SECTION VIII

FORMATION AND TRANSPORT OF ACID MINE DRAINAGE

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To correct the conditions cited in the previous sections a number of abatement and treatment techniques exist. The degree of success or failure for individual applications of abatement or treatment methods is dependent upon the correct matching of a remedial technique with the known cause or causes of the acid discharge. To insure the application or appropriate abatement techniques, the nature of acid mine drainage formation and conveyance should be reviewed with abatement measures in mind.

THE FORMATION OF ACID MINE DRAINAGE

The initial step in the production of mine drainage is the oxidation of insoluble iron pyrite to (FeS_2) to a soluble ferrous sulfate ($FeS0_4$) with the by-product production of sulfuric acid (H2S04). The reaction which takes, place is the following:

$$2\ FeS_2 + 7O_2 + 2H_2O \text{ ----> } 2\ FeS0_4 + 2\ H_2SO_4 (1)$$

This reaction converts an immobile insoluble sulfide into a soluble sulfate which may now be carried in solution wherever water is flowing.

A second reaction may occur converting $FeSO_4$ to an intermediate $Fe\ (S0_4)_3$ or ferric sulfate. This ferric sulfate is produced by the following reaction:

$$4\ FeS0_4 + 0_2 + 2\ H_2S0_4 \text{ -4 } 2\ Fe_2\ (S0_4)_3 + 2\ H_20\ (2)$$

A final reaction produces an insoluble iron precipitate plus additional acidity.

This reaction may take the form of:

$FeS0_4 + 2\ H_20 \qquad Fe\ (OH)_2 + H_2S0_4$ (3)

$Fe_2\ (S0_4)_3 + 6\ H_2O$ ---> $2\ Fe\ (OH)_3 + 3\ H_2SO_4$ (4)

Note that reaction (4) replaces the H_2SO_4 utilized in (2) in addition to producing additional acid.

SUBSURFACE FORMATION AND TRANSPORT

The factors necessary for subsurface acid formation were noted by the Appalachia Regional Commission as the following:

> "The volume, depth and fluctuation of water in the mine plays a critical role in the balance of acidity and alkalinity in effluent mine drainage. In the Appalachian region, liquid water is not neces sary for the initial oxidation of pyritic materials due to the availa-bility of sufficient moisture in the mine air . . . oxidation is actually faster in air than in water. Liquid water acts primarily as the vehicle for dissolving and transporting the solutes in mine drainage. Only minimal amounts of water are necessary for transporting the iron and aluminum sulfates causing acidity , since these salts are extremely soluble and high concentrations can be readily carried, more than 12 percent (120,000 ppm) total dissolved solids has been observed in mine drainage. Fluctuations in water

depth promote the solution of salts formed on mine walls."[17]

The role of water in the formation of mine drainage is paradoxical. If water can be 100 percent excluded from pyrites (zero relative or absolute humidity), no acid producing reactions will take place. If water cannot be absolutely excluded, then 100% flooding will severely retard mine drainage reactions by limiting the availability of oxygen. Any condition between these two extremes will permit the formation of acid mine drainage. The effectiveness of 100 percent flooding of a mine (even if the water is oxygen saturated) in reducing AMD formation can be demonstrated by the following mass balance.

From equation (1) the following GMW (gram molecular weights) of materials are needed to initiate the acid forming process.

2 FeS_2	= 2 (56 + 2(32))	240
7 O_2	= 7 (2 (1 6))	224
2 H_20	= 2 (2 (1) + 16)	36
		500

The following products are formed:

2 FeS04 = 2 (56 + 32 + 4 (16)) = 304

2 H_2S0_4 = 2 (2 (1) + 32 + 4 (16)) = 196

500

This balance indicates that for each 224 grams of oxygen reacted, 196 grams of H 2 so 4 are produced. If 10 grams of 0 2 are reacted, then 10 x 196 %224 or 8. 75 grams of H 2 so 4 are produced. Acidity as defined by equivalent weight of $CaCO_3$ is (100/98) (H_2S0_4) or 9 grams of acidity produced per 10 grams of oxygen reacted.

If a flooded mine contains water which is at dissolved oxygen saturation (10 ppm approximately), and the pyrite oxidation reaction used all available oxygen, a discharge with an acidity of 9 mg/L would be produced. (For comparison, the discharges in the Loyalhanna watershed from nonflooded mines contain from 13 to 2400 mg/L acidity. The major discharges contain 350 to 600 mg/L acidity.

If oxygen could be completely excluded from the mine environment, then the reaction would cease.

