Kinetics of the Reaction of SO_2 with Calcined Limestone

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Processes in which limestone and dolomite are used to desulfurize flue gas are being intensively investigated under the sponsorship of the National Air Pollution Control Administration. Such processes include dry injection of pulverized stone into boiler furnaces and the use of fluidized bed contactors, fluid bed combustion, and thin fixed-beds.

It is generally assumed that limestone absorbs SO_2 by a mechanism involving two consecutive steps, dissociation of the calcium carbonate followed by reaction of CaO with sulfur dioxide. It is expected that the rate of the second step will be important in any of the proposed pollution control processes, and especially in the dry injection process (Potter, 1968). Several investigators (Harrington, 1968, Potter, 1969) have determined the saturation capacities of a large number of naturally occurring limestones and dolomites under various conditions of reaction with SO_2. Other studies under way will define the rate of reaction of uncalcined limestones in the disperse phase (Lougher and Coutant, 1968). The purpose of the investigation reported in this paper is to determine the rate of reaction of limestones after calcination under standardized conditions.

Experimental

Complete geological descriptions of the stones used in this work are given in a separate report (Harvey, 1968). The chemical composition and primary physical characteristics of the calcined stones are given in Table I. Calcination was carried out in 180-gm batches in a Inconel kiln 12.5 cm. long and 8 cm. in diameter rotated at 1 rpm. It was heated to 980°C in a muffle furnace and then charged with 10/28-mesh stone. The kiln was maintained at 980°C and purged with air for 2 hours to remove CO_2 during calcination. Conversion to the oxide was complete under these conditions (CO_2 < 0.5%). The calcined stone was cooled, crushed, and screened into size ranges of 14/16, 28/35, 42/65, and 150/170 mesh (Tyler). The calcined samples were stored in air-tight containers until used.

The rate of reaction with SO_2 was determined in a differential reactor (Figure 1) constructed of Inconel alloy. In this type of reactor the thin layer of solid and high gas flow prevent gas-phase concentration gradients in the reacting solid. The gases enter the bottom of the reactor housing, are passed upward through an annular preheat section 73 cm. long and 5.25 cm. in diameter and then back downward through the inner, concentric reactor tube containing the limestone sample. The outer diameter of the reactor tube is 4.13 cm., and the inner diameter 3.42 cm. The sample is supported on a 30-mesh Inconel screen in a removable carrier. The carrier is sealed against a flange in the center of the reactor tube so that the entire gas flow passes through the solid during exposure.

In this investigation a sample consisted of 30 milligrams of calcined stone, which was distributed uniformly over the 2.65-cm. diameter screen. For small particle sizes a disk of woven refractory fabric was placed on the screen and a 1-cm. thickness of refractory (fused quartz) gauze on the fabric. The lime particles were dispersed into the gauze.

The mass flow rate of gas through the screen was matintained constant at 0.075 gm/(cm^2) (sec), which at 870°C corresponds to a superficial velocity of 240 cm/sec. A high gas velocity reduced gas film resistance to a negligible value so that mass transfer to the particle surface did not affect rate measurements. The gas fed to the reactor was a flue gas generated by combustion of fuel oil containing carbon disulfide. The composition of the flue gas was 10.5% CO_2, 3.4% O_2, 9.9% H_2O, 0.27% SO_2, 0.003% SO_3, and 75.9% N_2. The sulfur dioxide concentration was monitored continuously with a Beckman Mod. 315 infrared analyzer.

The reactor was mounted in an electric furnace containing three heating sections. The center section was energized by a proportional controller acting on a thermocouple located 3.4 cm. above the screen supporting the lime sample. The other two sections were equipped with variable transformers set by thermocouples in the top and bottom of the reactor tube to maintain a uniform temperature over the full length of the reactor and preheater assembly. The thermocouples were calibrated in situ against a multiply shielded, high-veloicty thermocouple. A mulitpoint recorder continuously monitored reactor temperatures.

Before a run was started, the carrier and sample were allowed to heat up for 5 minutes to the reactor temperature. The time of exposure of the solid to the gas stream was controlled by solenoid valves that started the gas flow at the beginning of the run and purged the reactor with nitrogen at the end of the run. The sample was removed from the carrier after exposure (along with the refractory gauze, if used) and analyzed for sulfate. The exposed sample was dissolved by treatment with ion exchange resin, filtered, and titrated in 80% isopropyl alcohol with barium perchlorate using thorin indicator.

Results and Discussion

The chemical reaction between limestone and sulfur dioxide at high temperature in the presence of excess oxygen is:

$$CaO + SO_2 + 1/2\ O_2 \rightleftharpoons CaSO_4 \qquad (1)$$

Equilibrium data for the reaction have been summarized by researchers at Battelle Memorial Institute (1967). The reaction proceeds to the right at temperatures up to 1230°C at partial pressures of SO_2 corresponding to flue gas concentrations of about 3000 ppm. The MgO component of dolomite has been reported to participate in the reaction also in the presence of iron oxide impurities (Wickert, 1963). No distinction is made in this study between CaO and MgO, although the data suggest that CaO is the only significantly reactive component at the temperatures investigated. When reaction (1) takes place in flue gas containing high concentrations of carbon dioxide, equilibrium also favors a competing reaction (Battelle, 1967) below 770°C:

$$CaO + CO_2 \rightleftharpoons CaCO_3 \qquad (2)$$

Typical experimental results for the sorption of SO_2 are shown in Figure 2; the milligrams SO_3 found in 150/170-mesh particles (Dp = .0096 cm) after reaction is plotted against exposure time at various reaction temperatures. Figure 3 shows a similar plot for different particle sizes at a reaction temperature of 870°C. Total conversion of the CaO would correspond to an ordinate value of 23.2 mg. These figures illustrate the strong sensitivity of the reaction to temperature and the surprisingly low sensitivity to particle size, which were characteristic of all the stones examined.

The rate of sorption was measured as the tangent to the smooth curve drawn through the data and is defined as:

$$r = \frac{1}{W}\frac{dn'}{dt} \qquad (3)$$

where W is the grams calcined stone exposed in the reactor and n' is the gram moles of SO_3 in the stone at time t.

The data were correlated according to the rate expression for chemical reaction in a porous solid (Satterfield & Sherwood, 1963):

$$-\frac{dn}{dt} = k_v V C^m \eta \qquad (4)$$

since $dn'/dt = -dn/dt$

$$\frac{1}{W}\frac{dn'}{dt} = \frac{\eta}{\rho} k_v C^m \qquad (5)$$

The effect of SO_2 concentration, C, on the reaction rate is shown in Figure 4 for dolomite 1337. The SO_2 concentration was varied between 58 and 6000 ppm by changing the carbon disulfide content of the fuel oil burned in the furnace. The reaction rate was measured at a conversion of 10.5% of the CaO in 14/16-mesh stone reacted at 870°C. The line fitted to these data by the method of least mean squares has a slope of 1.088 or $m \doteq 1$, indicating that the reaction is first order with respect to the concentration of SO_2 in the gas phase. The SO_2 concentration was fixed at a value of 2.88×10^{-8} gm mole/cm^3 (3000 ppm, dry) for the remainder of the experimental work, which is reported below.

The rate constant k_v is a function of temperature and also some function of n'/W, the sulfate loading; it decreases as the reaction progresses and the solid reactant is consumed. The temperature dependency of the sorption rate was correlated by the Arrhenius equation:

$$k_v = Ae^{-E/RT} \qquad (6)$$

An Arrhenius plot for each of the four calcined stones is shown in Figure 5 for reactions at temperatures between 650 and 980°C. The rates were measured at a sulfate loading of 0.9×10^{-3} gm mole/gm of 150/170-mesh particle size sample. The data show a linear correlation between log r and 1/T, as specified by equations (5) and (6). The apparent activation energy determined from the slope of these plots was distinctly different from each stone, ranging from 8.1 to 18.1 K cal/gm mole. When rates were measured at higher CaO conversions - up to 20% - the plots shifted toward the abscissa, but remained parallel to the lines shown in Figure 5, thus indicating no significant change in the activation energy.

The high sensitivity of the rate of sorption to temperature suggests chemical reaction to be the predominant rate-controlling resistance. The apparent activation energy for sorption controlled solely by bulk diffusion would be only 3.4 K cal/gm mole. A summary of the empirical kinetic parameters estimated from these data are given in Table II.

The plots further indicate that reduction in rate of reaction with SO_2 as a result of completion with CO_2, was not important at 650°C. At 540°C, however, there was evidence that reaction (2) was significant and the Arrhenius plots could not be extrapolated to that temperature. The plots also failed when the reaction temperature was raised from 980 to 1100°C, sorption rates decreasing at the higher temperature. Subsequent experiments in which the calcine was heated for 10 minutes at 980°C and then reacted at 870°C showed the same difference in rate when compared to a sample which was not exposed to the high temperature. It was

concluded that the loss of reactivity was due to the changes in porosity and bulk density which occur when lime is "overburned" (Boynton, 1966).

The effect of particle size on reaction rate is shown in Figure 6 in which the value of r at a sulfate loading of 1.8×10^{-3} gm mole/gm is plotted against the inverse of particle diameter. If the particles are assumed to be spherical, the total exterior surface of a given mass of stone (specific surface) would increase with $1/D_p$ when the particle size is reduced. Also, if the reaction occurs only at the outer surface, the plot shown in Figure 6 would be expected to be a straight line through the origin. It is clear that the rate was not proportional to specific surface and in some cases was essentially independent of it. The results suggest that some reaction takes place within the interior structure of the solid and that the relative importance of the internal reaction becomes greater as the particle size decreases. These observations are similar to the effects associated with highly porous catalysts and are consistent with the fact that the pore space in calcined limestones usually accounts for 50% or more of the total volume of the particles. The porosities (or fraction of particle volume that is pore space) for the 4 calcined stones are given in Table 2.

Figure 7 shows the conversion vs. time response for different particle sizes of stones 1351 and 1343 over long periods of exposure at 870°C. An analysis of the response according to the method of Shen and Smith (1965) was made to test for intra-particle shell diffusion. This model is based on diffusion through the product crust as the rate limiting mechanism and a non-porous solid reactant in which reaction occurs only at the interface of the unreacted core. The data from this investigation could not be correlated by the shell diffusion model when different particle sizes were considered. Figure 6 shows that the shell diffusion model, which predicts that the rate of sorption at a given sulfate loading will increase with $1/D_p^2$ is clearly inconsistent with data on particle size vs. reaction rate. This anomaly can only be explained if the effective diffusion coefficient decreases with particle size. Stone 1343, for example, had a diffusion coefficient of 3.4×10^{-2} cm²/sec for 14/16-mesh particle size, but only 0.054×10^{-2} cm²/sec for 150/170-mesh particle size.

The data could be correlated empirically over the full course of reaction by a plot of log r against sulfate loading, n'/W, as shown in Figure 8. The data could be linearized in this manner for all particle sizes of each of the four stones examined at a reaction temperature of 870°C. The observed response can be interpreted in terms of a change in the frequency factor, A, of equation (5). The frequency factor, which relates the reaction rate to the number of molecular collisions occurring per unit volume per unit time, is dependent upon the amount of SO_2 and the amount of CaO present. As the reaction progresses and CaO is consumed, the frequency factor decreases in some manner related to the amount of sulfate formed. Figure 8 suggests a relationship of the type:

$$A = A_o e^{-\beta n'/W} \qquad (7)$$

where A_o is the frequency factor at zero conversion and β is an emperical factor dependent upon particle size.

The correlation of Figure 8 has several implications regarding reaction kinetics. First, it shows that the rate is more sensitive to sulfate loading for large particles than it is for small particles. Second, it shows that the initial rate at zero loading may be estimated so that the effectiveness factor may be evaluated. The data shown for stone 1337 indicate that the effectiveness factor was not unity in this case. Other stones showed less change in η with particle size.

The results of this study show that the rate of sorption of SO_2 by calcined limestones is dependent to a very large extent upon the kinetics of the chemical reaction, particularly at small particle sizes and that the rate of reaction predominates as the overall rate-controlling resistance for conversion of at least the first 20% of the CaO.

Acknowledgement

The author thanks Mr. Robert Larkin for development of the procedure for analysis of sulfate in limestone.

Nomenclature

A	frequency factor, sec^{-1}
A_o	frequency factor at zero solid conversion, sec^{-1}
C	gas phase concentration of sulfur dioxide, gm moles/cm^3
$\overline{D}_p$	mean particle diameter, cm
E	activation energy, cal/gm mole
k_v	reaction rate constant per unit volume of solid, sec^{-1}
m	order of reaction with respect to sulfur dioxide
n'	sulfate in solid as SO_3, gm moles
R	gas constant, 1.987 (cal/gm mole °K)
r	reaction rate with respect to formation of SO_3 in the solid, gm mole/(sec)(gm)
V	total volume of solid, cm^3
W	weight of solid sample, gm
T	temperature, °K
t	time, sec
β	empirical correlation factor defined by equation (7)
η	effectiveness factor, ratio of reaction rate to the rate that would obtain if entire volume of particle participated equally in reaction
ρ	bulk density of solid, gm/cm^3

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Table I. Properties of Calcines

Sample	LoI[a]	% CaO	%MgO	% Fe_2O_3	% SiO_2	Bulk (particle) Density,[b] ρ gm/cm^3	Porosity[b] cm^3/cm^3
1337	47.4	55	43	0.33	0.92	1.41	0.60
1351	42.4	54	28.5	7.0	8.2	1.59	0.56
1343	42.8	94	0.8	0.66	2.98	1.88	0.45
1360	43.8	81	13.0	1.25	3.65	1.51	0.56

(a) weight loss on calcination

(b) 150/170 mesh particle size

Table II. Kinetic Parameters[a] for Sorption of SO_2 by Calcined Limestones

Stone	Activation Energy, E Cal./gm mole	Reaction Rate Constant, K_v sec^{-1}	Frequency Factor, A sec^{-1}
1337	10,000	4.8×10^3	2.4×10^5
1351	18,100	7.2×10^3	9.0×10^6
1343	14,200	4.0×10^3	1.1×10^6
1360	8,100	2.3×10^3	5.5×10^4

(a) evaluated at sulfate loading of 0.9×10^{-3} gm mole/gm, 150/170 mesh particle size.

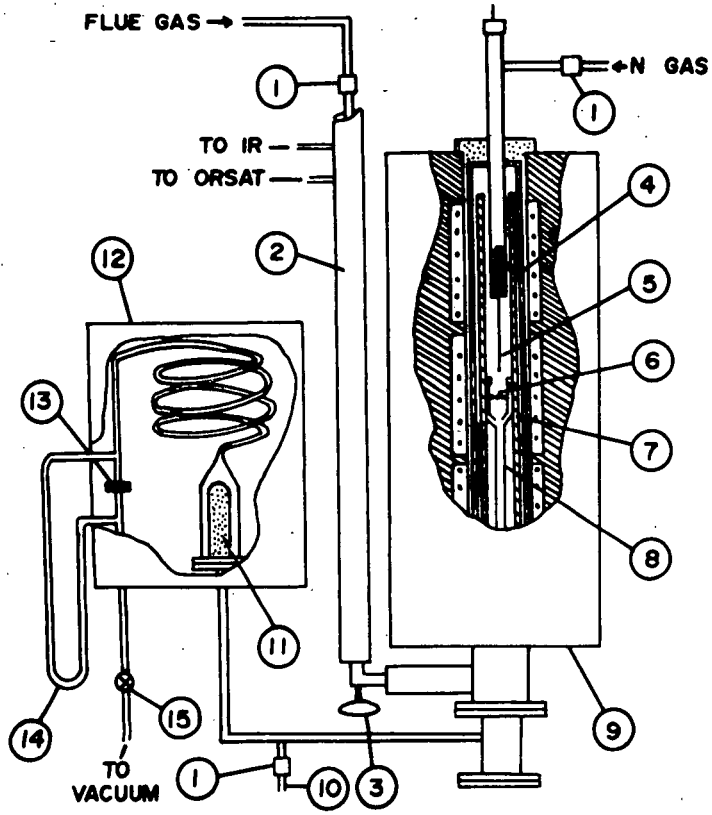

Figure 1. Apparatus

1. Teflon Solenoid valve 2. Heating tapes 3. Thermometer 4. Preheat section 5. Thermocouple 6. Sample 7. Reactor tube 8. Carrier 9. Heating Furnace 10. N_2 Purge exhaust 11. Alundum filter 12. Constant temperature oven 13. Orifice 14. Manometer 15. Flow control valve

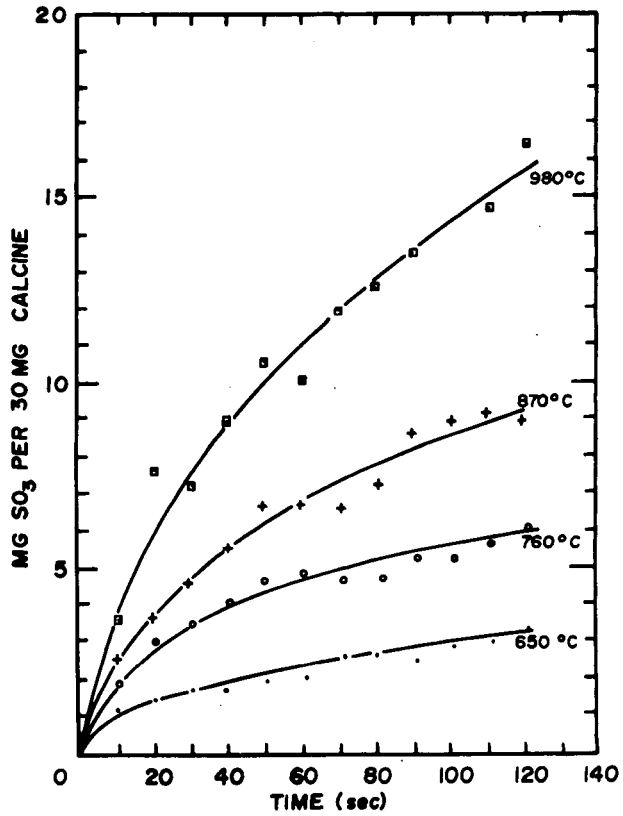

Figure 2. Sorption of sulfur dioxide by dolomite 1351 at various reactor temperatures

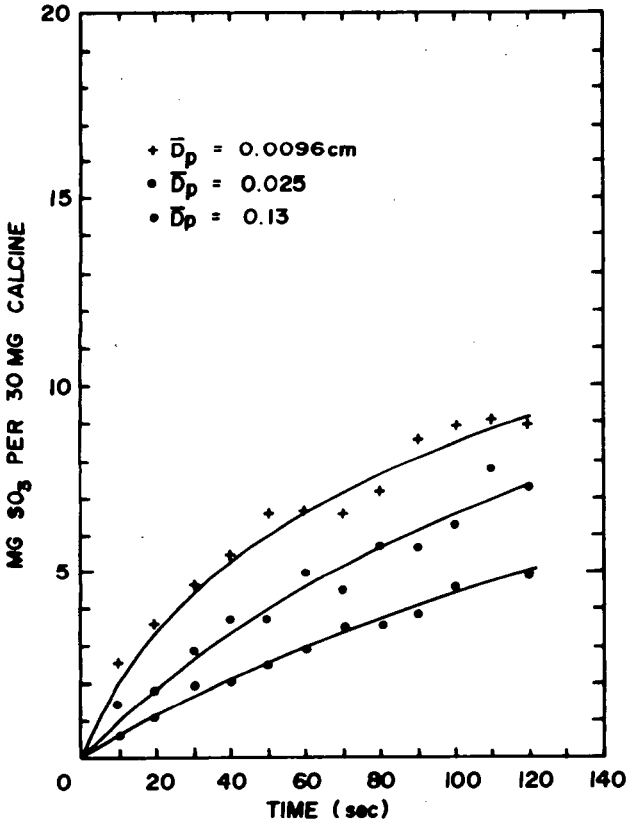

Figure 3. Sorption of sulfur dioxide by different particle sizes of dolomite 1351.

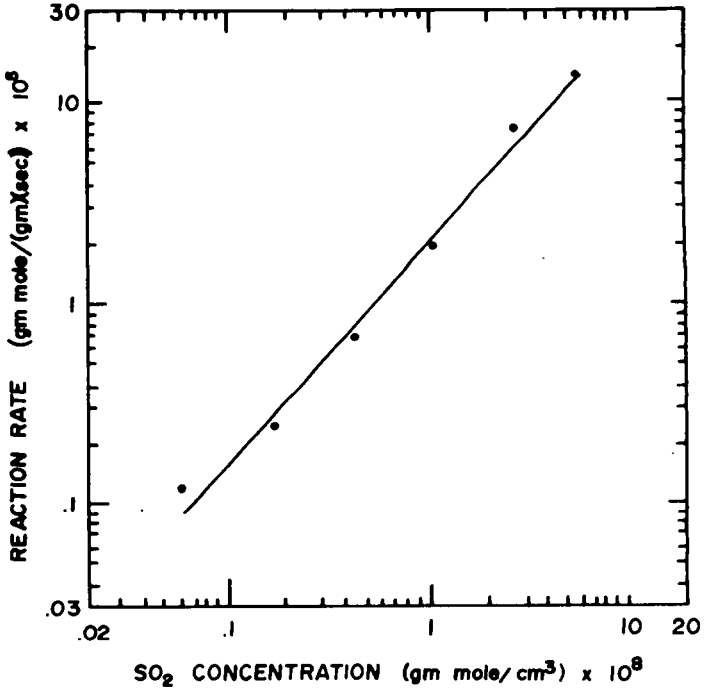

Figure 4 Log r vs. Log C to estimate m

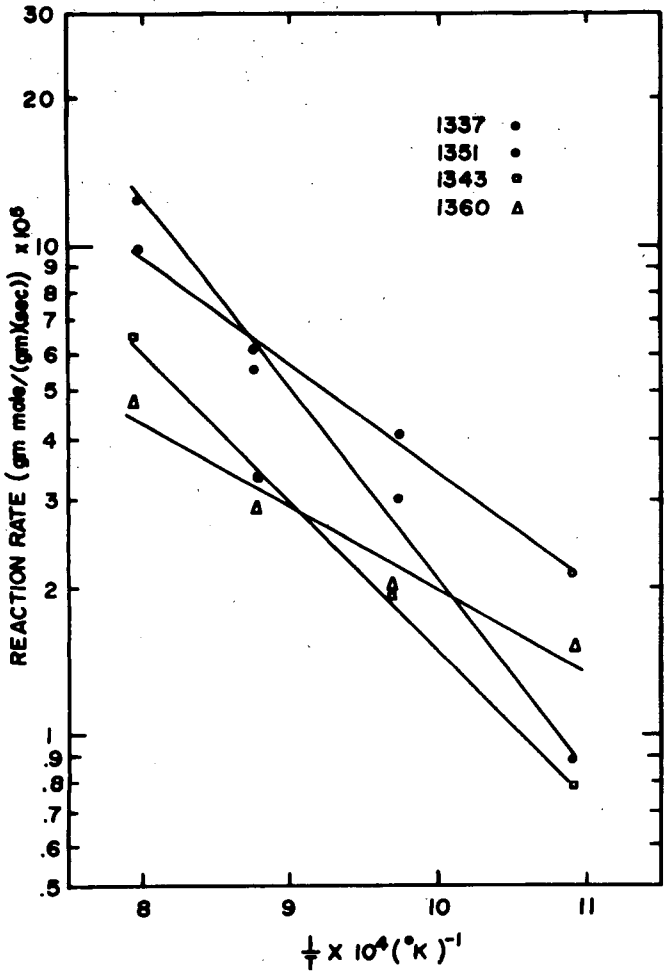

Figure 5. Arrhenius plots for the sorption of sulfur dioxide by four limestones

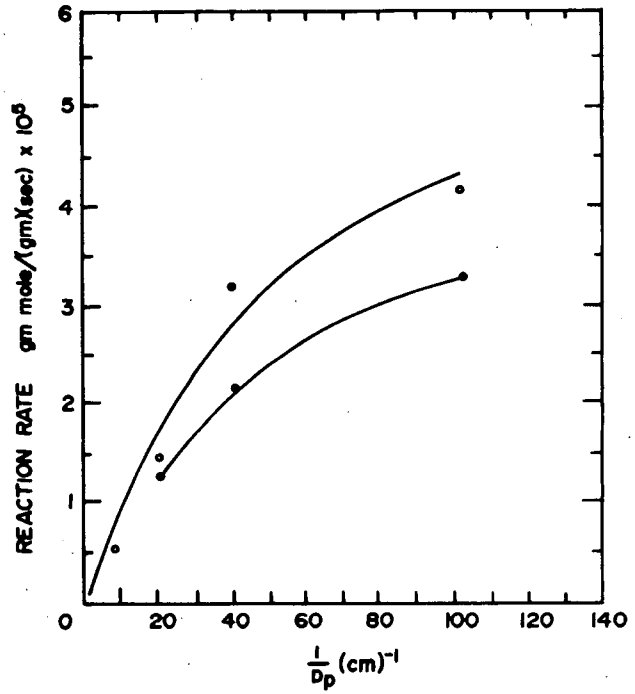

Figure 6. Reaction rate vs. $1/D_p$

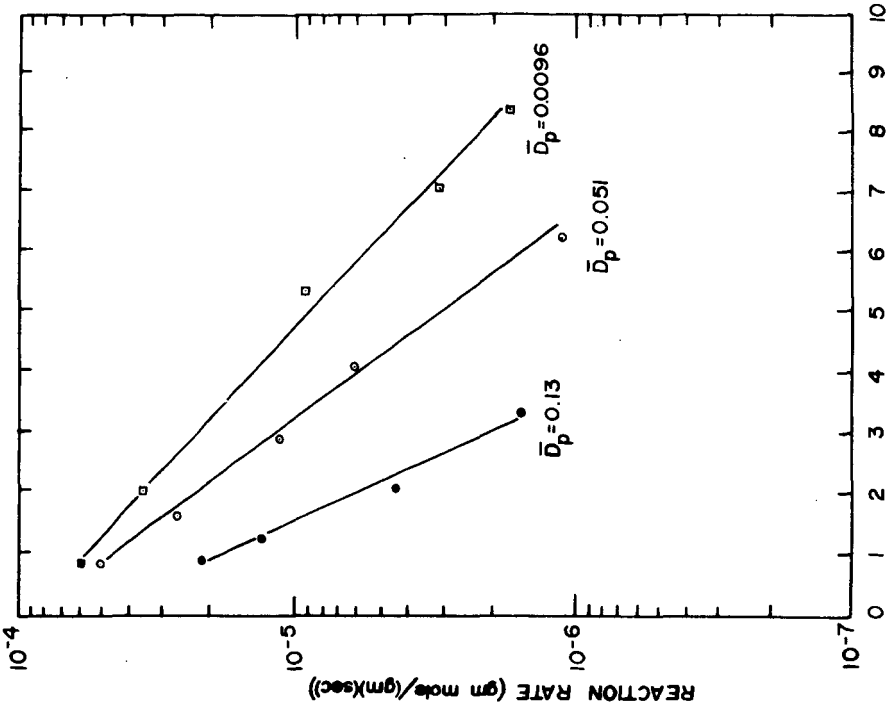

Figure 8 Relation of Sulfate Loading and Reaction Rate

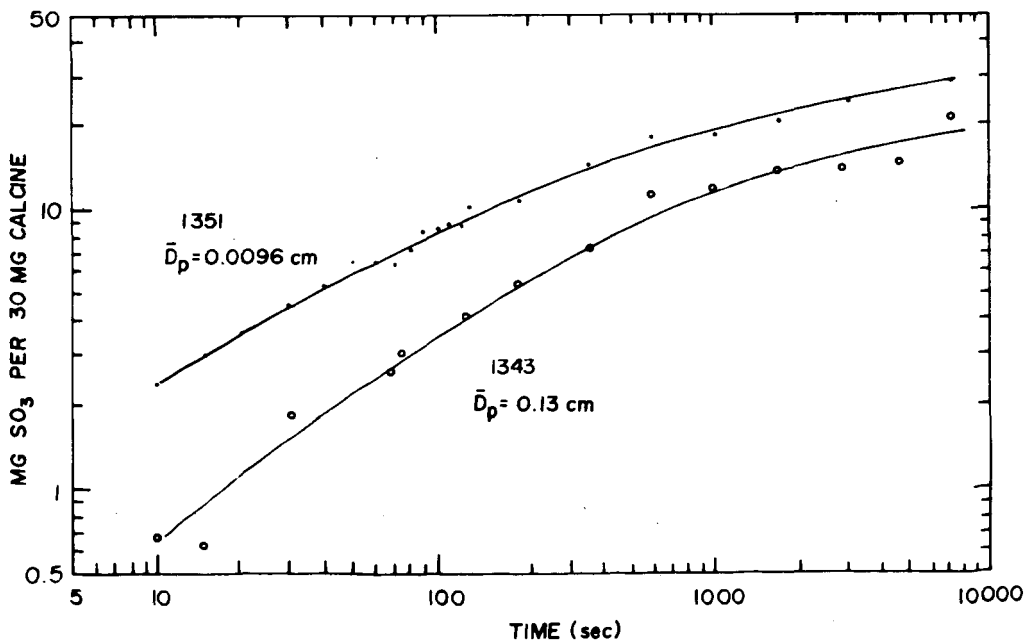

Figure 7 Sorption of sulfur dioxide by calcined limestone

KINETICS OF RECOVERING SULFUR FROM THE SPENT SEED IN AN MHD POWER PLANT

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ABSTRACT

The open-cycle magnetohydrodynamic power plant offers a unique means of profitably recovering sulfur from its effluent gases. This is due to the high affinity the potassium or cesium seeding materials have for sulfur and their ease of regeneration. These compounds are added to make the gas electrically conductive and, because of their cost, must be recovered and recycled to the MHD generator. A process which removes the sulfur with hydrogen as hydrogen sulfide from the seed-slag mixture before the seed-slag mixture is recycled to the MHD generator is described and experimentally confirmed. As a result of this process the seed maintains its capacity to remove sulfur from the combustion products and a sulfur-free effluent gas is produced. A kinetic interpretation of the experimental data is presented. This data is used to specify the design and operating conditions for a sulfur recovery reactor for a 1000 MWe MHD power station.

The kinetic model is shown to apply also to the regeneration of the absorbent in the alkalized alumina process presently under development for removing sulfur dioxide from power plant stack gases.

INTRODUCTION

The basic nature of the operation of an MHD-topped power plant offers a means not available in a conventional power plant of recovering sulfur from the combustion products.

In an MHD-topped power plant, the combustion products are seeded with a potassium or cesium seed to make them electrically conductive. The condensed seed and whatever slag contaminants it contains are then recovered and recycled to the MHD generator. For economical operation of the MHD-topped power plant this recovery of seed must be essentially complete. Experimental and theoretical studies (1-3) indicate that if there is any sulfur in the combustion products, the potassium or cesium seed will condense as the sulfate and that this reaction can be stoichiometric.

We propose taking advantage of the chemistry and nature of the MHD-topped power plant operation to eliminate air pollution from sulfur oxides as well as to provide an economically attractive means of recovering the sulfur in coal. To achieve these goals it is necessary to remove the sulfur from the seed-slag mixture before recycling the mixture to the generator. To be most desirable, this process should remove the sulfur from the seed-slag mixture in a form that can be readily converted to a salable product.

This paper describes our experimental and kinetic analyses of a process to convert the sulfur in the seed-slag mixture to hydrogen sulfide with a hydrogen feed gas. The hydrogen sulfide can then be separated from the hydrogen by stripping with an ethanolamine solution and converted to elemental sulfur via the conventional Claus oxidation process.

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

The kinetic model developed in this study is also applied to the regeneration of alkalized alumina with hydrogen.

EXPERIMENTAL PROCEDURE

Preparation of Simulated Seed-Slag Mixture

To simulate a seed-slag mixture such as would be recovered from an MHD plant (4), a 4.6/1 mole ratio of SiO_2/K_2SO_4 was mixed by ball milling and then fused at 2,100°F (the approximate dew point of K_2SO_4 in combustion products of sulfur-containing fuels) for 48 hours. The fused mixture was again ball milled and then formed into 1/8 x 1/4 cylindrical pellets. These pellets constituted the feed for the experiments.

Operation

Except where otherwise noted 55 g of sample were charged to the reactor, which was for most of the tests a "Vycor" tube 15/16 inches I.D. The reactor was heated under nitrogen pressure to the desired temperature and hydrogen was then admitted thru a quick opening valve. Hydrogen flow rates were maintained at 0.2 g mole/min for all the tests as this was found to approximate differential operation and, at the same time, to give measurable (0.1 to 2 mole percent) hydrogen sulfide concentrations. Except where otherwise noted by data points, gas samples were taken every two minutes over the first thirty minutes and every 10 minutes thereafter. The system was designed to minimize backmixing effects and the gas analyses indicate that these effects were negligible.

The sulfur removal rate was calculated from the data by the formula

$$r = Gy_{H_2S}/W_{SO}$$

where r is the H_2S formation rate in g-moles H_2S g-sample, min., G is the gas flow rate in g-moles/min, y_{H_2S} is the mole fraction of hydrogen sulfide, and W_{SO} is the initial weight of solid sample. The conversion to hydrogen sulfide as a function of solid residence time was obtained by graphically integrating r.

RESULTS AND DISCUSSION

The kinetic model is based primarily on the following experimental observations:

(1) The initial reaction rate is zero and increases over a time interval that depends on temperature to a maximum value, e.g. at 875°C, fig. 7, this time is one minute or less, at 800°C, fig. 6, it is approximately 6 minutes. Similar behavior is also shown in figs. 1 thru 5 for other temperatures.

(2) The maximum conversion level that can be achieved is also a function of temperature. For example, at 875°C only 4 percent of the sulfur can be converted before the reaction rate decays to zero, at 760° to 800°C roughly 50 percent of the sulfur can be converted to H_2S.

One interpretation of the above experimental results is that initially the sulfur is in a state which will not react to form hydrogen sulfide. However, upon exposure to the reaction conditions the original inactive sulfur compound transforms to an active intermediate which reacts to form hydrogen sulfide. Thus, the hydrogen sulfide production rate reflects the concentration of active intermediate which starts at zero, rises to a maximum, and then decays with increasing time.

The decay of the hydrogen sulfide production rate to zero before sulfur conversion is complete can be accounted for by assuming that concurrent with the formation of an active intermediate, which reacts with hydrogen to form hydrogen sulfide, is the formation of a sulfur compound which is refractory to hydrogen. With these assumptions about the chemistry several equally plausible reaction models can be proposed. However, the rate equations corresponding to these different models are all of the same form making it impossible to distinguish between them on kinetic grounds.

Also, although attempts by x-ray analysis have been made, chemical identification of the actual species present has not yet been achieved. Thus, we chose to use the simplest physically feasible reaction scheme to derive the rate equations with which to analyze the data.

In detail, what we assume in our model is that the sulfur is in an initial state I which, under reaction conditions, is transformed into an active sulfur containing species A as well as a sulfur species R refractory to hydrogen. The chemical reactions occurring in the system are

$$I \xrightarrow{k_1} A, \tag{1}$$

$$A + H_2 \xrightarrow{k_2} H_2S, \tag{2}$$

$$I \xrightarrow{k_3} R, \tag{3}$$

where k_1, k_2 and k_3 are reaction rate constants. We take all of the above reactions to be first order with respect to the concentration of solid reactants.

Since the hydrogen partial pressure in this series of experiments is maintained constant, k_1, k_2, and k_3 are completely determined by the temperature although in general they are also dependent upon hydrogen partial pressure.

The reaction of primary interest is (2) since it is this reaction which removes sulfur from the solid sample and produces the hydrogen sulfide which can be converted to the desired elemental sulfur. At constant hydrogen partial pressure the rate of hydrogen sulfide production is taken to be

$$r = k_2(A).^{*/} \tag{4}$$

The concentration of A as a function of time can be found by solving the following differential equation

$$\frac{d(A)}{dt} = k_1(I) - k_2(A) \tag{5}$$

which describes A's net formation where the concentration of I is obtained by solving the differential equation,

*/ Quantities in parentheses are concentrations of solid reactants measured in g-moles/g-solid.

$$-\frac{d(I)}{dt} = (k_1+k_3)(I), \qquad (6)$$

describing I's disappearance. From (6) we have $(I) = (I_o)e^{-(k_1+k_3)t}$ where (I_o) is the initial concentration of sulfur in the solid. Substituting this value for (I) in (5) gives

$$\frac{d(A)}{dt} = k_1(I_o)e^{-(k_1+k_3)t} - k_2(A)$$

whose solution is

$$(A) = \frac{k_1(I_o)}{k_2-k_1-k_3}\left[e^{-(k_1+k_3)t} - e^{-k_2t}\right].$$

Thus, in view of (4), we see that the rate of hydrogen sulfide production is given by

$$r = \frac{k_1k_2(I_o)}{k_2-k_1-k_3}\left[e^{-(k_1+k_3)t} - e^{-k_2t}\right]. \qquad (7)$$

For the regeneration of fused K_2SO_4-SiO_2 mixtures our data indicate that in the neighborhood of 800°C k_1+k_3 is approximately equal to k_2.

Since

$$\lim_{k_1+k_3 \to k_2}\left(\frac{1}{k_2-k_1-k_3}\left[e^{-(k_1+k_3)t} - e^{-k_2t}\right]\right) = \frac{\partial}{\partial k_2}\left(e^{-k_2t}\right) = t\,e^{-k_2t},$$

we use the formula

$$r = k_1k_2(I_o)t\,e^{-k_2t} \qquad (8)$$

for the rate of hydrogen sulfide production when $k_1+k_3 = k_2$.

Equation (7) or (8) if appropriate, is used to correlate the directly measured rate data. Integration of (7) or (8) enables us to compare predicted conversion to hydrogen sulfide with experimentally determined conversion obtained by graphical integration of the measured rate data. Values for the coefficient $\frac{k_1k_2(I_o)}{k_2-k_1-k_2}$ or $k_1k_2(I_o)$ and the exponents (k_1+k_3) and k_2 are selected on the basis of the best least squares fit of (7) or (8) to the rate data.

Calculated values of hydrogen sulfide generation rates using these constants are shown for the fused K_2SO_4-SiO_2 mixtures in figs. 1 thru 7 for temperatures of 700°, 725°, 760°, 775°, 800°, and 875°C. Examination of these results indicates considerable scatter in the rate data between 725° and 800°C. We attribute this scatter to the large variation in reaction rate with temperature which is clearly evident in figs. 1 thru 7. Not only does the shape of the reaction rate versus time curve change drastically in the temperature span from 700° to 875°C but there is also a pronounced variation in the magnitude of the reaction rates. This variability of reaction rate with temperature coupled with our inability to reduce temperature gradients in the sample much below 10° to 20°C make it impossible to exercise better control over reaction rate fluctuations. Running many duplicate determinations of rate versus time as is shown in fig. 6 at 800°C and using the average value for each time tends to smooth the rate data considerably.

Experimental levels of sulfur production gotten by integrating the rate data are compared in fig. 8 with those calculated by analytically integrating (7) and (8). The agreement between predicted conversion and measured conversion is well within the experimental error, especially when one considers that the errors in the integral data are cumulative and that relatively few data points past 31 or 41 minutes are taken. The scatter that does exist would have been further reduced if the least squares fit were based on this integral data rather than on the rate data. Thus, the derived rate equations can be used with good accuracy to predict the effect of reactor size on sulfur production over a wide range in shape of r(t,T) curves.

Effect of Temperature

In fitting (7) and (8) to the rate data, the groups involving the reaction velocity constants are evaluated rather than the constants k_1, k_2, and k_3 themselves. That is, if $k_2 \neq k_1+k_3$ then the coefficient $\frac{(I_o)k_1k_2}{k_2-k_1-k_3}$, and the exponents k_1+k_3 and k_2 are the terms determined by the least squares fit, whereas if $k_1+k_3 = k_2$ then the coefficient $k_1k_2(I_o)$ and the exponent k_2 are the quantities calculated.

The effect of temperature on k_1+k_3, k_2, and $\frac{(I_o)k_1k_2}{k_2-k_1-k_3}$ is shown in figs. 9 and 10, respectively. The reason for the hyperbolic behavior of the group $\frac{(I_o)k_1k_2}{k_2-k_1-k_3}$ becomes clear when one takes into account that for small values of k_1+k_3 relative to k_2 its essential behavior is that of $(I_o)k_1$ but as k_1+k_3 increases the dominating effect becomes the fact that $\underset{k_1+k_3 \to k_2}{\mathrm{LIM}} \left(\frac{(I_o)k_1k_2}{k_2-k_1-k_3}\right) = \infty$. Although (8) is strictly applicable only when $k_1+k_3 = k_2$, it does provide a satisfactory fit even to data well away from this constraint. Thus the problem of the inherent inaccuracy in the evaluation of large values of $\frac{(I_o)k_1k_2}{k_2-k_1-k_3}$ can be avoided by using (8) when k_1+k_3 is near k_2. For $k_1+k_3 > k_2$, $\frac{(I_o)k_1k_2}{k_2-k_1-k_3}$ is negative and for large values of k_1+k_3 relative to k_2 its essential behavior is that of $\frac{-(I_o)k_1k_2}{k_1+k_3}$. Thus for high temperatures (above 800°C in our study) the values of this group lie on a curve which is similar to the reflection of its graph generated at low temperatures (below 800°C) in the opposite quadrant. At temperatures above 725°C, k_2 is independent of temperature. This indicates the reaction for the production of hydrogen sulfide may be gas film or particle diffusion controlled above 725°C.

Knowing the initial concentration of sulfur, (I_o), allows the calculation of separate values for k_1 and k_3. Fig. 9 shows the dependence of these separate values on temperature. With this information the behavior of the system as a function of time and temperature can be explained.

For example, the experimental limitations of sulfur conversion to hydrogen sulfide are explained in terms of the formation of the solid sulfur compound R which will not react with hydrogen. The rate of formation of R is, according to our model, $d(R)/dt = k_3(I)$ and, as was seen from (6) $(I) = (I_o)e^{-(k_1+k_3)t}$. Thus the concentration of residual sulfur is

$$(R) = \frac{k_3(I_o)}{k_1+k_3}\left[1 - e^{-(k_1+k_3)t}\right].$$

The maximum conversion level to hydrogen sulfide is achieved when $t = \infty$ and is, at any given temperature, $\frac{(I_o)-(R)_{(t=\infty)}}{(I_o)} = 1 - \frac{k_3}{k_1+k_3}$. The maximum conversion level of sulfur to hydrogen sulfide, shown in fig. 11, is therefore a function of temperature only. This maximum is approximately 80 percent and should occur around 730°C. Unfortunately, our experiments at 700° and 725°C were terminated well before the maximum conversion was approached. However, at the other temperatures studied residence times were sufficiently long to enable close approach to maximum conversion. These data are compared with those predicted by the model in fig. 11.

Both the maximum conversion data in fig. 11 and the reaction rate data in figs. 1 thru 7 indicate that operating at temperatures either above 800°C or below 725°C would not be practical. The optimum temperature depends on the sulfur level of the particular coal used and the effect of reactor size on the process economics.

Since the constancy of k_2 with respect to temperature indicates that the reaction rate to form hydrogen sulfide may be gas film or particle diffusion controlled, it is of interest to see what advantages may accrue by operating reactors at increased gas velocities or with finer particles in order to increase k_2. For values of k_2 much greater than k_1+k_3 and for $t > 0$ the reaction rate to form hydrogen sulfide is approximately given by $r_{max} = k_1(I_o)e^{-(k_1+k_3)t}$. Thus, increases in the specific gas flow rate above that used in our present experiments or operation with finer particles should at most allow conversion rates to increase to the values indicated by r_{max}. However, even with the higher values of k_2 the maximum conversion to hydrogen sulfide will remain fixed because it depends only on k_1 and k_3.

Application of the Model to the Regeneration of Alkalized Alumina

Hydrogen sulfide formation rates with hydrogen and sulfur-saturated alkalized alumina were measured at 680°C to see if the same kinetic model could be used to describe this apparently similar reaction system. The comparison, shown in fig. 12, of measured rates with rates calculated using the model verifies that the model also describes the kinetics of regenerating alkalized alumina. Comparison of the measured conversion level with that obtained by integration of the rate equation is shown in fig. 13. This similarity of regeneration kinetics indicates that techniques for regenerating alkalized alumina (5) can also be utilized to remove sulfur from seed-slag mixtures.

