THE USE OF PHOSPHATES FOR AMELIORIZATION

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A REVIEW OF THE EFFECT OF PHOSPHATE AS AN AMD AMELIORANT.

This paper is not restricted to the work completed on phosphate research during the past year, but rather, summarizes results of the past several years in order to show the evolution of the phosphate study from the test tube stage to a study of the effect of various phosphate materials on the acid producing potential of the different lithic units associated with the mining of coal. Through 'this paper the reader will gain a view of the logic used by the investigators to produce the information required to advance the proposed use of phosphate materials as AMD ameliorants from the lab to the field.

This paper is divided into three parts: (I) Initial studies of phosphate as an ameliorant for acid mine drainage. (II) Acid producing potential of the various lithic units associated with coal mining, and (III) The effect of phosphate materials on the acid production of the various lithic units associated with coal.

(I) INITIAL STUDIES OF PHOSPHATE AS AN AMELIORANT

When the first ton of coal was extracted, the ecological impact of acid mine drainage began. During the earth moving operations involved in surface mining, large volumes of rock overlying the coal are removed to expose the seam. The exposure of these strata to the atmosphere initiates the Process of chemical weathering. During this process. iron disulfide minerals, mainly pyrite, react with water and oxygen to produce soluble iron sulfates. These compounds first appear as white crusts of ferrous sulfate, occasionally accompanied by yellow-green ferric sulfate salts on the weathering rock faces. These sulfates are hydrolyzed to Produce sulfuric acid and iron oxides. This latter product is evidenced as the yellow-red rock coatings in streams affected by acid mine drainage.

Although the exact weathering process of pyrite-containing overburden which produces AMD has not been well established, a common accepted reaction sequence is given below:

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

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

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

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

Upon examination, it can be shown that this process is a chain reaction, that is, the product from Equation 2, the ferric ion Fe^{+3} is used in Equation 4 to oxidize Pyrite. In this process ferrous ion, Fe^{+2} , is Produced which is the reactant in Equation 2 where it is again oxidized to ferric ion to be used in Equation 4. The only reactant which is consumed is pyrite and the only product which is not consumed is sulfuric acid.

The purpose of the initial investigation was to better understand the limitations of the ferric ion-pyrite reaction with the goal of determining a method by which it could be arrested.

The method of arrest could then be applied to overburden materials to test the effect on acid mine drainage production.

EXPERIMENTAL

The goal of the first sequence of experiments was made to determine the equilibrium reaction potential of Fe^{+3} and FeS_2. This was accomplished by mixing 75 ml of various molar solutions of $FeCl_3$ with 5 am samples of -100 and -200 mesh pure Pyrite. Nitrogen was bubbled through these suspensions for 10 minutes to minimize the dissolved oxygen concentration. The samples were sealed to prevent oxygen absorption and shaken occasionally for two hour intervals. The pH and electrical potential of the solutions were measured against a standardized glass electrode and a standardized platinum electrode at two week intervals. Between measurements, the samples were stored under nitrogen to prevent non-ferric oxidations. The equilibrium voltage was taken to be that value which remained constant for a period of 3 months with non-changing pH (see Table 1). The common value appeared to be 0.42. v. It is possible to use this value to calculate the ion concentration ratio and predict conditions below which this voltage is not- reached so the reaction in Equation (4) can not proceed. By using the standard electrode potential of .77 v for the Fe^{+2} ---- Fe^{+3}. couple and the Nernst equation, it can be shown that 0.42 v can be obtained at a Fe^{+2} /Fe^{+3} ratio of $1/10^{-6}$ in ideal solutions. Thus, to eliminate oxidation of Pyrite by ferric ion, the concentration ratio of ferric to ferrous ion should be kept at less than 10^{-6}:1.

less than 10^{-6}:1.