The rate of pyrite oxidation and mine drainage fornation is a function of the area of reacting pyrite surface exposed to oxygen and water. The effect of coal mining and the subsequent collapseof mine workings is the significant increase in the surface area of pyrites exposed to these elements.

The result of pyrite oxidation is to transform an insoluble material into a soluble sulfate salt. This soluble salt is easily transported from its initial reaction site by the movement of moisture.

Investigators offer the following description of the removal process:

"The rate of (reaction) product removal is primarily a function of the hydrogeologic characteristics of the system. Such characteristics include the porosity and permeability of the overburden, the presence of large scale cracks, and the position of the oxidizing material with respect to the region of normal water table fluctuations . . . (It) is possible to visualize three parallel transport mechanisms. The first is . . . direct washing. As ground water percolates through flow channels in the coal seam, products from the walls of the pores are dissolved. These products may have formed at times when the channel was not filled with water

The second removal mechanism is the flushing of products from an inundated volume. The inundation occurs as the water table rises during the spring thaws or during heavy rains and covers a previously non-submerged volume. The oxidation products gradually dissolve and are carried to the receiving stream.

The final removal mechanism arises from the fact that the oxidation products form a highly localized concentrated acid and salt solution. This solution is hydroscopic and will absorb moisture from the air. Since the relative humidity in a mine atmosphere is usually 100 percent, ample water is available for absorption. Eventually, sufficient moisture is collected at the oxidized surface, and the droplets of acidic solution form. As the drops become heavier they begin to flow by gravity and eventually reach the receiving streams. This mechanism has been observed in laboratory studies."[18]

The following observations may be made about the process:

3) If atmospheric oxygen and water vapor are accessible to an exposed pyritic surface, ferrous sulfate and sulfuric acid or acid mine drainage will inevitably result.

2) Once this material forms, it will continue to form, the reaction rate not being influenced by the removal rate or degree of local sulfate concentration.

3) If the pyritic materials do oxidize, they will eventually be carried away from the site, even if it is by means of water removed from the mine atmosphere.

It might then be concluded that:

1) The removal of a source of flowing water will not prevent the a) formation or b) transport of acid drainage. Efforts to exclude surface waters from abandoned coal seams will accomplish only the reduction of flows to a smaller but more concentrated flow of drainage. The long-term acid production (in pounds of acid produced) will remain unchanged. (only if this acid is to be contained within the mine is flow reduction advantageous).

2) All other factors being equal, the raising of the water level in an abandoned mine will decrease the rate of acid formation, lowering of the water table will increase the rate of formation.

3) The lowering of the water level in an abandoned mine by decreasing inflow, will temporarily reduce acid discharge volume but will increase the exposed pyritic surface area and in turn generate more acid.

4) The accumulation of sulfate salts in a nonflooded mine over a period of time will create a situation conducive to the release of slug loadings should future flooding occur.

SURFACE FORMATION AND TRANSPORT

Secondary sources of mine drainage are the gob or refuse piles of waste materials and associated strip mine pits. The contribution of gob piles to the short term deterioration of water quality is disproportionate to their total acid generation. Gob piles are primarily responsible for the surges in acidity or slugs which occur with high precipitation and associated run-off.

The mechanism of surface acid production and transport involves the oxidation and erosion of the outer pyritic layers of the refuse pile. Gob piles are a more significant source of acid run-off than strip mines because of the greater density of pyrites and their more even distribution throughout the pile. The process of formation of acid drainage is thus described by the research findings of three investigators at Ohio State University.

> "Preliminary examination of the pile indicated that it can be
>
> broken into three zones. The first (zone) is the outer mantle of the pile consisting of a layer 4 to 10 inches thick, from which much of the clay has been washed out by precipitation. From the standpoint of permeability to air and water, this outer mantle is relatively open and essentially all the pyrite oxidation can be assumed to occur in this layer. The second zone, having a low permeability is comprised of a layer of clay fines, an inch or more thick, packed tightly by rain action into the refuse immediately beneath the outer mantle. This layer has discontinuities which provide points of entry for water into the main body of the pile; however, it presents

an effective barrier over most of the pile surface to further penetration of water and oxygen. The third zone is the main body of the pile which shows little evidence of weathering or pyrite oxidation. Water entering through the discontinuities in the clay layer provides recharge for the ground water pool observed within the pile. This storage pool is a source for several continuously flowing springs found around the periphery of the pile."