Economic Feasibility of Removing Sulfur from Recycling Seed-Slag Mixtures

While no detailed estimates have yet been made on the costs of removing sulfur from recycling seed-slag mixtures, it is possible to make a rough cost estimate using the data in this paper. For example, the sulfur production rate of a 1,000 MWe MHD-topped power plant having a thermal efficiency of 0.47 and using a 13,610 Btu/lb 3 wt-percent sulfur coal for fuel will be 383,000 lbs/day which, at a value of $40/2,240 lbs, is worth $6,830/day. Such a plant will be seeded with about 2 g-moles of K_2O/kg-coal. With this seeding level 47 percent of the sulfur content in the recycling seed-slag mixture will have to be converted to hydrogen sulfide each pass to ensure a sulfur-free power plant effluent gas. Using a fluid-bed seed-slag regeneration reactor (to avoid complication of varying hydrogen partial pressure in the reactor) operating at a pressure sufficient to maintain a

1 atm hydrogen partial pressure, we find from the data in fig. 8 the solids residence time needed to achieve the desired conversion level is 40 minutes at 775°C. This residence time requires a reactor volume of 145 m^3 for the bulk density of the material used in our experiments. The total reactor pressure which will be needed to maintain the 1 atm hydrogen partial pressure is approximately 1.2 atm for a hydrogen sulfide concentration in the product gas of 15 volume percent. A ball park estimate of the sulfur price necessary to realize a profit from its recovery in an MHD plant is given in table 1.

TABLE 1
Summary of unit cost/day which includes taxes and profit and is based on a 365 day year

Pelletizing	383	(3 times the cost of pelletizing iron ore)
Seed-slag sulfur removal reactor	639	(estimated from (6))
Hydrogen	1,820	@ $0.40/1,000 SCF
Claus unit for converting H_2S to S	2,300	(estimated from (7))
Selling price	$5,142	

Since the value of the sulfur produced will be $6,830/day and because the sulfur recovery system is so simple sulfur recovery will be part of any coal-fired MHD-topped power plant and high-sulfur coals will be considered a premium fuel.

CONCLUSIONS

Sulfur can be economically eliminated from the effluent gases of open-cycle MHD-topped power plants by recovering it from the recycling seed-slag mixture with hydrogen. The incorporation of this recovery step is a simple matter in the MHD power station because a potassium or cesium seeding material, which has a great affinity for sulfur, is added to make the combustion gas electrically conductive, and this seed must be recovered and recycled. Our kinetic model for the stripping of sulfur as hydrogen sulfide from seed-slag mixtures can be used to design reactors for this purpose. This model also describes the regeneration of the absorbent in the alkalized alumina process for removing sulfur dioxide from power plant stack gases.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Raymond W. Hiteshue and Donald M. McCrea, Pittsburgh Coal Research Center, and Warren M. Mahan, Bureau of Mines, Hibbing, Minn. for providing some of the cost data and to Armido DiDonato of the Naval Weapons Laboratory, Dahlgren, Va. for testing the stability of the least squares constants to errors in the rate measurements.

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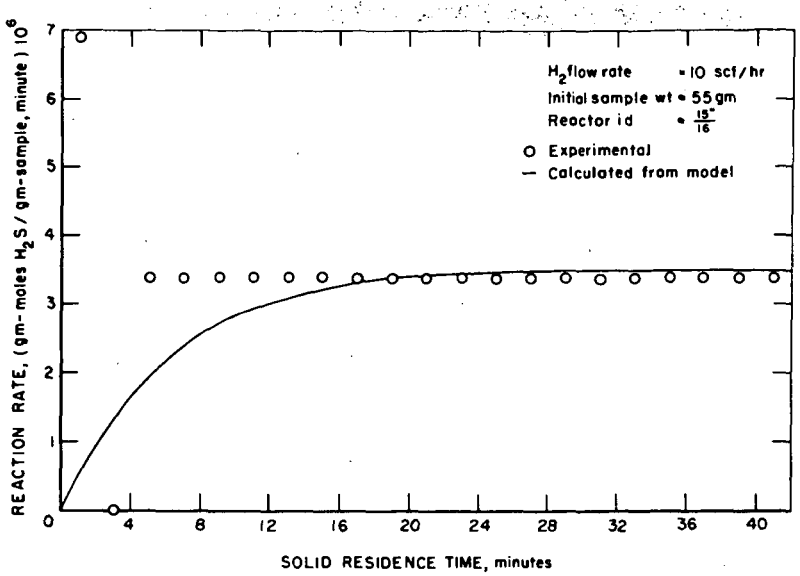

Figure 1.- Differential H_2S formation rate for the reaction of fused $K_2SO_4 - SiO_2$ with H_2: temperature = 700°C, H_2 partial pressure = 1 atm.

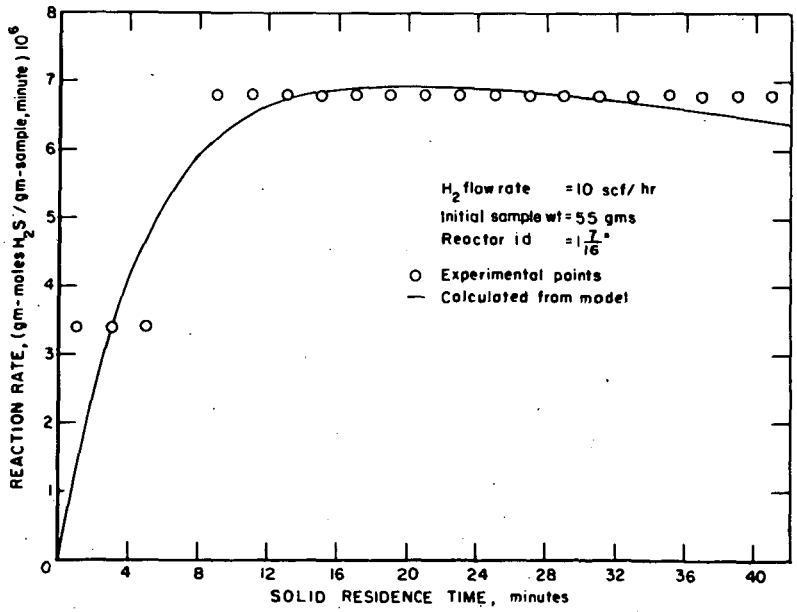

Figure 2.- Differential H_2S formation rate for the reaction of fused $K_2SO_4 - SiO_2$ with H_2: temperature = 725°C, H_2 partial pressure = 1 atm.

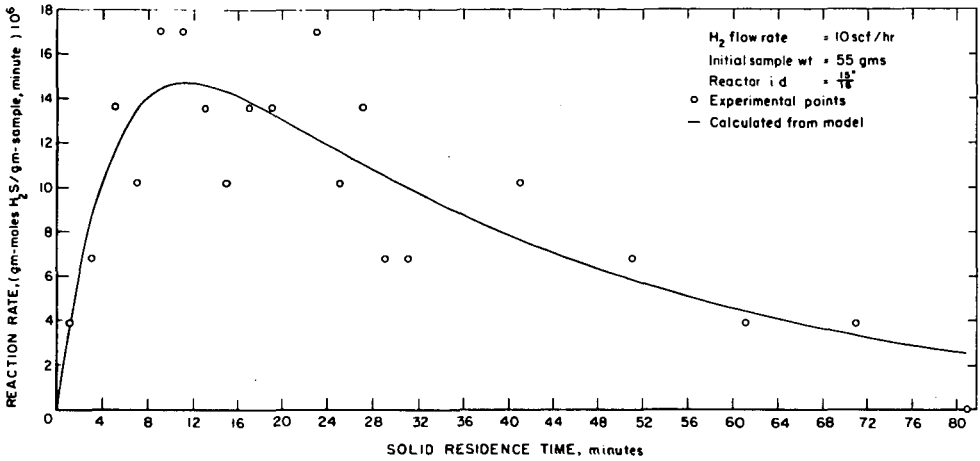

Figure 3.– Differential H_2S formation rate for the reaction of fused K_2SO_4 - SiO_2 with H_2: temperature = 760°C, H_2 partial pressure = 1atm.

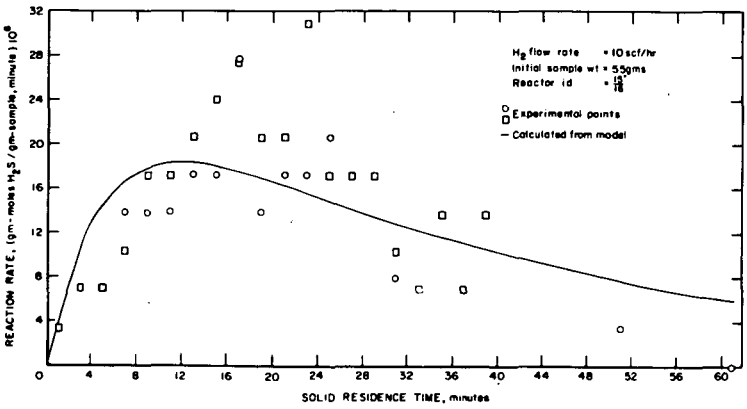

Figure4 – Differential H_2S formation rate for the reaction of fused K_2SO_4 – SiO_2 with H_2. temperature = 775°C, H_2 partial pressure = 1atm

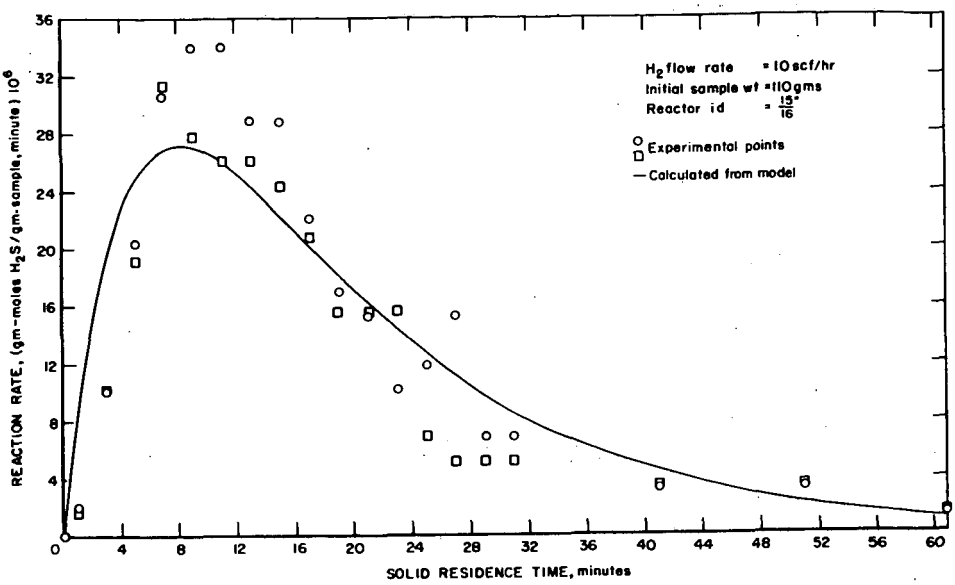

Figure 5 – Differential H_2S formation rate for the reaction of fused $K_2SO_4-SiO_2$ with H_2: temperature = 775°C, H_2 partial pressure = 1 atm.

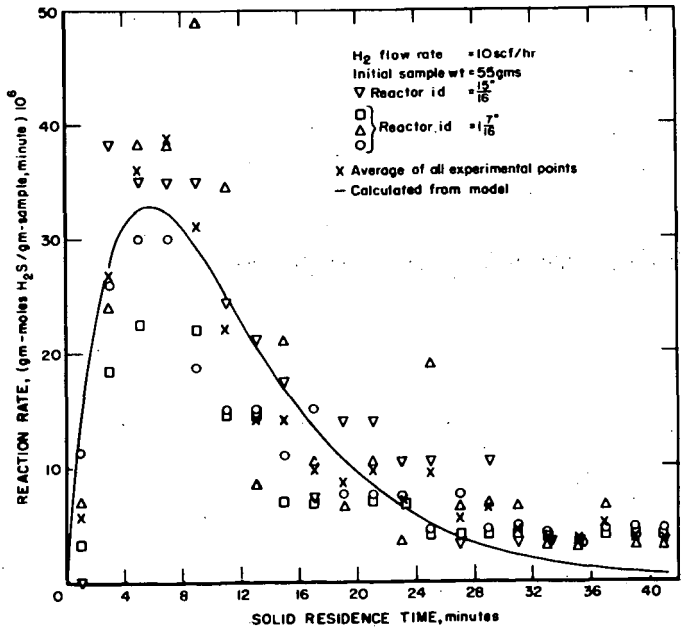

Figure 6 – Differential H_2S formation rate for the reaction of fused $K_2SO_4-SiO_2$ with H_2: temperature = 800°C, H_2 partial pressure = 1 atm.

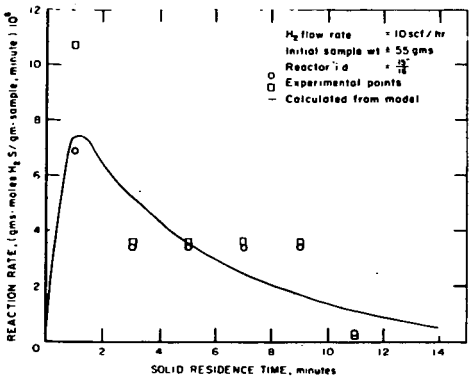

Figure 7. – Differential H_2S formation rate for the reaction of fused K_2SO_4 – SiO_2 with H_2 : temperature = 875°C, H_2 partial pressure = 1 atm.

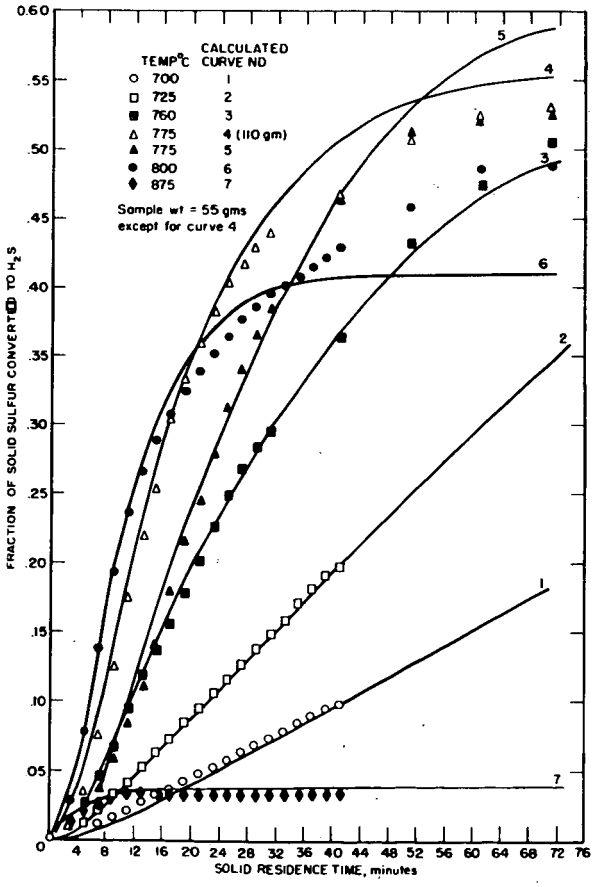

Figure8 – Effect of temperature and solid residence time on sulfur conversion to H_2S : H_2 partial pressure = 1 atm.

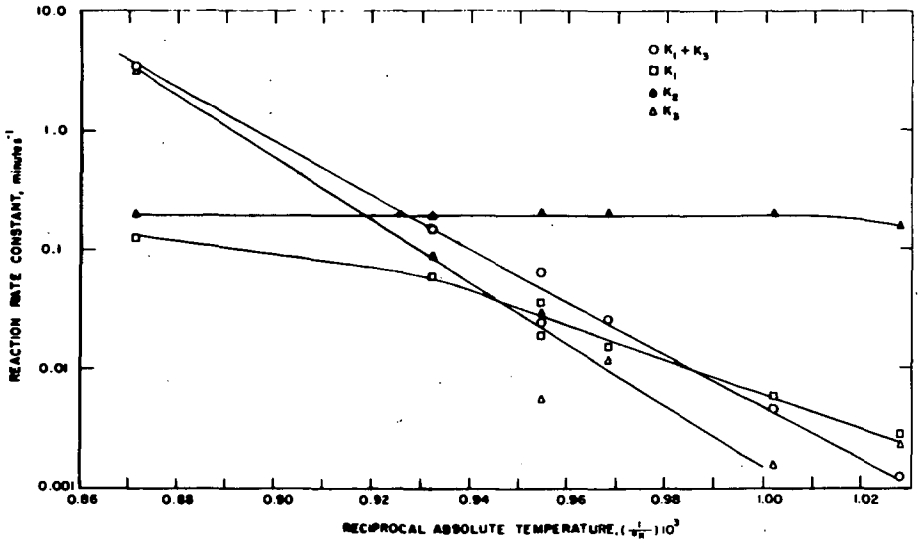

Figure 9 – Effect of temperature on reaction rate constants for the reaction : fused $(K_2SO_4 - SiO_2) + H_2 \rightarrow H_2S$.

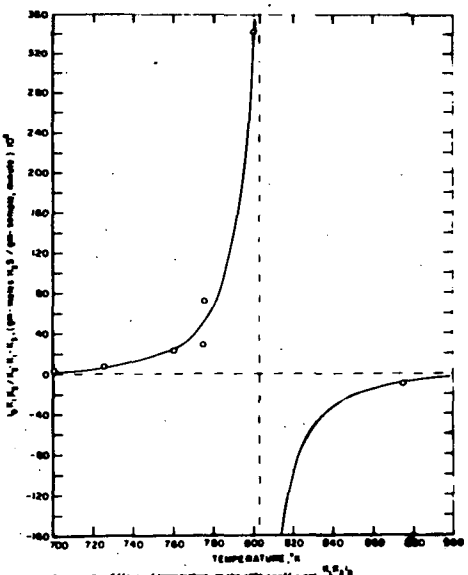

Figure 10 – Effect of temperature on the rate constant $\frac{K_1 K_2 K_3}{K_2 K_1 - K_3}$

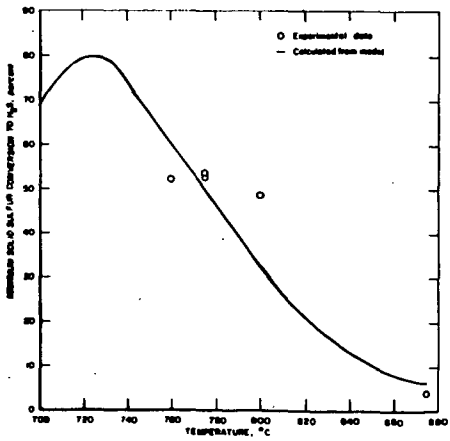

Figure – Variation of maximum sulfur conversion to H_2S with reactor temperature; H_2 feed, K_2SO_4-SiO_2 fused mixture

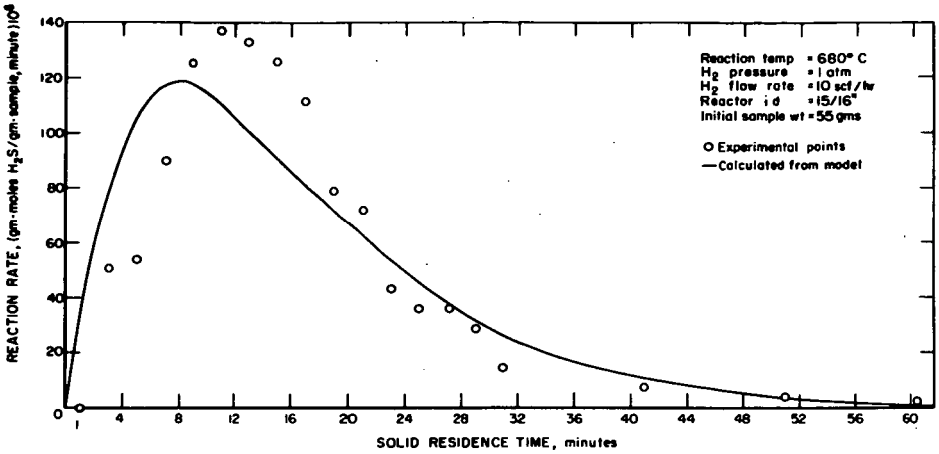

Figure 12.—Comparison of measured differential H_2S generation rates with that predicted by kinetic model for regeneration of spent alkalized alumina with H_2.

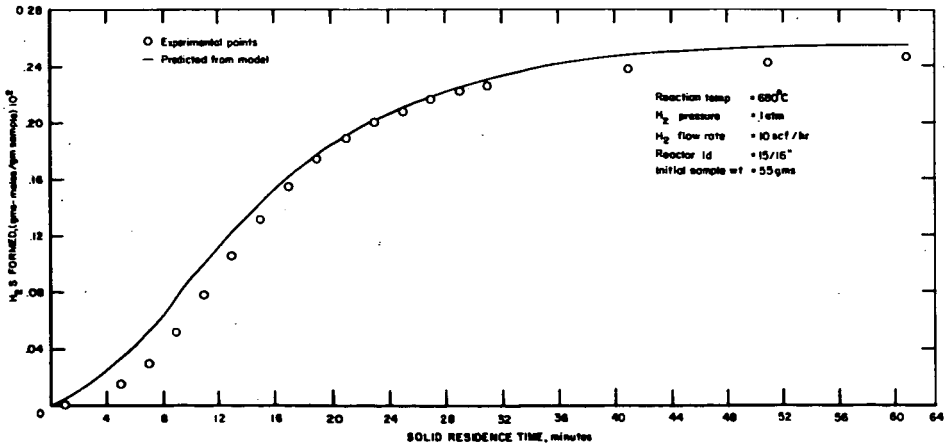

Figure 13.— Comparison of measured H_2S conversion with that predicted by kinetic model for the regeneration of spent alkalized alumina with H_2.

RECENT ADVANCES IN EXTINGUISHMENT OF BURNING COAL REFUSE BANKS FOR AIR POLLUTION REDUCTION

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INTRODUCTION

THE BURNING REFUSE BANK PROBLEM

A coal refuse bank is an accumulation of rejected material resulting from the mining and preparation of coal. These banks usually contain rock, coal, bonded coal, carbonaceous shale, pyrites and other debris from the mining operations; including possibly, paper, grease containers, rags, timbers and miscellaneous discarded mining supplies and equipment. In some cases, the refuse bank may also be a site where indiscriminate trash and/or garbage from nearby dwellings accumulates which adds to the possibility of combustion.

One of the problems important to the health and safety of the people of the coal producing areas, as well as to overall economic development in the coal regions, is that of burning coal refuse banks or piles. It is estimated there are at least 200 of these burning banks in Pennsylvania at the present time. Many of these burning piles are located in areas remote from urban development, however, many are causing air pollution in built-up areas.

For over 300 years, fires in accumulations of coal refuse and stored coal have been and still are occurring as a result of spontaneous combustion or other means of ignition. Currently, due to state and national regulations on air pollution and smoke control, attention is focused on the burning of discarded coal refuse, produced during the preparation of coal or from selective mining techniques. For many years these unsightly refuse areas were deemed a necessary evil of coal mining regardless of the devaluation of adjacent property, and the particulate matter and noxious sulfurous gases which they release into the atmosphere when burning.

The fate of many of the early refuse banks with respect to spontaneous, accidental, or deliberate combustion is not known. It may be concluded that many did burn, particularly in view of the inclusion of small coal with the spoil discharged to the piles. The large tipple-formed piles were particularly liable to spontaneous combustion. It may be assumed from the many examples of burned out colliery spoil banks which had been formed during the first half of this century that combustion was the rule, rather than the exception in many of the coal fields.

PUBLIC CONCERN

Passage of the Pennsylvania Air Pollution Act required the owner of a mine to employ all practical means to prevent the ignition of the refuse disposal from the mine and to prevent or minimize the emission of smoke and fumes from the refuse. An important exception was that the liability did not extend to deposits of refuse made before the passage of the Act, which at the time, were no longer in use and which were not under the control of the mine owner.

In Pennsylvania prior to 1963, the Department of Mines and Mineral Industries was not authorized by law, nor did it have the funds to attack burning bank fires. A few brief efforts had been made at extinguishment in the past, using the Governor's Emergency Fund or Civil Defense Funds. In 1963, legislation was passed which authorized funds to begin extinguishment of these bank fires. During 1964, two fires were extinguished with funds provided by the State Legislature. Through research and demonstration projects, varied techniques have been attempted in an effort to seek more efficient and less costly methods to extinguish burning refuse banks.

As far as existing non burning abandoned refuse banks are concerned, a continuous surveillance or patrol system is required, in order to promptly initiate abatement work as soon as a fire occupies a portion of a bank.

OCCURRENCE AND CAUSES

A 1963 survey conducted by the U.S. Bureau of Mines indicated that there are more than 495 refuse piles on fire in the United States. This report which is approximately six years old, is of necessity, inaccurate at the present time because new fires are constantly starting and through government and private efforts, fires are being extinguished and some piles are burned out.

The main cause of these difficulties, apart from the high carbonaceous content of piles, is said to be the tippler form of pile construction. This form of construction encourages the segregation of the larger pieces of spoil to the toe of the pile which allows the easy passage of air into the center. The rising bedding planes and the lack of consolidation allow internal convection currents to flow and the steep faces encourage penetration by the wind. The steep faces increase the difficulties of controlling any combustion which starts in particular, it is almost impossible to blanket the faces of these piles with clays, etc.

At the present time, approximately 25% of the run-of-mine coal reports to the refuse disposal area. Coal refuse material, when stockpiled at random, reaches ignition temperatures readily. The resulting combustion occurs in many different degrees from smoldering to active burning. Atmospheric conditions have a marked influence on this burning. Heat is liberated continuously, although this is not visible under warm, clear conditions. Cool, damp atmospheric conditions produce excessive vapor and smoke and together with the obnoxious gases high in hydrogen sulfide and sulfur dioxide produce an air pollution problem in the immediate vicinity and down wind from the refuse piles.

Modern coal mining practices and coal cleaning facilities increased the proportion of waste handled. Mechanical mining machines used in most anthracite and bituminous mines today are not selective and mine a considerable amount of rock and other non carbonaceous material which reports to the refuse pile after having passed through the preparation plant.

Ignition of a refuse bank can be initiated in several ways. A recent U.S. Bureau of Mines report outlines the following possible sources of combustion:

1. Spontaneous ignition:
   a. Sufficient air must enter the refuse dump to oxidize the coal and other combustible materials.
   b. Air must be insufficient in quantity to carry away the heat generated during the oxidation, thus permitting the heat to accumulate.

2. Careless burning of trash on or near the bank.

3. Forest fires.

4. Camp fires left burning.

5. Intentional ignition to create residue which may be used for road base materials.

BASES OF EXTINGUISHMENT METHODS

Coal and the carbonaceous minerals which form the major component of most refuse begin to oxidize as soon as they are exposed to the atmosphere in the course of mining. When small quantities of refuse are involved, the heat evolved will be dissipated, but when large masses such as banks are exposed to the atmosphere, thermal chain reactions may develop and active combustion may appear.

Any attempt at extinguishing a burning refuse bank and the elimination of resulting air pollution, must be based on the usual time honored extinguishment theories. The usual components of any combustion process must be eliminated through one technique or another. Air may be kept away from the carbonaceous material in such a way that no ignition is possible. A refuse bank may be re-cleaned in order to eliminate the fuel and lower the possibility of combustion. Cooling processes may be applied to lower the kindling temperature below the threshold for ignition. The ignition temperatures of Pennsylvania bituminous coals range from 327° to 420°C. The ignition temperatures of Pennsylvania anthracite range from 450° to 510°C. Pyrite and slate mixtures found in anthracite have been found to ignite at 417°C. Waste materials from mining operations, including powder boxes and timber will ignite at temperatures as low as 219°C. Most efforts aimed at extinguishing refuse bank fires have dealt with one of the three key ingredients of combustion - removal of oxygen, lowering of kindling temperature, or removal of fuel.

REFUSE BANK EXTINGUISHMENT

PREVIOUS WORK

During the period October 1, 1949 to May 31, 1951, a research project on mine refuse fires was conducted by the staff of the Department of Mineral Preparation at the Pennsylvania State University under the direction of Dr. H. B. Charmbury. The project was sponsored jointly by the Pennsylvania Department of Mines and Mineral Industries, the Central Pennsylvania Coal Producers Association, and the Western Pennsylvania Coal Operators Association. The research was concerned with an investigation to control mine refuse fires. Over 350 coal companies were contacted regarding the problem and data were obtained on over 800 piles. At only 81 of the locations were special efforts being made to pile the refuse to minimize possible ignition. These methods included

layer piling, layer piling with clay, sealing the pile with clay and fly ash, digging out and backfilling, and using trenches for storage. Some efforts were being made to extinguish burning piles. These included the use of water and the use of bulldozers to isolate the burning section. Neither of these methods was entirely successful.

Many methods such as flooding, blanketing, slurry injection, compacting, loading out, and sealing have been attempted in the past to control bank fires. A review of the pertinent literature regarding spontaneous combustion, refuse bank extinguishment efforts, coal - refuse storage, and related topics will be found in the attached bibliography (Appendix A).

RECENT WORK

Work has been conducted with funds made available by the Legislature of the Commonwealth of Pennsylvania and in certain instances, matched with Federal funds from the National Air Pollution Control Administration of the U.S. Department of Health, Education and Welfare. Demonstration projects have been devoted to finding newer and more practical methods of extinguishing burning refuse banks. In each of the various extinguishment techniques, the overall program followed the procedure outlined below:

1. Initial engineering and planning of the work and investigating possible problems and solutions.

2. Arrangements with qualified contracting firms to do the physical work.

3. Actual performance of the prescribed extinguishment program by the contracting firm with on the job consultation and surveillance by representatives of the Pennsylvania Department of Mines and Mineral Industries.

4. Evaluation of the extinguishment project by the project contractor and departmental staff in order to evaluate the extinguishment technique.

In most cases, the subject bank was chosen on the basis of finding areas where a demonstration project would serve the dual purpose of demonstrating and evaluting a new or modified technique and concurrently abating pollution which was creating a nuisance in a nearby community. Such refuse bank fires were located in both the Pennsylvania Anthracite and Bituminous fields. The contractor in each case was under obligation to secure the necessary permits from the State regulatory agency, (the Air Pollution Commission of the Pennsylvania Department of Health), and any required easements from private property owners.

In many of the demonstration projects, the approach taken was suggested by the Department's representative. However, in a few cases, the demonstration project was based on a plan or procedure presented to the Department by an engineering and/or contracting firm. The methods explored are listed on the following pages.

Accelerated Combustion and Quenching: A research project was conducted in the anthracite region involving the lifting of burning refuse material by a dragline and dropping the hot material through an air drop of 50 to 100 feet into a water filled lagoon. In the process of dropping the hot refuse material through the air, a considerable amount of combustible material was burned off, in some cases with a flash - explosion, while allowing the hot material to fall into a water filled lagoon. Following the water quench, another dragline lifted the quenched material out of the lagoon floor and placed the extinguished material to the rear of the operating equipment where bulldozers spread the material and compacted it into a tight, dense fill material. The work performed in this technique appeared to successfully extinguish the material and place it in a form in such a way that it would not further ignite. One shortcoming of the above mentioned technique, is the concurrent evolution of particulate matter during the air drop of the burning refuse. It may be possible that the technique described above may lend itself to extinguishment of refuse bank fires in areas remote from populated areas. This technique is applicable to large refuse banks.

Isolation: If the bank fire is in a very early stage of combustion, the burning area may be isolated from the remainder of the burning bank by ditches which cut completely through the bank to the bare soil underlying the bank. The isolated hot material can then be quenched with water or moved to an area and mixed with cold incombustible material. In some cases, the trench or ditch which is so created is lined with clay or earth to minimize the entrace of air into the porous bank material.

Foam Covering: In this project, a polyurethane foam was applied to a terraced-contoured refuse bank. The bank was contoured into a number of equal steps approximately 50 to 70 feet high and with a one to one slope between the roadbed and the rising slope to the next level. After shaping the pile, water sprays were applied to cool the surface material. Following such cooling, polyurethane foam was applied to all sidewall and roadbed surfaces. The pile temperature has decreased and continues to decrease over a period of 18 months following the application of the foam cover. In certain areas, excessive temperatures caused a charring of the foam and it was necessary to remove and rebuild a foam coating following a deep water spray and cooling of the localized "hot spot." It is felt that this technique lends itself to small refuse banks that are not excessively hot. It should be noted that certain shortcomings are obvious in this technique and this includes the possible damage to the coating surface by children or vandals and that a pile extinguished via this smothering method will need constant maintenance until the entire pile has cooled beyond the kindling temperature. In a subsequent project, based on a similar foam covering principle, further work is being done to reduce the thickness of the foam cover in order to reduce costs and additional steps are being taken to prevent surface degradation by sunlight through the use of paints applied to the foam surface. Fiberglass and/or other strengthing materials may be laid on the horizontal traveling surfaces to reinforce these areas. Additionally,

surface treating materials will be applied in order to reduce surface temperatures and provide a firm non-absorptive base for foam application.

Vermiculite and Sodium Bicarbonate Injection and Coating: This project aims at filling voids and reducing oxygen entry, as well as, sealing the surface. A mixture of vermiculite, sodium bicarbonate, limestone dust and resin, has been injected into and applied on to a shaped refuse bank. Some promise is shown by this method due to the expansion of vermiculite with the application of heat. The technique has not been completely evaluated. Preliminary results, however, would indicate that void filling with such materials is beneficial for a short period of time, but may, in fact, be too costly to justify the end results. The materials used, do not form a tight seal on the surface of the bank which is sufficient to exclude oxygen from the interior of the bank. Further work using this technique may be done, however additional emphasis would be placed on surface sealing in addition to the injection of these materials.

Injection of Fine Mineral Matter: Fly ash, coal silt, and rock dust, have been injected through drilled holes in the periphery of a burning refuse bank in order to fill voids and reduce air intrusion. This technique appears to be relatively successful, but again, the process of void filling must be followed by adequate surface treatment in order to prevent erosion and gully formation on the refuse bank surface. Heavy rain may often lead to the wash-out of the injected fines and the renewed porosity and oxidation problems along the sides of the eroded gully. The availability of such mineral materials adjacent to refuse banks and from the fine coal cleaning circuits of a normal preparation plant does offer considerable promise to this technique, especially if it were coupled with some relatively inexpensive surface sealing techniques.

Mine Drainage Sludge Injection: A project is now in progress in which acid mine drainage containing a high amount of iron and calcium salts is neutralized and the resulting iron hydroxide and gypsum sludge is injected into the burning refuse bank. The sludge of iron hyroxide and gypsum mixture forms a tight impermeable cake or crust on the pile and appears to merit further consideration. The small project which has been initiated has not been concluded, but present evidence would indicate that there is considerable merit in this procedure and is a relatively low cost disposal site for the troublesome treatment plant sludge and could concurrently help with refuse bank extinguishment efforts.

The Use of Anti-Oxidants: The discovery of a cheap reagent which could be applied to refuse to retard the rate of oxidation of the exposed pyrite would be an excellent solution to this and several allied problems. Unfortunately despite continued research, the prospects of finding such a reagent is still going on.

Laboratory experiments with chromates, phosphates, and sodium hydroxide were reported to be unsuccessful and a full scale test in which liquid ammonia was applied to abandoned mine refuse in an attempt to control the oxidation of the pyrite had also been unsuccessful. Tests involving up to 1 per cent of limestone powder added to small coal stock piles did retard the acidity initially, but after six months, the effect disappeared, even though most of the limestone had not been consumed. For the time being, it must be concluded that no specific reagents for the retardation of the rate of weathering of pyrite are known.

However, the use of oxidation inhibitors is being reviewed under a project which is continuing in Pennsylvania. A candidate group of inexpensive organic and inorganic anti-oxidants and flame retardants was evaluated by a chemical company. Small prototype piles or firing chambers were constructed by the firm and various

concentrations of candidate materials were added in the solid and/or solution form and the degree of ignition retardation was measured. The product which was found to be best has been applied in an aqueous solution to a burning refuse bank. Four areas have been laid out on this bank in order to establish the degree of success attainable through the above application. A control strip involving no treatment was laid out, a similar area was sprayed with only water, another area was sprayed with water and a surfactant, and the test area was sprayed with a water solution containing the anti-oxidant. Results to date indicate that the retardant has some desirable properties and the desired effect on the pile. H wever, applications must be at a much higher dose rate than originally anticipated.

Saturation Through Serpentine Canals: A refuse bank located in the anthracite field was covered with an array of interconnected serpentine canals or troughs, in an order to allow water maximum time to percolate through the pile. It is necessary to apply water through such a remotely located canal system so that personnel will not be in danger by secondary explosions or evolution of clouds of gases and/or steam at the point of water and refuse contact. The interconnected array of canals was constructed by bulldozers. The operators were equipped with oxygen breathing apparatus. Following the construction of the interconnected canals, water was pumped to the highest point in the canal system and allowed to flow in a "zig zag" pattern down the side of the bank. While this water treatment and cooling procedure was proceeding, other equipment was preparing another canal system in another part of the pile. After several months of canal construction and wetting, the technique was abandoned. The procedure did not allow sufficient percolation of water from the surface to the area beneath the superficial surface crust. Only percolation to the depth of two to three feet was noted.

Ponding Technique: A series of adjoining lagoons was constructed on the top of a relatively flat refuse pile which had been built across a valley bottom. Retaining walls were constructed around the perimeter of the refuse bank area, subdividing the surface into a series of level discrete areas or "rice paddys." Upon construction and in sequence, water was admitted through a series of canals into the flat impoundment areas. Evolutions of vapors and steam were immediately evident. Pools of water were retained on the top of such flooded areas for periods extending to a period of several weeks. Flooding may be hazardous inasmuch as explosions have been known to occur when a large quantity of water was rushed onto the fire area. After several weeks of soaking, an area would be allowed to drain and experimental cuts were made into the lagoon floor. In some cases, it was found even after several weeks of standing under several feet of water, penetration of the water into the refuse material was only two to three feet and temperatures in excess of 400° were found only several yards beneath the water. Work following this procedure has been continued and in spite of the necessity to continue to maintain a water cap on such ponded areas for an extended period of time, the technique is considered to be of relatively low cost per unit refuse extinguished.

Cooling and Dilution: This method involves the preliminary cooling of the refuse pile by remote application of a water spray from multiple nozzles. The cooled refuse is then mixed in a one to one volume proportion with soil and/or burned out coal refuse from a nearby borrow area. The mixing of extinguished but warm, damp coal refuse and the inert material is carried out by the bulldozer operator. The material is then laid down in a new portion of the tract and compacted by heavy equipment. Where cooling and diluting material is available and sufficient land is available, the above technique appears to be most promising and one of the least costly on a cost per cubic yard extinguished basis.

Blanketing With Clay and Cement Waste: A bank was covered with a mantle of clay along all sidewalls following conventional practice which has been performed many times with mixed success by the coal industry. (Experience has shown that complete clay covering of a refuse bank often leads to the formation of a "baked" clay seal which in due course, cracks and allows the re-entry of air and the re-firing of the cooling refuse bank.) In the technique attempted by the Pennsylvania Department of Mines, sidewalls of the refuse bank were covered with clay and the clay was compacted. The open top was covered with a layer of two to three feet of cement kiln waste dust. This dust which contains a certain amount of portland cement is a waste product from the nearby cement industry. The material was delivered by tank truck and placed on the flat top surface of the refuse bank. The surface of the cement dust layer was sprayed in order to form a crust to the depth of one to two inches. The dust beneath the surface crust remains fluid and filters down into cracks and fissures in the bank as they may occur. This technique appears to be successful and may be applicable to small piles that are adjacent to or near the cement industry.

Blanketing - Quarry Wastes: This technique involves shaping of a refuse pile followed by the application of minus 1/2"limestone quarry wastes to the top and sides as a sealant and the revegetation of the pile by hydroseeding. The compaction of the pile followed by the limestone covering of the sides and top appears to be rather successful. The evolution of carbon dioxide at the site of any hot spots may be useful in extinguishing the fire in the bank. The use of quarry wastes again carries the dual benefit of finding a useful outlet for this mining wastes material, concurrent with the blanketing and fire extinguishment purpose. Any run-off, following precipitation, from such a quarry waste covered bank would be of an alkaline nature. Due to the soil characteristics, an experimental planting has been done on the sidewalls of such a treated bank and a substantial stand of grass has established itself on this bank.

Use of Explosives Followed by Quenching: Many large refuse banks do not lend themselves to water quenching due to the previously mentioned fast run-off of water which is applied to the surface. A surface crust of impenetrable ceramic like clinker material does not allow the penetration of quenching water. In order to penetrate such a partially burned bank, the Department of Mines and Mineral Industies has placed horizontal boreholes into the burning area of the bank and placed heat insensitive explosives into the boreholes. The explosives are detonated and the broken up material is then quenched with water jets. This material has been used in an urban pile with a high degree of technical success and with reasonable economics. This technique is considered to be among one of the better procedures for application on piles which had heavy crusts of partially burned out material.

Hydraulic Jets: Projects conducted by the U. S. Bureau of Mines and the Pennsylvania Department of Mines have involved the application of "hydraulic giants" or high pressure or high velocity water cannons similar to those used in the placer mining industry. The application of high velocity streams of water undermines larger portions of the bank as well as quenching the bank material. The quenched material will fall or roll into a lagoon from which it is lifted by draglines. The quenched material is removed from the lagoon and placed behind the hydraulic jets and compacted by bulldozers. The effect of this technique is to extinguish large volumes of very hot materials while attaining a high degree of safety for operating personnel. In addition to the cooling and quenching action of the water jets, there is a good deal of particle size reduction and degradation which takes place in this material handling technique. When the material is then

relayered and compacted by the dragline - dozer combination, the material attains a cement like very dense characteristic which is considered to be virtually incombustible.

Water Sprays Only: The use of water sprays to control combustion in refuse piles has been deprecated by some authorities, but is still practiced. At best, this method can be considered to be only a temporary expedient for temperature and fume control until permanent abatement work can be initiated. Work by the U.S. Bureau of Mines recently and the British National Coal Board, has shown that once water spraying is discontinued, combustion takes place again, often with renewed vigor.

Run off from refuse banks is a problem closely related to the fire problem. The thermal reactions have no direct effect on the quality of the drainage from a bank but the indirect effects may be important. Active combustion may generate sufficient heat to evaporate all water precipitated on the bank so that no drainage appears. Provided that the heat is sufficient, the sulphur acids may be dissipated into the atmosphere as sulphur oxides so that acidic contamination of the drainage will not occur, but if the heat is insufficient, the acidic salts may accumulate in the pile and be washed out after the fire has subsided. On the other hand, if the heat is insufficient to evaporate all the precipitation while the fire is burning, the drainage will have a higher than average risk of becoming acidic due to the enhanced oxidation of pyrite at the elevated temperatures. Water applied to a pile to suppress a fire would probably increase the volume of drainage without any corresponding decrease in the degree of contamination.

CONCLUSION

The work involved in the various projects which have been initiated by the Pennsylvania Department of Mines and Mineral Industries requires the application of tried and proven techniques in combination with unproven theoretical applications of engineering and technology. The extinguishment project must be technically feasible and economically practical. The extinguishment project can not be conducted in such a manner that the emission of dust and fumes create an unwarranted nuisance in the immediate area and in the downwind inhabited areas. The creation of such dust and fumes by the extinguishment operation not only creates atmospheric conditions unfavorable for the residents of the area who are in the downwind direction, but make the operation exceedingly difficult for contractors' employees.

Because of the varied shapes, sizes, and elevations of different banks, various methods of movement and materials handling must be explored and tailored to the conditions at any given bank. The availability or lack of water at the project site, also plays an important role in choosing the particular method which can be applied to a bank. Other facts which are of importance include the size of tract and the proximity of homes to the fire area. The availability of inert or diluting solid material either in the form of an earth borrow pit, or completely burned out refuse, also must be taken into consideration in choosing the method to be applied. The extinguishment of small banks is, of course, more readily accomplished and less expensive than large banks. In

addition, techniques which are applicable to large banks do not always work equally well with small banks. For example, it is obvious that the use of a hydraulic jet is not warranted in a pile of only several hundred cubic yards of material. Conversely, foam covering could not readily be applied to a multi-million ton refuse bank.

It should be added that following extinguishment, maintenance is required to protect the private or public investment in the abatement project and to minimize the liklihood of any re-ignition. It is known that extinguished material, after having been cooled with water and rehandled and recompacted, becomes a stable, hard surfaced material which produces no dust or fumes and should be relatively immune to any rekindling. Refuse areas should be maintained and regularly inspected in order that hot spots which might develop could be spotted at once and removed and/or filled with an inert material such as clay or earth. Erosion to surface areas must be prevented as gullying allows air entry into the extinguished bank which might rekindle the fire. Following extinguishment, good insurance against further combustion is to deposit a clay and earth layer on the extinguished bank. The earth material should then be seeded with grass in order to minimize erosion and to consolidate the surface and prevent loss of the protected cover. The earth seal covered with a vegetated growth, while it does not reduce the necessity for maintenance, will reduce the maintenance to a minimum and provides protection against re-ignition and also prevents a more aesthetically appealing view for the community.

It should be noted, that virtually all reports indicate that a technique that is successful on one bank, may not be successful on another bank. Each bank represents an individual problem. The engineer, government agency or other organization who wishes to extinguish a fire, must find a technique which can be tailored to the situation at the given bank. It should also be noted that extinguishment may take years, but control is possible to the extent that the fume problem is reduced by gradual steps.

