PREVENTION OF ACID DRAINAGE
FROM STORED COAL[a]

By Harvey Olem,[1] Tracey L. Bell,[2] and Jeffery J. Longaker[2]

ABSTRACT: A method has been identified for controlling acid production and subsequent dissolution of toxic pollutants in drainage from coal storage piles. Results of laboratory and field experiments indicate that it may be possible to prevent, rather than treat, acid drainage by periodically applying an environmentally safe detergent formulation to the coal. These experiments showed that a mild solution of sodium lauryl sulfate (SLS) effectively blocks the activity of the bacteria that promote acid formation and chemical leaching. Drainage from coal treated once with 50 mg/L of SLS remained neutral for 60 days, about three times longer than the untreated control sample. An extrapolation of results to an industrial-scale application revealed that the cost of the SLS needed for a single application would likely be no more than $200 per acre of coal storage area ($500 per hectare) or, expressed per unit weight of coal, $4,000 per million metric tons.

INTRODUCTION

As more and more utilities and industries throughout the United States shift from the use of oil and natural gas to the more abundant supplies of coal, on-site storage of coal will increase. It has been projected that by 1985 the amount of coal in storage in the United States will increase from its present level of 128,000,000 metric tons (1978 estimate) to 227,000,000 metric tons (1). By the year 2000, the total amount of coal stockpiled could reach 680,000,000 metric tons (1). This projected increase in coal storage has renewed interest in the environmental effects of contaminated drainage from coal storage facilities.

The most efficient method now used for storing large quantities of coal is placement on the ground. Because the coal is exposed to the elements, rainwater falling on the pile can become contaminated by the action of chemolithotrophic bacteria on pyritic materials (usually iron disulfides). This occurs by the same series of reactions that are known to produce acid drainage from coal mines. Drainage from coal storage areas usually has an extremely low pH (pH 2–3) and generally contains high concen-

[1]Projects Mgr., Div. of Water Resources, Tennessee Valley Authority, Chattanooga, Tenn. 37401.

[2]Environmental Engr., Div. of Water Resources, Tennessee Valley Authority, Chattanooga, Tenn. 37401.
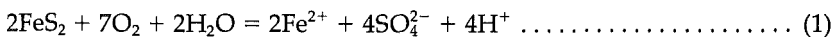
103

trations of metallic ions (aluminum, iron, manganese, mercury, nickel, zinc, etc.) sulfates, and suspended solids. To prevent such problems, this drainage is typically collected in a central pond and treated, usually by addition of hydrated lime. Consequently, runoff and leachate from coal storage piles have the potential for polluting both surface and ground water.

Results of laboratory experiments indicate that it may be possible to prevent, rather than treat, acid drainage by periodically applying an environmentally safe detergent formulation to the coal. For these experiments, two anionic detergents were applied to columns filled with coal that had been rinsed with water until the pH of drainage was neutral. This was done to simulate freshly mined coal or, more nearly, coal that had been processed by coal washing. As a control, a third column was filled with coal and did not receive any detergents. Because only one test has been performed to date, the results are considered preliminary.

BACKGROUND

One of the most common and most troublesome impurities in coal is a metallic sulfide, iron pyrite. When mining exposes pyrite (FeS_2) to water and oxygen, a chain of chemical reactions begins:

$$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \dots\dots\dots\dots\dots\dots (1)$$

$$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O \dots\dots\dots\dots\dots\dots\dots\dots (2)$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \dots\dots\dots\dots\dots\dots\dots\dots\dots (3)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \dots\dots\dots\dots\dots (4)$$

As shown in Eq. 1, pyrite is oxidized to produce ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}), and some acid (H^+). The ferrous iron can then be oxidized with this acid and some oxygen (Eq. 2) to form ferric ions (Fe^{3+}). Under certain conditions, the ferric ions will hydrolyze (Eq. 3) to form the yellow-orange ferric hydroxide precipitate ($Fe(OH)_3$) that typically appears in streams contaminated by acid mine drainage. Ferric iron can also react with more pyrite (Eq. 4) to form more ferrous iron and acidity. These reactions produce acid at a constant rate.