A consideration of the structure of the reactive outer mantle, which is continuously exposed to atmospheric oxygen suggests that the rate of pyrite oxidation will proceed relatively uniformly with the products of oxidation accumulating in the mantle. These acid salts will be flushed out during periods of rainfall with a portion appearing as acid load in the direct run-off and the remainder being carried into the main body of the pile by the infiltrating water. <u>If this model describes the true situation, then the amount of acid appearing in the run-off resulting from a storm should be proportional to the period of time elapsed since the previous flushing of the mantle.”</u>

The average rate of acid formation for the pile (found by the investi - gators was). . . 185 lbs. acidity/acre /day, as $CaCO_3$”

Erosion during periods of precipitation constantly renews the reactive mantle, and in its present state the pile can be expected to produce acid at a more or less constant rate until the pile is completely eroded away."[19]

SURFACE GENERATED ACIDITY - MODEL VERIFICATION

Sufficient data to verify this model hypothesis could not be obtained using a 1 in 30 day sampling program. To truly verify this hypothesis, continuous sampling would be required to insure the measurement of first flush runoff acidity after each rainfall. The constraint of a prescheduled sampling program precluded the analysis of each first flush runoff as it occurred as would be needed to determine the exact relationship of elapsed time between precipitation and acidic intensity of runoff. However, an analysis of data obtained during the normal sampling program which included several sampling days during which precipitation occurred tended to confirm this hypothesis.

Through a retrospective analysis of watershed acidity production as evidenced by in stream acidity at mainstream sampling stations and precipitation and runoff records, a degree of confirmation of the model describing the method of surface acidity production was obtained.

This analysis was based upon the estimated 480 acres within Loyalhanna watershed which are covered with potentially acid producing gob piles. 450 of these 480 acres are upstream of the dam. This total surface area of exposed gob and refuse piles could theoretically produce a potential loading of 83,000 lbs. of acid per day, if acid produced in the watershed was generated at the rate of 185 lbs. per acre/day as proposed by Good, Ricca and Shumate of Ohio State University.

To estimate the acid load contribution of surface refuse and gob piles to watershed acidity without continuous sampling it was necessary to rely on data obtained from regularly scheduled sampling dates which coincided with the occurrence of first flush runoff.

Fortunately two scheduled sampling dates coincided with first flush runoff and a third date with a midwinter thaw. The high runoff sampling dates and the previous seven day inflow data are given below in the following format:

Sample date	(1) calculated acid load day of sample (2) inches of precipitation day of sample	seven day flow ending on sampling date			
12/11/69	(1) 215, 000 lbs. Dec.	5	111. CPS	9	479 CPS
	(2) 1. 3611 (rain)	6	92 CPS	10	692 CFS
		7	156 CFS	11	3996 CPS
		8	507 CPS		
1/27/70	(1) 248, 000 lbs.	Jan. 21	303 CPS	25	291 CPS
	(2) 0. 07" (snow)	22	276 CFS	26	1180 CPS
		23	257 CFS	27	1150 CPS
		24	250 CPS		
6/27/70	(1) 164, 000 lbs.	June 21	1208 CFS	25	497 CPS
	(2) 0. 7411 (rain)	22	1908 CPS	26	543 CPS
		23	973 CPS	27	1511 CPS
		24	679 CFS		

The highest sampling date acid load discharging into the reservoir was measured at Station 3 on January 27, 1970 as 248,000 lbs. On January 27, only 0. 07" of precipitation as snow fell. However, during the previous two weeks, 0. 66" of precipitation was recorded at Loyalhanna Dam. During this two week period prior to the taking of the January 26 sample the daily high temperature (at Pittsburgh) rose above freezing on only three days (January 17, 18, 19). Flows into the reservoir were less than 300 CFS each day prior to January 26. On January 25, the temperature range was from -2 degrees to 31 degrees F. January 26 and 27 temperature ranged from 31 degrees to 48 degrees F and 31 degrees to 43 degrees F. The high flows of January 26 and 27 of 1180 and 1151 CFS correspond to the effects of a warming trend which produced a partial snowmelt. The high acid load measured January 27 might then be attributed in part to runoff of snowmelt from exposed gob piles.

In contrast to the January 27 peak discharge, on February 24, an acid inflow of 133, 000 lbs was measured at the reservoir. No significant rainfall occurred on the test date or during the previous 8 days. The inflow to the reservoir on February 24 was not significantly higher than that of the two preceeding weeks. Milder temperatures predominated and daily flows of 700 CFS or more for the 7 days prior to February 24 were recorded. If the 133, 000 lbs. of acidity measured February 27 are attributed primarily to subsurface discharges caused by high winter groundwater levels, then assuming 14,000 lbs. of subsurface acidity generated January 27, 100,000 lbs. of the 248,000 lbs. of acidity of January 27 might be attributed to refuse pile generated acidity. March 10th also represents an acid load measurement taken on a day of no significant precipitation or snow melt. An acid load of 85, 000 lbs. was measured which is close to that of February 27.