Although several successful bank extinguishment techniques are presently at hand, we anticipate that continued work in this area will provide worthwhile data and may lead to better and more economical methods for the control of this vexing problem.

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A Study of Inert Gas Atmospheres on the Oxidation of Coal Mine Pyrites

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The production of iron salts and sulfuric acid by the oxidation of pyritic material in coal mines is a substantial source of water pollution. These compounds are generally believed to be the result of the chemical reaction

$$2\ FeS_2 + 7\ O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$$

One means of controlling the rate of this reaction is to control the amount of oxygen in the atmosphere surrounding the pyrite. Investigators at Ohio State University[1] and Mellon Institute[2,3] have discussed the effect of limiting the oxygen concentration in such atmospheres. This paper describes the results of experiments in which pyrite is exposed to various gaseous atmospheres, in the presence of water.

The pyrite used was obtained from coal crusher reject material and was largely taken from strip mining sites in the Clearfield, Pennsylvania area. It was crushed from 6-8" lumps to less than 1" diameter, and loaded into six insulated cylindrical columns, 6' x 4" I.D. Approximately 40-45 lbs. of pyrite were used per column.

Demineralized water at a constant temperature of 56°F entered the top of each column, trickled over the pyrite bed, and was removed from the bottom. In a similar manner, the gases were injected into the top of each column and exited from the bottom. Each column was operated separately, with no interconnections.

TABLE 1

PYRITE ANALYSIS

Total Fe	40%
Total S	44%
Loss on Ignition	13%
Total Al	< 1
Total Ca	< 1
Total Mg	< 1

The results of the following gas systems are presented:

TABLE 2

COLUMN ATMOSPHERES

Air
Nitrogen
Nitrogen/Carbon Dioxide

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1 Shumate, K. S., and Smith, E. E., 2nd Symposium on Coal Mine Drainage Research, Mellon Institute, May, 1968.
2 Braley, S. A., Summary Report of Commonwealth of Pa. (Dept. of Health), Mellon Institute Fellowship No. 326B, February, 1964.
3 Personal Communication, R. A. Baker, September, 1968.

Column 1 - This column was loaded with 43 lbs. of pyrite having an average diameter of 3/8". After loading, the column was backwashed twice with demineralized water to flush soluble salts which had formed on the surface of the pyrite.

Air (40 cc/min) and demineralized water (12 cc/min) were percolated through the column continuously for seven days. Acid production was sporadic, as measured by frequent grab samples from the column effluent. It was surmised that the air, water and pyrite contact time was too short and therefore the procedure was changed to operate the column from 9 AM to 5 PM on Mondays through Fridays. The column was sealed at all other times with no water or air flow. This procedure produced a more or less steady production of acidic iron salts in the effluent, and was used as the method for operating the other columns.

After operating for twenty days under the modified alternate flow procedure, this column's gas atmosphere was abruptly switched from air to nitrogen, and was operated in a similar manner for thirty days. During each operating day, two grab samples and a daily composite sample were taken. This analytical data is plotted in Figures 1 and 2.

Column 2 - This column was loaded with the same size fresh pyrite as column 1, backwashed twice and then operated by trickling water from the top of the column to its bottom under a nitrogen atmosphere during eight-hour weekdays for a period of twenty days. Grab and composite samples were collected for analysis daily.

After twenty days, the nitrogen flow was discontinued and air substituted. The air/water system operated for thirty days until the termination of the experiment. The analytical data are plotted in Figures 3 and 4.

Column 3 - was loaded with fresh 3/4" O.D. pyrite, backwashed twice and exposed to a mixture of 90% $^{v}/v$ nitrogen and 10% $^{v}/v$ carbon dioxide, with the same water flow as before. This environment was maintained for fifty days until the experiment terminated. The analytical data are plotted in Figures 5 and 6.

Column 4A - was loaded with fresh 1/4" O.D. pyrite, backwashed twice and then exposed to a water/nitrogen atmosphere for thirty days the experiment terminated. The analytical data are plotted in Figures 7 and 8.

Column 5A - was operated exactly the same as column 4A, except air was used instead of pure nitrogen. The analytical data are plotted in Figures 9 and 10.

During the column experiments with the pyrite under study, two significant events common to all of the columns occurred.

a) An air leak was discovered sometime between the 10th and 11th of October, in all columns. The effects of this leak were immediately noted in plotting the grab sample analytical results, although the significance is masked in observing the data plotted for columns 2 and 5A, which were being operated in an air/water atmosphere.

b) Circumstances prevented taking the scheduled grab samples during the period of October 11th and October 21st, although the columns were in operation. Therefore, the point-to-point plot as

shown in the figures is possibly a distorted view of the overall reactions of the pyrite in each column.

DISCUSSION

The data obtained, as seen in the plotted figures (Figures 1-10), shows the definite trend for and rate of production of acidic salts to be markedly reduced when the atmosphere did not contain oxygen. Examination of the plots for columns 1-4 are particularly interesting, since the atmospheres in contact with the pyrite were switched to or from nitrogen and air. The pyrite response in each case was almost immediate when the atmosphere was reversed; the rate of acidic iron salt production decreasing when an oxygen-free atmosphere was used.

It is also of interest to note that the general shape of the curves plotted for total acidity, conductivity and iron content are the same.

None of the columns, when operated in an air free atmosphere completely ceased production of acidic iron salts. This could be due to small, undetected air leaks, or the more likely possibility that the reactions taking place had not reached a steady state.

Columns 4A and 5A represent nitrogen and air systems respectively, using smaller pieces of pyrite than used in columns 1 and 2. The increased surface area reduced the time for steady state conditions to be reached. Columns operated in nitrogen (4A and the latter 30 days of column 1) showed a steeper downward sloping curve for iron, acidity and conductivity when the smaller sized pyrite was used. The converse was true for the columns operated in air (column 5A and the latter 30 days of column 2).

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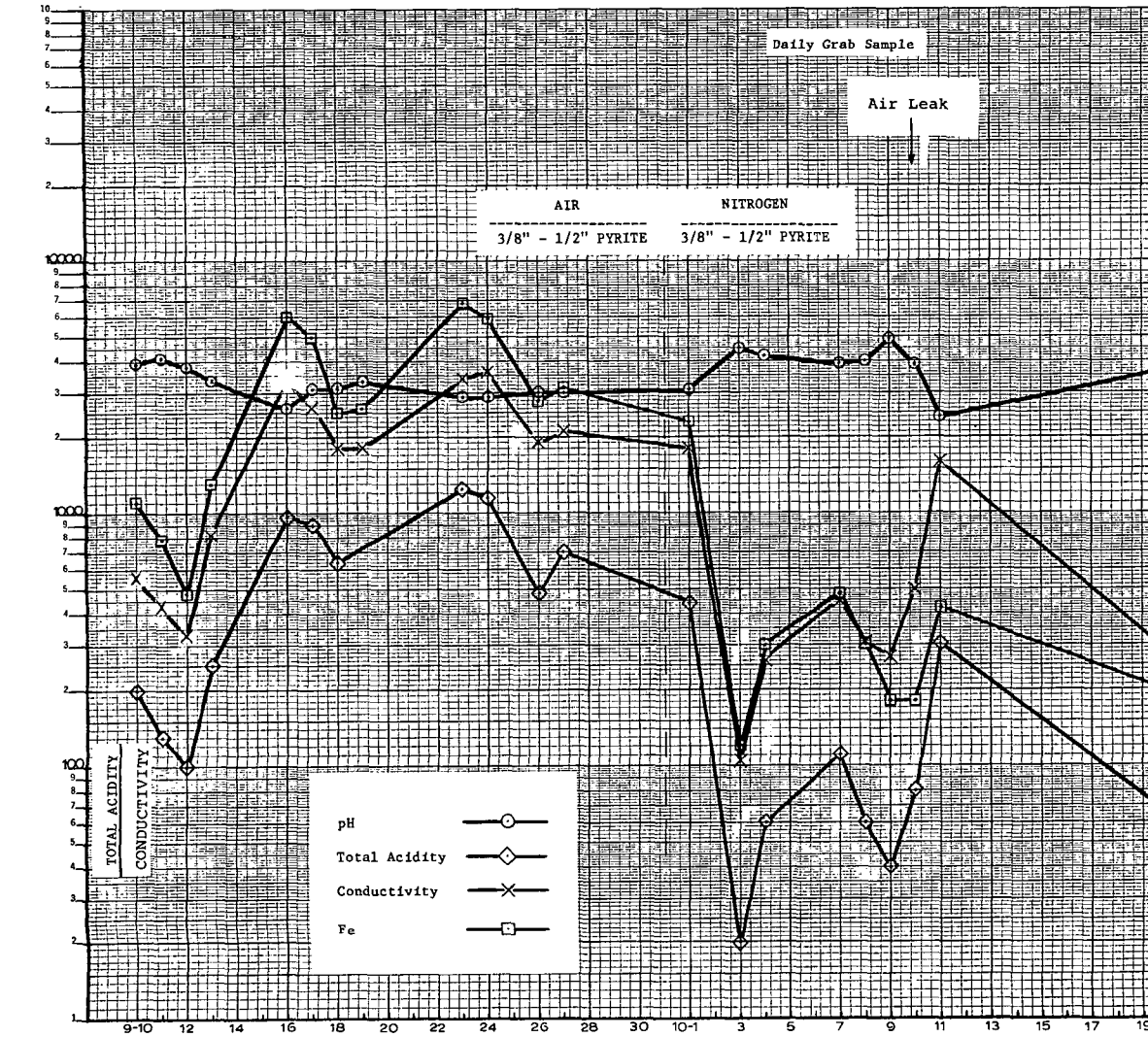
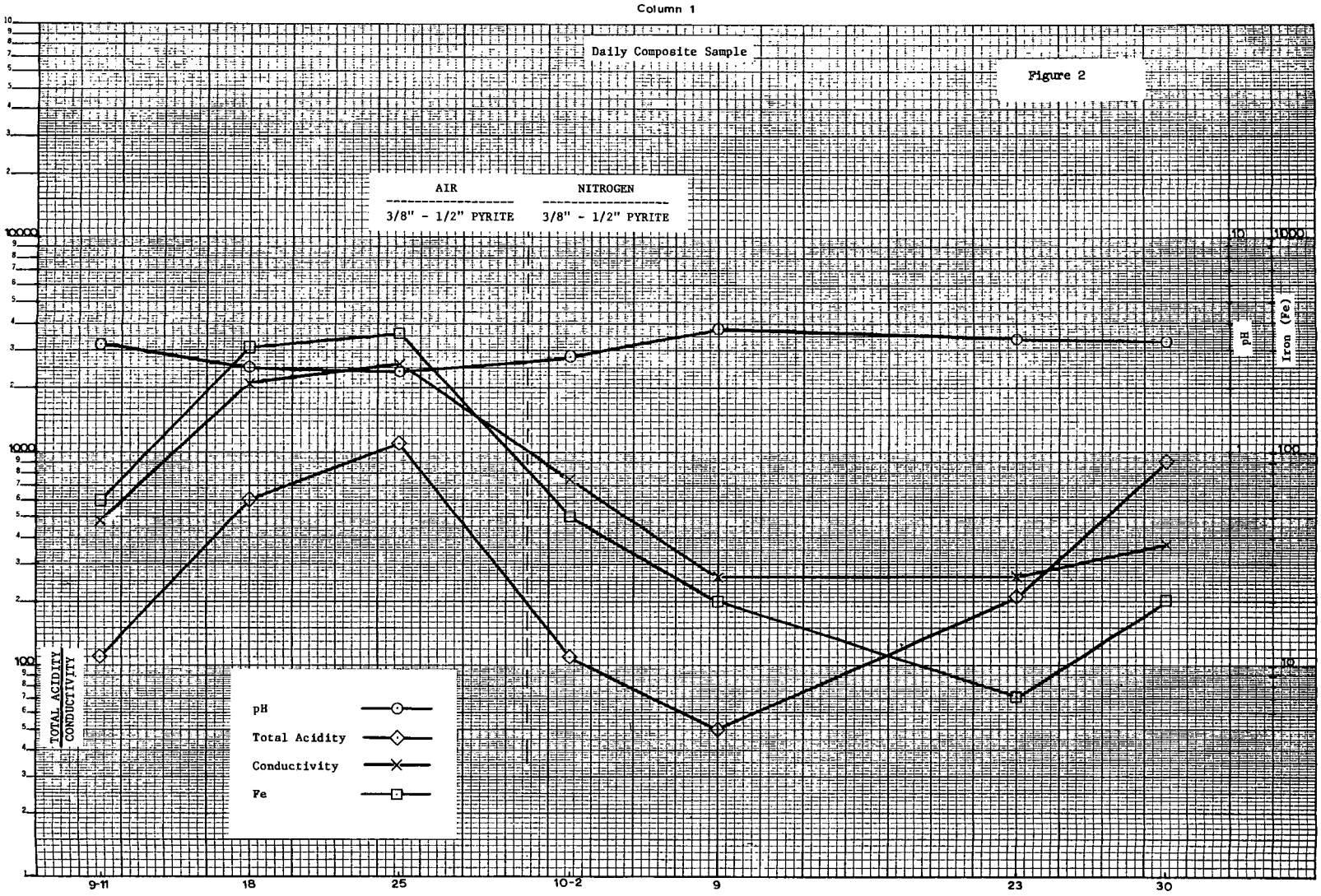
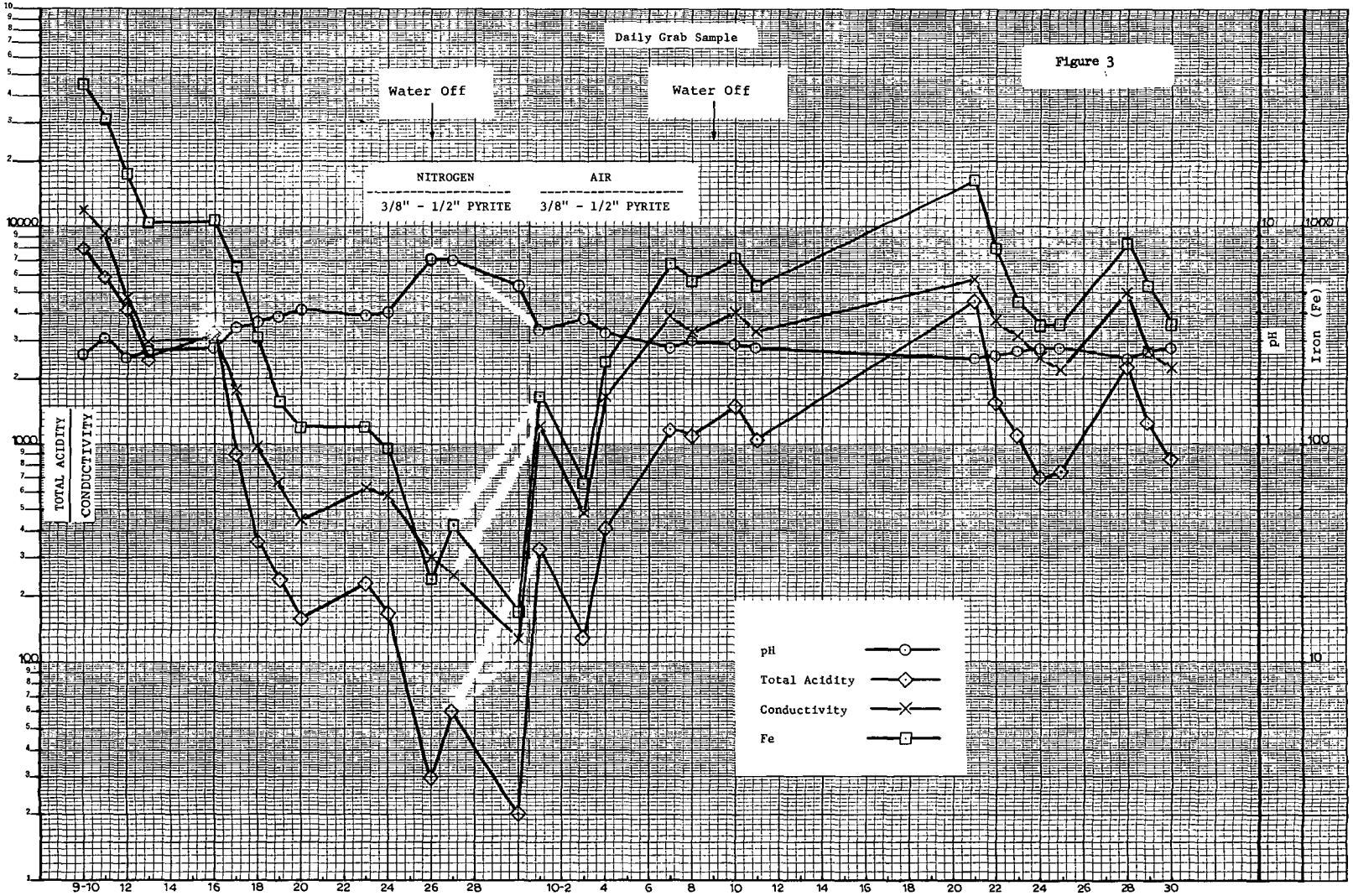
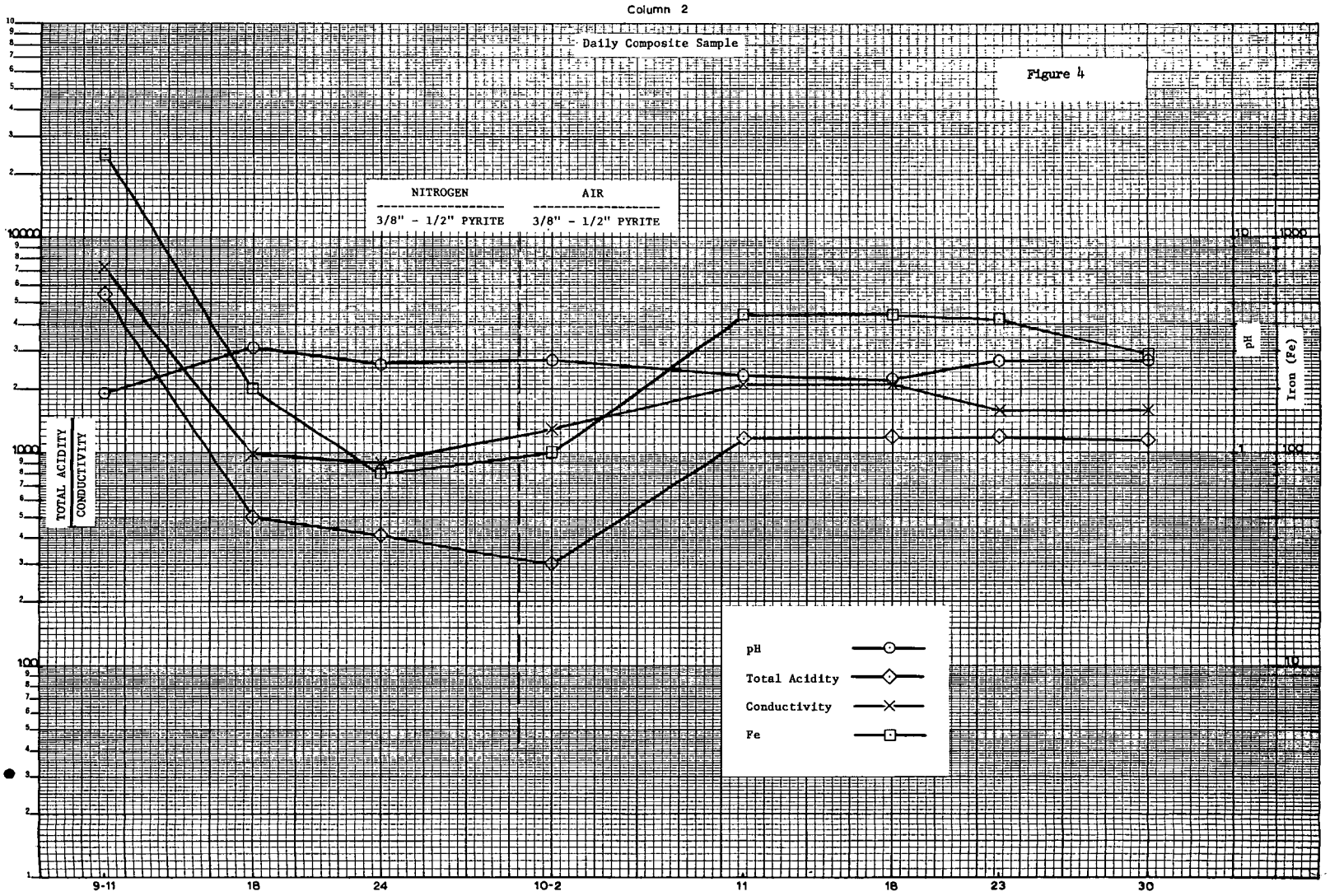
Column 1


Daily Grab Sample
Figure 1
Air Leak
AIR
3/8" - 1/2" PYRITE
NITROGEN
3/8" - 1/2" PYRITE
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
pH
Total Acidity
Conductivity
Fe
9-10
12
14
16
18
20
22
24
26
28
30
10-1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
31

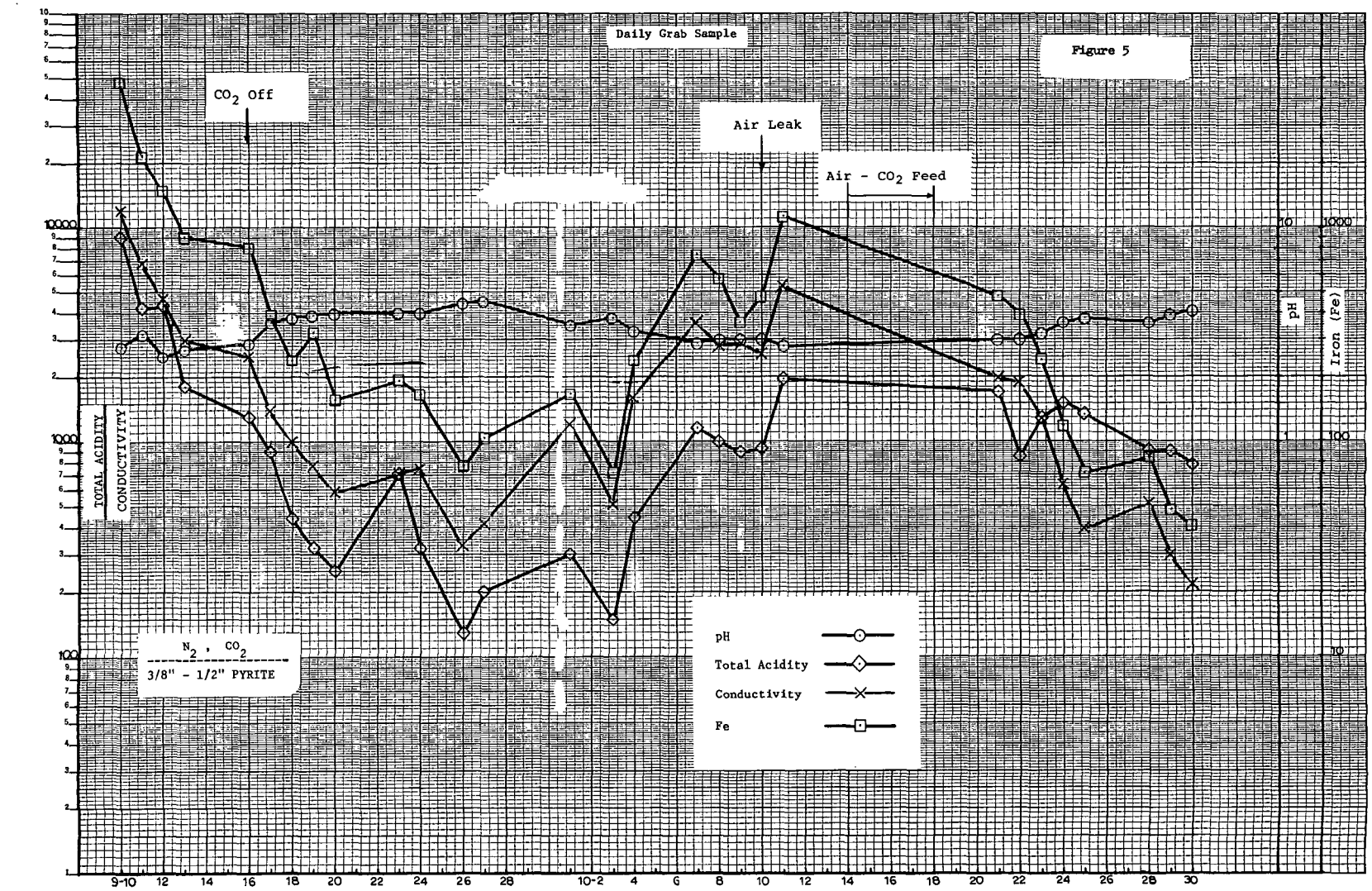

Column 1
Daily Composite Sample
Figure 2
AIR
3/8" - 1/2" PYRITE
NITROGEN
3/8" - 1/2" PYRITE
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
pH
Total Acidity
Conductivity
Fe
9-11
18
25
10-2
9
23
30

Column 2

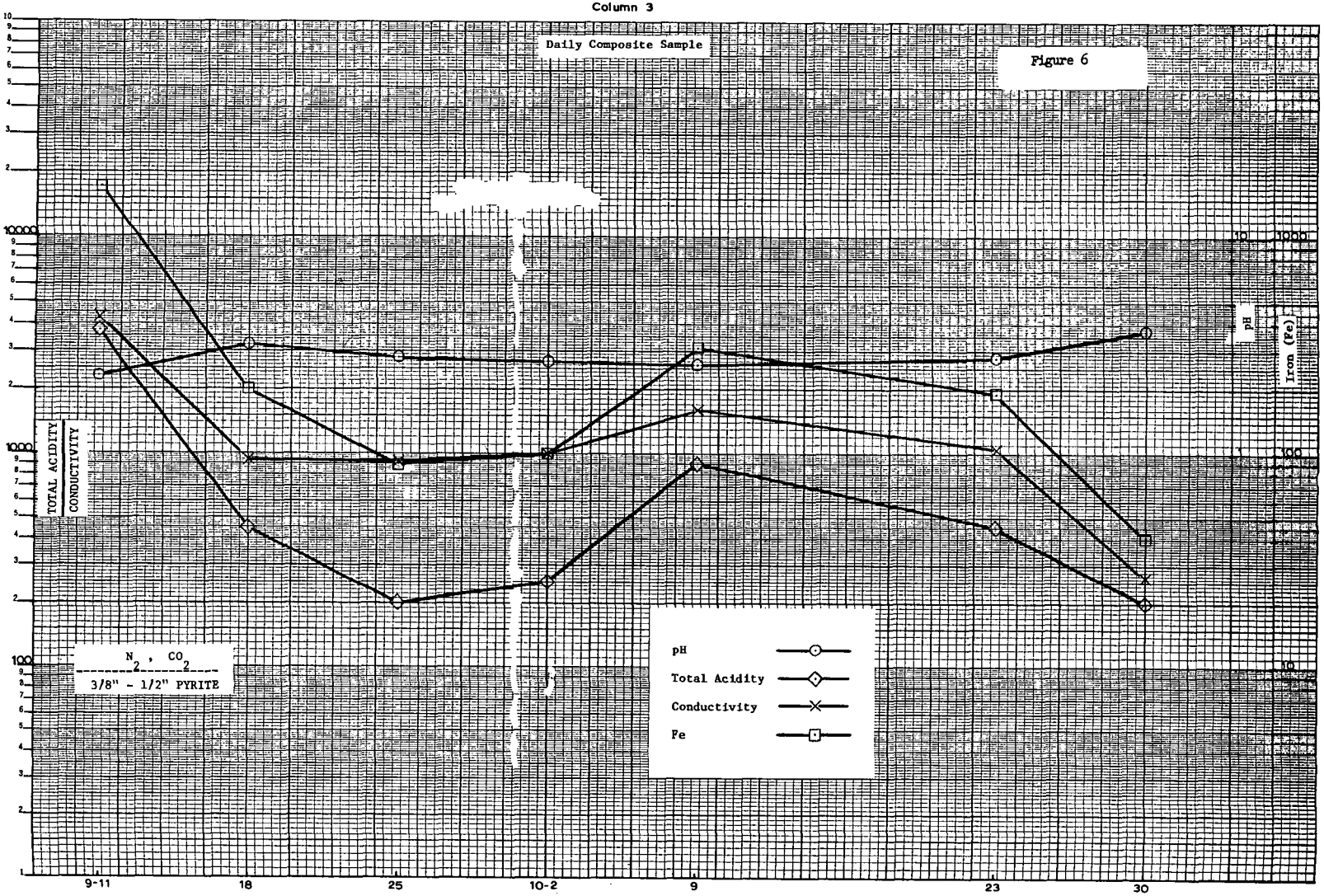

Daily Grab Sample
Figure 3
Water Off
Water Off
NITROGEN
AIR
3/8" - 1/2" PYRITE
3/8" - 1/2" PYRITE
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
pH
Total Acidity
Conductivity
Fe
9-10
10-2


Column 2
Daily Composite Sample
Figure 4
NITROGEN
3/8" - 1/2" PYRITE
AIR
3/8" - 1/2" PYRITE
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
pH
Total Acidity
Conductivity
Fe
9-11
18
24
10-2
11
18
23
30

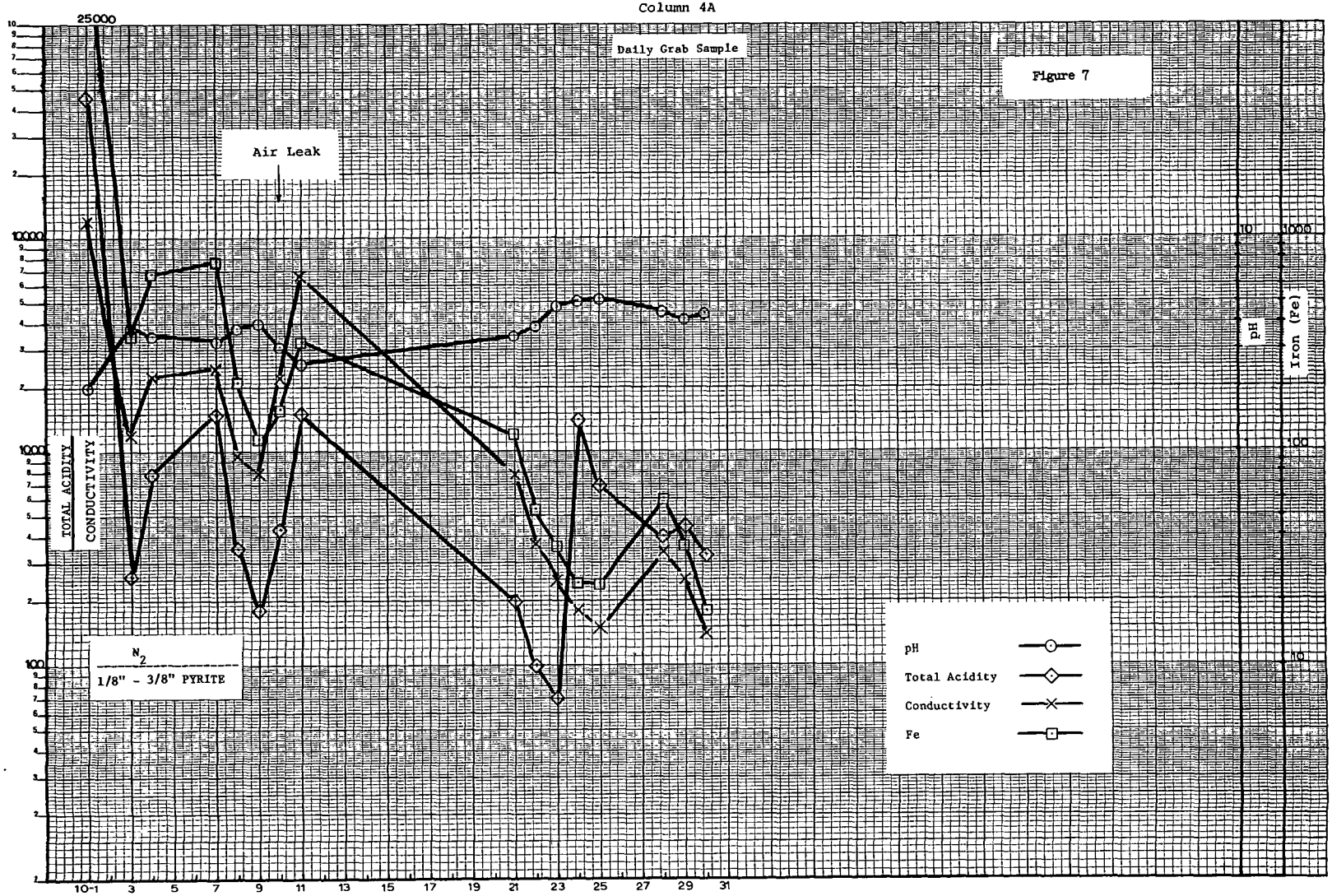
Column 3

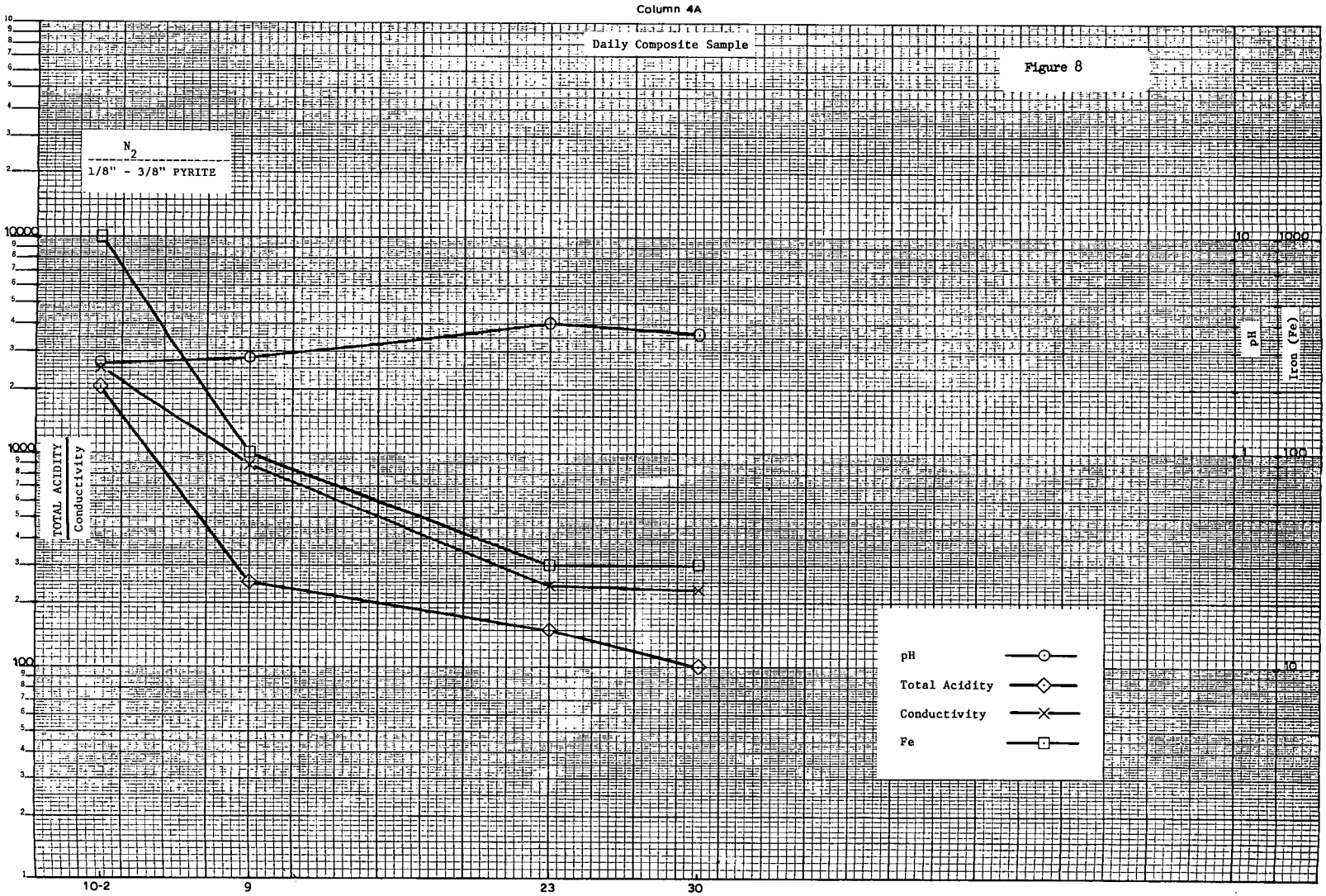

Daily Grab Sample
Figure 5
CO_2 Off
Air Leak
Air - CO_2 Feed
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
N_2 , CO_2
3/8" - 1/2" PYRITE
pH
Total Acidity
Conductivity
Fe
9-10
12
14
16
18
20
22
24
26
28
10-2
4
6
8
10
12
14
16
18
20
22
24
26
28
30

Column 3

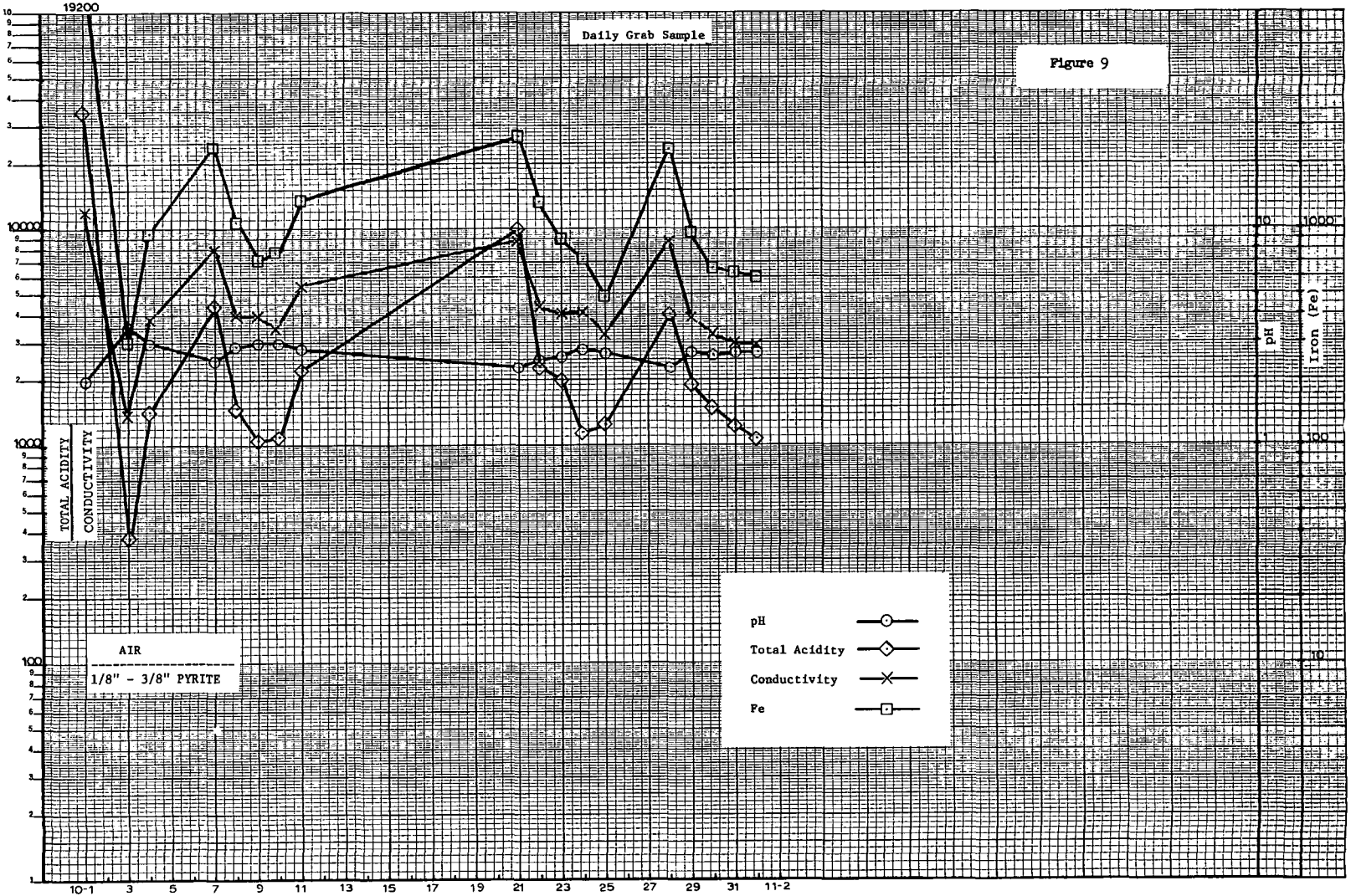

Daily Composite Sample
Figure 6
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
N_2 , CO_2
3/8" - 1/2" PYRITE
pH
Total Acidity
Conductivity
Fe
9-11
18
25
10-2
9
23
30

Column 4A


Daily Grab Sample
Figure 7
Air Leak
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
N_2
1/8" - 3/8" PYRITE
pH
Total Acidity
Conductivity
Fe
25000
10000
1000
100
10
1000
100
10
10-1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
31


Column 4A
Daily Composite Sample
Figure 8
N_2
1/8" - 3/8" PYRITE
TOTAL ACIDITY
Conductivity
pH
Iron (Fe)
10000
1000
100
10
1000
100
10
1
10-2
9
23
30
pH
Total Acidity
Conductivity
Fe

Column 5A


Daily Grab Sample
Figure 9
19200
10000
1000
100
10
TOTAL ACIDITY
CONDUCTIVITY
pH
Iron (Fe)
AIR
1/8" - 3/8" PYRITE
pH
Total Acidity
Conductivity
Fe
10-1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
31
11-2

Column 5A

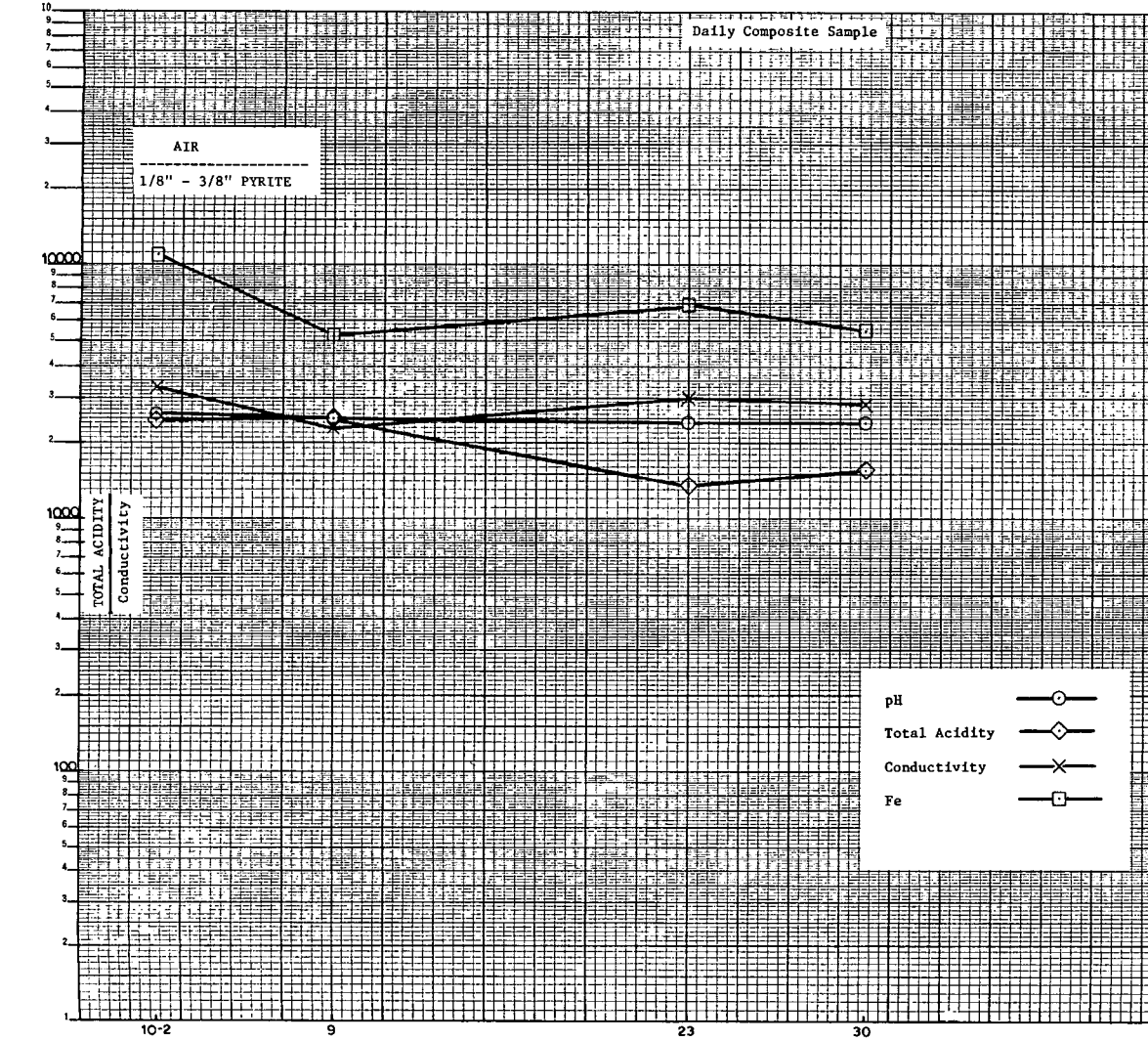


Figure 10

A Model for Pyritic Systems

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Introduction

The formation of acid mine drainage has been a subject of intense study for many years, and there have been extensive attempts to secure abatement in particular instances by such practices as mine sealing, establishing cover on spoil banks, and drainage control. It is becoming increasingly evident, however, that much of the consideration given to acid mine drainage formation and abatement has been taken out of context. In many instances, the problem has either been oversimplified, or assumed to be too complex to be handled by other than gross empirical approaches. This has resulted in difficulty in defining the rate controlling factors in specific mine drainage situations, and in both lack of communication and the accumulation of conflicting data. As a result, there appears to be a widespread element of doubt concerning the general feasibility of abatement of mine drainage pollution at the source, as an alternative to treatment. It may be that effective at-source abatement will be applicable to only a minor fraction of existing and future points of acid generation. It is just as likely, however, that through a more thorough understanding of pyritic systems,* economical abatement procedures can be developed which will eliminate the necessity of an interminable treatment program in the majority of cases. Further, it will provide a basis for more effective planning of mining operations with respect to optimizing abatement at the source.