Acid drainage would develop very slowly if this strictly chemical chain of events were not greatly accelerated by the biochemical action of certain bacteria. First isolated in 1947, *Thiobacillus ferrooxidans* were then believed to play some role in acid mine drainage formation, but their exact role was not well understood (1). More recently, Singer and Stumm (8) showed that direct oxidation of pyrite by oxygen (Eq. 1) was too slow to generate the amount of acidity observed in nature, and concluded that the oxidation of ferrous iron to ferric iron (Eq. 2) created a cycle in which the ferric ions produced in this reaction directly attack pyrite to form considerable amounts of acid (Eq. 4). Equation 2, however, is extremely slow under acid conditions in the absence of microorganisms. The half time for spontaneous ferrous iron oxidation in a sterile solution of pH 3.5 has been estimated to be 2,000 days (9). However, *T. ferrooxidans* were shown to accelerate this reaction by a factor of 10^6, thus producing significant quantities of ferric iron. The subsequent oxidation of

104

pyrite by these ferric ions produces more ferrous ions to allow the cycle to continue, producing more and more acidity until all the reactive pyrite is leached.

BACTERIAL INHIBITION

It is generally considered preferable to prevent the formation of pollutants than to provide continuous treatment after pollutants have already formed and contaminated surface or ground waters. It is with this objective in mind that bacterial inhibition of acid formation was investigated to prevent the contamination of rainfall draining through coal piles.

Anionic detergents, while normally considered cleansers rather than bactericides, do possess bactericidal properties. Dugan (3) found that anionic detergents can effectively stop iron oxidation by *T. ferrooxidans* at concentrations as low as 2 mg/L. Kleinmann (5,6) demonstrated the effectiveness of one type of detergent, sodium lauryl sulfate, in reducing acid formation in coal refuse piles and surface coal mines at somewhat higher detergent concentrations. The reason for this inhibition is not yet clear, but evidence indicates that semipermeable properties of the cytoplasmic membrane is altered so that H^+ is allowed to seep into the normally neutral interior of the cell (4). Thus, the bacteria are appropriately attacked by the acid they helped produce.

This study evaluated two types of anionic detergents: sodium lauryl sulfate (SLS) and neutralized benzene sulfonate (NBS). The common use for each detergent is shown in Table 1.

MATERIALS AND METHODS

Three acrylic plastic columns were set up in the laboratory to simulate a coal pile (Fig. 1). The columns were approximately 2 m high and 30 cm in diameter. A 1.5-cm diameter drain valve was located in the bottom of each column to facilitate collection of leachate. The underdrain system in the columns consisted of a 20-cm depth of thoroughly washed pea gravel under 25 cm of washed sand. To prevent the gravel from clogging the drain, a capped 10-cm diameter, 13-cm long perforated plastic column was glued over each drain hole. Compressed air was passed through water and fed through an L-shaped glass tube to simulate atmospheric conditions within a coal pile. The tube was located at mid-height in the sand layer. The sand also acted as a diffuser to distribute the air across the coal.

TABLE 1.—Detergents Tested to Prevent Coal Pile Drainage Contamination

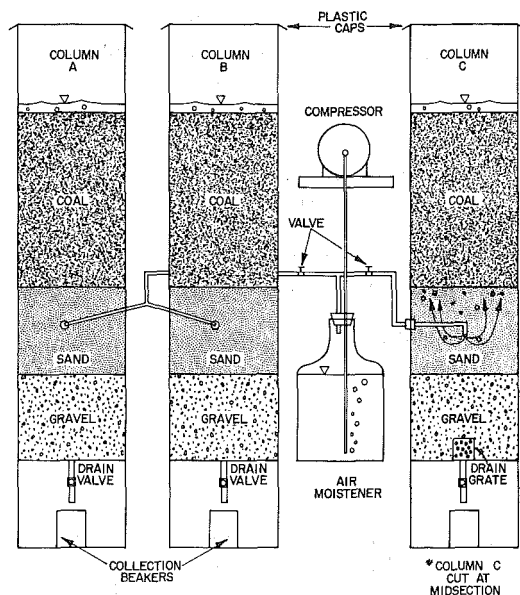| Detergent (1)	Common use (2)	Percent active ingredient in product tested (3)
Sodium lauryl sulfate	Active ingredient in many hair shampoos	30
Neutralized benzene sulfonate	Active ingredient in many laundry detergents	15