The second highest sampled acid loading was 215, 000 lbs. of acid measured December 11, 1969. The measurement was accompanied by 1. 36" of rain. On December 9, 0.67 inches of rain also fell which may have lessened the runoff effects. The magnitude of the surface contribution of December 9th may be compared to the acidic load of 42,000 lbs. measured on November 2, 1969. On that date 0.30" of rain were recorded but the streamflow had not yet risen to a crest indicating that the sample taken preceeded the first flush inflow. The possible effect of the December 11th flow is estimated to be about 175,000 lbs. of acid.

A similar increase in acid loading entering the reservoir accompanied by first flush runoff has also been observed under summer conditions. The acid inflows for May 30, 1970, June 27 1970 and July 28, 1970 were respectively 77,500 lbs., 164,000 lbs. and 25,000 lbs. On June 27th, .74" of rainfall were recorded, the first rainfall in 4 days. On June 22nd, 1.26" fell. On May 30 and July 28, no rain had fallen for the preceeding 4 days. The surface acid load generated on June 27th is estimated as 100,000 lbs.

The magnitude of surface generated acidity for the three days during which measurements were taken during or immediately after precipitation is estimated as:

		Days of non-precipitation preceeding	Acid produced lbs/acre/day
Dec. 11, 1969	170, 000 lbs.	2+2	97
Jan. 27, 1970	100, 000 lbs.	6*	37
June 27, 1970	100, 000 lbs.	4	55

*days since last thaw
** rainfall 2 days previously

Admittedly without continuous sampling at the major refuse piles it is impossible to verify these estimates of the production and discharge of gob pile produced acidity. However, the results of these crude attempts to estimate the average annual acid production of the refuse piles fall within a range of values encountered by Good, Ricca and Shumate in their experimental work. Estimates of acid production in their cited experimental work varied between 75 and 418 lbs. /acre/day. Allowing for variations between gob piles of different coal seams in composition, surface texture and exposure to runoff, an estimated acid production of 50 lbs. /acre/ day in the Loyalhanna watershed was used for refuse piles. The validity of this estimate derived. from limited sample data, is substantiated by its occurring within the same order of magnitude as other investigators' estimates of surface generated acid production.

If the figure of 50 lbs. of acid per day per exposed acre is applied to the 480 acres of exposed gob piles, an average load of 24, 000 lbs. of acidity per day, the equivalent of one major source is obtained. However, this acidity occurs at irregular intervals and only at times of relative high stream flow. The magnitude of each occurrence of surface generated activity is directly related to the elapsed time between discharges. The greatest discharge would occur following a major storm preceeded by a long drought. The peak acid discharge from surface sources could be predicted on a basis of historic meterological data. The estimated 50 lbs. per day of acidity per acre do not include the estimated 30% of acid production which leaches into the refuse pile and reappears as seepage. Such seepages from the refuse pile are accounted for in discharges such as #5351 and #5355.

STRIP MINES GENERATED ACIDITY

The remains of abandoned strip mines present an additional source of potential pollution in the watershed. Through the contamination of surface runoff as it flows through strip pits additional acid may be produced. A second contamination associated with strip mine, pits is the infiltration of water into the coal outcrop particularly through intercepted drifts and auger holes. However, this infiltration does not produce additional acid but provides flows for its more diluted conveyance.

The direct pollution effects of strip mine spoil banks in the Loyalhanna watershed is thought to be minimal. This conclusion is based in part upon the unpolluted nature of Whitehorn Creek. The Whitehorn Creek watershed does not contain any major subsurface or refuse pile dis charges. A large portion of the runoff flowing into the creek flows from the ridge overlying the northern section of the Greensburg syncline and must pass through a line of strip cuts along the western outcrop line of the Pittsburgh seam. Any acidity occurring in Whitehorn Creek would be attributable to these strip cuts. However, Whitehorn Creek is not acidic, maintains a pH above 7 and contains less than 150 ppm sulfates. Therefore, the acid contribution of these strip mine pits is minimal.

In other tributary watersheds of Loyalhanna Creek, the presence of other discharges tends to obscure the effects of strip cuts. This lack of effect on water. quality is felt to be the result of the shallowness and small scale of the cuts with highwalls rarely exceeding 301. These strip cuts and spoil banks should not be confused with gob piles which are prime sources of acid runoff.

The magnitude of the infiltration effects is harder to determine. However, since this infiltration does not generate additional acidic flows, its prevention is of minor priority. Strip mine cuts, when not associated with underground discharges, are a minor source of total acid loading.