The authors do not feel that the questions concerning at-source abatement versus drainage treatment can be answered on the basis of existing information. We strongly contend, however, that the time and expense required to arrive at these answers can be greatly reduced if the individuals, disciplines, and agencies associated with and/or dependent on mine drainage research and demonstration efforts can achieve a common basis for intensive and critical discussion. It is apparent that there are a host of widely held concepts concerning the nature of pyritic systems which differ primarily in emphasis on one or another aspect of the system. We have all experienced the frustration of argumentive discussions culminating in the realization that both parties were essentially in agreement from the first, or worse, in the realization that effective communication was not established at all.

The purpose of this paper is to present a model for the conceptualization of pyritic systems. The model draws principally on the type of descriptive framework commonly used in chemical engineering systems, and is neither new nor

* The term pyritic systems, as used in this paper, refers to the occurrence of pyrite in field situations; e.g.; gob piles, strip pits, spoil banks, and underground mines.

controversial. Rather, it is merely a restatement, in the context of pyritic systems, of the fundamental principles which describe virtually any reaction system. The model is intended to identify and provide a framework for integration of the numerous factors which determine the rate of acid release from any type of pyritic system associated with mining activity. It is hoped that this model will spark an increased level of critical discussion among those persons associated with acid mine drainage.

Rate versus Equilibrium and Rate Process Interdependencies

The acid mine drainage problem is essentially a rate problem, in which we are concerned ultimately with the rate at which products of pyrite oxidation (especially H^+, iron (Fe^{++} and Fe^{+++}), and $SO_4^{=}$) are released to receiving waters. Although thermodynamic considerations define the reactions which can occur in a given system, they do not define the rates at which they will proceed. Analysis of the rate of pollutant production requires the further delineation of the rate processes, which include:(a) rate of transport of reactants to the points of reaction, (b) rate of the reactions themselves, or reaction kinetics and (c) rate of transport of the products away from the points of reaction. Pyritic systems fall in the category of heterogeneous reaction systems, since the overall reactions involve gas, liquid, and solid phases. In any heterogeneous system there is, in general, a definite interdependency between the various rate processes. Often, one of the rate processes will be a rate limiting step in the overall sequence, and control of this specific rate process represents a potentially efficient means of controlling the rate of production of the system. The interdependency of rate processes will be discussed in more detail below.

Rate Processes in Pyritic Systems

The oxidation of pyritic materials associated with coal and other mined minerals has often been described by the following equations:

$$FeS_2(_s) + 3\ 1/2\ O_2 + H_2O \rightarrow Fe^{+++}\ 2SO_4^{=} + 2H^+ \quad (1)$$

$$Fe^{++} + 1/4O_2 + H^+ \rightleftharpoons Fe^{+++} + 1/2H_2O \quad (2)$$

$$Fe^{+++} + 3H_2O \rightarrow \underline{Fe(OH)_3}\downarrow + 3H^+ \quad (3)$$

As these are familiar to all involved in acid mine drainage work, it is convenient to outline the model in relation to these equations. It must be remembered that these are gross stochiometric equations, and although they indicate initial reactants and final products, they in no way indicate either the mechanisms of reaction or intermediate products which may be formed, but which may cancel out of the overall equations. It is significant that they do not define reaction kinetics, nor do they define the locations within a given system where the indicated reactions take place. It is likely that the simplicity of these reactions as they are popularly written may in itself be a factor in the tendency toward oversimplification in the analysis of pyritic oxidation systems.

Referring initially to equation (1), we might rewrite this equation as:

$$FeS_2(_s) + \text{electron acceptor} \rightarrow Fe^{++} + 2S^{+6} + \text{reduced electron acceptor} \quad (4)$$

This oxidation-reduction reaction provides for the oxidation of $FeS_2(_s)$ *, but does not imply that O_2 is a necessary electron acceptor or oxidizing agent. For example, it has been widely demonstrated that Fe^{+++} can be the oxidizing agent, in which case we could rewrite this oxidation reaction as :

$$FeS_2(_s) + 14Fe^{+++} + 8H_2O \rightarrow 15Fe^{++} + 2SO_4^{=} + 16H^+ \quad . . . (5)$$

The 14 Fe^{+++} ions in equation (5) would have to come from the oxidation of Fe^{++} iron formed by the previous oxidation of $FeS_2(_s)$. Rewriting equation (2) to provide the required 14 Fe^{+++} ion gives:

$$14Fe^{++} + 3\ 1/2O_2 + 14H^+ \rightleftharpoons 14Fe^{+++} + 7H_2O \quad . . . . . (6)$$

Adding equations (5) and (6) gives:

$$FeS_2(_s) + 3\ 1/2O_2 + H_2O \rightarrow Fe^{++} + 2SO_4^{=} + 2H^+$$

or the same net reaction as given in equation (1).

In any case, unless there is a continuous source of Fe^{+++} entering from outside the system, 3 1/2 moles of O_2 must be provided, at some point in the system, for each mole of $FeS_2(_s)$ put into solution. That is,oxygen can be regarded as the ultimate electron acceptor, within the context of the above reactions. For purposes of simplifying the presentation in this paper, oxygen will be regarded as taking part directly in the oxidation reaction. This in no way precludes the application of the model concept to the more complex and potentially very important case of pyrite oxidation by reaction with Fe^{+++} ions.

Taking equation (1) to represent the initial oxidation of pyrite, then equation (2) and (3) represent the eventual oxidation of Fe^{++} to Fe^{+++}, and the precipitation of $Fe(OH)_3(_s)$. These two steps may occur within the pyritic system, or in the receiving water, depending on environmental conditions and on residence time of the products of equation (1) within the bounds of the system.

The rate processes to be accounted for, then, are the reaction rates of the reactions shown in equations (1) through (3), the rate of transport of oxygen and water to the site of pyrite oxidation, and the rate of transport of the dissolved products of equation (1) away from the site, and eventually to the receiving water. In a high humidity environment, the water can be assumed to be present at the site, either as liquid water or water vapor, and thus will not be discussed in connection with reactant transport. Liquid water flow is of paramount importance in the dissolution and transport of products, however.

Description of a Pyritic System

Certain characteristics common to all pyritic systems can be summarized, which provide further definition of the factors to be included in any system model. These are:

(a) The reaction is heterogeneous, involving the reaction of crystalline (FeS_2) with oxygen in water. The initial reaction site is the pyrite surface, and it is the environment at this surface which determines the kinetics of the oxidation.

* In this paper, pyrite oxidation is taken to mean the type of reaction shown in equation (4), and does not include the subsequent oxidation of ferrous iron, leading to the precipitation of ferric iron, as shown in equations (2) and (3).

reaction. This rate may be expressed in kinetic terms as a function of the concentrations of reacting species, and of factors having a catalytic effect on the rate. The 'concentration' of FeS_2 is the number of reactive sites per unit area of pyrite, while other chemical species may be represented in conventional concentration terms.

(b) A calculation of the solubility of oxygen in water, together with a consideration of the stochiometry of equations (1) through (3) and the acid and iron concentrations commonly observed in mine drainages, shows that it is possible for only a trace of the oxygen required to have entered the system in the form of dissolved oxygen. Therefore, oxygen transport must be predominantly in the gas phase (1). This fact has far-reaching implications, one of the most important of which is the fact that pyrite undergoing oxidation cannot be covered by more than a thin film of water, due to the resistance to oxygen transport in water. One must look, then, to the factors controlling gas phase oxygen transport for a description of this major and indespensible link in the overall reaction train.

(c) 'Dry' pyrite will undergo oxidation at a rate similar to that observed for pyrite in water saturated with oxygen, as long as the relative humidity is near 100% (2). The products of oxidation are sufficiently hygroscopic to cause water to condense from the surrounding water vapor, resulting in an adsorbed liquid of high acid and salt content.

(d) Kinetic studies have shown that desorption of oxidation products does not influence oxidation rate of pyrite (in presence of water). (2) Thus, reaction rate is independent of the rate of transport of products away from the region of pyrite oxidation.

(e) In general, the reaction is not associated with pyrite exposed directly to the outside atmosphere, but instead with pyrite 'buried' within some type of porous structure.

Figure 1 shows an idealized example of a pyritic system, incorporating the major characteristics discussed thus far.

Interface A might be the ground surface in the case of a gob-pile, or the wall surface in an underground mine. The pyrite surface at C is buried at a distance L in the surrounding permeable material (e.g., coal, shale, etc.), and is covered by a film of water of thickness X. It should be noted that the term permeable media, as used here,does not imply a homogeneous permeability. It is likely that permeability to both oxygen and water is due largely to specific channels, such as cracks, partings, etc.

The boundary D marks the upper boundary of a region saturated with water, such as a saturated ground water flow region. Although products of pyrite oxidation might seep down to this region, and then be carried out of the system, pyrite buried in this region will not undergo significant oxidation, due to the resistance to diffusion of oxygen or any other electron acceptor in an unmixed (non-turbulent) volume of water. The distance and nature of water seepage from the point of oxidation to an area of active flow will determine the lag time between oxidation and appearance of products in the drainage.

Rate of Pyrite Oxidation:

Having defined the nature of this sample element of a large pyritic system, an expression can be developed to relate the rate at which the pyrite oxidation reaction proceeds to the system characteristics. This expression must be a function of the oxygen concentration at surface A, the mechanism of oxygen transport to the pyrite surface, and the kinetics of the oxidation reaction. For the purpose of discussion, it will be assumed that oxygen transport through the permeable media is by diffusion only. However, it should be noted that convective transport is very likely to be a major factor in oxygen transport in pyritic systems, due to the breathing action induced by atmospheric pressure fluctuations. Referring to Figure 1, let it be assumed that the oxygen concentration at the boundary A is c_1, that the oxygen concentration at the pyrite surface is c_3, and that the rate processes are proceeding under steady state conditions. Working with a unit area of pyrite,

$$r_r = k_1 c_3^n \quad \ldots \quad (7)$$

r_r = rate of reaction (moles O_2/hr consumed)
k_1 = reaction rate constant
n = empirical constant

To simplify this example, it will be assumed that n = 1. At steady state,

$$r_r = r_{t1} = r_{t2} \quad \ldots \quad (8)$$

r_{t_1} = rate of O_2 transport through porous media (moles O_2/hr)
r_{t_2} = rate of O_2 transport through water film (moles O_2/hr)

further, $r_{t_1} = \frac{D_1}{L}(c_1 - c_2)$ and $r_{t_2} = \frac{D_2}{X}(c_2 - c_3)$ . . . . . (9)

where D_1 = Diffusivity of O_2 through the permeable media
D_2 = Diffusivity of O_2 through the water
L = Length of diffusion path through porous media
X = Length of diffusion path through water film
c_2 = O_2 conc. at porous media - water film interface

rearranging euqations (8) and (9) ,

$$c_1 - c_2 = \frac{L}{D_1} r_{t_1} = \frac{L}{D_1} r_r \quad \ldots \quad (10a)$$

$$c_2 - c_3 = \frac{X}{D_2} r_{t_2} = \frac{X}{D_2} r_r \quad \ldots \quad (10b)$$

adding equations (10a) and (10b)

$$c_1 - c_3 = r_r \left(\frac{L}{D_1} + \frac{X}{D_2}\right)$$

and

$$r_r = \frac{1}{\frac{L}{D_1} + \frac{X}{D_2}} (c_1 - c_2) \quad \ldots \quad (11)$$

Note that for a given value of $c_1 - c_3$ (the overall driving force for oxygen transfer), an increase in L or X or a decrease in D_1 or D_2 will lead to a decrease in r_r. However, for a given reaction site in a given system, L, X, D_1, and D_2 will be constant and equation (11) can be rewritten as

$$r_r = k_m (c_1 - c_3) \quad \ldots \quad (12)$$

where k_m is the overall mass transfer coefficient for the system. Combining equations (7) and (12) (with n = 1 in equation (7))

$$k_1 c_3 = k_m (c_1 - c_3) \quad \text{or} \quad c_3 = \frac{k_m}{k_1 + k_m} c_1 \quad \ldots\ldots\ldots (13)$$

This gives the oxygen concentration at the pyrite surface in terms of the concentration of oxygen at boundary A, the mass transport characteristics of the system (k_m) and the kinetic rate constant (k_1).

Rearranging eq. (13),

$$k_1 c_3 = \frac{k_1 k_m}{k_1 + k_m} c_1 = \frac{1}{1/k_m + 1/k_1} c_1$$

$$r_r = \frac{1}{1/k_m + 1/k_1} c_1$$

Thus, the rate of oxidation can be expressed as a function of k_m, k_1, and the concentration of oxygen at the outside atmospheric boundary of the system c_1.

This is analogous to a simple electrical circuit with two resistances, R_1, and R_2, in series. In this case,

$$I = \frac{1}{R_1 + R_2} E$$

where I = current flow

E = potential drop.

In looking at the problem in the manner shown above, it is not necessary to assume a first order reaction as in eq. (7), nor is it necessary to assume a single site with single values of L and X. The model can be expanded to fit complex situations, with the major limitation at this time being valid data on the factors determining mass transport and kinetics.

For example, k_m is a function, in general, of the scale of the system, and the factors determining both molecular diffusion and cnnvective transport (breathing) of oxygen. Similarly, k_1 is a function of oxygen, ferrous, and ferric ion concentrations at the pyrite surface, the nature and surface area of the exposed pyrite, and catalytic factors such as bacterial activity. All of these factors must by incorporated in a description of the reaction system.

In any specific case, either mass transport or kinetics might be the rate determining factor, depending on the relative values of k_1 and k_m. For example, as above, let $r_t = k_m (c_1 - c_3)$, and $r_r = k_1 c_3$. As before, $r_r = r_t$, and the simultaneous solution of the expressions for r_t and r_r will yield the rate of transport (or of reaction) and the concentration of oxygen at the pyrite surface which will be maintained at steady state. This solution, which was carried out analytically above, can also be demonstrated graphically, as shown in Figure 2. Three cases are shown: Case A, $k_1 = k_m$; Case B, $k_1 <<< k_m$; and Case C, $k_1 >>> k_m$.

In Case A, it is seen that a change in either k_1 or k_m will yield a significant change in the steady state reaction rate : that is, both are rate controlling. In Case B, the steady state reaction rate is very sensitive to changes in k_1, but is insensitive to changes in k_m: thus, the reaction kinetics are rate controlling. To control acid formation at the source, attention should be given to the identification and control of the rate controlling step, which may well vary from one

situation to another. It is the ultimate effect of such procedures as mine sealing on the rate controlling step which is of importance.

Rate of Acid Release:

Just as reaction rates can be modeled rationally, so also can product release rates be modeled. Referring to Figure 1, products of oxidation will move away from the site by either diffusion or convection, depending on whether the water film on the pyrite is moving or stagnant. If there is no water film, the products will remain at the site. The rate and frequency with which the products are removed from the system will depend on the mechanism of transport away from the site, and the proximity of regions of active water flow. As the position of regions of active flow change (e.g., ground water levels, or percolating drainage from precipitation). they may flush out products held at or near the site of pyrite oxidation. It is significant to note that changing positions of flow channels may 'flood out' oxidation sites, temporarily decreasing the rate of acid formation, but at this same time, the rate of removal of oxidation products from the system may be at a maximum value. The overall process of product removal can be represented mathematically by established expressions describing mass transport and ground water flow. The primary factor to bear in mind is the fact that the distance from the site to a region of active water flow is variable with time, and related to seasonal changes in flow patterns. The 'lag time' of product removal may be considerable (1) and the overall retention time of oxidation products will be a factor in the determination of the Fe^{++}/Fe^{+++} ratio in the system's effluent.

Value of Model

It is believed that through the descriptions of pyrite oxidation systems in the context of the model outlined here, the discussion of such systems can be classified,and problems of communication can be considerably lessened. Several points warrent particular emphasis at this time. In planning and executing laboratory investigations, due consideration must be given to the problem of extrapolating laboratory data to field conditions. For example, in studying reaction kinetics, it should be recognized that water in the immediate vicinity of pyrite oxidation sites will be extremely high in both hydrogen ion and salt content. This may have a very direct bearing on the conditions to be simulated in experiments dealing with microbial catalysis of pyrite oxidation. Second, in the application of bacterial agents or agents intended to block the oxidation reaction, it is likely that they must be applied in the vapor phase, (following the oxygen transport paths) since liquid phase applications are not likely to come in contact with the majority of oxidation sites. Finally, in demonstration efforts such as mine sealing, due consideration should be given to the lag time between oxidation and the appearance of oxidation products in the drainage. Also, every possible attempt should be made to directly measure environmental conditions well within the interior of a given system. Observed overall abatement effects must be broken down into specific effects on specific rate processes, if the results of a demonstration program are to be correctly interpreted with the intention of yielding generally applicable results.

Acknowledgement

The financial support of the Federal Water Pollution Control Administration, through Research Grant 1-WP-01328-01 , is gratefully acknowledged.

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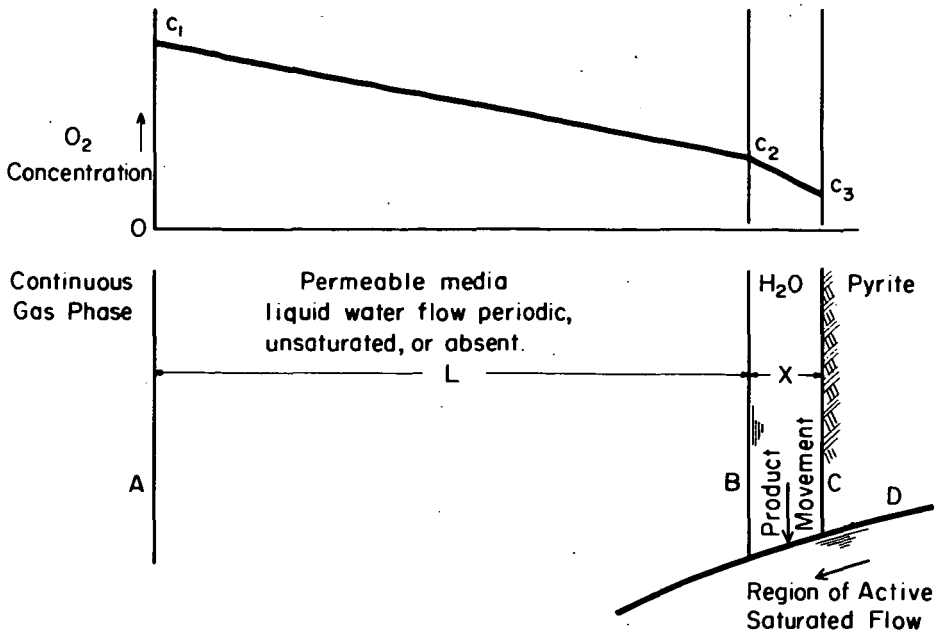

Figure 1
Generalized Element of Pyritic System

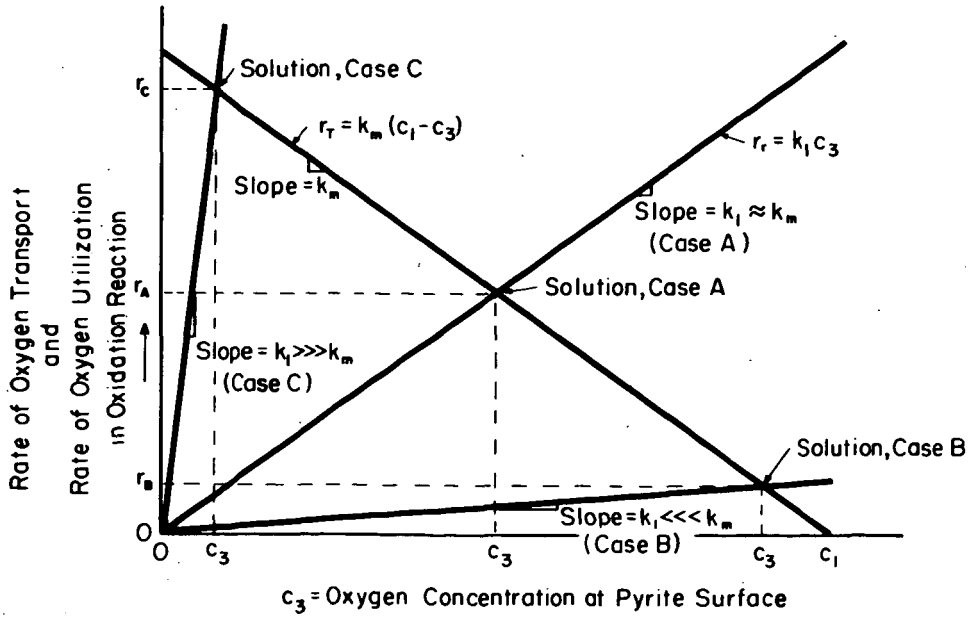

Figure 2
Solution of Steady State Rate Process Equation

REVIEW OF PENNSYLVANIA'S MINE DRAINAGE POLLUTION ABATEMENT PROGRAM

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ABSTRACT

The 1965 amendments to Pennsylvania's Clean Streams Law prohibit the discharge of acid mine drainage into the streams of the Commonwealth after January 1, 1967. Because of this new legislation the coal mining industry and state government are extremely aware of the necessity for new techniques in treatment and prevention of the flow of acid mine drainage from the active mines of the Commonwealth in order to keep the coal mining industry in Pennsylvania. Approximately one third of the total volume of mine drainage presently polluting the streams of the Commonwealth originates from "active coal operations" and two thirds come from "abandoned mine discharges." To date, the Commonwealth has allocated grants totaling $2,805,631 for mine drainage research. The Commonwealth is tackling its abatement activities on a "watershed-by-watershed" basis. Engineering studies are being made to pinpoint sources of pollution and then remedial action programs are defined and initiated on a priority basis. The basic premise of the Department approach divides the abandoned mine abatement problem into two logical divisions: (1) Volume reduction or contamination prevention; (2) Treatment of mine drainage. The treatment approach can be further divided into two basic approaches, i.e., treatment soley for the return of a minimum quality but acceptable discharge to streams and complete regeneration of mine drainage to prepare a satisfactory water for reuse.

This presentation will be made through the use of colored slides.

BIOCHEMICAL ECOLOGY OF METAL SULFIDE OXIDIZING BACTERIA

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INTRODUCTION

Metal sulfides in the presence of oxygen will oxidize to their corresponding metal sulfates and sulfuric acid; these reactions are accelerated by the metabolic activities of acid-loving iron oxidizing bacteria. The various mechanisms of metal sulfate oxidations have been reviewed (20). Microbial oxidation of sulfide metals have harmfull effects by contributing to stream pollution. Pyrites and marcasites, both associated with coal mining, when in the presence of oxygen, water and iron-oxidizing bacteria oxidize to sulfuric acid and iron sulfate. The acid is corrosive to equipment, kills aquatic life, dissolves rocks and minerals, and contributes to the hardness of water. The iron sulfate, soluble under acid conditions, eventually hydrolyzes and precipitates from solution to form colored complexes of ferric sulfates and hydrated oxides.

Considerable thought has been given to the prevention of biological iron oxidation as a means of controlling water pollution (28). However, as this report demonstrates, any thought of microbiological control must consider the metabolism of the whole organism. Attempts to inhibit iron oxidation can result in the organism oxidizing sulfur and/or organic compounds. A complex biochemical relationship exists in these bacteria and a particular metabolic expression depends upon regulatory mechanisms (11); the latter are subject to influence by the environment.

It is now recognized that the iron-oxidizing thiobacilli can grow and metabolize iron, sulfur, or glucose. It is the purpose of this presentation to discuss aspects of the cells' metabolism when oxidizing the different substrates for their primary energy source; emphasis is given to sulfur oxidation.

MATERIALS AND METHODS

Cultures. *Ferrobacillus ferrooxidans* was grown in the following ways:

I. Growth of ferrous iron. Cells were grown under conditions as reported previously (13). The organism was propagated in 16-liter glass carboys on the ferrous sulfate-9K medium (9,000 ppm of Fe^{++}, pH 3.3) under forced aeration and was harvested after 48 to 54 hr by use of a Sharples Centrifuge.

II. Growth on elemental sulfur. Cells were grown in 2-liter Fernbach flasks containing 500 ml of the 9K salts solution (pH 3.3), 1.0 ppm of $FeSO_4$, and 5 g of precipitated sulfur. These flasks were autoclaved for 5 min at 121°C prior to inoculation and were cooled rapidly to prevent sulfur from coalescing. Flasks were agitated on a reciprocating shaker for 5 to 6 days at 28°C and cells were harvested, after the pH had dropped below 2.0, with a Sorvall RC-2 refrigerated centrifuge. The sulfur in the flasks was not depleted during this time. The inoculum consisted of cells trained to sulfur by repeated transfers on the sulfur medium.

III. Growth on glucose. Cells were first grown in the regular 9K medium containing 0.5% glucose. Subsequent transfers were made into fresh media containing decreasing concentrations of ferrous

sulfate. Cells trained to grow on glucose grew well in the absence of iron. Culturing was done in 250-ml Erlenmeyer flasks and the pH of the medium at the time of transfer was 3.2.

Cell-free extracts and enzyme purification. Washed cells were suspended in 0.5M Tris-HCl buffer, pH 7.8 (25-30%, w/v), and passed three times through a cold French-pressure cell (15,000-20,000 p.s.i.) or treated with sonic energy. All operations were performed in the presence of 0.01M sodium thiosulfate. The broken cells were treated with 300 μg each of RNase and DNase at room temperature for 20 min after which the whole cells and debris were removed by centrifugation at 13,000 x g for 20 min. The resulting supernatant, the crude extract, was adjusted to pH 5 by slow addition of cold 1 N acetic acid and stirred in an ice bath for 20 min. Precipitated protein was removed by centrifugation and discarded. Ammonium sulfate was added to 25% saturation and the pH adjusted to 5.0 with stirring for 30 min, after which the precipitate was removed and discarded. More ammonium sulfate was added until 90% saturation was obtained and again the pH was adjusted to 5.0 with stirring for 30 min. The precipitate was collected and suspended in Tris-HCl buffer in .01M sodium thiosulfate and dialyzed against 4 liters of the same buffer.

The dialyzed extract was treated with 20 ml of a slurry of CM-cellulose in 0.025 acetate buffer, pH 5.0, for 1 hr at 4°C. Cellulose with the enzyme absorbed was recovered by centrifugation, and washed with the same volume of buffer at 0.05, 0.1, 0.2 and 0.3 M in the same manner. The enzyme was finally eluted with the same buffer at 0.50 M.

Protein was determined colorimetrically (Lowry) with crystalline bovine albumin as the standard.

Rhodanese assay. The assay for rhodanese was essentially that described by Bowen, Butler and Happold (4) where thiocyanate formed is measured colorimetrically. The reaction mixture contains 500 μmoles of Tris-HCl buffer (pH 8.5), 50 μmoles of sodium thiosulfate, 50 μmoles of potassium cyanide and partially purified enzyme. The reaction vessel was a screw cap test tube and the time of the reaction was 10 min. The reaction was stopped by the addition of 0.5 ml of the ferric nitrate reagent. The tubes were centrifuged to remove protein and the absorbancy measured in a Klett-Summerson 800 colorimeter equipped with a blue filter. A value of 36 Klett units equals 0.1 μmole of thiocyanate.

Electron microscopy. Cells were washed with a low concentration of EDTA solution prior to fixation and then fixed in 1.5% glutaraldehyde in s-collidine buffer (pH 7.6) for 10 min at room temperature, washed once in the same buffer and finally fixed overnight in osmium tetroxide (1.0%) in distilled water. Fixed cells were enrobbed in agar, cut into cubes, dehydrated in an alcohol series, embedded in an epoxy resin contained in gelatin capsules, and following polymerization sectioned in an ultra microtome. Sections were first stained with uranyl acetate and post stained with lead citrate.

RESULTS

Electron microscopy. Figure 1 shows thin sections of *F. ferrooxidans* following growth on the different substrates. Certain structural differences are apparent which reflect metabolic changes associated with changes in substrates. Structural differences are not the major endeavor of this paper, but certain changes are obvious when cells are grown autotrophically (iron or sulfur) or heterotrophically

(glucose). Glucose-grown cells (Fig 1b) contain poly-beta-hydroxybutyrate (P), a bacterial storage product, which is not present in iron or sulfur-grown cells. Also, there are no electron dense bodies (g) in glucose-grown cells compared to autotrophically-grown cultures (Fig 1a). Sulfur-grown cells have a more localized nuclear area (n), rather than a diffuse nucleus of the other cells. We are still uncertain as regards structural changes in the cell envelope; this is being studied for the envelope is important in substrate oxidations.

Iron oxidation. The oxidation of ferrous iron has been studied more extensively than the oxidation of sulfur and glucose, and the status of iron oxidation has been reviewed (7, 15). In simplest terms the oxidation is described as involving:

$$Fe^{++} \longrightarrow \text{cytochrome c} \longrightarrow \text{cytochrome a} \longrightarrow O_2$$

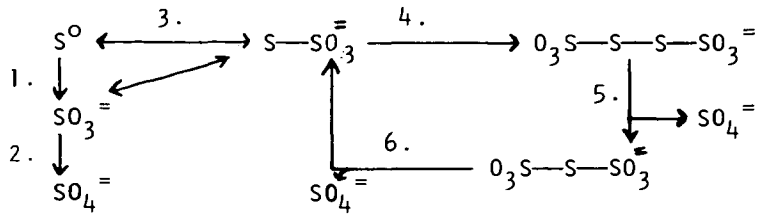
A model has been published for how oxidation might function in ferrobacilli (8).

Glucose oxidation. Iron oxidizing bacteria were once considered to be obligate autotrophs and therefore unable to grow heterotrophically. Results from our laboratory have shown that iron-grown cells could be trained to grow on glucose as the sole energy source (12, 16). How autotrophs might differ from heterotrophs as regards the utilization of simple organic compounds has been discussed (9,23). In iron-oxidizing bacteria, it has been shown that both a glycolytic pathway and a Krebs cycle are probably present (3). Since these are major metabolic routes in heterotrophy for energy and biosynthesis, any transition from autotrophic growth to a heterotrophic way of life for these bacteria should not be a difficult task.

Sulfur oxidation. Sulfur oxidation provides a link to iron oxidation through the $SO_4^{=}$ anion and its associated H^+ ions. The latter contributes to an acidophilic environment whereas the anion is required for iron oxidation (10); the mechanism by which $SO_4^{=}$ functions is not known. Earlier reports from this laboratory have described the organisms growth on sulfur (13) as well as the effects of glucose upon sulfur and iron oxidation (19).

The exact pathway for the oxidation of reduced sulfur by the sulfur oxidizing bacteria (Thiobacillus Spp.) is still in doubt, and it is possible that different species of organisms have different oxidative pathways. The status of inorganic sulfur oxidation has been reviewed (27).

For the iron-oxidizing bacteria, which are considered by us to be members of the Thiobacillus group, the below model has been constructed to serve as a guide for the study of sulfur oxidation.



Reaction 1 is catalyzed by the sulfur oxidizing enzyme with the formation of sulfite. This reaction is probably the central reaction for all pathways involving the oxidation of sulfur (24, 25, 15). The sulfur oxidizing enzyme has been found in iron oxidizing bacteria (18). It is possible that $SO_3^{=}$ exists bound rather than free (15). Sulfite can be oxidized to sulfate (reaction 2) via APS reductase (14) or

mediated by a cytochrome system (5). Both of these reactions can be coupled to energy generation. No energy is associated with reaction 1 for it is not coupled to oxidative phosphorylation. When elemental sulfur is oxidized, thiosulfate is formed enzymatically. Thiosulfate is the substrate for the thiosulfate splitting enzyme rhodanese, (reaction 3) which forms $SO_3^{=}$. This enzyme may function to keep the level of $SO_3^{=}$ high and counteract the nonenzymatic formation of thiosulfate. Thiosulfate may also be oxidized via the thiosulfate oxidizing enzyme (reaction 4). This reaction is found in other bacteria including thiobacilli (2, 6, 22) and may represent the major oxidative pathway for thiosulfate (27). Reactions 5 and 6 which involve tetrathionate and trithionate are suspected of being physiological reactions but enzymes catalyzing these reactions have yet to be found (21). It is known that both trithionate and pentathionate are formed non-biologically and are likely to be present whenever other forms of inorganic sulfur are present. In the proposed scheme $SO_4^{=}$, important for iron oxidation, would be a by-product.

Our present research effort is directed towards the demonstration of these reactions in iron oxidizing bacteria. The latest reaction demonstrated is that catalyzed by the enzyme rhodanese. The enzyme has been isolated and partially purified from both sulfur-grown and iron-grown cells. Rhodanese was purified about 50 fold over crude cell-free extracts, and all preparations are stable at room temperature for about 4 hr and can be stored at 0°C for 5 days with little loss in activity. Table 1 shows that enzyme, thiosulfate and cyanide are all required for the formation of thiocyanate. Neither cysteine, mercaptoethanol nor reduced glutathione (GSH) could replace thiosulfate.

TABLE 1. Requirements and specificity of rhodanese*

Deletions	Additions	μmoles SCN formed
---	---	1.06
KCN	---	0.08
S_2O_3	---	0.11
Enzyme	---	0.07
enzyme	boiled enzyme	0.38
S_2O_3	50 μmoles cysteine	0.12
S_2O_3	0.1% mercaptoethanol	0.14
S_2O_3	50 μmoles GSH	0.11

*The enzyme activity was determined under standard conditions outlined in the Methods. Additions and deletions are as indicated. 0.45 mg protein was used.

The pH optimum of the enzyme ranges from 7.5 to 9.0. Table 2 shows the effects of some inhibitors upon rhodanese activity. The thiol-alkylating agent, iodoacetamide, was the most effective inhibitor. Glucose, not shown in the table, had no effect upon the enzyme.

TABLE II. Effect of various inhibitors on rhodanese activity*

Addition	Concentration	Activity	% of control
None	---	0.87	100
p-hydroxymercuribenzoate	10^{-3}M	0.86	98.9
EDTA	10^{-2}M	0.88	101.1
arsenate	10^{-2}M	0.86	98.9
arsenite	10^{-2}M	0.88	101.1
o-phenanthroline	10^{-3}M	0.87	100
NaF	10^{-2}M	0.85	97.7
$HgCl_2$	10^{-3}M	0.62	71.3
GSH	10^{-2}M	0.83	95.4
N-ethylmaleimide	10^{-3}M	0.69	79.3
Na_2SO_3	10^{-3}M	0.55	63.2
iodoacetamide	10^{-3}M	0.14	16.1
mercaptoethanol	0.1%	0.86	98.9
NaN_3	10^{-3}M	0.88	101.1

*The enzyme activity was determined under standard contitions with additions as indicated. 0.45 mg protein was used. Activity is expressed as the number of μmoles of SCN^- formed per 10 min.

DISCUSSION

From a metabolic standpoint, the iron-oxidizing bacteria represent a very sophisticated group of organisms. They are biosynthetically complete and have evolved in an ecological niche where reduced iron and sulfur as well as acid (H^+) predominate. The organisms are able to use both reduced iron and sulfur for growth and since iron is the more soluble substrate probably prefers it to sulfur even though the energy yield per gram atom of substrate is lower. The requirement for $SO_4^=$ for iron oxidation is met through sulfur oxidation. Also, the acid from the oxidation maintains an acid environment. The organism is able to grow heterotrophically giving it an additional survival advantage. It is not known whether all members of the bacterial population adapt to glucose for an energy source or whether selective cells (mutants) adapt to heterotrophic growth and are selected out by the cultural procedures.

The metabolic-diversity possessed by these bacteria means that any attempt to control their growth with metabolic inhibitors will be difficult, and one must be cognizant of the whole metabolic potential before control is considered.

Acknowledgements

The contributions of Dr. M. Silver and A. Wang graduates from these laboratories are acknowledged. The work was supported under Contract 14010 DAY by the Federal Water Pollution Control Administration, Department of the Interior.

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Fig 1. Sections of iron-oxidizing bacteria grown on (a) iron, (b) glucose, (c) sulfur. Label n, nucleus; g, granule; p, poly-beta-hydroxybutyrate. a, 58,000X; b, 30,000X; c, 29,000X.

AEROBIC-ANAEROBIC OXIDATION OF PYRITE

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Abstract:

There are two general approaches to control acid mine drainage: treatment of mine effluent, or prevention or abatement of the sulfide oxidation which is responsible for acid mine drainage.

This paper describes one phase of a basic study on the kinetics and mechanism of sulfide (pyrite) oxidation, a study which has provided information necessary to the analysis and evaluation of methods for abatement of acid mine drainage at its source. This study was made to clarify the mechanism by which bacteria catalyze the oxidation of pyrite by using what is assumed to be a chemically analogous system. The regime of bacterial influence are described in terms of conditions at the reaction site. Bacterial-enhanced oxidation rates are compared to rates in a chemical system and the independence of the two mechanisms demonstrated.

Introduction:

Quantitative data on kinetics of pyrite oxidation in a chemical system are available. A general discussion of the thermodynamics and chemistry of pyrite oxidation was given by Clark (4). More quantitative kinetic studies on the effect of oxygen concentration (in vapor or liquid phase), water, and pH on the rate of pyrite oxidation were given by Morth and Smith (11), and Smith, Svanks, and Shumate (16). The latter paper also described work on oxidation of pyrite by ferric ions, here referred to as anaerobic oxidation. Where rate of oxidation is determined by the partial pressure of oxygen, the term aerobic oxidation is used.

Earlier work by Garrels and Thompson (7), who investigated the oxidation of pyrite by ferric sulfate solutions, showed the dependence of ferric/ferrous ratio on anaerobic oxidation rate, and suggested that the rate-controlling mechanism is related to adsorption of ferric and ferrous iron on pyrite surface. They also concluded that the rate of oxidation was chiefly a function of the oxidation-reduction potention (E_h) of solution and independent of the total iron concentration. Over the range of E_h that could be examined by Garrels and Thompson their conclusions are valid; however neither conclusion is basically correct.

A number of publications (2, 3, 6, 12) have taken a geochemical approach to evaluating the effect of E_h, pH, iron concentration, etc. on mine drainage. Unfortunately the geochemists have confused the kinetics of pyrite oxidation by using the E_h - pH stability diagrams to analyze pyritic systems. First, phase equilibrium diagrams give little information regarding kinetics, other than "go, no-go" limitations. But most serious is the implication that the effluent water from a mine or other pyritic system is representative of the water in contact with the reacting site of pyrite. The very fact that the geochemists have great difficulty explaining the source of oxygen or oxidizing agent from analysis of effluent water supports the conclusion (13, 15) that the vast majority of pyrite being oxidized is pyrite exposed to a vapor phase. Only an adsorbed layer or thin film of water acts as the reaction medium. This adsorbed layer of water has very little relation to the effluent stream from a pyritic system such as an underground mine. The designation of aerobic- or anaerobic- controlled regimes is therefore not possible from analysis of effluent water. Relative oxidation rates in natural systems are determined by oxygen partial pressure (aerobic rate) and ferric/ferrous ratio (anaerobic rate) at the site of the reaction.

A recent paper by Barnes and Romberger (3) discusses the effect of bacteria in

pyrite oxidation and confirms earlier statements (16) that the chemical (non-microbial) ferrous ion oxidation rate by dissolved oxygen is negligibly slow. Dugan and Lundgren (5) report the energy supply for Ferrobacillus ferrooxidans to be the oxidation of ferrous to ferric ions. Remarkable increases in pyrite oxidation rate were noted (9, 10) when large quantities of these bacteria were added to the reaction system. The same order of increase was reported (16) for anaerobic oxidation at high ferric/ferrous ratio.

Silverman (14) suggested that bacteria operate through both a "direct" and "indirect" contact mechanism in oxidizing pyrite. Direct oxidation implies the oxidation of pyrite through direct electron transfer between the cell and pyrite on which the cell is adsorbed. Indirect oxidation occurs by oxidation of pyrite by ferric ions, the ferric ions being generated by bacterial oxidation of ferrous ions in solution.

Bailey (1) followed the rate of pyrite oxidation as a function of ferric ion concentration in a biological system and observed no significant change in rate until the bacteria had oxidized the iron in solution to 70 or 80% ferric. This indicates "indirect" oxidation is of primary importance although it does not rule out a significant contribution by direct oxidation. A comparison of anaerobic and bacterial rates as a function of ferric/ferrous ratio in solution will indicate the relative rates of the two mechanisms.

In order to provide the basic kinetic information needed to compare oxidation rates in biological systems and analogous chemical systems, the following work was performed.

Experimental Program:

Equipment described by Smith, Svanks, and Shumate (16) was used for the anaerobic and combined aerobic-anaerobic runs. In place of the nitrogen purge line, a metered oxygen supply was added to the titration vessel for aerobic runs. The amount of make-up oxygen required to maintain a constant system pressure (including volume above permanganate burette) was used to determine aerobic oxidation rate.

Stoichiometry of both anaerobic and aerobic oxidation was checked experimentally and found to require 14 moles of ferric ion, and three and one half moles of oxygen to oxidize one mole of pyrite (iron as ferrous). Rates are thereby calculated in terms of micromoles of pyrite oxidized per hour per gram of pyrite, based on oxygen consumed and ferric ions reduced.

Two different types of pyrite were used here: one a 48-70 mesh "sulfur ball" material from the Mc Daniels mine in the Middle Kittanning No. 6 coal in Vinton County, Ohio and the other a "museum grade" sample of the same mesh size. Data on the Sulfur Ball #2 sample of Ref. (16) is also presented.

For some as yet unknown reason, data on the museum grade pyrite could not be consistently reproduced.

Consistent data were obtained on a set of runs, for example, a series of runs at different ferric/ferrous ratios, if operated continuously. But if the reactor were shut down overnight, the rate the following day would often be higher or lower by 25 to 50%. Sulfur ball material was much more predictable, the rate decreased slowly and regularly with reaction time. Over 25% of the original sample was consumed over the series of runs reported. All rates were recalculated to the same base rate; that of Run 23, the Rate vs. Concentration data set shown in Fig. 1. pH of all solutions varied between 0.2 and 0.5. The ferric/ferrous ratio was calculated from the equation: $EMF = 0.430 + 0.059 \log (Fe^{+3}/Fe^{+2})$, as determined experimentally for our system.

Two consistent sets of data for the museum grade pyrite are given in Tables 1 and 2.

Similar data for McDaniels Sulfur Ball sample are given in Table 3 and graphically in Fig. 2. Results of the combined aerobic-anaerobic oxidation runs are summarized in Table 4.

Treatment of Data:

A simple "dual site" adsorption model gives an equation that correlates experimental data within limits of experimental error.

As one possibility, assume a $Fe(OH)^{++}$ complex is adsorbed on two "reactive sites" of pyrite (dual-site adsorption). Also assume ferrous ions (Fe^{++}) compete for these dual sites. The activated complex formed by ferric ion adsorption is decomposed by electron

transfer from one of the reactive sites to the ferric complex, forming an adsorbed ferrous ion, which is then desorbed.