105

FIG. 1.—Laboratory Columns Used to Simulate Coal Pile Drainage

Coal was obtained from the Tennessee Valley Authority (TVA) Cumberland Power Plant located near Nashville, Tennessee. Small samples of the coal were collected from different locations and depths around the coal pile. The samples were than composited. To simulate freshly mined coal or coal that had been processed by coal washing, the composite was rinsed with water until the pH of drainage was neutral. A portion of the washed coal was analyzed for total sulfur, moisture, volatile matter, ash, fixed carbon, and energy content.

Approximately 0.057 m^3 of the coal was divided equally between the three columns. The three coal samples were prepared identically except for the application of different solutions.

Each coal sample was initially placed in a large bucket and saturated with the necessary solution for one hour. The excess water was poured off, and the resultant slurry was poured into the appropriate column. The coal placed in the first column was treated with deionized water only. Coal in the second column was treated with a solution containing 50 mg SLS per liter of deionized water. Coal in the third column was treated with a 50-mg/L solution of NBS and deionized water. These 50-mg/L detergent solutions corresponded to an approximate application rate of 10 $\mu g/g$ of coal.

The columns were dosed twice a week with 1,500 ml of deionized water to simulate a 1 in. (2.5 cm) rainfall. Leachate was then collected from the drain valves at the bottom of the columns.

Leachate samples were routinely analyzed for acidity, pH, conductivity, iron, manganese, and the most probable number (MPN) of iron-oxidizing bacteria. Selected trace metals and detergent concentrations were also analyzed periodically during the experiment. The deionized water

106

used in the experiment was routinely analyzed for pH. All chemical analyses were performed according to procedures outlined in *Standard Methods for the Examination of Water and Wastewater* (10). Populations of iron-oxidizing bacteria were estimated by use of the inorganic salts culture medium and the combination multiple tube and microtitre plate procedure described by Olem and Unz (7).

RESULTS AND ANALYSIS

Coal Characteristics.—Table 2 shows the characteristics of the coal used in these experiments. The total sulfur content was typical for coal burned at most TVA power plants. Coal with these characteristics has been found to produce strongly acidic drainage when exposed to the elements.

Simulated Rainwater.—The deionized water used to simulate rainfall had a pH of approximately 5.5. The acidity present in the deionized water was due to contact with atmospheric carbon dioxide.

Leachate Characteristics.—Table 3 shows the quality of leachate from each coal column three days after the beginning of the experiment. As expected, the drainage was initially pH 7.2 for all three columns. Most other water chemistry characteristics were similar for the drainage from all three columns, although certain parameters varied widely. After remaining nearly neutral for about 20 days, the leachate suddenly became ten-thousandfold more acid in the control column, as pH decreased from 7 to about 3 (Fig. 2). The pH continued to decline for another 20 days until it leveled off at about pH 2.

Drainage from the test column treated with NBS became slightly more alkaline at first but remained approximately neutral only about five days longer than the control. Then it paralleled the same pattern of rapidly increasing acidity, reaching pH 2 after about 50 days.

Drainage from the coal treated with SLS became even slightly more alkaline for the first 20 days. After a slight decrease in pH, it remained neutral for two and one-half times longer than the control. Even when the pH finally dropped after about 60 days, it hovered for another 25 days between pH 4 and 5. The acidity at this pH was approximately 100 mg/L, compared to 5,000 mg/L for the control column. This difference could be extremely important in terms of the treatment that would be needed to neutralize it.