Table 1

Emf and pH of Pyrite Fe^{+3} Solution

(at equilibrium)

	pH	E	Initial $[Fe^{+3}]$
150 mesh	3.35	+0.360	10^{-4}
5 gm/75 ml	3.00	+0.430	10^{-3}
	2.45	+0.400	10^{-2}
200 mesh	3.35	+0.430	10^{-4}
5 gm/75 ml	3.10	+0.430	10^{-3}
	2.35	+0.410	10^{-2}
	3.50	+0.420	10^{-4}
	3.00	+0.396	10^{-3}
	2.80	+0.390	10^{-2}
	3.00	+0.396	10^{-3}
	2.60	+0.420	10^{-2}
	2.95 avg	0.41 avg	

A lower ratio can be produced by the addition of a precipitating and/or coordinating agent. The low solubility of the phosphate salts would Precipitate both ferrous and ferric ions from solution. The differences in solubility product of these salts establish an ion concentration ratio of Fe^{+2} /Fe^{+3} of approximately $1/10^{-11}$, Thus, the resulting solution voltage would be less than 0.42 v and Pyrite could not be oxidized as in Equation (4).

Attempts to test this hypothesis by using PO_4^{-3} , which serves as both a coordinating and a precipitating agent, were carried out. Five gram samples of pure pyrite were mixed with 75 ml of various molar concentrations of $FeCl_3$. Apatite rock, $Ca_5(OH)(PO_4)_3$. was added to this mixture at three times the ferric molar concentrations. The solutions were stored under N_2 and periodically shaken as before. After 6 months, the time normally required for synthetic acid mine drainage reactions to reach equilibrium, the results showed no AMD and an emf of 0.23v. These experiments were conducted on idealized samples of pure pyrite and no applicable conclusion can be reached except by using actual pyrite containing rock samples from an acid producing environment.

The effect of apatite rock on acid producing mine waste was tested on overburden materials obtained from Garret County, Maryland and Monongalia County, West Virginia. A sample of Bakerstown overburden and one of Freeport overburden from Garrett County, Maryland and one sample of Berea sandstone were obtained from Monongalia County, West Virginia. The Garrett County overburden samples were known AMD producers, while the Berea sandstone was not considered an AMD producer. The samples were ground to -200 mesh in a porcelain mortar and pestle. Weighed portions of the ground overburden were soaked overnight with 3M HC1 to dissolve various hydrated iron sulfates or oxides and any leachable iron from clay minerals. The mixture was filtered and analyzed for dissolved iron. This concentration of iron is referred to as acid soluble iron. The residue was soaked with 6M HNO_3 . refiltered and the filtrate analyzed to determine the amount of iron bound as pyrite. This indicates the acid producing potential.

The overburden samples were then divided into three portions and treated as described below.

Sample 1. 75 ml of distilled, deionized H_2O was added to 5 gm samples, the samples were sealed under N_2 and were periodically stirred for two hour intervals. After 6 months, they were tested for acid production and the electrode potential was measured. The results can be seen in Table 2.

Table 2

Effect of Phosphate Treatment on Oxidation Potential

and Acid Production of Overburden Material

SAMPLE 1

Before Addition of $Ca_5(OH)(PO_4)_3$

Bakerstown		Freeport		Berea	
E	pH	E	pH	E	pH
0.498	2.9	0.660	2.3	0.264	4.0
0.540	2.8	0.612	2.5	0.270	4.1
0.498	3.2	0.630	2.5	0.282	4.1
0.456	3.9	0.510	2.7	0.300	4.2
0.438	3.8	0.504	2.7	0.300	4.0
0.534	3.0	0.540	2.7	0.300	4.0
		0.486	3.3	0.276	4.1
		0.522	3.1	0.282	4.1
				0.281	4.0

SAMPLE 2a

After Addition of $Ca_5(OH)(PO_4)_3$

Bakerstown		Freeport		Berea	
E	pH	E	pH	E	pH
0.335	5.2	0.348	5.3	0.378	5.1
0.330	5.4	0.348	5.2	0.354	5.2
0.330	5.5	0.354	5.2	0.348	5.4

SAMPLE 2b

After Addition of Air and $Ca_5(OH)(PO_4)_3$

Bakerstown		Freeport		Berea	
E	pH	E	pH	E	pH
0.240	5.2	0.240	5.5	0.240	5.5
0.340	5.6	0.384	5.4	0.378	5.6
0.380	5.8	0.378	5.5	0.390	5.6

Sample 2a. $Ca_5(OH)(PO_4)_3$ was added at three times the molar concentration of acid soluble iron. These samples were sealed under N_2 and periodically stirred for two hour intervals. After 6 months, they were tested for acid production and oxidation potential. The results can be seen in Table 2.