Using the Hougen-Watson (8) concepts for calculating the rate equation, the following rate equation was derived:

$$r = \frac{k_{3f}\left(\sqrt{K_1} - \frac{\sqrt{K_2}}{K}\sqrt{\frac{Fe^{+2}}{Fe^{+3}}}\right)}{\frac{1}{\sqrt{Fe^{+3}}} + \sqrt{K_1} + \sqrt{K_2}\sqrt{\frac{Fe^{+2}}{Fe^{+3}}}} = \frac{k - k'\sqrt{\frac{Fe^{+2}}{Fe^{+3}}}}{\frac{1}{\sqrt{Fe^{+3}}} + \sqrt{K_1} + \sqrt{K_2}\sqrt{\frac{Fe^{+2}}{Fe^{+3}}}} \quad (5)$$

where:

k_{3f} = rate constant, electron transfer reaction

K = equilibrium constant, electron transfer reaction

K_1 = adsorption equilibrium constant for ferric ions

K_2 = adsorption equilibrium constant for ferrous ions

Fe^{+2}, Fe^{+3} = concentration of ferrous and ferric ions

At high EMF's, where the square root of the ferrous/ferric ratio (Fe^{+2}/Fe^{+3}) is negligible, this equation may be written:

$$r = \frac{k}{\frac{1}{\sqrt{Fe^{+3}}} + \sqrt{K_1}} \quad (6) \quad \text{or} \quad \frac{1}{r} = \frac{1}{k\sqrt{Fe^{+3}}} + \frac{\sqrt{K_1}}{k} \quad (7)$$

A plot of 1/r vs. $1/\sqrt{Fe^{+3}}$ for anaerobic oxidation at high EMF's should give a straight line with a slope equal to 1/k and an intercept equal to $\sqrt{K_1}/k$.

These data for the three pyrite samples shown in Tables 1, 3, and Table 2 of Ref. (16) are plotted in Fig. 1.

After k and $\sqrt{K_1}$ are calculated from the slope and intercept, k' and $\sqrt{K_2}$ can be determined in the following manner: Assume that reaction rate goes to zero as EMF approaches o.37* ($\sqrt{Fe^{+2}/Fe^{+3}} = 3.0$). Then setting the numerator of Equation 5 equal to zero when $\sqrt{Fe^{+2}/Fe^{+3}} = 3$; $k' = k/3$.

K_2 can be determined from one value of the Rate vs. EMF data where the ferric/ferrous ratio is significant.

The data presented in Ref. (16) for Sulfur Ball #2 may be used to illustrate the calculation of the Rate Equation.

From Fig. 1, slope of line for Sulfur Ball #2 = 0.0061 and Intercept = 0.02, then:

$k = 1/0.0061 = 165$

$k' = 165/3 = 55$

$(\sqrt{K_1})' = \text{Intercept} \times k = 3.3$

(Note: since $\sqrt{Fe^{+2}/Fe^{+3}}$ is not negligible at EMF = 0.650, the intercept value

*From potentiostat measurements of pyrite, these values appear reasonable in systems where the pH is below 1.0.

of 3.3 includes $\sqrt{K_2}$ times $\sqrt{Fe^{+2}/Fe^{+3}}$. By trial and error. $K_1 = 3.3 - 70 \times 0.0137 = 2.3$, when K_2 is calculated from rate at EMF = 0.477. Therefore the rate equation, as calculated using Fig. 1 and one point from Rate vs. EMF data is:

$$r = \frac{165 - 55\sqrt{Fe^{+2}/Fe^{+3}}}{\frac{1}{\sqrt{Fe^{+3}}} + 2.3 + 70\sqrt{Fe^{+2}/Fe^{+3}}} \qquad (8)$$

Table 5 compares calculated and experimental rate for these data.

In like manner, the rate equations for the experimental points given in Fig. 2 can be calculated. The solid lines on Fig. 2 are loci of the calculated rates for different total iron concentrations. Calculated and experimental rates for museum grade pyrite are compared in Table 2.

Interpretation of Data:

The excellent correlation of experimental data by Equation 5 indicates that the form of the adsorption equation, if not the specific mechanism used to derive it, is relevant. It appears that the relative adsorption of ferrous and ferric ions is rate-determining in anaerobic oxidation. A comparison of adsorption equilibrium constants for ferrous and ferric ion is surprising. For sulfur ball pyrite the ratio of K_2/K_1 (ratio of adsorption equilibrium constants for ferrous and ferric ion, respectively) is 900 for Sulfur Ball #2, 2500 for Mc Daniels Sulfur Ball, and 45,000 for Museum Grade pyrite. In other words, the relative adsorption of ferrous ions is much greater than ferric for all types of pyrite. The selective adsorption of ferrous ions is particularly great in museum grade pyrite -- over 20 to 50 times greater than the sulfur ball. It is also interesting to note that the reactivity of the pyrite samples is inversely related to K_2/K_1. The rate curves for the three pyrite samples are compared in Fig. 3

The data show that anaerobic rates are a function of total iron concentration, and are determined by ferrous/ferric ratio, not E_h (EMF). As the E_h of solution is raised to the point where all iron is ferric, the rate becomes constant. Further increase in E_h has negligible effect on rate.

The combined aerobic-anaerobic oxidation runs show the independence of the two reaction modes. The aerobic rate is not influenced by solution E_h or ferric/ferrous ratio, and the anaerobic rate is not changed by the partial pressure of oxygen. This leads to the conclusion that the "reactive sites" for the two oxidation mechanisms are not the same.

It is interesting to note that the increase in oxidation rate, over the aerobic rate, is approximately the same for samples heavily inoculated with Ferrobacillus ferrooxidans (9) and samples subject to anaerobic oxidation at high EMF's. This observation, together with those of Silverman (14) and Bailey (1) leads to the conclusion that bacteria such as Ferrobacillus ferrooxidans function to generate a high ferric/ferrous ratio in solution. The rate of oxidation by ferric ions would then be the same in both a biological or chemical system, and determined by the ferric/ferrous ratio and total iron concentration.

These data provide a basis for defining the reaction regime, i. e. aerobic or anaerobic, if data on oxygen concentration and ferric/ferrous at the reaction site are known. Aerobic and anaerobic rates are approximately the same, at oxygen partial pressures of 21%, when EMF = 0.450. This corresponds to a ferric/ferrous ratio of 2.2 or 70% of iron ions in the ferric state. At an EMF of 0.40, where 24% of iron is ferric, the anaerobic rate is one-fifth to one-tenth the aerobic rate in air. Only with microbial-enhance oxidation can ferric/ferrous ratios this high be attained. In other words, if the ferric/ferrous ratio is less than 0.3 (24% ferric), and the partial pressure of oxygen is 15 to 20%, the system is in an aerobic regime - i. e., the oxidation rate is determined by the chemical aerobic mechanism. If oxygen vapor concentration is under 2% and 70% of the iron is in the ferric state, the system is in a anaerobic regime, generated by microbial activity. It must be emphasized that the term "anaerobic" as used here does not mean that the ultimate electron acceptor

is not oxygen. "Anaerobic" implies only that the electron acceptor at the reaction site is a ferric ion. These descriptions are applicable to natural systems where active oxidation sites are exposed to vapor phase. Pyrite immersed in normal ground water is not oxidized.

Summary:

Anaerobic oxidation rate of pyrite is determined by the ferric/ferrous ratio and total iron concentration in solution. The adsorption equilibrium constant for ferrous ions on pyrite is much greater than ferric ions. At least for the three different pyrite samples examined, the reactivity is inversely related to the ratio of the adsorption constants, ferrous-to-ferric.

Aerobic oxidation rate is a function of oxygen concentration at the reaction site. It is not affected by the presence of either ferric or ferrous ions nor the total iron concentration. Since the two rates are also independent, it appears that different "reactive sites" are involved in aerobic and anaerobic oxidation.

The aerobic and anaerobic rates are approximately equal for sulfur ball pyrite when 70% of the iron in solution is in the ferric state and the solution is in equilibrium with air of 21% oxygen. Since such a high ferric/ferrous ratio is only possible in a microbial system in a natural environment, oxidation by ferric ions (anaerobic oxidation) can be significant only in bacteria-catalyzed systems. The oxidation regime can be determined from oxygen and iron concentrations and the ferric/ferrous ratio at the reactive site. Note that the effluent water can not be used to determine these factors since this water is in no way representative of the water in contact with the "reactive sites."

Figure 4 graphically describes the regimes in terms of oxygen concentration and ferric/ferrous ratio at the reaction site. The boundry lines were drawn where the ratio of rates (anaerobic and aerobic) differ by a factor of 5.

Since aerobic and anaerobic oxidation rates are independent and additive, the rate of pyrite oxidation (per unit surface area exposed) can be determined in terms of the equations for anaerobic and aerobic oxidation.

This type of information presented here furnishes the basic data which, combined with a relevant model of a pyritic system e. g. drift mine, gob pile, spoil bank, etc., enables one to evaluate abatement measures or predict acid formation that will develop under various conditions. The kinetics of the total system can be derived only if the basic chemical kinetics are adequately described.

ACKNOWLEDGEMENT

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TABLE 1

Museum Grade Pyrite
Rate vs. Conc. at EMF = 0.700

Total Iron (gm./liter)	r	$\frac{1}{\sqrt{Fe^{+3}}}$*	$\frac{1}{r}$
0.125	0.83	21.1	1.21
0.250	1.25	14.9	0.80
0.500	1.[illegible]	10.[illegible]	0.83
1.00	2.2	7.45	0.45
2.00	3.1	5.3	0.34
4.00	4.0	3.73	0.25
8.00	4.9	2.64	0.20
10.00	5.2	2.3[illegible]	0.195

*Fe^{+3} in moles/liter

TABLE 2

Museum Grade Pyrite
Rate vs. EMF; Iron Conc. = gm/liter

EMF.	$\frac{Fe^{+3}}{Fe^{+2}}$	$r_{exp.}$	$r_{calc.}$*
0.700	37,100	5.2	5.2
0.650	5,360	3.8	2.[illegible]
0.600	760	1.36	1.35
0.550	108	0.54	0.59
0.500	15.4	0.23	0.23
0.477	7.3	0.15	0.14

$$*r_{calc.} = \frac{20 - 6.7\sqrt{Fe^{+2}/Fe^{+3}}}{\sqrt{\frac{1}{Fe^{+3}}} + 1.4 + 300\sqrt{Fe^{+2}/Fe^{+3}}}$$

Note: "r" (Rate) in units of microgram-mole FeS_2 oxidized per hour per gram of sample.

TABLE 3

Rate vs. Iron Concentration
EMF. Setting = 0.650; pH = 0.5
Mc Daniels Sulfur Ball

Run 23		Run 50	
r	Fe Conc. (gm/liter)	r	Fe Conc. (gm/liter)
19.3	5.0	19.1	4.3
18.7	3.85	14.2	2.26
14.3	2.15	11.3	1.26
10.9	1.10	9.1	0.675
8.5	0.59	4.8	0.193
6.5	0.31	11.7	1.28
5.3	0.183	8.2	0.54
		6.2	0.29

TABLE 4

Combined Aerobic and Anaerobic Oxidation

Run No.	EMF	Iron Conc. (gm/liter)	Rate by 100% O_2	Rate by Fe^{+3} Ions
31	-	-	3.6	- (aerobic only)
33	500	1.00	3.6	4.5
34	-	-	3.5	- (aerobic only)
35	500	1.00	3.4	4.4
38	500	0.40	3.5	3.5
41	550	0.20	3.4	5.1
45	550	0.20	3.5	5.0

TABLE 5

Rate vs. EMF, Sulfur Ball #2, Ref. 16
Iron Concentration = 1 gm./liter, pH = 0.2

EMF	$r_{exp.}$	$r_{calc.}$*
0.65	14	14
0.60	12.5	12.3
0.55	11	9.2
0.50	6.1	5.4
0.477	3.6	3.6
0.460	2.1	2.7
0.430	0.56	1.3

$$* \; r = \frac{165 - 55\sqrt{Fe^{+2}/Fe^{+3}}}{\frac{1}{\sqrt{Fe^{+3}}} + 2.3 + 70\sqrt{Fe^{+2}/Fe^{+3}}}$$

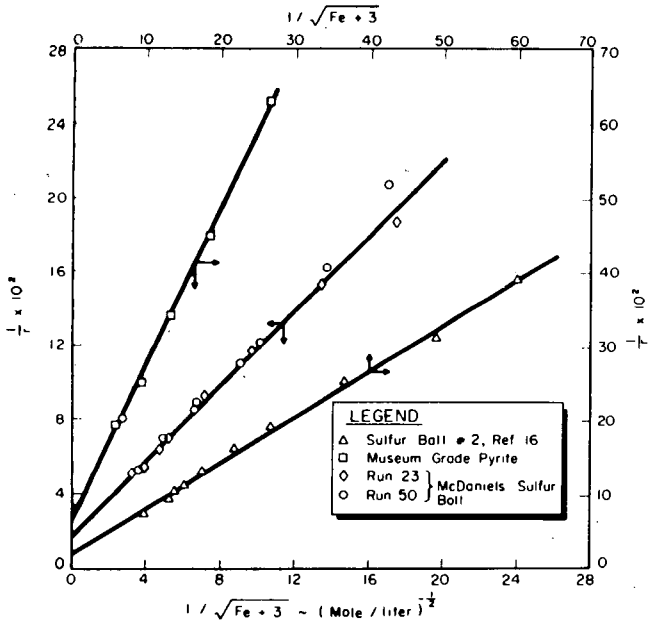

FIG. 1
Reciprocal Rate vs. Reciprocal Ferric Conc.

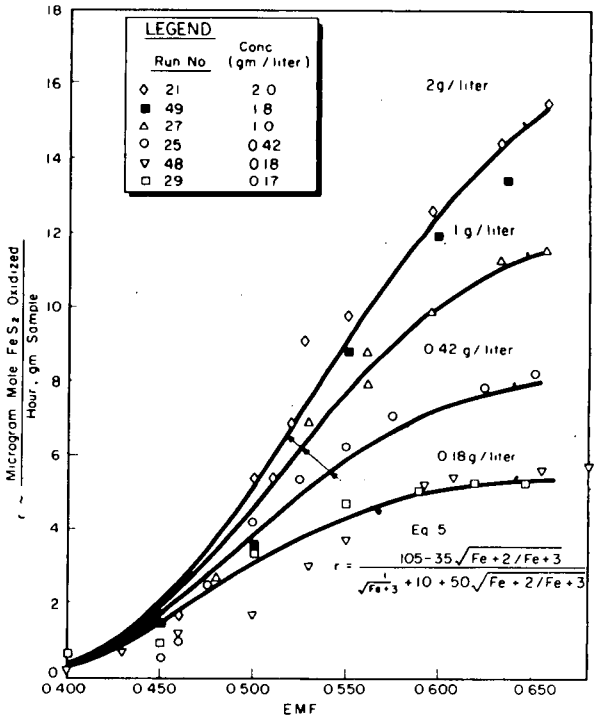

FIG. 2
Rate vs. EMF for McDaniels Sulfur Ball

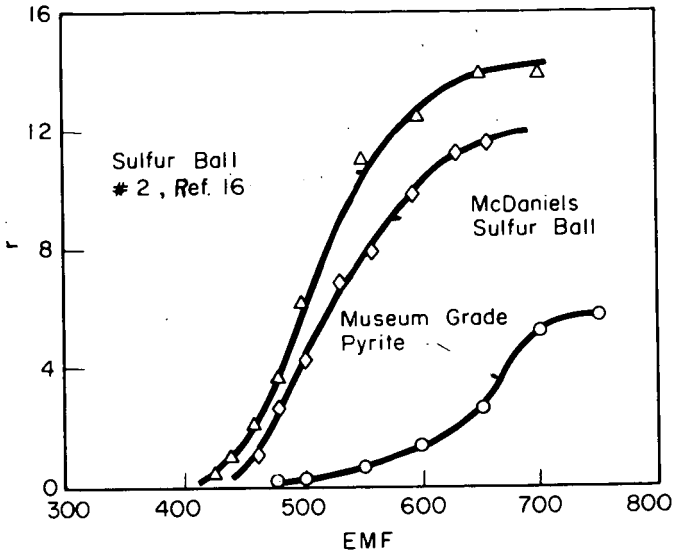

FIG. 3
Rate vs. EMF for Three Pyrite Samples

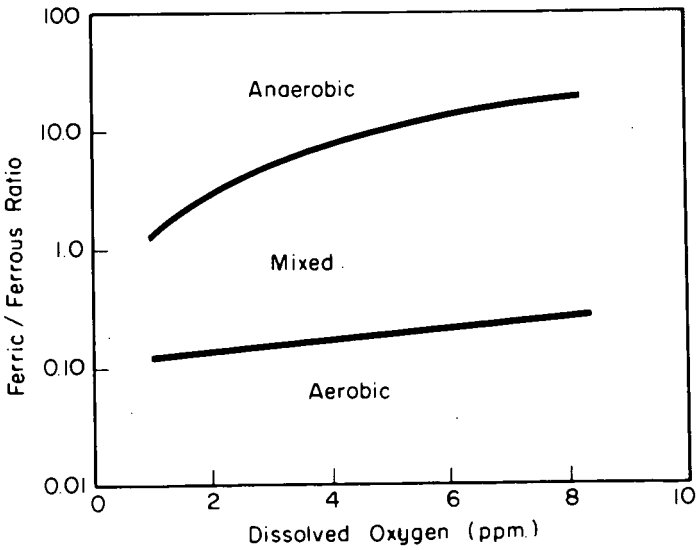

FIG. 4
Reaction Regime for High Iron, Low pH Systems

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THE MICROBIOLOGICAL OXIDATION OF FERROUS IRON IN MINE DRAINAGE WATER

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ABSTRACT

Acidophylic iron bacteria have been investigated at the laboratory level for their abilities to grow and oxidize soluble ferrous iron in synthetic and natural mine drainage waters. The influence of pH, temperature, aeration and other variables on the metabolic activities of these microorganisms were determined using both batch and continuous culture techniques. The results of these studies, as they would affect the use of these microorganisms in treating mine drainage water, are discussed. Plans for constructing a large scale field test system are also presented.

THE RATE-DETERMINING STEP IN THE PRODUCTION OF ACIDIC MINE WASTES

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Previous studies of the oxidation of iron pyrite and the subsequent release of acidity into mine drainage waters have provided no conclusive results in ascertaining which of the steps in the overall reaction is rate-determining. Although microorganisms have frequently been implicated as the causative agents in the production of acidic mine drainage, the activity of these microorganisms in natural systems has rarely been evaluated. Furthermore, few studies have been conducted in order to assess the catalytic influence of several chemical agents which are indigenous to mine drainage waters and which have been cited in the literature, in various circumstances, as exhibiting catalytic properties in the oxidation of ferrous iron. This paper represents a quantitative evaluation of the individual factors controlling the oxidation of iron pyrite; the relative rates of the various consecutive reactions have been considered in order to elucidate the rate-determining reaction. The laboratory results are complemented by results of a field investigation of iron(II) oxidation in natural mine waters.

The mine-water system can be characterized by the following stoichiometric reactions:

$$FeS_2(s) + 7/2\ O_2 + H_2O = Fe^{+2} + 2\ SO_4^{-2} + 2\ H^+ \qquad (1)$$

$$Fe^{+2} + 1/4\ O_2 + H^+ = Fe^{+3} + 1/2\ H_2O \qquad (2)$$

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

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

The reactions demonstrate that the dissolution of one mole of iron pyrite leads ultimately to the release of four equivalents of acidity: two equivalents from the oxidation of S_2(-II) and two from the oxidation of Fe(II) and the ensuing hydrolysis of Fe(III). It should be noted that two oxidants of iron pyrite are readily available: oxygen and iron(III).

OXYGENATION OF FERROUS IRON

LABORATORY STUDIES

The rate of oxygenation of ferrous iron over the pH-range of interest in natural waters is shown in Figure 1. These results were obtained in clean laboratory systems and were not subject to the various chemical and biological

complexities imposed by nature. In the acidic pH-region corresponding to conditions encountered in mine drainage waters, the reaction proceeds relatively slowly ($t_{50} \sim 1000$ days) and is independent of pH. However, the composition of natural mine waters is such that the oxidation reaction may be accelerated. Inorganic ligands, such as sulfate (2), which coordinate with Fe(II) and Fe(III), soluble metal ions, such as copper(II) (3), aluminum, and manganese(II) (1), suspended material with large surface areas and high adsorptive capacities, such as clay particles, materials which accelerate the decomposition of peroxides in the presence of ferrous iron, such as charcoal (4), and microorganisms (5) have all been mentioned in the literature, in various instances, as being capable of catalyzing the oxygenation of ferrous iron. Table 1 presents a summary of the experimental results of a study in which the catalytic properties of the various chemical agents were investigated. The specific results themselves and the experimental procedures employed are described elsewhere (6). It was found that the data obtained in the presence of the various catalysts studied, at constant partial pressure of oxygen, constant pH, and constant concentration of catalyst, could be suitably fitted by a relationship which is first-order in the concentration of ferrous iron:

$$-\frac{d\,[Fe(II)]}{dt} = 2.3\ k''\ [Fe(II)] \qquad (5)$$

In addition to the effective catalysts listed in the table, Mn(II), aluminum, amorphous ferric hydroxide, kaolinite, powdered charcoal, and crushed iron pyrite were examined, but no catalytic effects were observed. The studies were conducted in the absence of the microorganisms which are reportedly capable of accelerating the oxygenation reaction. Table 1 shows that the greatest influence on the rate of oxidation of Fe(II) was exerted by the clay particles or their idealized counterparts, alumina and silica, but at areal concentrations much greater than those encountered in most natural mine waters.

FIELD STUDIES

In order to compare the experimental results describing the kinetics of ferrous iron oxidation in synthetic mine waters with the rate of the reaction in nature, field investigations were conducted in the bituminous coal region of West Virginia, near Elkins. An underground mine which had been air-sealed by the FWPCA served as a source of mine water having a high concentration of dissolved ferrous iron. Measurements by the FWPCA had indicated that the partial pressure of oxygen inside the mine had been reduced to 7% (7). Samples of the water draining out of the air-sealed mine were collected and

TABLE 1. Chemical Catalysis of the Oxidation of Ferrous Iron

pH	log k'' $(day)^{-1}$ (k'' = - d log [Fe(II)]/dt)					
	Uncatalyzed Reaction	Catalysis by:				
		10^{-2}M SO_4^{-2} at 50°C	10^{-4}M Cu^{+2}	Al_2O_3 8000 m^2/l	SiO_2 3000 m^2/l	Bentonite 10 gm/l
3.0	-3.8	-3.1	-3.4	-	-	-
3.5	-3.6	-	-	-2.5	-	-
3.8	-3.4	-	-	-2.1	-	-
4.0	-3.3	-	-	-1.8	-2.2	-2.2

allowed to stand back in the laboratory exposed to the atmosphere. Aliquots were removed at various intervals and titrated with standardized solutions of permanganate. Figure 2 is an arithmetic plot of the change in [Fe(II)] with time; curve A represents a sample which was acidified at the time of collection, in order to serve as a control; curve B corresponds to a sample which was millipore filtered (0.8μ pore diameter) immediately after collection; and curves C and D represent untreated samples. The linearity of curves C and D indicates that the oxidation of Fe(II), in its native solution, is zero-order in Fe(II). The zero-order nature of the oxidation is suggestive of a biological reaction in which the substrate is non-limiting and in which the concentration of microorganisms remains relatively constant, i.e.,

$$- dS/dt = \mu_{max}B/y = \text{constant} \qquad (6)$$

where S is the concentration of substrate (Fe(II)), μ_{max} is the maximum specific growth rate of the microorganisms, y is the yield of microorganisms per unit of substrate utilized, and B is the instantaneous concentration of microorganisms, assumed here to be constant (8). Curves C and D in Figure 2 satisfy equation 6.

Since the energy released by the oxidation of Fe(II) is so small, the oxidation of 10^{-3}M Fe(II) would not be expected to significantly change the bacterial concentration if a large number of bacteria were present in the mine water, i.e., B should remain constant. If, however, the bacterial concentration were diminished, as by filtration of the mine water, B would be expected to increase logarithmically as the substrate, Fe(II), is utilized so that

$$- dS/dt = \mu_{max}B_o e^{\mu_{max}t}/y \qquad (7)$$

which, after integration, gives

$$S_o - S = B_o e^{\mu_{max}t}/y \qquad (8)$$

at $\mu_{max}t \gg 1$, or

$$\log (S_o - S) = \log B_o/Y + \mu_{max}t/2.3 \qquad (9)$$

S_o and B_o are the initial substrate and bacterial concentrations, respectively. Figure 3 shows the data from curve B of Figure 2 to fit such a microbial relationship. The specific growth rate constant is 0.076 hrs.$^{-1}$, corresponding to a generation time of 9.1 hours. (Silverman and Lundgren observed generation times of about 7.0 hours in their laboratory studies of Fe(II) oxidation in the presence of Ferrobacillus ferrooxidans (9).)

To further substantiate biological significance, sterile solutions of ferrous sulfate were inoculated with acid mine drainage. Two sterile controls were maintained: one in which aseptically filtered mine water (220 mμ pore diameter) was used as the inoculum, and another containing sterile ferrous sulfate alone. A decrease in the concentration of ferrous iron was observed, but only for the non-sterile specimen.

Therefore, the oxidation of ferrous iron occurs more rapidly in natural mine water than in any of the synthetic solutions investigated in the laboratory subject to the various chemical catalytic additives. The rapidity of the reaction in nature is apparently the result of microbial catalysis.

OXIDATION OF IRON PYRITE

With the exception of the study by Garrels and Thompson (10), previous investigations of the oxidation of iron pyrite have been concerned almost entirely with oxygen as the oxidant. In most cases, the potentiality of ferric iron as an oxidant of pyrite has been overlooked.

Figure 4 shows the decrease in Fe(III) with time in the presence of various concentrations of iron pyrite, under a nitrogen atmosphere. The concentration of pyrite is large compared to that of Fe(III) so that $[FeS_2]$ remains relatively constant during the course of the reaction. The study was conducted below pH 2, where the rate of oxidation of pyrite is independent of pH (10) (11).

The rapidity of the oxidation of iron pyrite by Fe(III) is readily apparent. For 1 gm/l of pyrite, the time required for the reduction of 50% of the ferric iron is approximately 250 minutes, which is considerably less than the half-time for the oxidation of Fe(II) even when accelerated by the chemical catalysts found in natural mine waters.

The rate of reduction of Fe(III) by pyrite in the presence of oxygen is demonstrated in Figure 5, showing that there is virtually no difference between the rate of reduction of Fe(III) by pyrite, or the rate of change of soluble

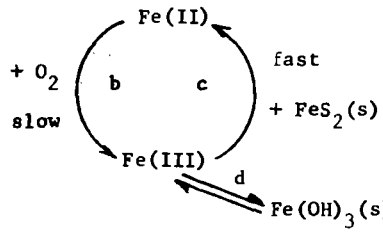
Fe(II), under aerobic and anaerobic conditions. In the presence of 0.20 atm. of oxygen, the oxidant of iron pyrite is ferric iron.

CONCLUSIONS

In accordance with the experimental results presented, the following model is proposed to describe the oxidation of iron pyrite in natural mine waters:

<u>Initiation Reaction</u>: $FeS_2(s) \xrightarrow{(+\ O_2)} Fe(II) + S\text{ - compound}$ (10a)

<u>Propagation Cycle</u>:



(10b,c)

(10d)

The model is similar to and carries with it the same overall consequences as that suggested by Temple and Delchamps (12). The rate-determining step is a reactive step in the specific oxidation of ferrous iron, reaction 10b. As this investigation has demonstrated, the rate of oxidation of Fe(II) under chemical conditions analogous to those found in mine waters is very slow, indeed considerably slower than the oxidation of iron pyrite by Fe(III), reaction 10c.

Reaction 10a serves only as an initiator of the overall reaction: ferrous iron may be released by simple dissociation of the pyrite, or by oxidation of the pyrite by oxygen. Once the sequence has been initiated, a cycle is established in which ferric iron rapidly oxidizes pyrite and is slowly regenerated through the oxygenation of the resultant ferrous iron, reactions 10b and c. Oxygen is involved only indirectly in the regeneration of Fe(III). Precipitated ferric hydroxide deposited in the mine serves as a reservoir for soluble fe(III); a significant supply of Fe(III) is readily available as an oxidant of pyrite.

The pertinent consequences of the model are as follows:

1.) Ferric iron cannot exist for long in contact with pyritic agglomerates.

2.) The elimination of oxygen is inconsequential with regard to the <u>specific</u> oxidation of iron pyrite. The exclusion of oxygen, however, does prevent the regeneration of Fe(III).

3.) The overall rate of dissolution of pyrite is independent of

its surface structure, since the specific oxidation of pytite is not the rate-limiting step.

4.) Microorganisms can be influential only by mediating the specific oxidation of ferrous iron, since it, alone, is the rate-determining step.

The solution to the problem of acid mine drainage appears to be dependent upon methods of controlling the oxidation of ferrous iron. Microorganisms, presumably the autotrophic "iron bacteria", markedly enhance the rate of oxidation of ferrous iron, thus accelerating the overall rate of pyrite oxidation. Control measures must be aimed at halting the catalytic oxidation of ferrous iron.

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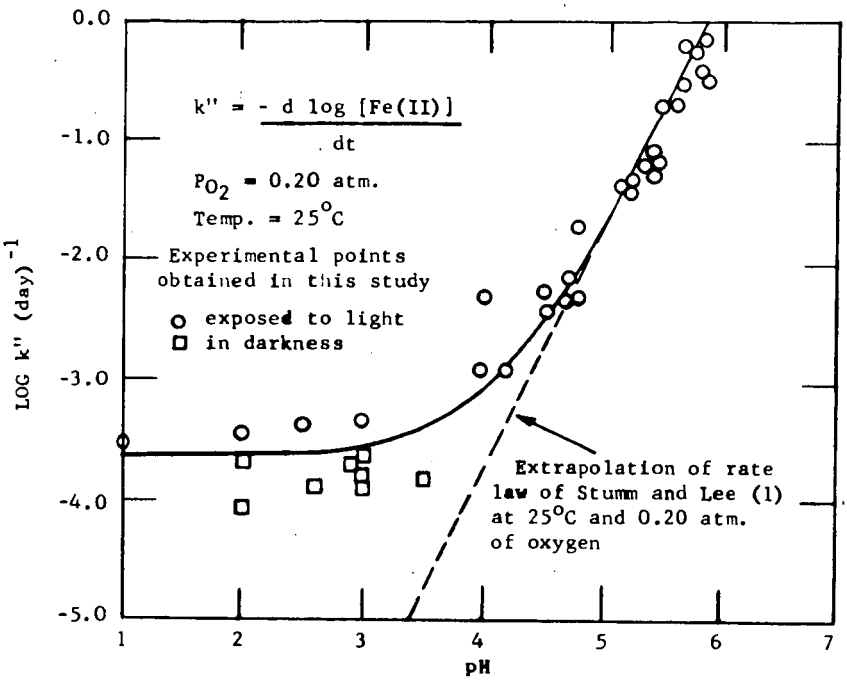

Figure 1. Oxygenation rate of ferrous iron as a function of pH.

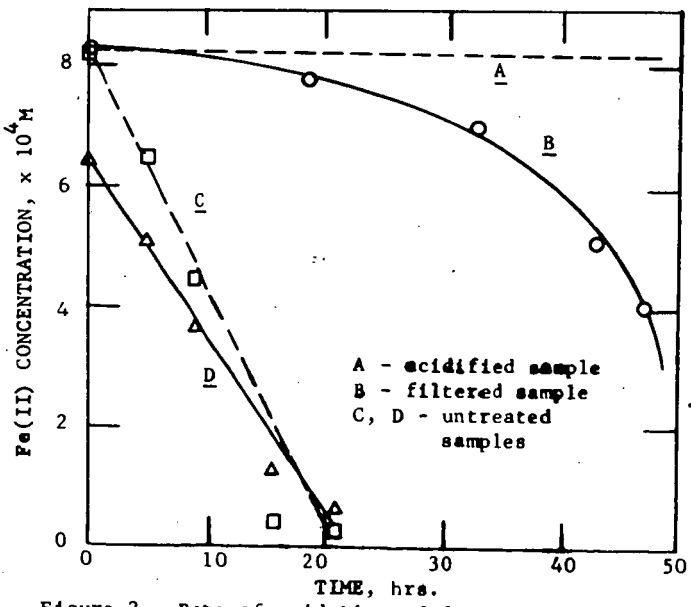

Figure 2. Rate of oxidation of ferrous iron in water collected from air-sealed underground mine.

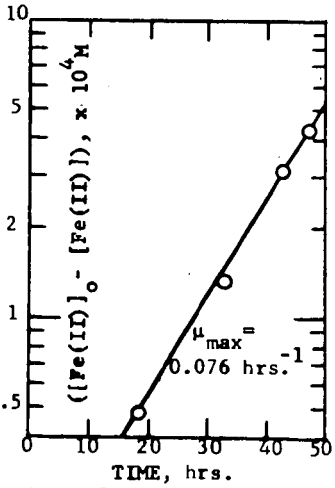

Figure 3. Change in ferrous iron concentration in millipore filtered water.

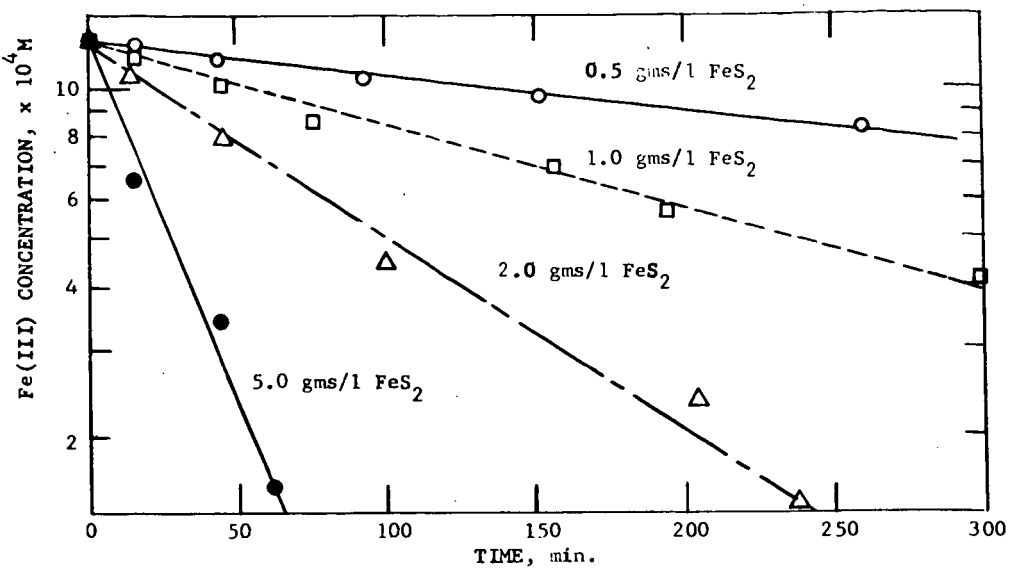

Figure 4. Reduction of ferric iron by iron pyrite in the absence of oxygen.

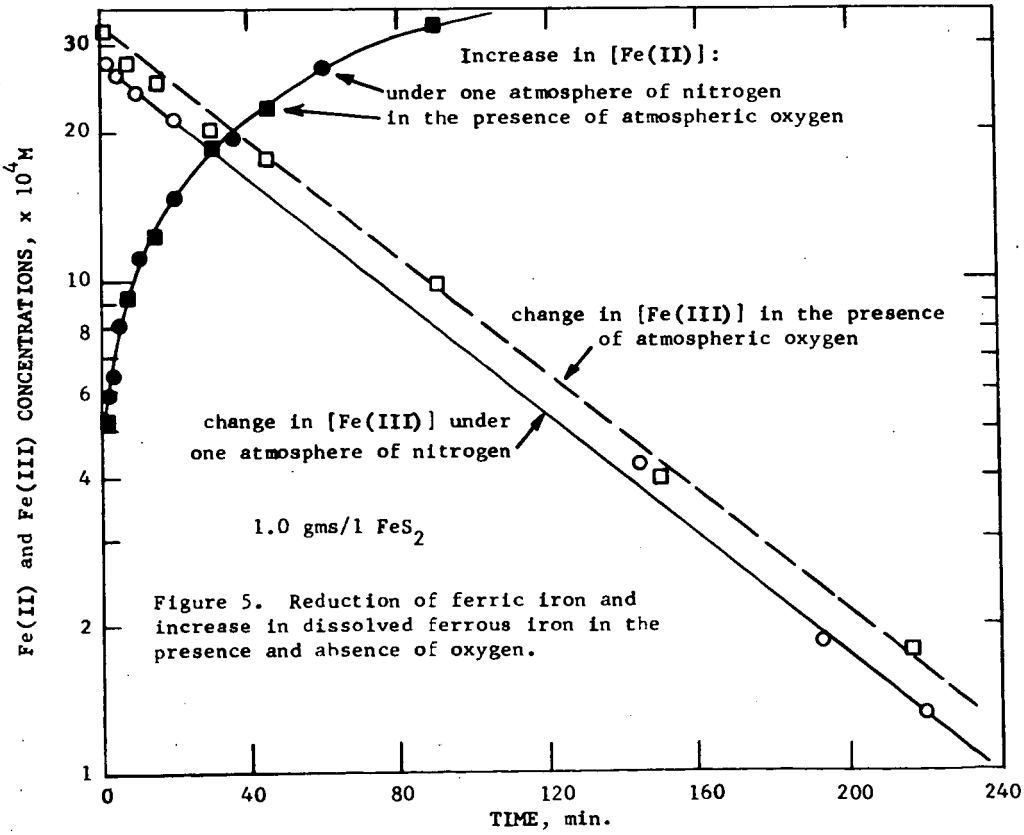

Figure 5. Reduction of ferric iron and increase in dissolved ferrous iron in the presence and absence of oxygen.

The Oxygenation of Iron II Solutions Relationships to Coal Mine Drainage Treatment

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INTRODUCTION

Most coal mine drainage waters, containing sulfuric acid, iron, and aluminum as major impurities, require treatment to reduce the contaminant concentrations to meet recent State regulations prior to their entry into natural waterways. The present, most widely employed treatment process includes neutralization of the waters and subsequent oxidation and precipitation of the iron along with most of the aluminum present. An impurity sludge product is separated for disposal.

Iron occurs in these waters predominantly as the soluble iron (II) ion. Its desired removal as an insoluble hydrated ferric oxide usually involves air oxidation with the associated production of further acid. A knowledge of the oxidation kinetics of the iron (II) ion is of significance in the development of control measures that could prevent formation of these contaminated waters and in providing efficient methods of treatment. In the treatment, the parameters involving this oxidation not only regulate the reaction rate, thus process-equipment design, but also have implications regarding the neutralization reactions and the nature of the resulting sludge.

This paper deals with the oxygenation of iron (II) ions and indicates the relative response of the more important reaction parameters on the measured rates. It is taken from a more extensive study by the authors.[5] The experimental conditions employed were similar to those prevailing in the treatment of mine drainage. The parameters considered were: pH, temperature, iron concentration, and aluminum concentration. Aluminum in mine drainage though commonly considered innocuous as a contaminant, has significant affects during treatment. There are other variables which are not discussed herein such as sulfate concentration and catalytic responses of trace constituents such as copper.

BACKGROUND

The oxygenation of iron (II) ions and the subsequent precipitation of iron (III) can be represented as follows: [1]

$$Fe^{++} + 1/4\ O_2 + 5/2\ H_2O = Fe(OH)_3\downarrow + 2H^+ \qquad \text{(a)}$$

This overall reaction involves oxygenation, hydrolysis, and precipitation, of which oxygenation, is believed to be the rate-determining step.[1] Stumm's studies of iron (II) in the pH range 4 to 8 indicate the oxidation rate can be described by the following equation:

$$\frac{-d(Fe(II)^{++})}{dt} = K\ (Fe(II)^{++})\ (O_2)\ (OH^-)^2 \qquad \text{(b)}$$

Below pH 3, however, the rate law follows the equation:[2 3]

$$\frac{-d(Fe(II)^{++})}{dt} = K\ (Fe(II)^{++})\ (O_2) \qquad \text{(c)}$$

In the pH range 4 to 8, for a given pH and oxygen concentration,

the rate expression becomes:

$$\frac{-d(Fe(II)^{++})}{dt} = k' \ (Fe(II)^{++}) \qquad (d)$$

$$\text{where } k' = K \ (OH^-)^2 \ (O_2)$$

which represents a first-order reaction rate.

EXPERIMENTAL

A jacketed reaction chamber was employed in which aeration was achieved by introducing air through a fritted glass disc at the bottom. The gas movement provided violent agitation within the chamber. Glass and calomel electrodes were supported through a stopper at the top of the chamber to lead a signal to a Sargent Recording Titrator, Model D. By proper adjustment of a cam limit switch, the titrating mechanism automatically controlled injection of the alkaline titrant (1.5N NaOH) to maintain a constant pH. A constant temperature bath and pump were employed to circulate water through the glass jacket surrounding chamber to maintain a constant temperature. A schematic representation of the apparatus is shown in Figure 1.

Reactant solutions were prepared with boiled, distilled, deionized water and reagent grade ferrous sulfate heptahydrate, $Fe(SO_4) \cdot 7H_2O$ and hydrated aluminum potassium sulfate, $AlK(SO_4)_2 \cdot 12H_2O$. Reactant solutions were adjusted to pH 2.8 with sulfuric acid prior to addition of the ferrous sulfate salt to insure oxidation would not occur before the experiment was initiated.

Approximately 600 ml of solution were used for each test. The solutions were placed in the reaction chamber and aerated for 30 minutes to ensure saturation of the solution by O_2. The rate of air introduction appeared to maintain this saturated condition since a plot of the pseudo-first order reaction rates conformed to a straight line dependent only upon the decrease in iron (II) concentration. The reaction rate was followed by withdrawing samples at measured time intervals, dowsing them immediately in 2 ml of concentrated HCl and titrating with potassium dichromate solution to determine the concentration of iron (II) ion.

In the initial test series only the pH of the reaction was varied by employing iron solutions (1000 ppm Fe(II)) at 22°C. A second series was conducted at two different levels of the four parameters as a 2^4 factorial experimental design. The variable levels of the second series of tests are given in Table 1.

TABLE 1

VARIABLE LEVELS USED IN RATE STUDIES

Variable	Min	Max
x_1 : pH	5.5	5.7
x_2 : Temp °C	15	25
x_3 : ppm Fe(II)	400	800
x_4 : ppm Al(III)	200	400

The pH values chosen were those which gave reasonably measurable rates by titrimetric techniques. Additional tests were conducted employing an ice bath, which verified the temperature dependence to 5°C.[5] The concentrations of iron and aluminum employed were representative of levels of mine drainage waters in Pennsylvania.

RESULTS

The rates for iron solutions at constant pH were found to conform to a pseudo-first-order reaction as indicated by equation (d). The reaction rate constants, k', are listed in Table 2.

TABLE 2

RATE CONSTANTS FOR OXYGENATION OF IRON $(II)^{++}$ CONSTANT pH

pH	k' ($min^{-1} \times 10^{-5}$)
4.50	1.5
4.70	263.
4.75	348.
4.80	517.
5.10	809.
5.18	1190.
5.35	3030.

Iron $(II)^{++}$ = 1000 ppm. T = 22°C

The reaction rate curves (shown in Figure 2) are represented by the following function:

$$\ln (Fe(II)_t) = \ln (Fe(II)_o) - k't \qquad (e)$$

where $Fe(II)_t$ = % Fe(II) remaining at time t (in minutes)

The least-squares-method was used to establish k' values (the slopes of the curves), however, the concentration at t = o was not used due to the bias that would have been created during the initial phase of the reaction while the hydroxyl ion concentration was changing.

There was nearly 2000-fold increase in the reaction rate with a pH increase from 4.50 to 5.35. The change in rate with pH appears to be nearly linear between 4.5 and 5.1 with a very major increase occurring within the next few hundreths of a unit, attaining rates which could not be evaluated by the experimental procedures employed.

The introduction of iron concentration, aluminum concentration, and temperature as additional parameters developed major changes in the reaction rate. Table 3 presents the levels of variables and the calculated rate constants, k', for these tests in the experimental design. With the subsequent observations it is critical to stress that iron (II) ion concentration at t = o was not used to calculate k'. The four reaction rate curves shown in Figure 3 are typical of the plots for all of the tests.

It appears from the curves of these reactions that during the initial phase, i.e. with the introduction of alkali until the particular desired pH was reached, either a different reaction rate or reaction mechanism was taking place than the one plotted for the reaction at a constant pH. The initial rate is much more rapid than that established at constant pH. The curves extrapolate only to 60-85 percent of the known iron (II) concentration at t = o.