The coal treated with SLS eventually produced drainage with the same

TABLE 2.—Analysis of Coal Used in Laboratory Simulation of Coal Pile Drainage

Characteristics (1)	Value (2)
Total moisture, percent	3.8
Volatile matter, percent (dry)	39.8
Ash, percent (dry)	9.8
Fixed carbon, percent (dry)	50.4
Total sulfur, percent (dry)	3.1
Energy content, in British thermal units per pound (dry)[a]	13,161

[a]To convert to kJ/kg, multiply by 2.321.

107

TABLE 3.—Quality of Leachate from Laboratory Coal Columns Three Days After Application of Detergents[a]

Characteristics (1)	Concentration in Leachate		
	Control (2)	Treated with SLS (3)	Treated with NBS (4)
pH	7.2	7.2	7.2
Acidity, in milligrams per liter $CaCO_3$	0.6	0.3	0.3
Conductivity, μmhos/cm	480	210	600
Metals, in micrograms per liter			
Fe	1,020	299	1,680
Mn	96	22	100
Pb	4	<1	11
Hg	0.7	0.3	<0.2
As	1	<1	1
Cd	0.2	<0.1	<0.1
Cu	<1	<1	4
Se	1	<1	2
Cr	2	320	1
Ni	<50	<50	<50
Zn	<5	<5	<5

[a]Coal was saturated with a 50 mg/L solution of the necessary detergent, which corresponded to an approximate application rate of 10 μg/g of coal.

low pH of about 2, but only after 140 days, three and one-half times longer than the 40 days for the untreated control.

Other constituents generally followed the same pattern as the changes in pH. Table 4 shows the quality of leachate from each column 56 days after the beginning of the experiment. At this point in the experiment, only the drainage from the SLS-treated coal was neutral; the acidity of drainage from the control and NBS-treated coal was over 100 times higher. Conductivity and concentrations of Fe, Mn, As, Cd, Cu, Cr, Ni, and Zn were also significantly lower in drainage from the SLS-treated coal. Compared to the control, drainage from SLS-treated coal contained higher concentrations of only Pb and Se, and these concentrations were almost at the limits of detection.

Drainage from both treated columns had detergent concentrations below detection limits (<0.1 mg/L measured as methylene blue active substance). This is important because these detergents are toxic to aquatic life. For example, Dalela, et al. (2) reported an LC_{50} value of 11.2 mg/L for a freshwater fish, *Saccobranchus fossilis*, exposed to SLS. Subacute stress was observed at SLS concentrations above 0.75 mg/L.

Apparently, not much SLS was washed out of the coal. Most of it was probably adsorbed onto the coal particles and remained there until its chemical structure was broken down into simple degradation products such as carbon dioxide, water, and sodium and sulfate ions.

Kleinmann and Erickson (6) performed a detergent adsorption capacity test on refuse from a coal-cleaning plant and determined that one
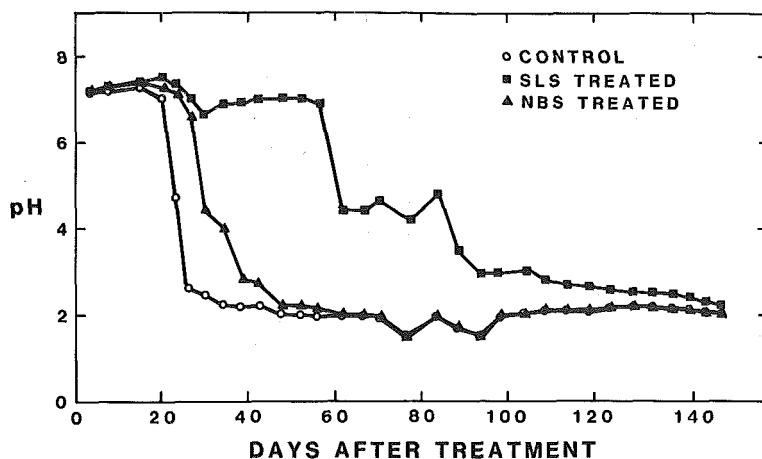
108