Sample 2b. The Sample 2a, which was already treated with phosphate, was subjected to aeration in order to test the effect of oxygen on the system. Hydrated air was forced through the sample suspension daily for two 10 minute periods over an interval of a week. The suspension was removed and exposed to hydrated air for 2 months after which time it was tested for acidity and emf. The results can be seen in Table 2.

Sample 3. Another overburden sample identical to Sample 1 was permitted to Produce acid mine drainage. It was then treated with phosphate and aerated as Sample 2b. The samples were filtered and the residues were permitted to stand exposed to air for one month during which time the samples were occasionally moistened to encourage the oxidation reaction. After 1 month, the samples were placed in 75 ml of distilled, deionized water and they were stirred for two hours. The pH and emf can be seen in Table 3.

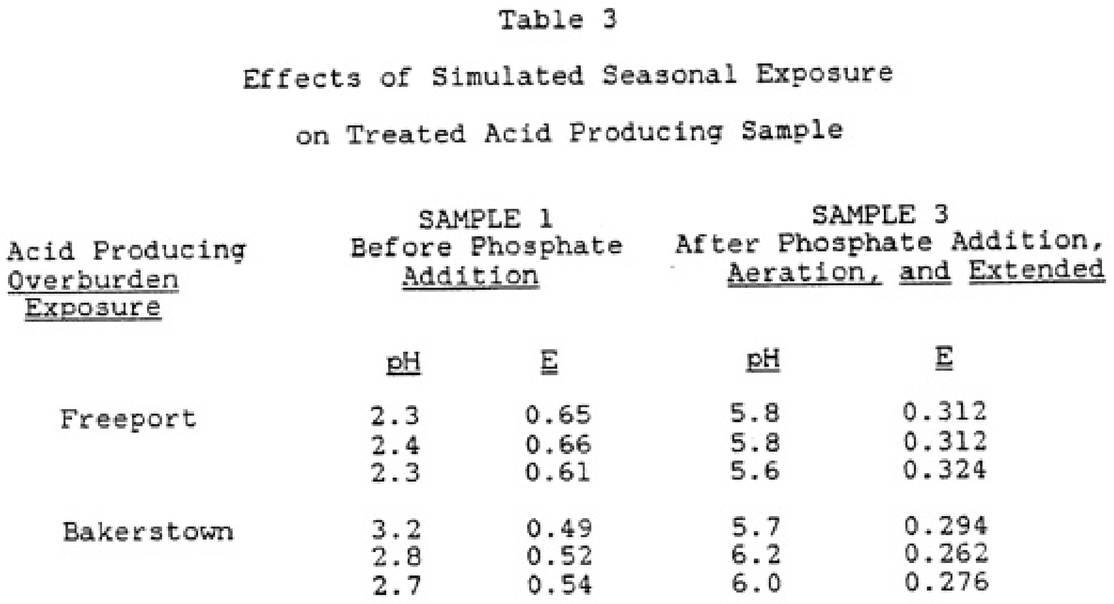


Table 3

Effects of Simulated Seasonal Exposure on Treated Acid Producing Sample

Acid Producing Overburden Exposure	SAMPLE 1 Before Phosphate Addition		SAMPLE 3 After Phosphate Addition, Aeration, and Extended	
	pH	E	pH	E
Freeport	2.3	0.65	5.8	0.312
	2.4	0.66	5.8	0.312
	2.3	0.61	5.6	0.324
Bakerstown	3.2	0.49	5.7	0.294
	2.8	0.52	6.2	0.262
	2.7	0.54	6.0	0.276

RESULTS AND DISCUSSIONS

The results of the initial reaction Fe^{+3} /FeS_2 couple showed that the ferrous-ferric couple which controls the reaction has an -average equilibrium voltage of 0.421. It follows that if the electrode potential of that couple can be reduced to below 0.42 v, no pyrite oxidation can occur by Equation (4).

The role of $Ca_5(OH)(PO_4)_3$ is to reduce the concentration of ferrous to ferric to less than $1:10^{-6}$, resulting in an electrode potential for that cell of less than 0.42 v.