During this initial phase, the alkali was injected into the reactant solution at the maximum rate attainable with the equipment (3.5 ml/min). When the desired pH was reached, the minimum injection rate was employed (1/3 ml/min.). The lapsed time for the initial

TABLE 3

LEVELS OF ALL VARIABLES AND RATE CONSTANTS FOR EACH OXIDATION RATE TEST WITH ALUMINUM PRESENT

Test	pH	Temp°C	Fe(II) ppm	Al(III) ppm	k' ($min^{-1} \times 10^{-5}$)
E-1	5.5	15	400	200	11.0
E-2	5.7	15	400	200	50.9
E-3	5.5	25	400	200	66.5
E-4	5.7	25	400	200	583.
E-5	5.5	15	800	200	102.
E-6	5.7	15	800	200	1930.
E-7	5.5	25	800	200	1060.
E-8	5.7	25	800	200	6870.
E-9	5.5	15	400	400	5.6
E-10	5.7	15	400	400	31.8
E-11	5.5	25	400	400	23.4
E-12	5.7	25	400	400	239.
E-13	5.5	15	800	400	35.2
E-14	5.7	15	800	400	123.
E-15	5.5	25	800	400	333.
E-16	5.7	25	800	400	1780.

alkali introduction during the multiparameter tests was slightly longer (3-4 min.) than during the pure iron solution tests (2-3 min.).

During the initial rapid injection of alkali, a typically greenish precipitate (assumed to be ferrous hydroxide) was formed at the point of injection, due to the high localized concentration of hydroxyl ions in this region. When no aluminum was present, it appeared that the reaction rate was not appreciable different during this initial phase than after the desired reaction pH was reached.

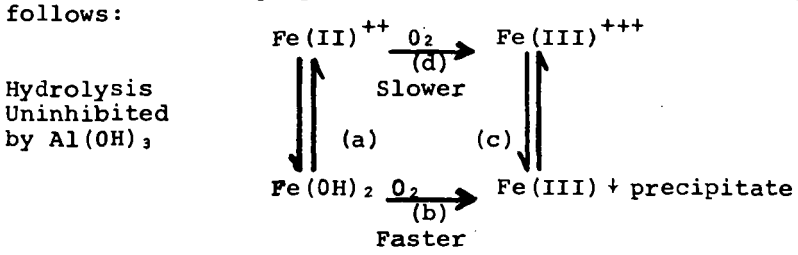
Thus it seems that the presence of aluminum ions in the reactant solution somehow modifies the oxidation rate of iron (II) in a complex manner. The effect of aluminum hydroxide on the hydrolysis of Fe(II) and Fe(III) has been investigated by Kakabadse and Whinfrey.[4] Their results show that $Al(OH)_3$ changes the rate of precipitation of $Fe(OH)_3$ but does not interfere with $Fe(OH)_2$ precipitation.

The oxidation rate of iron (II) ion continues to increase with pH beyond 5.35 to 5.7 even in the presence of aluminum ions. A 10° temperature increase resulted in a similar change in the oxidation rate by a factor between 3 and 15 times. This temperature dependence was indicated over the temperature range between 5 to 25°C.

The reaction rate constant may appear to vary with the initial iron (II) concentration. However, as the reaction rate for pure iron solution was first-order with respect to iron (II) concentration, the rate constant is independent of the initial iron (II) concentration (see equation d). With interference of $Al(OH)_3$ [2,4] on the hydrolysis rate of iron (III), these changes in the measured rate constant must be attributed to changes in the Fe(II):Al ratio, i.e. the overall oxidation-hydrolysis reaction rate of iron (II) $^{++}$ is proportion to this ratio. Consequently, it was found that a two-fold increase in the Fe(II):Al ratio resulted in increases in the oxidation rate of iron (II) ion between 2 and 40 fold. The effect on reaction rates of

aluminum concentration increasing corresponds with a decreasing iron concentration, temperature and pH.

A notable consequence of this study was the observation that the oxidation rate during the initial few minutes of the reaction, while $Fe(OH)_2$ was forming and oxidizing, was extremely rapid and did not appear to be affected by the presence of aluminum, even though the $Al(OH)_3$ precipitate was observed, also, during this period and throughout the test. A proposed explanation is schematically represented as follows:



Reaction (d) in this schematic diagram is slowed due to the inhibition of the hydrolysis reaction (c) caused by the interference of $Al(OH)_3$. Reaction (b), on the other hand, continues at the same relative rate as it would regardless of the presence of aluminum.

Accordingly when aluminum occurs in mine drainage water as a major constituent it is anticipated that reaction rates during treatment will be greatly retarded. If the above proposal is accurate, superior results should result when the waters are completely neutralized and the Fe(II) precipitated as the hydroxide prior to the oxygenation step, i.e. the pH be kept as high as feasible subject to other variables and processes. Further studies are being planned to resolve and quantify these relationships which can result in major changes in process conditions.

ACKNOWLEDGEMENT

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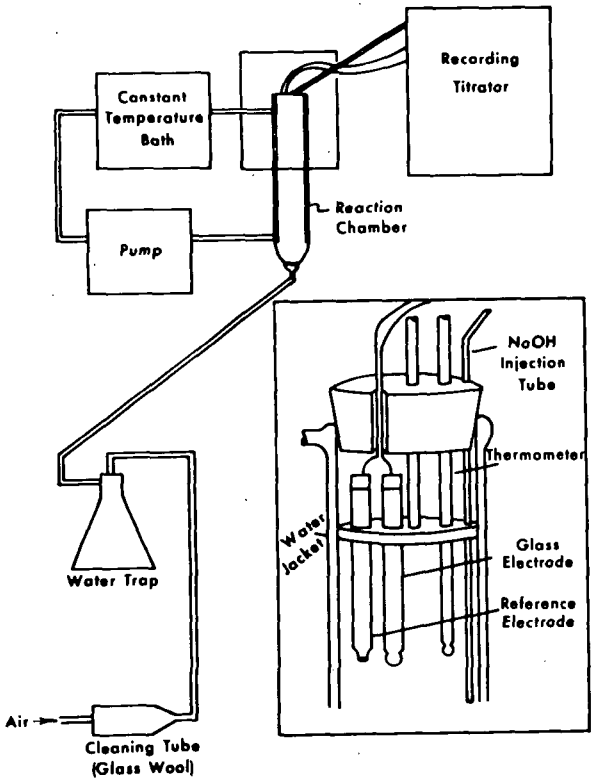


FIGURE 1. SCHEMATIC DIAGRAM OF APPARATUS USED IN IRON (II) OXIDATION TESTS

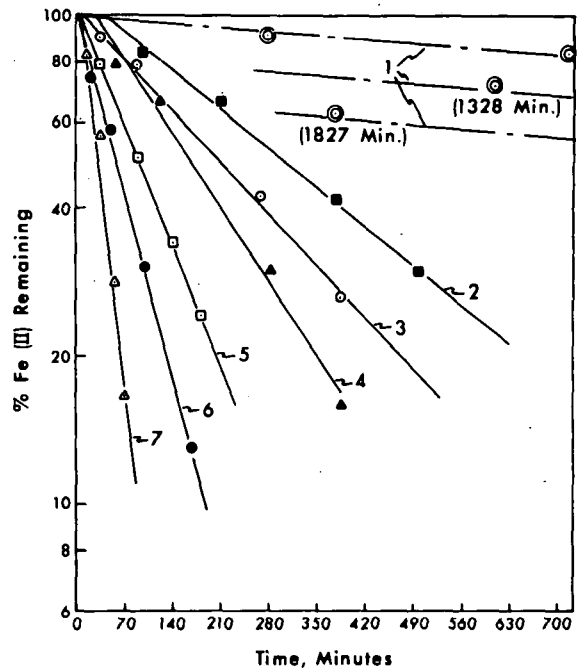
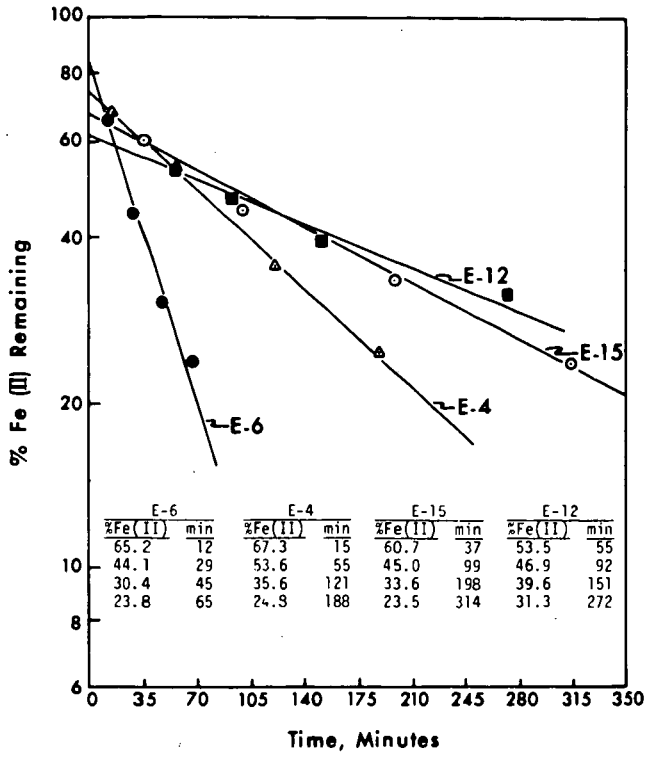


FIGURE 2. OXIDATION RATES OF IRON (II) IN SULFATE SOLUTION AT VARIOUS pH VALUES



E-6		E-4		E-15		E-12	
%Fe(II)	min	%Fe(II)	min	%Fe(II)	min	%Fe(II)	min
65.2	12	67.3	15	60.7	37	53.5	55
44.1	29	53.6	55	45.0	99	46.9	92
30.4	45	35.6	121	33.6	198	39.6	151
23.8	65	24.3	188	23.5	314	31.3	272

FIGURE 3. EXAMPLES OF OXIDATION RATES OF Fe(II) WITH ALUMINUM PRESENT

SUBSURFACE DISPOSAL OF MINE WATER

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Introduction

The concept of disposing of liquid industrial wastes by deep-well injection is not a new one. During the past ten years, a variety of industries have resorted to subsurface disposal, some of the details of which are given elsewhere[1,2]. The list reveals wide variations in injection rate, pumping pressure, cost, and waste disposition. Enactment of more restrictive clean water legislation in Pennsylvania recently had a great impact on the coal industry. When a feasibility study of deep-well disposal was proposed to the Pennsylvania Department of Mines and Mineral Industries, the Coal Research Board approved it. To evaluate the potential of deep-well disposal, geologic studies were undertaken.

Contiguous with the bituminous producing areas of Western Pennsylvania are a great number of formations containing petroleum and natural gas. This was a mixed blessing: providing important information from numerous drill holes but presenting a serious legal problem of water disposal. With the aid of hundreds of driller's logs, four cross-sections were constructed through southwestern Pennsylvania to determine potential water disposal strata. From the cross-sections and all other available geologic data it appeared that the Homewood sandstone and Connoquenissing sandstone, referred to collectively as the "Salt Sands" by most drillers, were very promising disposal formations because: they underly all coal seams; no commercially producible minerals are present in the formations; the formations contained brine under nearly hydrostatic pressure; driller's logs indicated high porosity and permeability and adequate thickness over a large area; the Salt Sands are bordered by impermeable rocks; and the formations were at a shallow depth of about 1500 ft.

After viewing the feasibility report[2], the Bethlehem Mines Corporation, a subsidiary of the Bethlehem Steel Corporation, agreed to cooperate in developing a test disposal well at its No. 58 Mine. Subsurface contour maps indicated that the Salt Sands were approximately 130 feet thick at the proposed well site and were covered by 1400 feet of overburden. The exact position of the well was chosen between the mine discharge point and a 1,500,000 gallon emergency storage pond on the surface that coincided with the location of a rectangular pillar in the mine, Fig. 1. This selection would permit an underground installation of the pumping unit if the disposal technique proved feasible. It also was a good surface choice allowing adequate sludge pond construction, proximity to acid water discharge and a supply of fresh water for preliminary testing. Bethlehem offered to finance completely the development, completion, testing, equipping and operation of the well. Ownership and supervision of the well were to remain Bethlehem's responsibility, but the information obtained from the well was to be released to the general public through the Coal Research Board. The Department of Mining at Penn State was to act as the agent of the Coal Research Board for this project, and also was to assist Bethlehem in an engineering capacity

Experimental Well Development

Appropriate surface arrangements were made and cable tool drilling began. A 20-inch bit was used to penetrate the 25 feet of unconsolidated material be-

tween the surface and bedrock, and a 16-inch conductor pipe was set to prevent spalling of loose material into the hole, Fig. 2. Drilling continued to a depth of 535 feet with a 13 3/8-inch bit, penetrating the Pittsburgh coal seam between the depths of 497 and 502 feet. Drill cuttings were removed by bailing out the hole with a conventional "dart" bailer. Representative samples of these cuttings were dried and visually examined to determine the rock types penetrated. In addition, the drill rig operator kept a "driller's log" of the subsurface units encountered. This latter record was based primarily on relative drilling rates. Ten-inch H40 steel casing was set from a depth of 532 feet to the surface and was cemented in place with circulated cement in accordance with the Oil and Gas Laws of the Commonwealth.

Cable tool drilling continued below the 535-foot depth using a ten-inch bit to a depth of 1302 feet. Cutting samples were also collected during this phase of drilling, and the driller's log similarly was recorded. Examination of these two records indicated that considerable disagreement existed in the indentification of the stratigraphic sequence encountered. Both logs showed, however, that the strata encountered were beds of sandstone, shale, limestone, claystone and coal of varying thickness and order of deposition, and both logs showed the presence of at least 30 feet of shale cap rock above the 1302-foot level. After Caliper and formation density logs were performed on the uncased portion of the well between 532 feet and 1302 feet, a seven-inch J55 steel casing was cemented throughout the entire hole. Diamond core drilling which followed in the interval from 1302 to 1588 feet provided 2 5/16-inch diameter cores, after which the cored zone was enlarged to a diameter of 6 1/2 inches by reaming the well to the 1565-foot depth. Examination of the cores disclosed that much less sandstone existed in this zone than had been expected. Although the lithology of this zone was quite complex, it could be approximated and is presented in Table 1.

Table 1

General Lithology of Cored Interval of Disposal Well

Depth From Surface (Feet)	Rock Description
1302 - 1314	Shale
1314 - 1365	First Salt Sand *
1365 - 1428	Shale and Siltstone
1428 - 1518	Second Salt Sand **
1518 - 1547	Shale with Minor Coal
1547 - 1565	Maxton Sand ***
1565 - 1588	Shale and Claystone

* Interbedded shale, siltstone, claystone and minor sandstone (16 feet).

** Approximately 64 feet of sandstone with minor shale and siltstone.

*** Entire interval sandstone.

The combined thickness of sandstone in the Salt Sands was 80 feet, considerably less than the 130 feet predicted by the isopach map of these units. The Maxton sand furnished an additional 18 feet of sandstone to make the total of 98 feet of uncased sandstone in the well. Strata encountered in the proposed disposal zone were quite different than those recorded for three nearby gas wells.

Density, Guard and Nuclear Logs were run to determine porosity and water saturation of the formations penetrated by the well. A 3-Dimensional Velocity

Log was performed to determine the quality of the bond between the cement and the seven-inch casing. The well was bailed dry following the logging program. Subsequent bailings revealed that water from the uncased interval was entering the well at rates between 8.5 and 10 gallons per hour. This was considered an exceptionally low influx of water for the Salt Sands.

Several aspects of the well were not as favorable as had been expected prior to well development. The main potential problems were the relative thinness of the sandstone units in the proposed disposal zone and the low porosity of these units. A low influx of formation water in the well also was a point of concern. A washout of claystone beds in the uncased part of the well also presented a potential problem in the maintenance of the well under injection. Nevertheless, since the well represented an investment of $40,000 at this stage, a decision was made to proceed with fresh water injection tests on the disposal well.

Water Injection Tests

Treated and filtered municipal water was injected through the seven-inch casing into the entire uncased portion of the well below the 1302-foot depth. No flow occurred until a pumping pressure of 1550 psig was reached, at which point water began to enter the well at the approximate rate of 84 gallons per minute (gpm). This phase of the test was continued a little over 2 hours; the flow rate increasing to 150 gpm with a pumping pressure in the range of 1700-1800 psig. A radioactive tracer log was run simultaneously with the initial injection test to determine which zones in the well were taking fluid. The log chart indicated that most of the injected fluid initially was leaving the well between the depths of 1472 and 1485 feet. As the injection rate was increased, other zones in the well began to take water, specifically the interval from 1496 to 1508 feet and the caved zone between 1340 and 1350 feet.

Fresh water injection was resumed and continued for an additional period of approximately 4 1/2 hours. Flow rates varied from 93 to 218 gpm and the pressure fluctuated from 1475 to 1940 psig. A total of 48,654 gallons of fresh water was injected during this nearly 7-hour period with no apparent change in the hydrological properties of the disposal zone. There was concern for the magnitude of the pumping pressures. At disposal capacity of 150 gpm, the pressures recorded during the injection test varied from 1650 to 1940 psig as opposed to a calculated theoretical well head pumping pressure of approximately 600 psig. As a result of the high injection pressure encountered during this first test, a decision was made to hydraulically fracture the uncased part of the well. Radioactive material was injected during the fracture treatment to indicate the location of the fracture. Approximately 30,000 gallons of fresh water and 34,000 pounds of 20-40 mesh sand were used in the treatment. Radioactive beads were added to the injected sand during the tailing-in period of the operation. Although the highest pressure recorded during the fracture treatment was 2200 psig, flow rates during the treatment were as high as 1500 gpm in the pressure range of 1500-1600 psig. This large flow was largely due to the fact that four large pumping trucks were used.

The well was allowed to back flow following the fracture treatment to release the pressure build-up in the disposal zone. A radioactive tracer log was run on the well to attempt to locate the fracture and to determine its orientation. The log chart indicated a high radioactivity level at a depth of 1508 feet which was interpreted to result from radioactive beads mixed with sand holding an induced fracture open. This fracture was thought to be oriented horizontally, as

the radioactive peak was confined to a small vertical interval. According to this interpretation, the well had been fractured at one of the most porous and permeable zones. A second fresh water injection test was run to determine if the fracture had improved the flow characteristics of the well. The test began at an injection rate of 147 gpm at a well head pressure of 600-800 psig. A flow rate was maintained at 150 ± 10 gpm for the duration of the test. The injection pressure gradually rose to 1800 psig during the first 1 1/2 hours and leveled off at this value. The test was stopped one-half hour later after 15,942 gallons of water had been pumped into the well because it was assumed that the high pumping pressure may have been caused by fine particles in the well plugging the pores of the sandstone beds. Thus the well was allowed to back flow in the hope that the flow of water out of the disposal zone would remove any loose particles in contact with these formations. Flow of water from the well continued for about four hours when the well was shut in.

Attempts to bail down the well three days later revealed that frequent bridging, or plugging, of the hole was occurring below the 1350-foot level. This bridging could be knocked free by running the drill bit down the well. Pebble to cobble sized pieces of claystone, similar in color to silt observed in the back flow after the second injection test, were removed from the bailer. This rock was identified as claystone from the spalled zone between the depths of 1340 and 1351 feet. This development implicated two threats to the future of the well. One, fine clay particles from these zones could permanently plug the pores of the sand face. The second possibility was that a continuation of spalling of this clay zone could initiate large scale caving, resulting in the loss of the well. Therefore, a bridge plug was set at a depth of 1370 feet, about 20 feet below the caved area, and cement was introduced into the well from the bridge plug upward to a depth of 1205 feet. After the cement had set for four days, it was drilled out with a 6 1/2-inch bit, hopefully leaving an irregular "doughnut-shaped" plug of cement in each of the caved areas. The bridge plug also was drilled out at this time. A caliper log was run on the uncased portion of the well to determine the effectiveness of the cementing operation. A comparison of this log with the previous caliper log indicated that the cement had blocked off at least part of the lower clay seam, but gave inconclusive evidence regarding the upper seam.

A third injection test was then performed to determine if the partial sealing of the caved area would result in lower pumping pressures. Approximately 46,000 gallons of fresh water were pumped into the disposal zone at injection rates from 105 to 250 gpm. Very little pressure change was recorded for the various flow rates used, the pressure remaining in the range of 1800 to 2000 psi through the five-hour test. Therefore, a decision was made to hydraulically fracture an isolated zone in the well. Examination of the core records showed that the interval from 1480 to 1520 feet had the highest porosity and permeability and should be most receptive to a fracture treatment. Therefore, it was decided to isolate this zone, notch and fracture it, and conduct another injection test. The zone was isolated from the lower part of the well by filling the well with a cement mixture of Calseal and Hydromite below the 1520-foot level. A retrievable packer was set at a depth of 1482 feet on 3 1/2-inch casing that ran from the packer to the surface. The setting of this packer completed the isolation of the zone to be fractured. Notching pipe was run into the zone through the 3 1/2-inch casing and the zone was hydraulically notched at 1491, 1492 and 1493 feet. The notches were cut in an attempt to create a locus for fracture initiation.

The fracture treatment was designed to rupture the sandstone and then place 40,000 pounds of sand, suspended in 30,000 gallons of water, in the fractures as a propping agent. Formation breakdown pressure for this treatment was 3000 psig. Water and sand were pumped into the well at a flow rate of about 850 gpm at 2500

psig until the treatment was about 75 per cent completed. At this time water was observed flowing out of the top of the well from the annulus between the seven-inch casing and the three and one-half-inch tubing. This flow was continuous and increased in volume. The fracture treatment was concluded after 34,000 pounds of sand and 26,000 gallons of water had been pumped into the well as the benefits to be derived from further pumping were dubious. This leak indicated that water was entering the formation, by-passing the packer, re-entering the well bore and flowing to the surface, Fig. 2. An induced vertical fracture, which bridged the packer, would cause this type of flow pattern. The possibility of a wash-out around the packer seemed unlikely, as the rock at this depth appeared competent enough to withstand rapid erosion.

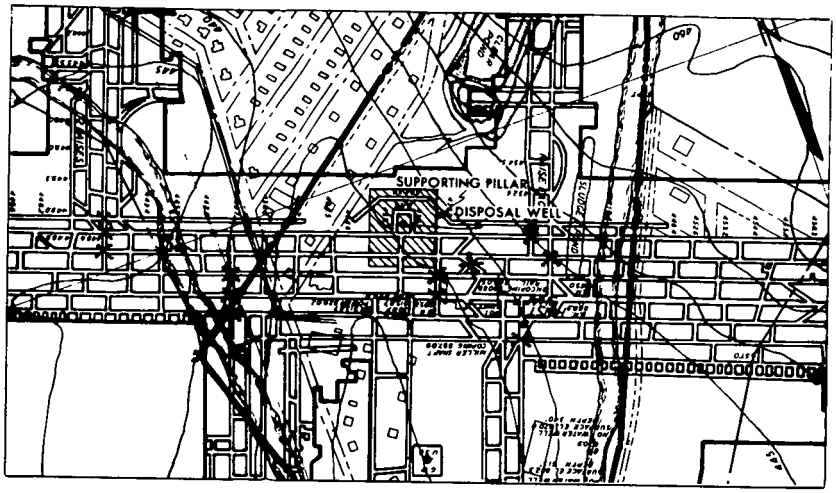
After the pressure had been bled off the well, the packer was unseated and reset at the depth of 1480 feet in an attempt to isolate the entire fracture. Fresh water injection was resumed after the packer had been reset. The flow rate varied from 145 to 160 gpm and the pressure ranged from 1600 to 1700 psig. After 12,700 gallons of water had been injected, water again began to flow out of the annulus at the top of the well. Injection was halted and the packer was raised and reset at the depth of 1472 feet. Injection into the well began again at the rate of 150 gpm. The pumping pressure ranged from 1600 to 1800 psig. After the injection of 18,400 gallons of water, the leak recurred and the injection test was stopped. No further attempt to relocate the packer at a higher elevation was made, as the caliper log indicated the upper well bore was unsuitable for this purpose.

Geologic sections revealed two other potential disposal zones in this area. The first was the Buffalo and Mahoning sandstone (Dunkard Sand) formations approximately 600 feet above the Salt Sands and the Burgoon Sandstone (Big Injun Sand) located at approximately 400 feet below. However, experimental work for steam injection oil recovery was contemplated for the former in this area, and the latter was a gas producer. Therefore, permission could not be obtained for disposing in these formations and all work ceased.

Discussion

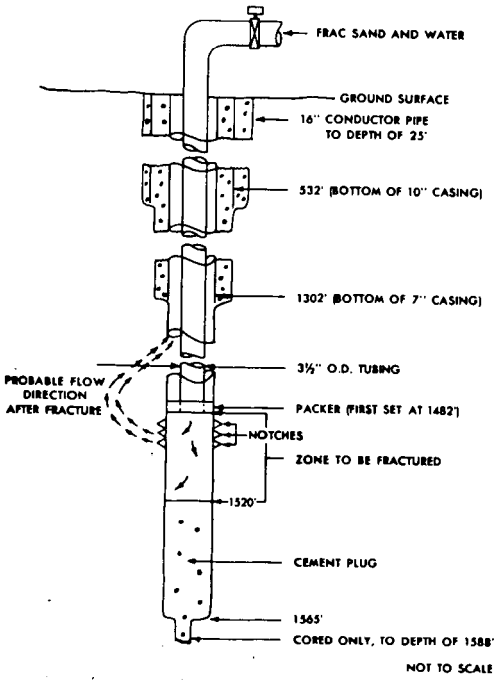
The decision to halt work on the disposal well was brought about by the high pumping pressure of about 2000 psi required to inject 150 gallons of acid mine water per minute into the well and the development of a more economical water treatment process at this mine. The high pumping pressures indicated higher operating and capital costs than originally anticipated. A total of $57,080 had been spent by Bethlehem Mines Corporation on the development and testing of this disposal well, this sum being broken down elsewhere[3]. This phase of the project was well within the expected cost range. Despite thorough planning, careful execution and exhaustive remedial measures, the disposal well did not approach expected performance. The pumping pressure ranged from 1500 to 2000 psig for a flow rate from 84 to 250 gpm. Furthermore, during the flush stage of the first fracture treatment, water was injected into the well at a rate of 1430 gpm with a pressure of 1600 - 1650 psig. Any benefits gained from the first hydraulic fracture treatment were not evident. For a given flow rate, the pumping pressure after the fracture treatment should be less than the pressure prior to treating. Strangely enough, most of the post-fracture pressures were higher than the pre-fracture pressures for comparable flow rates.

The phenomena described above indicate clearly that the particular region of the Salt Sands penetrated by this well was not a good disposal zone. The Homewood and Conoquenessing sandstones, which comprise the Salt Sands, are members of the Pottsville Series of Carboniferous rocks. One of the main reasons



WELL LOCATION

Figure 1



CONDITION OF WELL DURING SECOND FRACTURE TREATMENT

Figure 2

THE EFFECTIVENESS OF MINE DRAINAGE POLLUTION CONTROL MEASURES ELKINS, WEST VIRGINIA

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INTRODUCTION

The seriousness of water pollution by acid drainage from coal mines is highlighted by the following figures: In Appalachia(1) during 1966, more than 6,000 tons of acidity per day were discharged from active and inactive mines, polluting more than 10,000 miles of streams.

In 1962, an authoritative report, "Acid Mine Drainage"(2) was issued by the Committee of Public Works of the U. S. House of Representatives. Recognizing the extent of the problem, the report pointed out that elimination of this form of pollution would restore vast quantities of water for municipal and industrial use, propagation of fish, aquatic life, and wildlife, recreational purposes, and other uses. After pointing out that most of the various methods developed to abate acid mine drainage had been abandoned because of high costs and technical failure in field applications, the Committee concluded that mine sealing was the most promising method.

The report recommended (1) a sealing program directed at sealing abandoned mine shafts and other drainage openings, (2) a stepped-up research program by federal, state, and interstate organizations to develop other measures, and (3) a stream and acid flow regulation program to be employed where sealing or other methods are unable to sufficiently reduce the acid content of the stream to meet water quality requirements for all legitimate purposes.

The report also called for a demonstration program to evaluate mine sealing procedures and results, suggesting that the work be done in "three appropriate watersheds containing between 50 and 100 abandoned coal mines each from which acid water is now draining." Funds for the demonstration grant, $5 million, were authorized by Congress in 1964.

The work was to be under the direction of the Water Supply and Pollution Control Program of the Department of Health, Education, and Welfare, the forerunner of the Federal Water Pollution Control Administration which later was transferred to the U. S. Department of the Interior. Other participating agencies were the U. S. Bureau of Mines, U. S. Geological Survey, U. S. Bureau of Sport Fisheries and Wildlife(2), and West Virginia agencies in charge of mining, water pollution, and reclamation.

In March 1964, the first demonstration project site was selected in the Roaring Creek-Grassy Run watershed near Elkins, West Virginia. The areas contained one large drift mine (3,000 acres) and a number of smaller underground mines which had been extensively strip mined along the out-crop. The surface mine intercepted runoff and directed it into the underground mine, which in turn flushed more mine drainage from the underground workings. These streams were contributing 12 tons per day of acidity to the Tygart River. Chemical characteristics of the two streams are presented in Table I.

The demonstration project was carried out in three phases: (1) site, (2) mine sealing, regrading, and revegetation, and (3) project evaluation. Phase 1, begun in March, 1964 and completed in July, 1966, was devoted to water quality surveillance (FWPCA); stream gaging (USGS): surface mapping, investigation of mine conditions, and design control measures and reclamation planning (USBM); securing land permits (W. Va.),

and award the construction contract (FWPCA, USBM). Sealing of the mines and concurrent reclamation measures (Phase 2) were begun in July 1966 and completed in September 1967. Disturbed areas were vegetated in the spring of 1968. Phase 3, evaluation of the effectiveness of mine sealing and reclamation measures is continuing.

Table I
Water Quality Characteristics[a]

	Grassy Run		Roaring Creek	
	mg/l	Tons/day	mg/l	Tons/day
pH[b]	2.55		3.3	
Acidity, (Hot), $CaCO_3$	656	10.6	110	1.8
Iron, Total	110	1.8	5	0.08
Iron, Ferrous	4	0.06	1	0.01
Sulfate	992	16.0	168	2.7
Hardness, $CaCO_3$	446	7.2	99	1.6
Calcium, $CaCO_3$	293	4.7	76	1.2
Aluminum	38	0.6	12	0.2
Specific Conductance[c]	1,723		530	
Flow[d]	6		40	

a - Average values for period March 1964 to June 1966
b - Unit not mg/l, median value
c - Units - micromhos per cm
d - Units - cfs

CONTROL MEASURES

The control measures planned were as follows:

1. Air sealing of the underground mine: Since oxygen was felt to be necessary for the oxidation of pyrite and the production of iron and acidity, preventing oxygen from reaching the pyrite should reduce or eliminate acid pollution. Air sealing was to be accomplished by filling all bore holes, subsidence holes, and other air passages into the mine. "Wet" mine seals, which allow water to leave the mine, but prevent air from entering, were to be constructed at all openings discharging water.

2. Water diversion: Since water is the transport media for carrying acid and iron from the mining environment, reducing the amount of water passing through a surface or underground mine will reduce the amount of pollution. To prevent water from entering underground mines, subsidence holes were filled, streams were rechanneled away from mines, and "dry" seals, a solid seal through which water could not pass, were constructed in mine portals.

3. Burying of acid-producing spoils and refuse: Since these materials were major contributors to pollution they were buried in surface mine pits.

4. Surface mine reclamation: Although surface mines were to be regraded primarily to prevent water from entering the underground mine, regrading also reduces the time that water is in contact with acid-producing material in the surface mine itself. During regrading attempts were made to bury the highly acid material.

5. Revegetation: All disturbed areas were revegetated to prevent erosion and stablize the backfills.

Both "wet" and "dry" seals were constructed from concrete block and coated with urethane foam on both sides to protect the block from acid attack. The mine opening was timbered on both sides of the seal in order to keep the weight of the roof off the seal. Dry seals were composed of one wall, while the wet seals had three walls; one wall was solid except that two blocks were removed from the bottom, the inner wall was approximately 12 feet from the seal and 2½ feet high, and the outer wall was 5 feet from the seal and 2½ feet high. The latter two walls formed a pool which prevented air from entering the mine. Clay seals were used in areas where the highwall was badly fractured and deep mine workings lay behind the wall. For this type of seal, clay was compacted against the highwall to a height well above the underground mine workings.

Three types of backfills were used on the surface mines - contour, pasture, and swallow-tail. For a contour backfill, the spoil was graded back to as close as possible to the original contour of the land. Usually the top of the highwall was pushed down to complete the backfill. In constructing the pasture backfill, the spoil was graded to form a small slope away from the highwall and the highwall was left standing. The pasture type backfill was used when the highwall was sound. The swallow-tail backfill was similar to the pasture backfill except that in the swallow-tail, a waterway was constructed paralled to the highwall. The waterway was located away from the highwall and finial cut. Where possible, soil low in acidity was hauled in and placed on top of the backfill to facilitate revegetation and reduce acid production. Most of the subsidence holes within 100 feet of the highwall were filled with soil during the backfilling operation.

The construction contract for the reclamation work, except revegetation and the filling of subsidence holes located over 100 feet from the highwall, was entered into on June 30, 1966. Because of the many unknowns that might be encountered in working with abandoned mines, the contract was cost-plus-fixed-fee. Estimated construction cost was $1,640,382. Work begun on the south half of the major mine (3,000 acres) dealt primarily with water diversion, surface reclamation and some air sealing. By mid-1967, it became apparent that the cost for the entire project would exceed the original estimates. A decision was made to complete only the south half of the mine to conserve funds. No further work was done on the north half. This change in plans meant that the major mine would not be air sealed, however, a small isolated mine had been sealed and was available for evaluation. Thus, the project as curtailed would give information on the effectiveness of water diversion and surface mine reclamation on the south half of the major mine and the effectiveness of air sealing and water diversion on a smaller mine.

In the spring of 1968, approximately 700 acres of land disturbed during reclamation were revegetated. The most up-to-date technology was used in the revegetation program. Soil samples were taken as a guide to the fertilizer and lime requirements and for choosing the best type vegetation. The entire area was planted to grass for quick erosion control which reduced acid water drainage. Hydroseeding was used in difficult areas to assure establishment of grass. Trees were planted on the steeper slopes and the more toxic areas for long term erosion control. A summary of the reclamation and revegetation work is presented in Table II.

UNIT COST

The final determination of the unit cost for the various control measures has not been made; however, some preliminary data are available. The cost for building masonry mine seals ranged between $2,000 and $6,000 per seal; clay seals averaged $88.00. This cost included clean-up of mine opening, temporary and permanent timbering, concrete footers, concrete block walls, urethane foam coating, portal, all equipment, direct labor, 75 percent overhead, and 6 percent G and A. A preliminary cost estimate for earth moving was $0.41 per cubic yard. This cost, derived by subtracting

the cost of the seals from the total cost, is unrealistic, higher than the actual earthmoving cost.

A complete analysis of the unit cost for revegetation was made and is presented in Table III.

RESULTS

This reclamation work was completed, except for revegetation, in the fall of 1967, thus a little over a year's data are available for evaluating the effectiveness of the control measures.

MINE SEALING

As noted earlier, a small isolated mine was completely air sealed. This mine was a combination of underground and surface operations. Two seams had been surface mined (78 acres) the seam in which the underground mine was located and the seam above the deep mine. The size of the underground mine is unknown, but it is estimated to cover only a few acres, as the mine was never developed.

The surface mines were regraded to facilitate rapid runoff. A pasture type backfill was used on the upper areas and a contour backfill on the lower. There were two portals into the underground mine. One portal was sealed by packing clay into the opening and a "wet" seal was installed in the second opening to allow water to discharge.

Table IV shows the air quality within the mine and the quality of the discharge. Within two months after the mine had been sealed, the oxygen content of the mine atmosphere had been reduced to 9.1 percent. Since that time, the oxygen content has varied between 7.0 and 10.8 percent, indicating that air has access to the mine. The presence of oxygen in the mine may be due to movement of air through the overburden as a result of barometic changes.

The acidity concentration of the discharge decreased to a value less than any obtained in the 44 months of pre-construction monitoring in less than a month after sealing was completed. The lowest acidity value during pre-construction was 438 mg/l, while the highest post-sealing value has been 388 mg/l. Over the long-term, the acidity is expected to continue to decrease, but at a much slower rate than the initial decrease. For example, the acidity in November 1968 was 247 mg/l compared to 388 mg/l in November 1967. A similar large initial decrease in acidity followed by a smaller decrease has also been observed by Moebs.(4) No explanation for the initial decrease has been developed; however, it would not appear to be due to the reduction of the oxygen content within the mine because the acid being discharged at any given time is an indication of the pyrite oxidation at some previous time. Thus, a lag occurs between the time the oxidation rate of pyrite is reduced and the time this reduced rate will be noted in the discharge. During the period of initial decrease the oxygen content was just beginning to decrease and no lag period had occurred. Shumate and Smith(5) found this lag to be several months. The long-term decrease in acidity is probably an indication of reduced oxidation of pyrite.

The total iron content of the discharge has decreased very little, if any. Approximately 90 percent of the iron before sealing was in the ferric form and after a year the ferrous content has not increased, indicating that sufficient oxygen is available within the mine to oxidize the ferrous iron resulting from pyrite oxidation. At the low pH's occurring in the discharge, ferric iron is highly soluble, therefore, the opportunity for the iron to precipitate within the mine is small.

The sulfate, a product of pyrite oxidation, has decreased since the mine was sealed.

In many months the sulfate content was less than the minimum concentration observed before sealing. This reduction in sulfate may be another indication that the rate of pyrite oxidation has decreased.

In summary, the data from this mine seal indicate that some reduction in pyrite oxidation may be occurring, however, the water quality is still extremely poor.

Although the major mine in the project area was not completely sealed against air the discharges from the 11 "wet" seals in that mine are still being monitored. Ten of these discharges have shown no significant changes in water quality. The eleventh has shown improvement as given in Table V. This "wet" seal is located in a mine portal. In general, the mine drainage in this area is away from the mine portal; however, there is a localized dip in the coal and the drainage from a small area drains out the portal.

The pH of this mine seal discharge has increased, reaching as high as 6.4 in September. The acidity, total iron, and sulfate concentration show some decreasing trends. No air samples have been collected from the mine, therefore, data are not available to determine if the oxygen content has decreased. It was originally felt that this portion of the mine was not air sealed since there are many known holes into the mine. However, there is a chance that due to subsidence within the mine this section is isolated from the major mines and thus air sealed. Air samples are to be collected to check this premise.

Table II
Reclamation Work Performed

Reclamation	
Land disturbed	710 acres
Surface mines reclaimed	12.5 miles
Backfill, total	3,600,000 cubic yards
Backfill, compacted	61,269 cubic yards
Subsidence holes filled	450
Mine seal, dry	43
Mine seal, wet	12
Mine seal, clay	41
Mine seal, other	5

Revegetation	
Total	710 acres
Grass only	322 acres
Hydroseed only	16 acres
Trees only	57 acres
Hydroseed grass and trees	195 acres
Grass and trees	120 acres

SURFACE MINE RECLAMATION

The effectiveness of surface mine reclamation on water quality was evaluated by collecting samples of runoff during wet periods and by monitoring the streams to which the surface mines discharge. Six areas were isolated and evaluated.

Site RT 8F-1. This sampling point was used to measure the effect of reclamation on 49 acres of surface mines. One underground mine discharge remains in the area. The opening has been sealed. As seen in Table VI, the acidity has varied considerably since the reclamation was completed. With the exception of December 1967, the acidity has been less than the average for the pre-reclamation period, and during five months the acidity level was less than the minimum value obtained prior to reclamation.

The pH has been greater during post-reclamation and the sulfate has a decreasing trend. In general, the water shows improvement, however, it has not recovered to its natural state. This area was discharging 59 pounds per day of acid in September 1966 and in September 1968 was discharging 38 pounds per day, a decrease of 35 percent. The high acidity in December 1967 was due to a flushing of material from the underground mine.

Site RT 9-2. This sampling point was used to measure the effect of reclamation on 160 acres of surface mines. One underground mine discharge is in the watershed, however, its contribution of mine drainage is minor. The data collected for the watershed are presented in Table VII. The acidity since reclamation has been less than the mean concentration during pre-reclamation. Even during the dry months of July, August, and September when the concentration is the greatest, the water had a lower acidity than the mean during pre-reclamation. The sulfate concentration with the exception of two months, has been less than the average for pre-reclamation. The pH has been somewhat higher, while the total iron concentration shows only marginal improvement. The acid load during the project from this area for the month of October is given in Table VIII. The data show a decrease in load after reclamation.

Site RT 9-23. This sampling point was used to measure the effect of reclamation of 256 acres of surface mines. One minor underground mine discharge is located in the area. As seen in Table IX, the acidity and sulfate concentration has been less after reclamation than the mean value before reclamation, except during September 1968 for acidity and August and September for sulfate. These high concentrations occurred during a very low flow period and it is questionable if the acidity was due to surface mines. The pH was greater than the pre-reclamation value in all but one month, again the low flow period. A comparison of the loads for October before and after reclamation is presented in Table X. A reduction in the acid load can be noted.

Site RT 6-20. This sampling point was used to measure the effect of reclamation on 45 acres of surface mines. Two large underground mine discharges are located in the watershed. In Table XI, the data collected at this site are reported.

These data indicate that there has been no improvement in the water; if anything, the water is worse. Upon investigating the source of the acid pollution, it was found that before reclamation 24 to 50 percent of the acid load was from the underground mines. After surface mine reclamation, the underground mines are contributing 75 percent of the acid load. It appears, therefore, that some benefits have occurred from surface mine reclamation.

Site RT 6-21. This site is located at the mouth of Kittle Run. A total of 140 acres of surface mines were reclaimed. Two major underground mine discharges are located in the watershed. The streambed of Kittle Run was completely destroyed during surface mining and a large portion of the runoff and the discharge from an underground mine were diverted into another underground mine. During reclamation the stream channel was reestablished, therefore, more water should be passing Sample Site RT 6-21, however, to date this has not occurred. In Table XII, the data collected at this site

Table III
Cost of Revegetation[a]

	Dollars Per Acre		
	Maximum	Minimum	Average
Conventional Grass[b]	462.08	71.13	165.22
Hydroseeding Only[c]	370.72	238.60	323.43
Trees Only[d]	194.76	55.02	106.73
Hydroseeding and Trees[e]	537.06	362.95	429.40
Conventional Grass and Trees[f]	380.53	204.47	230.56

a - Cost includes labor, equipment, materials, and overhead
b - Fertilizer (0.5 ton/acre of 10-10-10), lime (2 - 4 tons/acre) applied from truck, grass planted by seeder box.
c - Lime (2-4 tons/acre) spread from truck or from farm type fertilizer spreader, hydraulic application of grass seed, fertilizer (0.5 ton/acre of 10-10-10) and organic mulch (1 ton/acre).
d - Hand planted (900 - 1,000/acre).
e - Hydroseeding plus hand planted trees (900 - 1,000/acre).
f - Conventional grass as in b, plus hand planted trees (900 - 1,000/acre).