FIG. 2.—Changes in pH in Laboratory Generated Coal Pile Drainage Following Application of 50 mg/L of Sodium Lauryl Sulfate (SLS) and Neutralized Benzene Sulfonate (NBS)

gram of refuse adsorbed between 50 and 68 μg of SLS. These values were an order of magnitude higher than results for similar tests performed on overburden material from surface mines. When the same test was performed on the coal used in the laboratory column experiments reported here, adsorption capacity was found to be 60 μg SLS/g coal. Because of the lower adsorption capacity of overburden materials, Kleinmann (6) incorporated SLS into rubber pellets, which gradually release the detergent into infiltrating rainwater. This method may not be needed for coal storage and coal refuse disposal areas.

The NBS and SLS detergent applications apparently did not kill all the iron-oxidizing bacteria, because small numbers of live but apparently inactive bacteria were present even in samples collected after the coal was treated. For example, bacterial numbers in the drainage 28 days after treatment were 160,000 per 100 ml for the control column, and 7,900 per 100 ml for the SLS-treated column. Toward the end of the experiment, when drainage from the treated and control columns was acid, bacterial numbers were more similar. One hundred and nineteen days after treatment, drainage from the control and SLS-treated columns contained 1,100,000 and 920,000 iron-oxidizing bacteria per 100 ml.

The reasons for the relative effectiveness of SLS treatment compared to NBS are not known. SLS is the active ingredient in many shampoos used to remove protein buildup from hair. On the other hand, NBS is the active ingredient in many laundry detergents used to remove soil particles, not proteinaceous matter. If detergents alter the semipermeable properties of the cytoplasmic membrane and allow H^+ to seep into the interior of the T. ferrooxidans cells, as has been reported, then it is plausible that a detergent that removes protein would be more effective than one that removes soil.

Projected Costs.—A rough extrapolation of these laboratory scale results to an industrial scale application indicates that the cost of SLS needed

109

TABLE 4.—Quality of Leachate from Laboratory Coal Columns 56 Days After Application of Detergents

Characteristic (1)	Concentration in Leachate		
	Control (2)	Treated with SLS (3)	Treated with NBS (4)
pH	2.0	6.9	2.1
Acidity, in milligrams per liter $CaCO_3$	5,000	10	5,500
Conductivity, μmhos/cm	6,000	1,950	5,500
Metals, in micrograms per liter			
Fe	1,560,000	365	1,004,000
Mn	48,900	1,780	74,500
Pb	<1	2	7
Hg	0.3	<0.2	<0.2
As	200	1	220
Cd	310	2.3	340
Cu	1,050	7	1,160
Se	<1	4	1
Cr	295	<1	2
Ni	1,500	<50	3,300
Zn	13,700	<5	16,700

for a single application might be about $200 per acre of coal storage area ($500 per hectare). Expressed per unit weight of coal, the estimated cost would be $4,000 per 1,000,000 metric tons. These estimates assume a delivered cost of $0.75 per lb ($1.65 per kg) for the SLS used in the experiments and allow for a 50% decrease in the efficiency of detergent application in the field. Because only one experiment has been performed to date, these costs must be considered preliminary.

Methods of Application.—Results of laboratory experiments showed that SLS may be effective in preventing problems of acidity and dissolved metals in coal pile drainage for about two months. If an operating facility stored less than a 2-month supply of coal and always burned the oldest coal first, a single application to each new coal delivery might prevent the development of acid drainage. However, there are probably few plants where these conditions would be met at all times. In the tests performed thus far, it was assumed that it would be necessary to treat all the coal from the top to the bottom of an entire pile each time it is required. There are some indications, however, that bacteria are active mainly in the top layer of coal, where the temperature and availability of air best suit their needs. If that is the case, it might be necessary to treat only the surface of the pile, or it might be possible to extend significantly the time between full-pile treatments by means of supplementary surface-layer treatment.

