used on all sites. Such use might aggravate an existing problem.

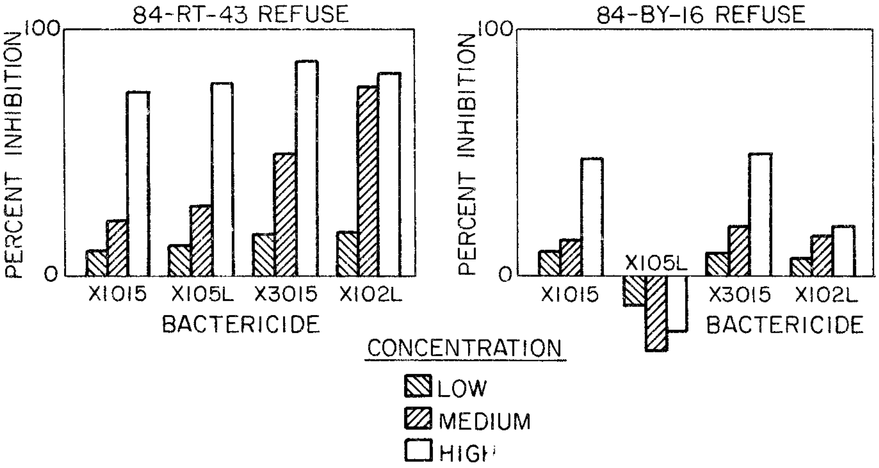

Figure 6. Relative efficacy of bactericides on refuse materials. Different levels of inhibition demonstrate the site-specific nature of bactericides.

Physical application of controlled release products and spray materials are easily incorporated into the reclamation plans with standard equip-

Table III. Lysimeter sample results.

| Parameter | Treated Area | Untreated Area | Percent Reduction in Treated Area |
|---|---|---|---|
| Acidity | 882 mg/l | 6,620 mg/l | 87% |
| Specific Conductance | 2,725 umhos | 5,332 umhos | 49% |
| Total Iron | 156 mg/l | 1,254 mg/l | 88% |
| Ferrous Iron | 31 mg/l | 535 mg/l | 94% |
| Aluminum | 31 mg/l | 568 mg/l | 95% |
| Manganese | 6 mg/l | 60 mg/l | 89% |
| Sulfate | 2,100 mg/l | 11,388 mg/l | 82% |

trol areas were present. In contrast, the treated areas possessed no detectable loss of vegetation and had established a strong vegetative cover. Initial results from another but more recent field site are similar to those described above.

## SUMMARY

A practical bactericide system for controlling acid mine drainage has been developed. Data obtained from field projects are being used to refine formulations for increased life of controlled release systems and improvement of bactericide application rate determinations. These systems aid permanent reclamation, and provide environmental protection for active coal refuse piles and mine tailings.

Improvements in the environment for plant life for prolonged periods of time, thus aiding nature to complete the reclamation process, is of primary concern with current reclamation techniques. The controlled release system outlined in this paper promotes such improvements. Further, it reduces the need for lime, soil cover, creating and revegetating borrow areas, and subsequent site maintenance.

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