Table IV
Effectiveness of Mine Seal - Area 24

	Oxygen[e] Within Mine, %	Acidity (Hot) $CaCO_3$, mg/l	pH	Iron, mg/l	Sulfate, mg/l
Before Sealing[a] (Mean)	___	591 (65)[b]	2.8[c]	93 (25)[b]	1035 (155)[b]
Minimum	___	438	3.1[d]	48	710
After Sealing					
Oct. 67	___	388	3.1	86	835
Nov. 67	9.1	365	3.2	83	770
Dec. 67	___	325	3.2	87	785
Jan. 68	7.8	315	3.1	75	655
Feb. 68	___	328	3.2	69	700
March 68	8.8	332	3.2	77	703
April 68	___	277	3.3	60	625
May 68	10.8	344	3.3	64	620
June 68	___	382	3.0	81	860
July 68	7.0	354	3.2	73	780
Aug. 68	___	318	3.2	70	665
Sept. 68	___	360	3.0	74	680
Oct. 68	7.2	279	3.2	74	630
Nov. 68	7.6	247	3.2	78	660

a - March 1964 - August 1967
b - Number in parenthesis is standard deviation
c - Median value
d - Maximum value
e - Data collected by U. S. Bureau of Mines

Table V

Effectiveness of Mine Seal - Area 44

	Acidity (Hot) $CaCO_3$ mg/l	pH	Iron Total mg/l	Sulfate mg/l
Before Sealing[a] (Mean)	39	3.6[b]	1.1	214
Minimum	17	4.0[c]	0.3	160
After Sealing				
Oct. 67	20	3.9	0.3	230
Nov. 67	7	3.9	0.7	205
Dec. 67	40	4.0	0.6	207
Jan. 68	31	3.9	0.5	215
Feb. 68	28	3.9	0.3	215
March 68	20	4.2	1.5	140
April 68	8	4.7	0.5	81
May 68	12	5.2	0.2	120
June 68	0	5.2	2.5	156
July 68	21	4.2	0.8	180
Aug. 68	0	6.1	2.0	145
Sept. 68	17	6.4	0.9	160
Oct. 68	4	5.0	0.6	115
Nov. 68	0	5.8	0.7	96

a. Mean of 25 samples collected between March 1965 and November 1966
b. Median value
c. Maximum value

Table VI

Effect of Surface Mine Reclamation in Watershed RT 8F-1

	Acidity (Hot) $CaCO_3$ mg/l	pH	Iron Total mg/l	Sulfate mg/l
Before Reclamation (Mean)	199	3.0[a]	19	290
Minimum Value	73	3.4[b]	4	140
After Reclamation				
Oct. 67	107	3.4	28	220
Nov. 67	145	3.4	19	220
Dec. 67	921[c]	3.4	20	215
Jan. 68	38	4.8	6	78
Feb. 68	111	3.5	14	180
March 68	95	3.3	17	190
April 68	54	3.9	8	112
May 68	71	3.8	14	140
June 68	83	3.6	12	185
July 68	27	4.1	0.8	190
Aug. 68	135	3.5	13	175
Sept. 68	89	3.5	10	150
Oct. 68	55	3.7	8	155
Nov. 68	37	4.1	3	135

a. Median value
b. Maximum value
c. A flush of mine drainage from the deep mine occurred

Table VII
Effect of Surface Mine Reclamation in Watershed RT 9-2

	Acidity (Hot) $CaCO_3$ mg/l	pH	Iron Total mg/l	Sulfate mg/l
Before Reclamation (Mean)[c]	178	3.3[a]	5.2	313
Minimum Value	79	4.3[b]	1.9	48
After Reclamation				
Oct. 67	73	3.6	4.9	180
Nov. 67	68	3.6	5.4	175
Dec. 67	69	3.8	5.4	195
Jan. 68	74	3.7	3.2	220
Feb. 68	111	3.7	7.4	360
March 68	95	3.7	5.5	220
April 68	56	3.9	1.9	135
May 68	62	3.9	2.5	135
June 68	73	3.8	2.6	225
July 68	125	3.5	4.3	210
Aug. 68	105	3.5	3.4	220
Sept. 68	141	3.4	4.5	335
Oct. 68	74	3.6	4.1	240
Nov. 68	49	3.7	2.5	190

a. Median value
b. Maximum value
c. March 1964 to September 1967

Table VIII
Pollution Load from Area RT 9-2

	Flow cfs	Acidity (Hot) mg/l	Acid lbs/day	Rainfall Inches
Before Reclamation				
Oct. 65	0.226	241	293	1.43
Oct. 66	0.895	212	2,165	2.63
After Reclamation				
Oct. 67	0.67	73	263	3.33
Oct. 68	0.14	74	56	4.04

Table IX
Effect of Surface Mine Reclamation in Watershed RT 9-23

	Acidity (Hot) $CaCO_3$ mg/l	pH	Iron Total mg/l	Sulfate mg/l
Before Reclamation (Mean)[c]	178	3.3[a]	5.5	313
Minimum Value	79	4.5[b]	1.3	48
After Reclamation				
Oct. 67	40	4.1	1.5	47
Nov. 67	26	4.1	2.3	44
Dec. 67	34	4.0	5.0	62
Jan. 68	38	4.0	3.1	57
Feb. 68	43	4.0	3.4	54
March 68	49	4.0	4.7	68
April 68	25	4.1	1.2	36
May 68	22	4.3	1.1	57
June 68	35	4.0	0.7	37
July 68	116	3.6	6.6	190
Aug. 68	127	3.5	11.4	450
Sept. 68	446	3.2	15.9	340
Oct. 68	87	3.6	8.8	205
Nov. 68	44	3.9	2.9	119

a. Median value
b. Maximum value
c. March 1946 to September 1967

Table X
Pollution Load from Area RT 9-23

	Flow cfs	Acidity (Hot) $CaCO_3$ mg/l	Acid lbs/day	Rainfall Inches
Before Reclamation				
Oct. 64	0.7	191	720	2.00
Oct. 65	0.4	233	502	1.43
Oct. 66	4.7	87	2,203	2.63
After Reclamation				
Oct. 67	6.2	40	1,336	3.33
Oct. 68	1.22	87	572	4.04

are presented. The data show a small trend toward improvement of the water quality. The amount of improvement that can be expected at this site is limited by the underground discharges. Currently the deep mine discharges are contributing 70 to 80 percent of the acid. For example, on June 4, 1968, 4,320 pounds of the 6,278 pounds of acid per day flowing down Kittle Run originated at the two deep mine discharges.

Site RT 6-19. This site was chosen to measure the effect of reclamation on nine acres of surface mines. As shown in Table XIII, the runoff from this area has shown marked improvement since reclamation. Part of the increase in pH and decrease in acidity is due to the lime applied to the watershed as part of the revegetation program.

Table XI
Effect of Surface Mine Reclamation in Watershed RT 6-20

	Before Reclamation	First Eleven Months After Reclamation
pH (median)	2.7	2.9
Acidity, mg/l, $CaCO_3$	487	550
Total Iron, mg/l	91	130
Sulfate, mg/l	616	630

Table XII
Effect of Surface Mine Reclamation in Watershed RT 6-21

	Before Reclamation	First Eleven Months After Reclamation
pH (median)	2.5	2.8
Acidity, mg/l, $CaCO_3$	1,554	1,107
Total Iron, mg/l	328	310
Sulfate, mg/l	1,768	1,100
Flow, cfs	0.628	0.58

Table XIII
Effect of Surface Mine Reclamation in Watershed RT 6-19

	Before Reclamation	First Eleven Months After Reclamation
pH (Median)	2.8	6.4
Acidity, mg/l, $CaCO_3$	576	5
Total Iron, mg/l	107	0.04
Sulfate, mg/l	726	12

Summary - Surface Mine Reclamation. One year has past since the surface mine reclamation was completed and six months since these areas were revegetated. The water quality in each of the watersheds, which were polluted primarily from surface mines, has shown improvement. However, in all cases, but RT 6-19, the water is still of very poor quality and has not recovered its natural condition. It was expected that the improvement in water quality would be slow. Although every effort was made to place the best material available on the surface of the reclamation area, the soil still had a low pH, high acidity and acid producing material. It will probably require a number of years for the acid materials in the backfills to leach out; and during this period the stream will recover slowly. The good grass cover established on the backfills will prevent erosion and the exposure of more acid producing material, thus the rate of improvement in the streams should increase during the coming year.

In those areas polluted by both underground and surface mine drainage, pollution from the underground mines should constitute the greater portion of the pollution load as the rate of discharge from the surface mines diminishes.

Water Diversion. The most difficult control measure to evaluate has been water diversion. Following the completion of water diversion projects, the flow of the stream to which the water was diverted should increase while the volume of underground mine discharge should decrease. A number of factors complicate an analysis of this nature. First, in order to compare a "before" and "after" condition, the hydrologic situation must be somewhat similar during the times comparative data are taken; e.g., the rainfall and antecedent moisture conditions. Second, continuous flow measurements are also desirable for evaluation. Continuous flow monitoring was established at the mouths of Grassy Run and Roaring Creek for this purpose. However, since only half of the mine was reclaimed, these stations lost their value. Flow determinations were made at the remaining sampling stations only when samples were collected (once a week or every other week).

A preliminary evaluation of the runoff from the reclaimed areas indicated that the streamflow has increased and thus less water is entering the mine. For example, in one watershed, which contains 227 acres of reclaimed surface mines, the instantaneous flow at the mouth of the stream after reclamation has increased severalfold over the flow before reclamation for a similar precipitation occurrence. A culvert which carried this stream without problem before reclamation has flooded a number of times since reclamation. A detailed water balance is being developed for each of the watersheds, which should provide a better proof that an increase in flow has occurred.

Underground mine discharges do not reflect changes of inflow immediately. Dye studies have shown that water flowing in one end of the underground mine at Elkins may take several months before it discharges. Thus, to determine a reduction in discharge will require an analysis of both the surface and underground flow patterns. A preliminary review of the underground mine discharges data revealed that insufficient information was available to draw conclusions as to whether water diversion had decreased the flow. Further studies of the hydrology of the area are being conducted to determine lag times within the mines and develop a water budget.

SUMMARY

The Federal Water Pollution Control Administration in cooperation with other federal agencies and the State of West Virginia conducted a project to demonstrate the effectiveness of mine sealing, surface mine reclamation, and water diversion on the preventing of acid mine drainage from coal mines. This paper reports on the effectiveness of these control measures during the first year following the completion of the reclamation.

Improvement in water quality from mine sealing and surface mine reclamation was predicated to be a slow process, probably taking several years, due partly to the accumulation of pyrite oxidation products within the mine that must be flushed out.

Reclaimed surface mines must be stablized with vegetative cover.

After one year the following conclusions can be drawn:

(1) A small mine sealed against air shows a reduced oxygen content and the water discharging from the mine shows improvement; however, the water quality is still very poor. If the current trend continues water quality will continue to improve.

(2) Surface mine reclamation in those areas where the mine drainage was predominantly from this source has improved the water quality. The water quality is improving slowly and the trend is that it will continue to improve.

(3) Evaluation of water diversion as a control method is difficult. A preliminary analysis indicates that streamflow has increased in those areas where water was diverted from the underground mine to the stream. Further analyses are being made to verify this finding. Whether a reduction in underground mine discharges is occurring due to water diversion has not bees established.

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ABATEMENT OF POLLUTION FROM ABANDONED COAL MINES BY MEANS OF IN-SITU PRECIPITATION TECHNIQUES

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BACKGROUND OF PROJECT

Coal, as we all know, has been mined in Pennsylvania for decades, leaving many underground caverns into which ground water percolates and eventually flows out into the streams. This water during its course through the mine workings becomes acidic.

Today, more than 2,500 miles of Pennsylvania's streams are polluted by mine drainage from abandoned mines, estimated at close to one billion gallons per day (plus an additional estimated half-billion gallons per day from active mines).

Before 1963, little hope was held for a comprehensive solution to what was an ever-increasing problem. However, in 1963, the Pennsylvania Department of Mines and Mineral Industries launched an intensive research program to ascertain the extent of the problem and to develop economical methods for abating stream pollution from both active and abandoned coal mines. Studies were initiated to establish the mechanism of formation of acid mine water, and to investigate its treatment and control. Means were sought for preventing water from entering coal mines, by diverting water flow, backfilling mine voids, etc. Much progress has been made but much remains to be done.

In 1968, the Parsons-Jurden Corporation received a contract from the Department of Mines and Mineral Industries, Commonwealth of Pennsylvania, for the development and demonstration of the use of in-situ precipitation of sludge resulting from the reaction of acid mine water with low cost additives in an abandoned coal mine to prevent mine drainage pollution. The work is supported in part by the Federal Water Pollution Control Administration, U.S. Department of the Interior, through a grant to the Commonwealth of Pennsylvania under Title II, Section 6 (a) of the Federal Water Pollution Control Act, as amended by the Clean Water Restoration Act of 1966. The demonstration mine would be the Hastings Fuels Company Mine No. 1 in Cambria County, Pa. The work would proceed in two phases, first in the laboratory, then in the field at the selected mine.

EXISTING APPROACHES TO POLLUTION CONTROL

Acid water pollution from coal mines manifests itself in the form of a large drainage outflow consisting of sulfuric acid, dissolved iron, and other mineral impurities, similar in character to waste pickle liquor from the steel industry. The acid stream is generated by water contacting the mine workings in the presence of oxygen and reacting with pyrites contained in unexcavated pillars and other surfaces of the deep mines.

Numerous approaches have been taken for reducing this acid water pollution, among which have been:

1. Air sealing of the mines.

2. Flooding the mines by sealing the exits.

3. Neutralizing the acid outflow with alkaline materials.

4. Diversion of subsurface waters from mine entrances.

5. Injection to underground strata.

6. Chemical sealing of surfaces within the mine.

PARSONS-JURDEN APPROACH

The in-situ precipitation approach proposed by Parsons-Jurden offers benefits of lower cost and ease in use and should have wider applications to mines of varying geological features.

The in-situ precipitation concept consists of injecting water slurries of low cost alkaline reactants (such as limestone, lime, and fly ash) directly into acid water contained in the mine voids, through bore holes drilled from the surface. Numerous reactions occur during the neutralization of the acidity, resulting in precipitates. In addition, as the pH goes up, various mineral constituents in the water (notably iron) precipitate as a gelatinous, voluminous sludge. Our proposal postulated a bulking ratio of 30:1, that is the sludge resulting from injecting a ton of reactant into the mine water would occupy 30 times the volume occupied by the same ton injected into pure water. Subsequent laboratory work has indicated that bulking ratios as high as 150:1 can be achieved, although practical considerations indicate such large ratios have limitations.

In-situ precipitation, as a technique for elimination of pollution from abandoned coal mines, is of interest from three standpoints:

(1) Filling of mine voids, to restrict entry and passage of water thru the mine;

(2) Sealing drainage openings to restrict outflow from the mine; and

(3) Continuous neutralization of any effluent acid mine water.

Use of this concept for filling mine voids is based on forming "bulking-type precipitates" (as mentioned above), thus providing an economic advantage over simple backfilling on a one to one ratio. This concept is also useful from the standpoint of sealing drainage openings because the water-borne precipitates so formed seek out the flow points (being carried by the water flow) and plug them, an action similar to "blinding" a filter cloth. Finally, in-situ precipitation is expected to be an efficient, economical means for continuous neutralization of effluent mine waters, without the usual waste sludge disposal problems.

The feasibility and economics of continuous external neutralization of acid mine water drainage from active coal mines has been demonstrated. However, the problem of disposal of the resultant sludge remains. When applied to abandoned coal mines, the sludge does not present any problem. The sludge is formed in the mine voids and gradually settles to the lower portions of the mine. The mine provides an extensive retention basin for the sludge. When the mine eventually fills up with sludge, the continuous neutralization station is no longer needed as the pollution problem no longer exists.

PRESENT STATUS OF PROJECT

Shortly after the Commonwealth of Pennsylvania issued its contract to us to proceed with this project, an unforeseen obstacle developed: one of the landowners refused to sign a release permitting access to the Hastings mine. A second mine was then considered, located in the Prince Gallitzen State Park. However, the water flow at this mine was deemed to low to be useful for the demonstration. A third mine was

then considered, and presently is expected to be the demonstration site: the Driscoll No. 4 Mine at Vintondale. This mine was active until January 1967, at which time the pump and fan were removed. The mine has subsequently been filling with water. When the water level reaches 1405 ft., the water will flow out of the mine through the entrance, at an anticipated rate of one million gallons per day. As this paper is being prepared, the water level has reached approximately 1376 ft. It is anticipated that by the time this paper is delivered (April 1969), the water will be flowing from the mine.

LABORATORY INVESTIGATIONS

The laboratory phase of this project is designed to serve two functions: first to develop data for laboratory confirmation that the in-situ precipitation concept can achieve what is expected of it; and second, to establish what materials and methods will be used at the demonstration mine. Because of problems in selecting the mine to be used for the field demonstration, the laboratory to date has been limited to developing data of a general nature. A synthetic acid mine water, consisting of ferrous sulfate, aluminum sulfate and sulfuric acid, was used to evaluate various types of materials rather than specific candidate materials. Laboratory tests were devised to determine the bulking ratios for precipitates produced, sealing properties (and conditions necessary for such sealing) of precipitates, and effectiveness of continuous neutralization of effluent mine water.

To determine the bulking ratio for a given reactant, a water slurry of the reactant was added to synthetic acid mine water at a specified ratio. The resultant mixture was allowed to stand for 18 hours at which time the volume of the precipitate was noted and compared to the volume obtained in pure water; pH was also measured. As previously noted, bulking ratios as high as 150:1 were achieved.

To evaluate the sealing properties of the precipitates, a glass tube 2 inches in diameter and 4 feet long was used to simulate a mine adit. The tube was placed in a "horizontal" position, with a 1% slope towards the effluent end. A wire gauze, backed up by a layer of coarse sand and one of fine sand was placed at the effluent end to simulate a rubble obstruction. Acid mine water was supplied to the tube at a controlled rate to simulate the flow of mine water in the adit. A water slurry of reactant material was injected, through a vertical side tube located a short distance behind the sand layers, at a controlled rate to maintain a fixed ratio of mine water to slurry. Reduction in flow rate, and pH of effluent was measured over an extended period of time. In most cases, the flow rate was reduced significantly, and in some cases stopped completely; pH of effluent was raised to acceptable levels, and could be brought up to the range of 12-13 without any difficulty (initial pH was 3).

To study the continuous neutralization of acid mine water, the "horizontal" tube set-up was used except that the tube now sloped away from the effluent end. Under these conditions, the precipitate formed rolled back down the tube to accumulate at the lower end. The pH of the water could be raised to and maintained at any desired level.

When the demonstration mine is finally selected, specific laboratory tests will be performed based on the actual mine water and on economically attractive, locally available alkaline reactants. Shortly thereafter, the actual field demonstration will be undertaken.

CURRENT CONCLUSIONS

At this time, it is too early to draw any definite conclusions as the actual demonstration has not started, but from the preliminary results of the laboratory investigations, we are extremely optimistic concerning a successful demonstration. It is also felt that after the completion of the program, we will be able to demonstrate the economic soundness of using this method of preventing stream contamination from most abandoned mines and some operating mines, utilizing the in-situ precipitation techniques. However, each individual mine must be evaluated to determine which one or more of the three results is the most economic, i.e.:

(1) filling of mine voids,

(2) sealing drainage openings,

(3) continuous neutralization of mine water.

ACKNOWLEDGMENT

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The laboratory work has been performed by G. & W. H. Corson, Inc. under subcontract to Parsons-Jurden Corporation.

CHEMICAL PROPERTIES OF TOXIC STRIP-MINE SPOIL BANKS IN PENNSYLVANIA

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Strip mining is a relatively safe and efficient method of mining bituminous coal. Nevertheless, many problems are created when the overburden is removed to get at the coal. The stripped area may be subject to runoff and erosion if not backfilled properly and revegetated. In addition to the silt from eroded areas, chemical substances leached from the spoil banks may further pollute the streams.

In 1945, the Pennsylvania Legislature passed the Conservation Act, which required reclamation of stripped areas. With consequent amendments the act now states that all stripped areas must be backfilled, graded, planted, and inspected by a Land Reclamation Board. For most of the strip-mined areas, revegetation has been satisfactory. Decades of research and experience have resulted in improved planting practices and the selection of the best performing species (Research Committee 1965). Yet, there are a substantial number of strip-mined areas which cannot be revegetated successfully by present methods. These spoils are characterized by being highly acid. However, it is possible that the revegetation failures are a result of toxic substances or lack of essential nutrients rather than acidity per se. For example, aluminum and manganese become soluble under conditions of high acidity and could possibly reach toxic concentrations (Berg 1965).

There have been few reports on either the actual chemical concentrations or the concentrations which limit plant growth on the highly acid spoils. Therefore, selected toxic spoils were analyzed to provide basic information for subsequent plant growth studies.

In Pennsylvania, four major coal seams, the Lower Kittanning, Middle Kittanning, Clarion, and Brookville, produce the most troublesome spoils. All are generally highly acid although there may be considerable variation in conditions from one area to another within the same bank. From each of these spoils five samples were collected from the surface layers of typically toxic portions. Five samples were also collected from a non-toxic spoil on the Lower Freeport coal seam. Since only one bank from each seam was sampled, no estimate of the variation between banks within the individual seams could be made. Each of the spoil samples was analyzed for pH, soil texture class, lime requirement, nitrogen, phosphorus, soluble salts, and exchangeable calcium, magnesium, potassium, iron, manganese, and aluminum. Since we were interested in the spoils primarily as a plant growth medium, agronomical analyses were made.

Among the first analyses made were pH determinations, since the majority of revegetation failures occur on spoils with a pH value below 4.0 (Wheeler 1965) and the availability of ions to plants in the soil is profoundly affected by the hydrogen ion concentration. The pH's were measured using a glass electrode pH meter with a 1:1 soil:water ratio (Jackson 1958). According to this technique, the pH values of most soils lie in the range between pH 4.0 and pH 8.5. The pH's of the toxic spoils were all well below pH 4.0 -- Brookville 3.3, Lower Kittanning 3.1, Middle Kittanning 2.9, and Clarion 3.1. In contrast, the non-toxic Lower Freeport spoil had a pH value of 5.2.

Also of major importance in soil chemistry are the exchange properties of soils which are dependent on the nature of the soil colloids. Since clay soils possess high surface areas per unit volume, they have higher cation exchange capacities (Slabaugh 1952) as well as different physical properties than those of coarse-textured soils. Hence, a mechanical analysis was made of the spoil material.

The material was first dry-sieved to determine the percentage by weight of soil-size particles (diam < 2mm). The percentages were as follows: Lower Freeport, 55; Brookville, 66; Lower Kittanning, 65; Middle Kittanning, 54; and Clarion, 55. Using the hydrometer method of separation (Bouyoucos 1928), the soil was fractionated into various groups of separates, and a textural designation based on the relative distribution of the soil separates was determined (Table 1). On the spoils studied, texture is evidently not a limiting factor since at least half the particles were of soil size and had a particle distribution in a loam class.

Table 1. Mechanical analyses of selected strip-mine spoils in Pennsylvania.

Seam	Sand	Silt	Clay	Texture Class
	percent	percent	percent	
Brookville	50	25	25	Sandy clay loam
Lower Kittanning	46	28	26	Loam
Middle Kittanning	33	32	35	Clay loam
Clarion	30	29	41	Clay loam
Lower Freeport	32	42	26	Loam

Both clay content and pH influence the cation exchange capacity (CEC) of the soil. This term refers to the capacity of a soil to absorb and hold the cationic nutrient elements that are used by plants. More precisely, it is a measure of the total quantity of negative charges per unit weight of soil and is equal to the sum of the exchangeable hydrogen and the exchangeable bases. The measured CEC varies somewhat according to the nature of the cation employed, the concentration of the salt, and the equilibrium pH. Hence it is not a highly exact but rather an equilibrium measurement under chosen conditions.

Exchangeable hydrogen was determined according to the method of Woodruff (1947) employing a buffered solution and glass electrode. The exchangeable bases were leached from the sample materials according to the method of McLean et al. (1965), and their concentrations were determined by atomic absorption spectroscopy. The results are presented as milliequivalents per 100 grams of soil in Table 2 and parts per million in Table 3.

Table 2. Exchangeable concentrations of cations and CEC in milliequivalents per 100 grams of soil on selected strip-mine spoils of Pennsylvania.

Cation	Brookville	Lower Kittanning	Middle Kittanning	Clarion	Lower Freeport
	me/100g	me/100g	me/100g	me/100g	me/100g
Ca	0.51	0.20	0.22	0.28	3.20
Mg	1.06	0.42	0.53	0.47	1.12
K	0.51	0.39	0.44	0.38	0.35
Fe	0.13	0.10	0.26	0.25	0.09
Mn	0.05	0.01	0.01	0.02	0.21
Al	1.00	1.60	2.01	2.18	0.05
H	12.00	16.00	16.00	16.00	6.00
CEC	15.26	18.72	19.47	19.58	11.02

Table 3. Exchangeable concentrations of cations in parts per million on selected strip-mine spoils of Pennsylvania.

Cation	Brookville	Lower Kittanning	Middle Kittanning	Clarion	Lower Freeport
	ppm	ppm	ppm	ppm	ppm
Ca	102	41	44	56	640
Mg	126	50	64	56	135
K	199	154	172	149	136
Fe	37	28	72	71	26
Mn	13	2	2	4	58
Al	90	144	186	197	5
H	120	160	160	160	60

A comparison of the spoils reveals that the toxic spoils as a group differed from the non-toxic spoil in the cation exchange capacity and in the concentrations of hydrogen, calcium, manganese, and aluminum. Although the four toxic spoils had higher exchange capacities than the non-toxic spoil, this was mainly a result of their much higher hydrogen concentrations. The essential nutrient calcium was very low on the toxic spoils in comparison to the non-toxic spoil. Since the potentially toxic manganese was considerably higher on the non-toxic spoil, it could be eliminated as a potential cause of the toxicity on the other spoils. However, another potentially toxic element, aluminum, was considerably higher on all of the toxic spoils. On three of the spoils, Lower Kittanning, Middle Kittanning, and Clarion, the low concentrations of magnesium could contribute to the revegetation failures. Neither potassium nor iron differ sufficiently among the spoils to be probable limiting factors.

Because of the high concentration of hydrogen ions and the low calcium content, the lime requirements of the toxic spoils are quite high. Based on the Woodruff (1947) method, it would take 6 tons of lime per acre on the Brookville, 8 tons on the Lower Kittanning, 8 tons on the Middle Kittanning, and 8 tons on the Clarion to neutralize the exchangeable hydrogen.

Concentrations of two additional essential growth elements, nitrogen and phosphorus, were also quite low on the toxic spoils (Table 4). Total nitrogen was determined by the Kjeldahl method (Bremner 1960), and phosphorus, by the extraction method developed by Bray and Kurtz (1945). Although the concentration of nitrogen on the Lower Freeport spoil exceeded that of the toxic spoils by an order of magnitude, it is still low in comparison to average cultivated soils.

The soluble salt content was determined by measuring the electrical conductivity with a Solu Bridge (Beckman Instruments Inc. 1967). As used in soils, this term refers to the inorganic constituents that are appreciably soluble in water. A well fertilized field soil optimum for plant growth would be between 1.0 and 2.0 millimhos/cm. The soluble salt content was thus quite low for all the spoils including the non-toxic Lower Freeport (Table 4).

Based upon the results of these analyses, it seems likely that the chemical properties of the spoil banks associated with the Brookville, Lower Kittanning, Middle Kittanning, and Clarion coal seams in Pennsylvania contribute to the revegetation failures. The two chemical properties which seem to be most serious are the low pH's and the high concentrations of exchangeable aluminum. We are currently conducting studies designed to evaluate the effects of various combinations of pH and aluminum concentration on the growth of selected species. The low concentrations of the essential nutrients, calcium,

nitrogen, phosphorus, and magnesium, suggest the possibility of improving growing conditions through liming and fertilizing.

Table 4. Total nitrogen, extractable phosphorus, and soluble salt content on selected mine spoils of Pennsylvania.

Seam	Nitrogen	Phosphorus	Soluble Salt
	percent	ppm	millimhos/cm
Brookville	0.003	3	0.36
Lower Kittanning	0.004	1	0.26
Middle Kittanning	0.002	6	0.53
Clarion	0.009	5	0.11
Lower Freeport	0.070	25	0.20

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EXPERIENCE IN OPERATING AN EXPERIMENTAL ACID MINE DRAINAGE TREATMENT PLANT*

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In 1967, the staff of the School of Mines designed and supervised the construction of an acid mine drainage treatment plant making use of lime slurry as a neutralizing agent for a plant size study of neutralization of acid mine water. This plant was constructed to handle at least 200 gallons of water per minute containing around 500 parts per million of iron, mostly in the ferrous state, and having a pH of approximately 5 with acidity running around 1,000 parts per million on the calcium carbonate equivalent basis. A description of the plant will not be given because it was described in a recent publication.[1] At the present time, we have a range of four mines that we can use for experimental purposes. The approximate analyses of the waters from these is shown in Table 1.

TABLE 1
ANALYSES OF ACID WATERS FROM MINES 1, 2, 3, and 4

Mine No.	Field pH	Iron Total	Iron Ferrous	Aluminum	Calcium	Magagese	Acidity*	Sludge Value**	Total Solids
1	3.14	912	783	116	259	69	2400	330	7951
2	4.64	573	545	36	331	60	1022	166	6014
3	2.40	2648	1096	580			6500	510	18890
4	2.85	602	242	69			1746	236	8164

* Calcium Carbonate Equivalent
** Milliliters of sludge per liter of water tested

Extreme distances between the wells is about one mile, but no well is much more than about one-half mile from the treatment plant.

The plant, shown in Figure 1, is located on the side of a hill about 180 feet above the floor of the valley. It was orginally intended to place the plant in the valley but the movement of ground water through the low-lying level lands offered a problem in that we would not know whether our treatment was effecting a change made in the water or whether it was due to the ground water. This site on the side of a hill eliminated this problem, but it did raise a problem of raising water from the bottom of the valley to the elevation of the plant which would not exist in most acid treatment plants.

In this plant, which was manually operated, the following operations were carried out.

1) It prepared a lime slurry to be used for neutralization. This slurry was usually prepared at a concentration of one pound of lime per gallon of water. This seemed to work very well and did not require excessive amounts of slurry to be used in the treatment process.

2) It was arranged to feed the slurry into the feed water at a rate that would effect neutralization and raise it to a pH of about 10. This high pH was made necessary by the ferrous iron in the water. As our neutralization curves indicated, such iron would not come out completely until the pH water was raised to about 10.

3) The treated water was passed through an aeration plant which was designed to handle about 200 gallons of water per minute to convert the ferrous iron to ferric iron and to reduce the pH to a value acceptable by the water laws of West Virginia.

1. Holland, C. T., Corsaro, J. L., Ladish, D. J., Factors in the Design of an Acid Mine Drainage Treatment Plant, Second Symposium on Coal Mine Drainage Research, 1968, Coal Industry Advisory Committee to the Ohio Valley Water Sanitation Comm.

* This project is sponsored by the Northern West Virginia and West Virginia Coal Associations and their associates by a grant that has exceeded $200,000 at this writing.

4) Following this operation the water was passed through a settling basin holding about 300,000 gallons which allowed the iron, both ferrous and ferric, aluminum, as well as the calcium sulfate formed to precipitate, and the clear water to flow into the streams of the state. The ponds were large enough to accommodate the accumulation of sludge for two days to four or five days operation depending upon the concentration of iron and acid.

5) By means of a diaphragm slurry pump this sludge was pumped from the receiving basins into a sludge storage basin.

6) Here arrangements were made to decant the water from the sludge as it separated and to expose as large an area as was possible to the atmosphere to encourage evaporation. The sludge pond was also constructed with the thought in mind that some water would seep through the walls of the earth-filled basin and aid in concentrating the sludge. As it will be noted later on in the paper, this sludge disposal basin did a very good job of concentrating the sludge and removing the water at the rate at which we operated.

OPERATION

The plant treated different waters in periods. From April 1 until December 16, it operated on water from mine No. 1. The operating rate was 16 hours per day five days per week with the time from August 21 until October 4 non-operative because of a breakdown in the deep well mine pump.

From December 18, 1967 to February 19, 1968, we were in the process of laying a pipeline between the plant and mine No. 2. The operation was delayed because of the severity of the weather.

From February 19 to August 12, we operated 16 hours per day five days per week on water from mine No. 2 with the exception of a week out from April 3 to April 10, because of a failure of the deep well pump at mine No. 2.

From August 12, 1968 to September 20, 1968, we operated on water from mine No. 2, No. 3, and No. 4 mixed. Again the operating time was 16 hours per day five days per week but considerable time was lost due to sulfation preventing operations in the plant.

From September 20, 1968 to October 20, 1968, we operated on mine waters from mine No. 3 and No. 4. Again considerable time was lost during this period because of sulfation difficulties.

The flow sheet of the plant is shown in Figure 2.

OPERATING RESULTS MAKING SLURRY

Our apparatus for making slurry proved to be quite acceptable. No trouble of any kind has occurred with this apparatus other than the normal amount of attention to keeping the apparatus securely fastened to the mixing tank and items of a like nature. Only one shut-down in nearly two years of operation was occasioned by this apparatus and this was the fault of the operator.

SLURRY FEED APPARATUS

Throughout the experiments, the slurry feed apparatus consisted of some kind of a constant or very nearly constant head arrangement. The one shown in the flow diagram (Fig. 1) is typical. Considerable trouble consisted of stoppage of the valves, stoppage of the pipe, and stoppage of the pump so as to refuse to operate. Lime slurry seems to have this property, of forming solids in pipes, valves, and pumps, and it is suggested that this apparatus be installed in duplicate so that one feeder can be repaired while the other operates.

TRANSPORTATION OF TREATED ACID MINE WATER TO AERATOR AND SETTLING BASINS

This part of the plant gave us considerable trouble also. At first we had a four-inch PVC* pipe through which we forced this water after adding the lime. This pipe became clogged rather quickly and was a constant source of trouble. Then we built a one-foot square wooden flume with sufficient slope to carry this material to the aerator. This proved to be an improvement over the pipe because it could be cleaned regularly every day. However, this flume has been the source of some trouble when treating strongly mineralized water, because of deposited material in the flume.

AERATION EQUIPMENT

The aeration equipment has proved to be one of the most difficult parts of the plant to keep in operation. This was because the treated mine water contains calcium sulfate usually in supersaturated solution as well as, in our particular waters, usually a large quantity of ferrous and ferric hydroxide, and some aluminum. Some four types of air dispersal equipment were used trying to overcome this difficulty. Type 1 consisted of a special type aerator devised for treatment of metallic ores. This one did not supply sufficient aeration. The second type of air dispersal equipment used was a ceramic pad, somewhat similar to that used by chemists for aeration in laboratories but on a much larger scale. This unit gave fine dispersal of the air and worked fairly well on water from mine No. 2, which was lower in acid and iron. When applied to a mixture of water from mines No. 2, No. 3, and No. 4, however, it was a complete failure. It was almost impossible to keep the pads operating. Type 3 dispersal unit was a home-made job that was made by drilling 3/64" holes in 2" PVC pipe and arranging this at the bottom of the aerator. This worked very well for a few days but shortly stopped up when water from mine No. 2, No. 3, and No. 4 were mixed and passed through the aerator. The best results were obtained by using an air dispersion device which consisted of a PVC tube that introduced the air inside of knitted socks.** This device comes in two lengths, one some two feet long and one about eight inches long, both worked very well. In water from mine No. 2, little trouble was experienced in this type of air dispersal unit. However in water from mines No. 2, No. 3, and No. 4 mixed, and No. 3 and No. 4 mixed, arrangements had to be made to clean these socks once every day. Consequently when using them, they should be purchased in duplicate sets. In general, we are not satisfied completely with any of the air dispersion units we have used. We did not try a surface aeration unit in our settling ponds because the ponds were comparatively shallow and did not have concrete bottoms; and we thought that the mud kicked up by this device would more than off-set its advantages.

The air to this plant is supplied by two blowers developing a pressure of 1 pound per square inch and rated 300 CFM.* These blowers are placed in series so they develop 2 pounds per square inch and deliver up to 475 CFM. These aeration units have two sections and in each section are 14 air dispersion units. The results obtained from the unit as a whole are shown in Figure 3. The unit in operation is shown in Figure 4.

Operating between the flume from the treatment plant and the aerator tank is a 200 GPM* centrifugal pump working against a 10 foot head. This pump works well in low-sulfate water but when the water begins to approach the saturation point with calcium sulfate, the impellers and eye of the pump became clogged with deposited sulfate. This has proved to be very troublesome, and it seems best to advise that such a unit be installed in duplicate so that plant operations may continue while repairs are being made to one pump.

SETTLING BASINS

The settling basins (shown in Fig. 1) are about 220 feet long and have a cross section area of about 150 square feet. Even though we at times, overloaded the design by a factor of 3, they have worked well. Two ways of removal of sludge from the basin were tried, continuous operation and cyclical operation. Both proved to be possible and satisfactory, but for our particular case the alternate use of basins and pumping them out cyclically seemed to give the better results.

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*Poly Vinyl Chloride (PVC) Cubic Feet Per Minute (CFM) Gallon Per Minute (GPM)
** Made of nylon

SLUDGE PUMP AND PIPING UNIT

This unit which removed the dilute sludge from the settling basins and deposited it in the sludge storage basin worked very well indeed, as throughout the work done at the plant, little trouble has been encountered. It is necessary to have a surge tank on both the suction and discharge of this sludge pump, which was a diaphragm type pump. If these are not there, it is difficult to prevent a great deal of vibration and considerable water hammer in the lines. No trouble was experienced with sulfation* with any part of this piece of equipment.

SLUDGE DISPOSAL BASIN

This basin, shown in Figure 1, proved to be adequate and it has performed better than expected throughout the operation of the plant. Troubles experienced here consisted principally of the water decantation system becoming clogged with sludge primarily, we believe, because of the amount of calcium sulfate that was carried into the sludge basin. This again acted to clog up the pipes and prevent as efficient decantation as we would have liked to have had.

WATER QUALITY OBTAINED

In Table II and III, we have presented analyses of the raw water fed to the plant and of the treated water flowing from the plant. It will be noted, we have presented two values for the water fed to the plant.

1) The average value of all the water fed.
2) An approximate one-week run showing the variation and results achieved during one representative week. In the overflow, we have presented the analyses for the treated water during the one-week sample run.

It will be noted, in the case of waters treated from mine No. 1 and No. 2, that results have been quite good and that we have, in general, kept the iron in the overflow water less than 5 parts per million, and in some cases even less than 1 part per million. This is only accomplished, however, by raising the pH to a value lying between 9.5 to 10.5 depending on the water. In the mixed waters from mines No. 3 and No. 4, and No. 2, No. 3, and No. 4 due to difficulties from sulfation and some trouble with the slurry feed apparatus, we were not able to maintain the pH at the value we would have liked to have had. It will be noted in these cases the iron in the effluent water has been quite high, although in the case of the mixture from mines No. 3 and No. 4, we have been able to keep it fairly close to the state limits. In the effluent water from mines No. 2, No. 3, and No. 4, we have not been able to do this quite so well. This is because we had not learned to cope quite so well with the effects of sulfation.

When the water was treated all of the water discharged was comparatively high in calcium which means that the water will be a hard water. In mine No. 2, the water discharged contains more total solids than did the water entering the plant. In the case of mines No. 1, and the mixture from mines No. 2, No. 3, and No. 4, and from mines No. 3 and No. 4, we have been able to appreciably lower the total solids in the water. Such total solids are not included in the standards of the state so this, at present, is not really a serious difficulty.

Not much tasting of the water fed to the plant was done by anyone, but it can be said, in general, the taste of the water, to put it mildly, was unsatisfactory. The treatment process greatly improved the taste, although even with the treatment which we have in this plant, the taste of the effluent water is not particularly desirable.

These results indicate that with high acid waters, treatment is going to be more difficult than with more amendable water and sulfation is going to pose some real serious problems.

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* Deposits of calcium sulfate mixed with iron hydroxide from the treated water

Table II
Operating Results of the
Acid Mine Drainage Treatment Plant
Water Quality

Feed Water

pH Lab	pH Field	Total Iron	Ferrous Iron	Aluminum	Calcium	Magnesium	Acidity	Sludge Volume	Solids Total	Solids Susp.
					Mine No. 1					
					Average of Complete Test					
3.14	3.63	912	783	116	259	69	2400	330	7951	
					Week Sample					
3.45	3.6	882	762	137			2160	280	7838	
3.35	3.55	900	787	144			2080	420	7937	
3.25	3.	870	782	98	312	22	2120	300	7715	
3.4	3.50	877	778	116			2060	340	8005	
3.2	3.3	346	391	151			2090	290	7522	
3.30	3.45	907	760	NLA	276	138	2110	380	7753	
					Mine No. 2					
					Average of Complete Test					
4.64	5.43	573	545	36	331	60	1022	166	6014	
					Week Sample					
5.00	6.00	578	546	35			1000	130	4858	
5.60	5.8	594	550	13			995	100	4780	
4.58	5.35	574	542	39			960	130	4930	
4.92	6.0	570	530	42			990	160	4890	
					Mines Nos. 2, 3, & 4					
					Average of Complete Test					
2.64	2.78	1372	831	270	110	37	3706	1398	10400	
					Week Sample					
2.52	3	1964	982	414			2790	536	13954	
2.53	3	1443	773	250			2278	464	10453	
2.55	3	1470	973	295	152	46	2155	270	10532	
2.59	2.9	1475	979	216			2109	456	9848	
2.72	3.25	1065	563	179			3027	272	9410	
					Mines 3 & 4					
					Average of Complete Test					
2.55	2.00	1925	1147	434	161	33.8	6473	490	15138	
					Week Sample					
2.53	2+	2040	1309	444			7406	546	16201	
2.61	2+	1572	908	333			5381	396	13539	
2.61	2+	1973	1282	475			7180	472	14582	
2.52	2+	1964	1198	450			7242	506	16164	
2.55	2+	1931	1248	452			7168	512	14182	
2.56	2+	1897	1206	435			7076	476	14996	
2.53	2-	1862	1025	456	165	46	7172	472	15427	
2.54	2+	1979	1301	451	174	4	7343	406	15372	

Table III
Operating Results of the
Acid Mine Drainage Treatment Plant
Water Quality

Treated Water

pH Lab	pH Field	Total Iron	Ferrous Iron	Alum-inum	Calcium	Magnes-ium	Acidity	Sludge Volume	Solids Total	Solids Susp.
					Mine No. 1 Week Sample					
9.80	10.7	5	Nil	35	576	83			4265	772
9.50	10.05	5	Nil	15					4000	607
9.90	10.85	2	Nil	17	504	70			3970	485
9.4	10.05	3	Nil	12					4450	101.5
10.5	11	5	Nil	8					3741	585
					Mine No. 2 Week Sample					
8.00	7.95	2	Nil	20	760	83			4193	150
8.68	9.0	4	Nil	19					4278	140
8.50	8.0	1	Nil	20					4360	180
8.22	8.5	3	Nil	26					4292	141
8.05	7.75	2	Nil	26	744	112			4587	88
6.30	6.65	20	Nil	22					4400	132
6.70	7.6	6	Nil	23					4253	60
					Mines 1, 2, & 3 Week Sample					
7.93	7.9	13.7	Nil	.82					4107	392
7.99	7.5	10.8	Nil	.83	692	135			4372	237
5.51	6.85	19.9	5.3	1.06					5059	3502
10.01	9.9	16.1	Nil	.51	746	99			13,921	1827
7.81		4.7	Nil	.68					4460	879
					Mines 3 & 4 Week Sample					
11.15	11+	Nil	Nil	7.4					5764	119
8.41	7-	35.1	21.5	3.02	972	111			5935	1753
11.13	9+	5.8	Nil	20.1	912	113			5087	737
10.28	7+	1.3	Nil	36					5898	296
8.29	6+	4.7	Nil	25.4	854	24			5368	1988
10.28	11	3.6	Nil	15.9	690	34			5419	155

HARDNESS

It will be observed in Table III, that the hardness of the treated water from mine No. 2 is quite high. As an experiment, it was decided to treat this water with sodium carbonate to reduce this hardness to some acceptable value. Consequently, a plant was designed that would treat 10 gallons of water per minute and feed the sodium carbonate in the required amounts automatically. The plant is shown in Figure 5. Both the inflow water and the sodium carbonate are arranged to operate under a constant head, through a fixed orifice. The results of this experiment are shown in Table IV. It will be noted that the calcium hardness was well taken care of by the sodium carbonate. The sodium carbonate method of neutralizing hardness, however, has some serious disadvantages. One is with high concentrations of calcium sulfate in the water to be removed by the sodium carbonate as in this case, it

leaves the water with a strong saline taste. This would be more undesirable than would the hardness. The cost of the sodium carbonate to correct this hardness is 41 cents per thousand gallons of water treated. The total cost of the treatment, including cost of plant, labor, electricity, etc., for correction of hardness would easily run twice this amount. A final disadvantage is it discharges the water at too high a pH to conform to the water laws of West Virginia.

Table IV
Results of Treating Water From Mine 2
From Treatment Plant With Sodium Carbonate
To Reduce Hardness

pH Lab	pH Field	Total Iron	Ferrous Iron	Aluminum	Calcium	Magnesium	Solids Total	Solids Susp.
			Feed Water From Acid Treatment Plant					
7.32	7.5	4	Nil	8			4616	26
8.10	8.5	2	Nil	20			4446	20
8.49		1	Nil	10	320	97	2814	315
7.70	8.4	1	Nil	15			4265	40
7.35	7.6	1	Nil	7			4336	65
			Overflow Water From Hardness Treatment Plant					
8.00	8.15	1	Nil		24	49	3870	170
9.30	9.3	1	Nil		Nil	50	4112	12
9.95	9.6	1	Nil		Nil	58	4480	121
10.20	9.85	1	Nil		Nil	52	4750	115
10.22	10.15	1	Nil		Nil	58	4886	83
10.15	10.85	2	Nil		Nil	58	4737	70
9.80	10.4	1	Nil		Nil	58	4374	58
8.30	8.65	2	Nil		80	117	3980	

SLUDGE FORMED

The cost of disposing of the sludge when treating acid mine drainage has always been a bug-a-boo. The results of our experimentation insofar as formation of sludge is concerned is shown in Table V. It will be noted in this table, that insofar as the formation of sludge is concerned, large quantities are formed in the settling basin. It will also be noted that even by as simple a process as letting it evaporate and decant the clear water from the sludge storing basin, a very good job has been done of reducing the large volume of sludge to a rather small one.