It might even be economical to treat each new coal delivery before it is added to the pile, either as a supplementary treatment or as the only treatment required. At many plants, the surface of the coal pile is routinely sprinkled with water to control dust, and a small amount of SLS might easily be added to the tanks of the sprinkler trucks. A spray sys-

110

tem might be installed to treat every truckload or trainload of coal with a small amount of SLS, either as it is dumped or as it moves along conveyors to the pile, so that the surface layer of new coal would continually be protected against acid formation. If significant time is expected to elapse between mining and delivery, the coal might even be protected with SLS as soon as it is mined and then treated again when it is delivered.

Additional Research Needs.—There is a question as to whether it would be possible to correct an existing problem by application of detergents. A modification of the methods described in these studies would likely be necessary because SLS breaks down rapidly in strong acid solutions. It may be possible to correct an existing problem by treating the coal with SLS in combination with some buffering agent. Further experiments using several buffers such as sodium bicarbonate and phosphate are in progress.

It is not known whether SLS affects the burning characteristics of coal. This must be determined, because laboratory results indicated that SLS was readily adsorbed onto the coal particles. Another potential concern, the sulfur added to coal by treatments with SLS, should not present a problem. The sulfur content theoretically added to the coal by the sulfate ions in SLS is insignificant relative to the much higher sulfur content of even "low-sulfur" coal.

CONCLUSIONS

1. Controlled application of anionic detergents may be useful in preventing acid drainage from coal storage piles.

2. Sodium lauryl sulfate was more effective than NBS in preventing acid production in laboratory simulated coal piles.

3. Laboratory studies indicate that a single application may prevent acid formation for 60 days.

4. The cost for the amount of SLS needed for a single industrial scale treatment was extrapolated from laboratory results to be $200 per acre of coal storage area ($500 per hectare) or, expressed per unit weight of coal, $4,000 per 1,000,000 metric tons.

ACKNOWLEDGMENTS

APPENDIX.—REFERENCES

1. Colmer, A. R., Hinkle, M. E., "The Role of Microorganisms in Acid Mine Drainage: A Preliminary Report," *Science*, Vol. 106, 1947, pp. 253–256.
2. Dalela, R. C., Tyagi, A. K., Pal, N., and Verma, S. R., "Subacute Stress Induced by Sodium Lauryl Sulfate (SLS) on Certain Haematological Parameters in *Saccobranchus fossilis*," *Water, Air and Soil Pollution*, Vol. 15, 1981, pp. 3–9.
3. Dugan, R. P., "Bacterial Ecology of Strip Mine Areas and Its Relationship to the Production of Acidic Mine Drainage," *Ohio Journal of Science*, Vol. 75, 1975, pp. 266–278.

4. Hugo, W. B., "The Mode of Action of Antibacterial Agents," *Journal of Bacteriology*, Vol. 30, 1967, pp. 17–50.
5. Kleinmann, R. L. P., in "Proceedings, Symposium on Surface Mining Hydrology, Sedimentology, and Reclamation," D. H. Graves, ed., *Report No. UKY BU123*, University of Kentucky, Lexington, Ky., 1980, pp. 333–337.
6. Kleinmann, R. L. P., Erickson, P. M., in "Proceedings, Symposium on Surface Mining Hydrology, Sedimentology, and Reclamation," D. H. Graves, ed., *Report No. UKY BU126*, University of Kentucky, Lexington, Ky., 1981, pp. 325–330.
7. Olem, H., Unz, R. F., "Acid Mine Drainage Treatment with Rotating Biological Contractors," *Biotechnology and Bioengineering*, Vol. 19, 1977, pp. 1475–1491.
8. Singer, P. C., Stumm, W., "Acidic Mine Drainage: The Rate Determining Step," *Science*, Vol. 167, 1970, pp. 1121–1123.
9. Singer, P. C., Stumm, W., "Oxygenation of Ferrous Iron: The Rate-Determining Step in the Formation of Acid Mine Drainage," Federal Water Pollution Control Administration, Report 14010, Washington, D.C., 1969.
10. *Standard Methods for the Examination of Water and Wastewater*, 15th ed., American Public Health Association, Washington, D.C., 1980.

112