It will be noted that insofar as total volume of water treated is concerned that as of October 20, 1968, only 2 per cent of it remained in the storage basin as sludge; and of the sludge estimated to have been deposited in the settling basin that only 7 per cent remains in the storage basin.

In connection with this though, it should be remembered that our plant has not been continuously operated, in that it is operated only five days per week and 16 hours per day; and there have been periods that it did not operate at all during the nearly two years the study has been going along. Our best estimate of the capacity of this sludge basin to concentrate sludge is, that if we had operated 24 hours a day, 365 days a year, we could have handled about 200,000 gallons per 24 hour day of water containing around 2500 parts per million acid, and 900 parts per million iron. With this type of feed water, the sludge remaining in the pond at the end of the year, we estimate, would not be more than 3 per cent of the water pumped.

When treating water such as existed in mine No. 2, we could have handled possibly three times this much water, but had we been treating water such as that water from mines No. 3 and No. 4 when mixed, the amount of water treated would probably have to be reduced by one third.

TABLE V
OPERATING DATA PERTAINING TO SLUDGE OPERATING DATA

Period	Water Treated		Estimated Volume of Sludge Pumped from Settling Basins	Sludge Remaining in Sludge Storage			Total Sludge in Pond as Overall Percentage	
	Average Total Acidity	Gallons Pumped		Gals.	Percent of Sludge Pumped	Water Treated	Sludge Pumped	Water Pumped
Apr. 1 to Dec. 18, '67	2399	21,801,000	7,200,000	596,000	8.3	2.7	8.3	2.7
Feb. 19 '68 to Aug. 12 '68	1022	11,628,000	1,850,000	24,000	1.3	.12	6.4	1.9
Aug. 12 '68 to Sept. 20 '68	3707	3,160,000	1,140,000	20,000	1.8	0.6	6.9	1.7
Sept. 20 '68 to Oct. 20 '68	6473	2,319,000	1,140,000	191,000	16.6	8.3	7.0	2.0

TABLE VI
SLUDGE ANALYSIS AT VARIOUS DATES

Date	Total Iron	Ferrous Iron	Alum-inum	Cal-cium	Magne-esium	Carb-onate	Sul-fate	Water of Hydra-tion	Insol-uable	Spec. Gravity	Total Solids
	Percentages of										
6- 6-67	23.1		2.3	15.5	19.4					1.34	14.3
9-19-67	14.7		1.7	10.4	2.1				2.8	1.37	20.3
10- 2-67	19.0		1.8	12.2	2.7				.5	1.22	16.8
2- 6-68	27.4	Nil	7.7	12.1	.2	3.9	29.4	19.6	.5	1.10	13.9
7-25-68	28.3	Nil	8.5	12.9	3.8	2.1	27.1	17.7	.2	1.09	20.5
11-13-68	26.9	Nil	8.0	9.9	.4	6.1	30.3	18.6	.6	1.09	11.1

LIME REQUIRED

Careful records were kept of the lime required as we went along with our program. These records were compared with the weights of lime, and the theoretical amount of lime required to neutralize the acid. The agreements are close in all cases. It will be noted by consulting Table VII that the amount of lime required to treat water in thousand gallon units and per part per million of acid in the water vary somewhat. This is due to several causes. (1) In the case of the water treated from mine No. 2, No. 3, and No. 4 a slight insufficiency in lime existed. This same is also true to a lesser extent in the case of the mixed water from mines No. 3 and No. 4. Other factors that entered were the (2) presence of bicarbonates and (3) dissolved CO_2.

TABLE VII

LIME REQUIRED FOR TREATING WATER AND COST AT $24/TON

Period	Water Treated In 1000 Gal. Units Treated	Lbs. of Lime Used Per 1000 Gal.	Lbs. of Lime/ 1000 Gal. Per Part Per Million of Acid in Water	Cost of Lime in Cents per 1000 Gals. per part per Million of Acid With Lime at $24 per ton
Apr.1-Dec.18,1967	21800	14.8	.0063	.0076
Feb.19-Aug.12,1968	11628	8.4	.0081	.0098
Aug.12-Sept.10,1968	3160	19.7	.0053	.0064
Sept.12-Oct.16,1968	2319	40.7	.0063	.0076
		Average	.0065	.008

ECONOMICS

Operating this plant has given us some insight into the economics of acid mine drainage treatment by lime neutralization. Three questions here are paramount; namely, what will it cost and how much and what kind of land will be required on which to build a plant.

Costs of treatment are difficult to estimate. This is true because the cost of lime varies with the location of the treatment plant with respect to the nearest lime producer. Also, costs of labor vary from one section to another. The costs of construction also vary with location and type of excavation required. Also, as shown in Table VII, some differences exist among mine waters in the amount of lime required for neutralization. So the costs given are based on our experience, and here the cost of the land for the plant was low. We allowed about $200 per acre and we had no hard rock excavation to do. Therefore our figures cannot be blindly applied, but we believe they give us some indication of costs. Our estimates for the cost of treating acid mine water are shown in Table VIII. It will be noted that the cost will be substantial, and it increases as the acidity of the water increases.

Our experience indicates that the sludge production will not be as large as at first feared; but it is still substantial. If it has to be stored in surface disposal units, then in a few years considerable areas of surface, in mine areas afflected by acid mine drainage, are going to be covered by sludge.

Also, it will be noted that where strongly acid water or if large quantities of acid water of less strength are to be treated, substantial areas for plant construction and sludge disposal will be required. In some areas of the coal fields, land of the nature required and acreage are scarce.

The lesson seems to be plain that the treatment of acid mine wastes will not be easily and economically achieved by lime neutralization, nor in most cases, will the problems associated with the sludge disposal be easily handled.

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TABLE VIII

ESTIMATED COSTS OF LIME NEUTRALIZATION OF ACID MINE DRAINAGE
ALL COSTS IN CENTS/1000 GALLONS

Plant Capacity Gallons/ Day	Approximate Acidity Concentration	Approximate Iron Content	Plant Cost (Except Sludge Removal)	Lime**	Labor	Sludge Disposal	Mainten- ance	Contin- gencies	Total	Sludge Accumulation Acre-Ft./Yr.
300,000	6500	2000	12.0	53	14.0	11.0	6.0	5.0	101	13
900,000	6500	2000	11.2	51	12.6	10.5	5.8	5.0	96	39
2,700,000	6500	2000	10.4	49	11.8	10.5*	5.5	5.0	92	117
8,100,000	6500	2000	9.8	48	11.0	10.5*	5.3	5.0	89	351
300,000	3400	1000	9.5	28.0	10.0	8.0	4.0	3.0	62.5	9.8
900,000	3400	1000	8.5	26.0	5.0	7.0	3.0	3.0	52.5	30.1
2,700,000	3400	1000	7.5	25.5	2.5	7.75*	2.5	3.0	48.5	91.0
8,100,000	3400	1000	7.25	25.5	2.0	7.50*	2.5	3.0	47.75	273.0
300,000	1400	650	9.5	12.9	8.0	4.0	3.0	3.0	34.8	4.9
900,000	1400	650	8.5	11.5	4.0	3.5	2.5	3.0	33.0	15.4
2,700,000	1400	650	7.75	11.0	2.0	3.75*	2.0	3.0	29.5	45.4
8,100,000	1400	650	7.25	11.0	1.6	3.75*	2.0	3.0	28.6	136.5
300,000	650	325	8.5	6.1	6.0	2.0	2.5	2.5	27.60	2.8
900,000	650	325	7.5	5.7	3.0	1.8	2.0	2.5	22.50	7.7
2,700,000	650	325	6.75	5.5	1.8	1.9*	1.5	2.5	19.95	23.1
8,100,000	650	325	6.5	5.5	1.0	1.9*	1.5	2.5	18.90	68.6

*These costs allow for excavating some hard rock.
**Cost of hydrated lime taken at $24.00/ton bagged, $22.00/ton bulk.

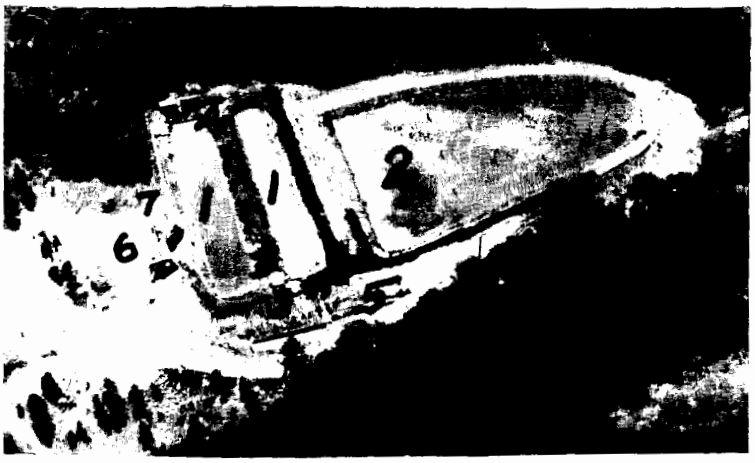


FIGURE 1

AERIAL PHOTOGRAPH OF THE ACID MINE DRAINAGE TREATMENT PLANT
(1) Settling basins, left one is full of treated water.
(2) Sludge disposal basin. (3) Sludge pump house. (4) Aeration plant. (5) Water softening plant. (6) Acid treatment house
(7) Flume to aeration plant.

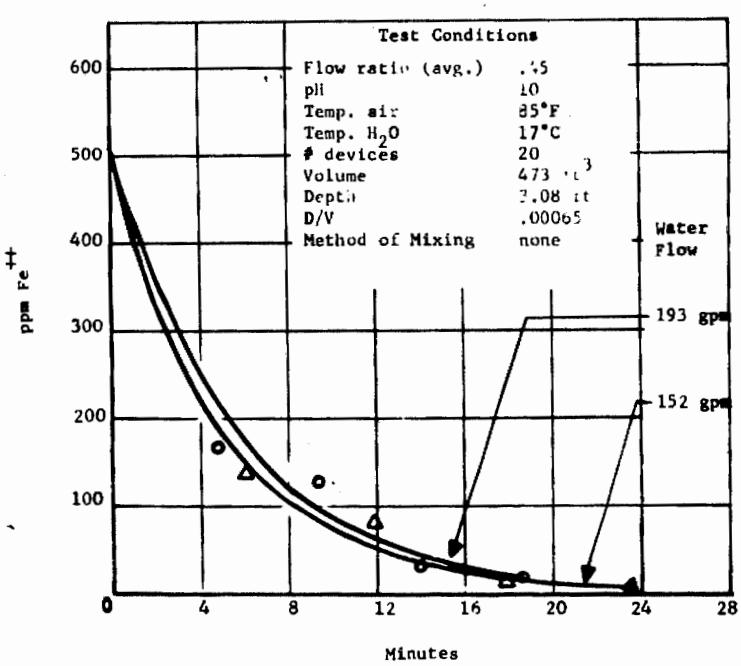


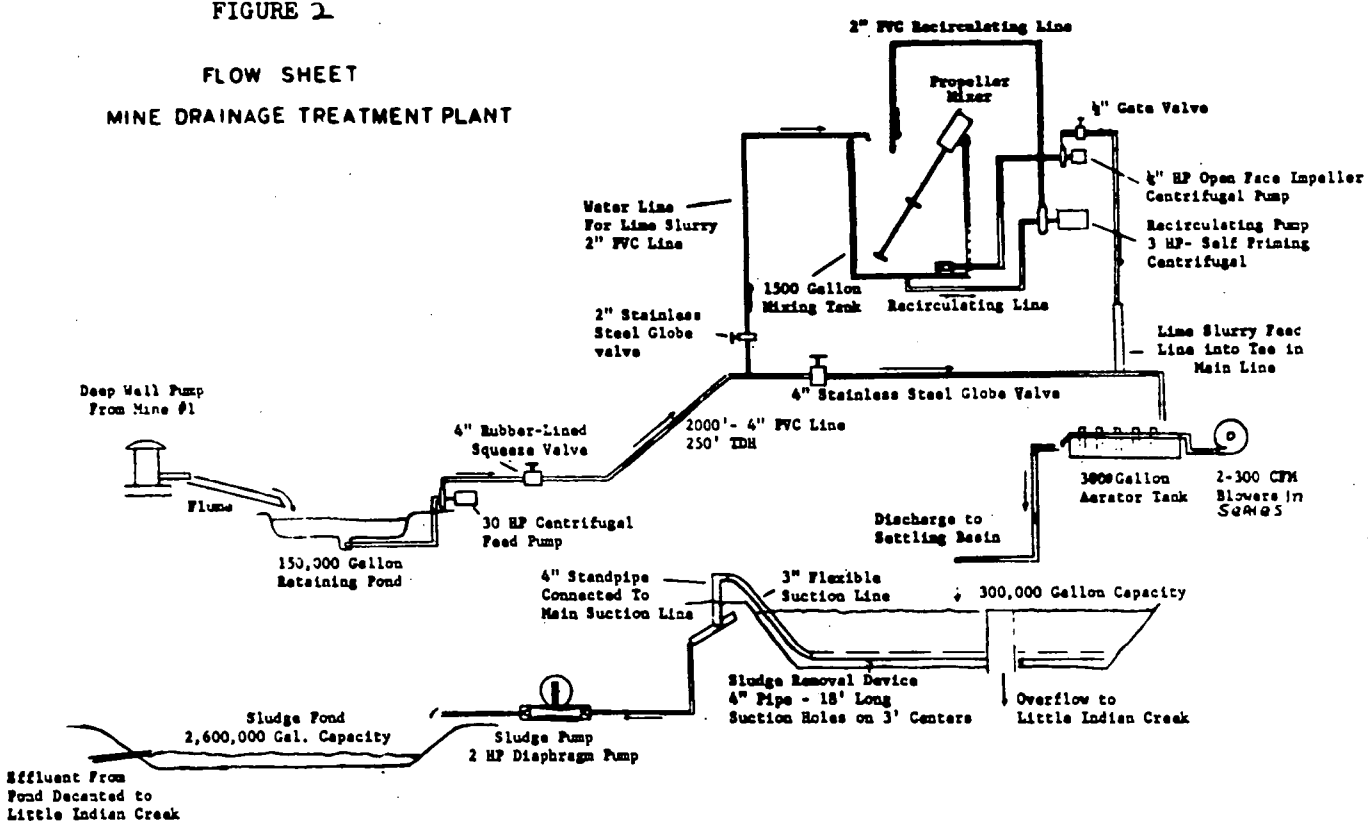
FIGURE 3

CURVES SHOWING AERATION RESULTS ACHIEVED
Note the abscissa description refers to the minutes the treated water has been in the aerator. The PPM on the ordinate refers to the parts per million of ferrous iron remaining in the treated water.

FIGURE 2

FLOW SHEET

MINE DRAINAGE TREATMENT PLANT



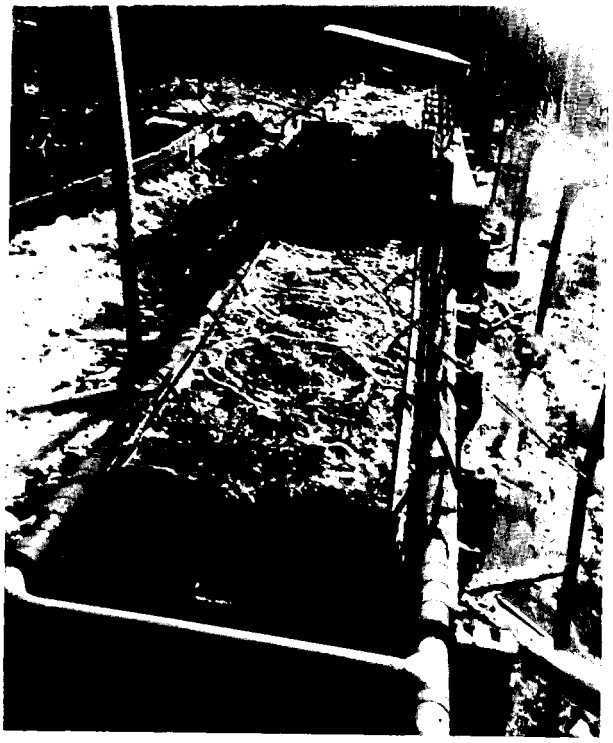


FIGURE 4
AERATION UNIT IN OPERATION

FIGURE 5
PHOTOGRAPH OF WATER HARDNESS TREATMENT PLANT
(1) Treated water. (2) Sodum Carbonate solution metering arrangement. (3) Water metering device and discharge of treated water. The overflow is through a pipe not visible in the lower foreground.

Hydrology and Chemistry of Coal-Mine Drainage in Indiana

by

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Introduction

In recent years it has become increasingly fashionable to speak of man's modification of his environment as another evidence of man's inhumanity to man, thus implying that all modifications are deleterious ones. Quickly we choose sides, and the debate is on. These debates make strange bedfellows, for they do not present scientists versus non-scientists as a battle of the two cultures, but rather, scientists and engineers are liberally sprinkled among others of the "pro" group and the "con" group.

If we adopt the definition of environmental pollution that it is the "unfavorable alteration of our surroundings", as was proposed by the Environmental Pollution Panel of the President's Science Advisory Committee (1965, p. 1), then we accept the fact that "these changes may affect man directly, or. . .his physical objects or possessions, or his opportunities for recreation and appreciation of nature".

In a recent article, Norman Brooks (1967) provided an excellent analysis of the closely interrelated problems of man, water, and waste, thus guiding us toward the subject of this paper.

Water from Coal-Mining Operations

Precipitation that reaches the ground must either: (1) evaporate or transpire back into the atmosphere, (2) infiltrate into the ground and become part of the underground water supply, or (3) run off at the surface of the ground into streams. Evaporation and transpiration losses vary both daily and seasonally, whereas runoff is sensitive not only to these two factors but to others such as the intensity and magnitude of rainfall, and the ability of the ground to store water. Surface runoff and infiltration are extremely important in the matter of acid-mine drainage.

Hydrologic effects of coal-mining operations include changes in the quality of the water in streams, as well as changes in the quantity. Both quality and quantity are closely related, and must be considered together when we attempt to evaluate their characteristics and possible effects in producing environmental changes.

Changes in the quality of water as a result of the mining process include chemical, physical, and biological ones. Taking these in reverse order, it is possible that the biological effects are more beneficial than not, because research has shown that: (1) acid mine waters are useful in at least partially restoring the quality of surface water in streams that have received improperly treated sewage (Anon, 1968), and (2) inhibition of bacterial growth in acid-producing underground mines can inhibit the production of acid waters (Shearer, Everson, 1965; Shearer and others, 1968).

Physical changes in water quality have been described usually as the unwanted increase in turbidity and objectionable colors, because of the presence of $Fe(OH)_3$,

$Fe(OH)SO_4$, and $Fe_2O_3 \cdot x\ H_2O$ in suspension in the streams and as a precipitate on the stream bottoms, along with the black sediment that results from coal fines coming from the washing operations in the coal-preparation plant.

Other physical changes, on the positive side, are the increase in ground-water flow to streams during dry times, and the decrease in flood runoff during wet times (Corbett, 1965; Agnew, 1966). The former is due to the infiltration of rainfall into the permeable, uncompacted cast-overburden material that is excavated and piled up before the coal can be extracted, and the latter is due to the arrangement of these ridges of displaced bedrock and sediment across drainage lines of pre-existing surface streams.

Surface runoff and infiltration are extremely important in the matter of acid-mine drainage, for the water reacts with pyrite (FeS_2) in an oxidizing environment to carry $FeSO_4$ and $Fe(OH)_2$ in solution, resulting in acid water and a suspension and precipitate known as "yellow boy" -- compounds present include H_2SO_4, $Fe(OH)(SO_4)$, $Fe(OH)_3$, and $Fe_2O_3 \cdot x\ H_2O$.

Often the "yellow boy" settles out on the stream bed, and reflections in the water make it appear that the flowing water is also yellow whereas it is only slightly murky. When the stream bed is free of "yellow boy" and there is no evidence of aquatic life, and the flowing water is clear, then the presence of acid is very probable.

We have recognized that the "flushout" phenomenon is most critical with regard to acid-mine drainage (Corbett, Agnew, 1968, p. 133-155). A flushout results from intense rainfall during a period of low streamflow or drought, and causes the following to be picked up by the stream or washed into it: (1) materials eroded from mine-waste piles or tailings ponds, (2) oxidized acid-forming materials previously collected on the banks and in the flood plain, (3) bottom deposits scoured from the stream bed, and (4) impounded water of poor quality.

These and other chemical aspects are discussed in greater detail in succeeding sections of this paper.

Water from Indiana Coal-Mining Operations

Indiana is not one of the states that has a major problem with chemical and physical pollution of its water resources, caused by coal-mining operations. Because its land is relatively flat or has a subdued rolling topography, the physical effects of erosion and deposition of sediment from hillwash and by landslides are not nearly so prominent as in the more rugged hilly or mountainous country of large parts of Appalachia; nevertheless, sediment rates are higher in Indiana during and for a short time after mining operations, until the new vegetation gets established on the slopes. Another source of physical pollution is the dry-coal residue resulting from washing in the coal-preparation plant; slugs of this material -- and even fairly continuous discharges of it -- are released to the streams, causing problems that are mainly unsightly. Sometimes the presence of these coal fines affects the chemistry of the water, but the effect can be beneficial, apparently because of the reducing action of the coal. Enforcement of the present Surface Mining Reclamation Act of 1967 in Indiana will assure that this problem is held to a minimum.

Similarly, Indiana's problem with chemical pollution of surface waters because of coal-mining activity has been relatively minor, for data gathered recently by the State Board of Health revealed that only some 300 miles of streams were so affected (Woodley, Moore, 1966, p. 268), from a total of approximately 15,000 miles in the southwestern part of the State.

However, our research has shown that the occurrence, character, and distribution

of this acid pollution is closely related to the amount of flow in the stream, so the stream hydrology is of utmost importance in obtaining a much more precise assessment of the matter. Thus, by careful sampling and analysis, the problem is shown to be restricted to localized geographic areas and to specific time periods. Accordingly, one of the major contributions of our research study is the fact that in an acid-producing area not all of the area is equally blameworthy, and what is even more important, the acid character of a stream is variable so that only during specific climatologic events does the major pH or acidity problem result.

Our research work has caused us to conclude (Corbett, Agnew, 1968, p. 133-155) that the flushout phenomenon is the cause of the major part of the acid-mine drainage problems in Indiana. This conclusion, first reached in the Busseron Creek Watershed of west-central Indiana, has been corroborated during the Summer of 1968 in the Patoka River area, 75 miles to the south (Corbett, 1969). It seems evident that the most damaging aspect of the flushout phenomenon is the erosion of the old mine-waste piles that are resistant to infiltration, and to erosion of abandoned railroad grades and haul roads, and discharges from coal-preparation plants.

Analysis of the flushout phenomenon has shown that its effect is dependent upon: (1) magnitude and intensity of the storm, (2) length of time since the last flushout, (3) ratio of area compacted during mining to the total area mined, (4) storage potential of last-cut lakes (lakes formed in the last cut resulting from the mining process) and adjacent cast-overburden material (rock, soil, and loose sediments lifted off the coal by a dragline and deposited in dirt stacks to the side) at the time of the storm, and (5) the ease of storm runoff from the compacted areas.

Thus we concluded (Corbett, Agnew, 1968, p. 4) that: (1) the magnitude and frequency of storm runoff has an appreciable effect on acid concentrations in a stream, and (2) present surface-mining operations, except for coal-processing plants, are not the cause of acid water in the streams; rather, it is due mainly to old waste piles and compacted areas within the disturbed area, and to old underground mines.

Busseron Creek Watershed

General Statement

To illustrate the foregoing statements, we wish to use the Busseron Creek Watershed and especially its Mud Creek Tributary, in the coal-mining area of west-central Indiana (Fig. 1). This area is one of the authorized Public Law 566 Small Watershed projects of the U. S. Soil Conservation Service, which contemplates the construction of 26 flood-retarding dams. Fifteen of these structures have already been built, some in watersheds that will be surface-mined at a future date; in fact, one dam site (in the Mud Creek Tributary Watershed) has already been mined out, and two others (in the Buttermilk Creek Tributary Watershed) are scheduled for mining in the near future. Furthermore, one site is planned in the Sulphur Creek Tributary Watershed, which contains acidic surface water at both low and high stream flows.

Mud Creek Tributary Watershed contains 11.9 square miles of drainage area, of which 5.2 square miles has been disturbed by surface mining for coal. About 87 percent of the mined area contains water of good quality in the last-cut lakes and ground water in the cast overburden. The remaining 13 percent is comprised of mine-waste piles, an abandoned tailings pond, and an 18-acre last-cut lake through which Mud Creek flows because of an artificial diversion; the purpose of this diversion was to permit settling out of fines eroded from the upstream mine-waste piles during intense storms.

The SCS and the U. S. Geological Survey, in cooperation with the State of Indiana, instrumented the Watershed with automatic recording stream gages so that

continuous streamflow data could be obtained at six water-sampling sites; in addition, we estimated the streamflow on numerous occasions at five additional sites, and less often at more than 100 supplemental locations.

Some 430 water samples were collected from these sites at various times during the two-year period, November 1965 - November 1967; the Federal Water Pollution Control Administration made analyses of approximately 400, and the Indiana State Board of Health analyzed the remaining 30, for pH, conductivity, acidity, alkalinity, total hardness, total iron, manganese, chloride, and sulfate (Corbett, Agnew, 1968 tables in appendix).

Within the Busseron Creek Watershed, three areas had been known to carry acid water -- the Big Branch - Mud Creek, the Sulphur Creek, and the Buttermilk Creek Tributary Watersheds (Fig. 2). Surface mining had disturbed 26, 7, and 12 percent, respectively, of these areas.

Our studies showed that the upper part of Big Branch has no acid-mine drainage problem, although sulfate occasionally is high. The upper part of Mud Creek did show an acid problem, but this was due to old mine-waste piles and underground mines rather than to recent or current surface mining. Further, the acid concentration of Mud Creek dropped considerably after it joined Big Branch.

Acid water is apparently contributed to Sulphur Creek by both old underground and old surface mines.

The Big Branch - Mud Creek Tributary and the Sulphur Creek Tributary drainages join the mainstem Busseron Creek (Fig. 2), where their acid waters are diluted and partially neutralized so that normally the pH and acidity are moderate to good -- except when flushouts occur.

Farther downstream is the Buttermilk Creek Tributary Watershed (Fig. 2), which contributes acid water that is derived from old mine-waste piles and an old underground mine. However, the mainstem Busseron Creek dilutes Buttermilk Creek so that water of acceptable pH and acidity is present at the lowest stream-gaging station on the Busseron -- except during flushouts.

The flushout phenomenon was studied carefully during three storms -- April 26-27, 1966; November 10-17, 1966; and May 1-5, 1967 (Corbett, Agnew, 1968). In general, the flushout effect was apparent at and before the time of the peak discharge of the stream, and was of short duration; chemical effects included an increase in acidity, total iron, and sulfate, and a decrease in pH and alkalinity.

Hydrology and Chemistry -- Flushouts

Unless he has automatic monitoring equipment, the hydrologist rarely is able to gather from streams all the chemical data that he wants, so he must make his interpretations and draw his conclusions by rather subjective extrapolations on the basis of his experience. Some hydrologists and chemists have felt forced to take these all-too-few data and project them throughout the year, thus arriving at total loads of ions on an annual basis. The hydrologist, however, should recognize the limitations of these data, and should help the water chemist interpret the hydrologic-chemical situation.

Thus, acid loads calculated for a stream for the year, but based on samples taken at only a relatively few times during the year, may be greatly in error because they may have sampled only the "normal" hydrologic events rather than some of the abnormal ones, or vice versa.

Examples of this procedure are not uncommon, such as the report of a private

research foundation (Clifford, Snavely, 1954, p. 12, 13), which was based on samples taken every three months, without measurements or estimates of streamflow. This report did cite scattered measurements of the USGS (Clifford, Snavely, 1954, Tables A-2 and A-3), wherein pH, acidity, and hardness were presented, but for only one sampling date. The authors stated that "complete chemical analyses are also available, but are not reproduced here as they would serve no purpose" (p. 13). The fallacy of this statement is brought out by a recent USGS report (Musser, Whetstone, 1964), wherein the effects of aluminum and silicon are considered as significant in addition to pH, acidity, sulfate, iron, and manganese.

The Federal Water Pollution Control Administration has made excellent progress in dealing with this matter of adequate and representative sampling in recent years, especially at its two Ohio River Basin Field Stations -- in Evansville, Indiana and Wheeling, West Virginia. Although the FWPCA still reports "average" parameters as well as "maximums" and "minimums", (1967, p. B-14, Figures 3-5; 1968a, Table 2; 1968b, Tables 6, 9-10, 12-13, 15, 17, 19, 21), it commendably recognizes the flushout effect that causes increased acid concentration along with increases in streamflow.

The flushout phenomenon was discussed briefly in a recent USGS report (Biesecker, George, 1966, p. 5), wherein they stated that "occasional flushing of mines by excessive precipitation produces temporary, but often more dramatic stream damage" than continuous mine drainage; they went on to corroborate our view that continuous mine-drainage problems (as contrasted with flushouts) "should be more serious during the June - November low-flow period when stream waters normally are more concentrated".

The flushout effect in the Busseron Creek Watershed is what we wish to discuss now, not only to show the relationship of increased concentration of ions with increased streamflow, but also to show the value of gathering water samples at many times during such an event.

Between the hours of 1455 and 1510 on June 24, 1968, a torrential rain storm swept across the Mud Creek Tributary Watershed, registering 1.04 inches in 15 minutes at the Minnehaha Mine gage near the lower end of the Watershed (Fig. 3). The junior author and microbiologist Richard Kindig were nearby when the rain began, and drove to the USGS stream-gaging station on Mud Creek near its mouth, arriving at 1520 hours.

They collected ten water samples in the next 90 minutes, catching a preliminary crest and recession and then the main crest at 1620 hours (Fig. 3). A final water sample was collected at 1710 hours, as the flood recession was beginning to taper off.

Table 1 and Figure 3 show significant trends in the acidity, sulfate, and conductivity, which increased in concentration during the rising discharge (although conductivity dropped just before the crest), and then continued to rise as the discharge was decreasing. (The final drop in conductivity is unexplained, and may be due to a sampling or analytical error.)

Table 1. -- Chemical quality of water samples obtained during flushout of June 24, 1968, at Mud Creek stream gage, Busseron Creek Watershed (analyses by FWPCA Evansville Field Station).

Real time C.S.T.	Conductivity a/	pH	Alkalinity b/	Hot Acidity b/	Total Hardness c/	Ca d/	Mg d/	Total Fe d/	Mn d/	SO_4 e/	Discharge (cfs)
1010	2450	4.3	0	180	1840	362	228	45	19	1900	4.6
1420	1000	4.4	0	310	1130	233	134	137	13	1400	13.0
1435	1050	4.6	1	210	1080	227	125	104	14	1300	10.0
1445	1200	5.0	3	270	1330	263	164	126	15	1200	17.0
1455	1350	4.9	10	790	1610	321	197	---	18	1900	52.0
1500	1150	4.6	2	850	1220	251	144	318	25	2100	61.0
1510	1200	3.5	0	1200	1140	257	120	560	20	2660	79.0
1515	1500	2.8	0	1300	1170	289	109	890	16	2600	82.0
1520	Peak Discharge -- No water sample collected.										84.0
1525	1800	2.6	0	1600	1180	321	93	700	15	2600	82.0
1540	2050	2.5	0	1800	1450	364	131	830	21	3200	74.0
1550	3100	2.5	0	2000	1470	375	131	780	26	3300	64.0
1625	3400	2.5	0	1900	1570	396	142	647	26	3300	35.0
1710	2600	2.5	0	2100	1670	396	153	592	21	3400	22.0

a/ micromhos at 25°C per centimeter
b/ potentiometric titration, mg/l
c/ calculated only from Ca and Mg, mg/l
d/ atomic absorption spectrophotometer, mg/l
e/ turbidimetric by precipitation as $BaSO_4$, mg/l

Hardness likewise increased, but experienced a marked decrease during the peak discharge, and then continued to increase during the discharge recession. Total iron also increased during the rise in discharge, experienced a dip during the discharge crest, again increased briefly while the discharge was decreasing, and then gradually decreased.

It was expected because of the flushout character of this storm, that the pH would decrease abruptly as the peak discharge was reached, and maintain that low level throughout the period of decreasing discharge; the latter occurred, but the pH decrease began earlier than expected, for the following reasons.

Coal fines from the tailings pond described on page 3, and mine-waste fines were simultaneously flushed out of the last-cut lake into Mud Creek on June 24, 1968. We believe that the reducing effect of coal fines in the tailings pond kept the pH of the water during the flushout from falling below 4.9 until the recharge from this area was depleted, whereupon pH decreased and acidity increased just before the crest of the discharge was reached, rather than at the beginning of the rise as was shown in an earlier published report (Corbett, Agnew, 1968) for the three flushouts of 1966 and 1967, because the stream gage sampling site is 1¼ miles downstream from the tailings pond and last-cut lake, and because of the reducing effect of the coal fines.

Obviously, if only one water sample had been taken during this flushout, and its analytical results projected for a much longer period, the projected data would have been highly unrepresentative of the stream's overall character. The concentration levels of all of the ions in this acidic stream were in excess of acceptable

potable water-quality standards even before the flushout (sulfate 1200-1400 mg/l; total hardness, 1100-1200; acidity, 200-300; iron 100-200), but the flushout increased these deleterious concentrations by 3, 1/3, 10, and 4 times, respectively.

Chemical Analytical Methods

In the final part of the paper we hydrologists wish to put some questions to the chemists, and ask for their help.

In our study, as mentioned earlier, we have relied on the FWPCA and the Indiana State Board of Health for water analyses. Further, we have combed the files and searched the professional literature for additional water data, obtaining it mainly from USGS publications. In the process, we have encountered the following problems of relating or correlating analytical results performed by different methods.

1) Difference between field pH and laboratory pH readings, taken from the same sample. From the standpoint of the fieldwork, it is very important that we obtain a reliable field pH reading. Both agencies report difficulty in relating the field and the laboratory pH determinations, whether sampled by us or by their personnel; the pH may differ by more than one unit, such as a field pH of 4.0 against a lab pH of 2.9. We recognize that several factors may be involved: importance of time, so that the laboratory pH should be run within a few hours of the field pH; relative precision of the field meter and lab meter; method of sampling by persons with different kinds of training; and adverse field conditions -- for example, the stream may have to be sampled at a temperature of $0^{\circ}C$.

2) Acidity and alkalinity. Some laboratories give a net acidity reading (the difference of the acidity and alkalinity measurements), whereas others list acidity and alkalinity separately. If only one is listed, this may give the impression that the other is zero, which is not always true. But a more important point is the method of determination of acidity. There are a variety of methods of acid determination in common use, which do not give the same results -- hot acid (at or near the boiling point), cold acid (room temperature), and methyl orange. If we are trying to reproduce what is happening in the stream, we are told that we should run it cold; however, if we want to obtain the total acidity, we should run it hot; furthermore, the accuracy of the older analytical method, methyl orange, depends on the speed of analysis. What we would like to have is a conversion factor that can be applied to these results, to make all of the available data useful. You may not be able to supply this, so we will be forced to continue to look for differences in samples run by the same method.

3) Relationship of total hardness to acidity-alkalinity. What is this relationship? It would be very helpful for us to know, as many water samples have been analyzed for total hardness, but not for the more definitive acidity-alkalinity. It would appear, according to our data and to FWPCA Evansville Field Station chemists, that acidity plus total hardness (Ca,Mg) approximates sulfate, as shown in the following tabulation. But is this more apparent than real? In alkaline streams they may differ considerably.

Table 2. -- Comparison of acidity, total hardness, and sulfate from water samples taken during flushout of June 24, 1968 at Mud Creek Gage.

Time	Total Acidity (Measured) +	Total Hardness (Calculated from Ca^{++} and Mg^{++})=	Total	SO_4 (Measured)
1010	180	1840	2020	1900
1420	310	1130	1440	1400
1435	210	1080	1290	1300
1445	270	1330	1600	1200
1455	780	1610	2390	1900
1500	850	1220	2070	2100
1510	1200	1140	2340	2660
1515	1300	1170	2470	2600
1525	1600	1180	2780	2600
1540	1800	1450	3250	3200
1550	2000	1470	3470	3300
1625	1900	1570	3470	3300
1710	2100	1670	3770	3400

This relationship of sulfate to total acidity is not an analytical problem but has been used as a check on the data; however, as it might possess greater significance for us we would like to refer it to the chemists for an answer.

4) Sulfate determination. Several methods are in common use by the two Federal laboratories, the FWPCA and the USGS -- turbidimetric, colorimetric, end-point titration, and gravimetric. Can we compare the results? We should be able to, for "normal" waters, but how about acid-mine drainage?

5) Total hardness determination. To determine the total Ca^{++} and Mg^{++}, the atomic-absorption spectrophotometer is being used more and more. However, a more common laboratory technique uses the EDTA method with an inhibitor; sometimes the EDTA method is run on the hot-acidity filtrate, but some of the Fe, Mn, and Al have already been precipitated. Thus results are not reliable in running mine-drainage samples because of the large quantities of interfering ions.

6) Conductivity. Despite the fact that the field meter is temperature-compensated, it is known that the cell constant in the field meters varies; thus field-meter readings and automatic-monitor readings are not always accurate. The FWPCA now requires that conductivity be performed in the laboratory at 25°C.

Our basic references to methods and techniques have included the excellent U. S. Geological Survey Water Supply Papers 1454 and 1473 (Rainwater, Thatcher, 1960; Hem, 1959), dealing with collection, analysis, and interpretation of water samples. The previously cited papers of Musser and Whetstone (1964) of the USGS, and of the FWPCA (1967, 1968a, 1968b) show that we need a different set of procedures and methods when dealing with mine drainage.

These recent papers, coupled with those contained in the two mine-drainage symposia (ORSANCO, 1965, 1968), are taking us a long step toward the solution of

these problems. However, we hydrologists still need some answers, and we appreciate this opportunity to present our needs to the chemical fraternity at this meeting.

Acknowledgments

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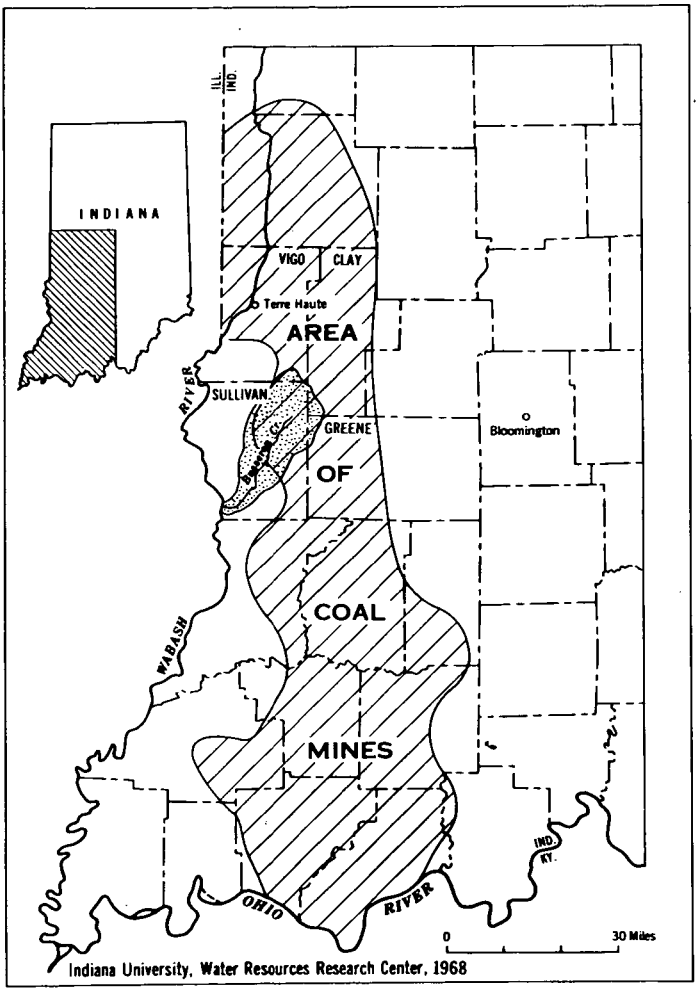

Figure 1. Map of southwestern Indiana showing area of coal mines and Busseron Creek Watershed.

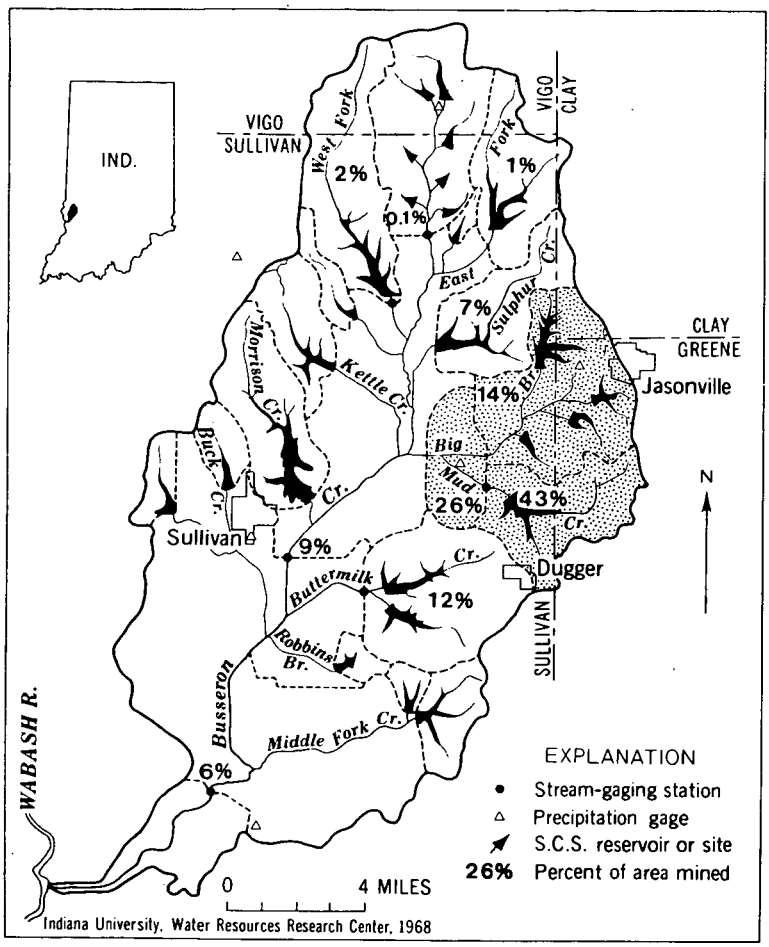

Figure 2. Map of Busseron Creek Watershed showing Big Branch - Mud Creek Tributary Watershed.

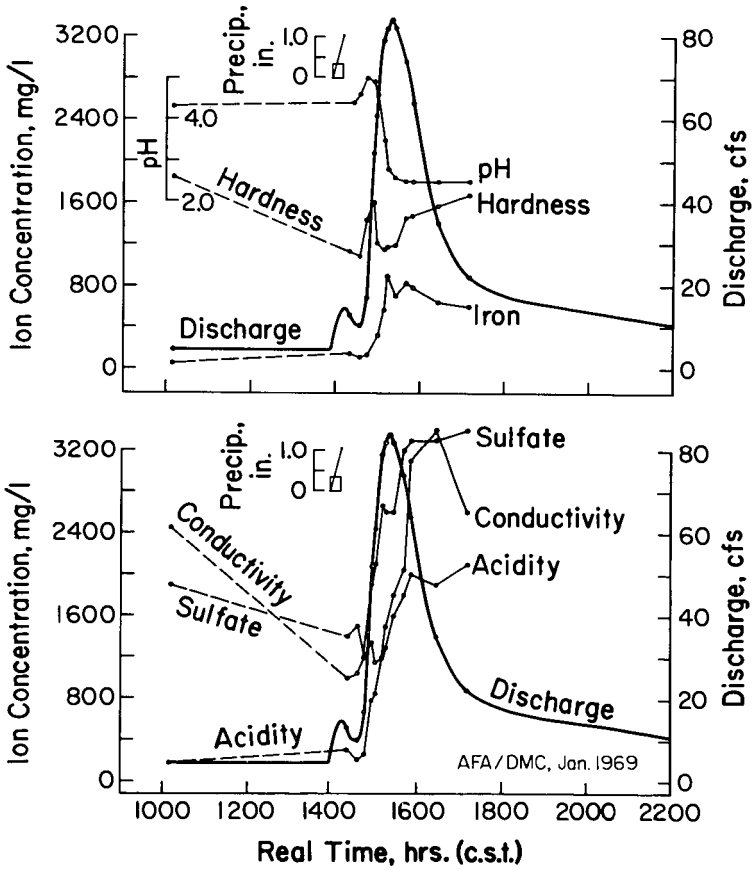

Figure 3. Graph showing effects of flushout of June 24, 1968 on water quantity and quality at Mud Creek Stream Gage, Busseron Creek Watershed.