Tables 2 and 3 show the dramatic effect of $Ca_5 (OH)(PO_4)_3$ on the AMD producing potential of that cell. The fact that the potential is less than 0.42v essentially eliminates the possibility of pyrite oxidation by reaction with Fe^{+3} Table 3 also shows that even upon vigorous aeration of samples treated with $Ca_5 (OH)(PO_4)_3$. the voltage still remained below 0.42 meaning that even with vigorous oxidation, no acid can be produced.

It is felt that the Fe^{+3} /FeS_2 reaction is the propagation step in the AMD reaction. This reaction is cyclic and could be the key to AMD production methods. Micro-biological evidence for the oxidation of Pure pyrite is controversial but thiobacillus ferrooxidans is known to oxidize Fe^{+2} to Fe^{+3} Their role in AMD production may be the reoxidation of ferrous ion to ferric ion for continuous reaction with pyrite, which results- in acid generation. However, if the Fe^{+3} does not directly contact pyrite because it is precipitated by PO_4^{-3}, no acid will be produced even in their presence.

The lack of AMD Production in calcareous overburden may not be due to "neutralization" as in acid base systems, but may be the result of chemically controlling the Fe^{+3} /Fe^{+2} voltage. It is realized that in basic solutions, the Fe^{+3} activity is greatly reduced over the Fe activity, thus causing a significant decrease in the electrode potential of the cell. If the resulting - voltage is less than 0.41 v, the oxidation of pyrite cannot proceed.

The overall conclusion is that treatment of acid -producing overburden by $Ca_5 (OH)(PO_4)_3$ is shown to be effective in eliminating the AMD Production of samples in the lab.

These initial experiments dealt with the synthetic weathering of small (less than 100 gm) samples. Before any practical statement could be made concerning the potential role of phosphate as an ameliorant, studies evaluating changes in AMD production between large dimension systems of treated and untreated samples had to be made. For these experiments, the samples were increased in mass 1-5,000 times from the dimensions of test tubes to 35 gallon plastic barrels.

EXPERIMENTAL DESIGN

The experimental Procedure used in this study was designed to evaluate the effect of phosphate rock addition to large volumes of potentially acidic material by comparing chancres in the quality of the leachate from a series of treated samples and controls. The reactors used in the study were six, thirty five gallon white, translucent polypropylene barrels. Each barrel was twenty inches wide and forty five inches high and capable of containing 300 pounds of mine waste material. Each was fitted with a distribution plate five inches from the bottom perforated with 200 1/8" diameter holes in a regular array. The plate supported the barrel contents and Provided for uniform flow of the leachate through the system. Below the distribution plate was a flow plate which directed the leachate to an exit Port and an air trap through which it Passed into five gallon polypropylene vessels for collection (see figure 1).

Coal cleaning plant waste material associated with the Upper Freeport coal in Grant County, WV was used in these experiments. The material was analyzed by LECO and shown to contain 3.15% pyritic sulfur. A portion of the sample was leached with 3M HCL to determine the weight percent of acid soluble iron in the sample. The phosphate loading schedule which equals three times the stoichiometric equivalent of acid soluble iron was calculated to equal 2.5 lbs of apatite rock in three hundred lbs of mine waste.

Six of the thirty five gallon barrels were filled with three hundred pounds of mine refuse material. Three barrels were untreated controls. In the three treatment barrels, 2.5 lbs of crushed apatite rock (-60mesh) was homogenized into the mine waste 40 days after the initiation of the experiments to test the effect of Phosphate on systems already producing acid. The barrels were exposed to normal weathering for 358 days. Two days after each rainfall event, the leachates were collected and analyzed for pH, specific conductivity, acidity to pH = 7 and pH = 8.3 and sulfate ion concentration. The total volume of leachate was recorded at the time of collection. These data were used to calculate the acid load leached from both the treated and control samples for the same rainfall event. In addition, the sulfate concentration of the leachate was used to calculate the amount of pyrite which has been oxidized. The data showed that significantly less acid was produced from the treated samples as compared to the untreated samples. The data showed that in addition only 35% of the pyrite in the control remains unreacted while 55% of the pyrite in the treated samples remains unreacted. At first this may not seem so impressive except for the fact that the phosphate treatment was not added to the sample until 40 days after the experiment began. At this time at least 35% of pyrite had already reacted, thus the real impact of phosphate addition had not been measured. It can be -concluded from these experiments that phosphate is capable of significantly reducing the amount of acid produced by the weathering of cleaning plant waste.

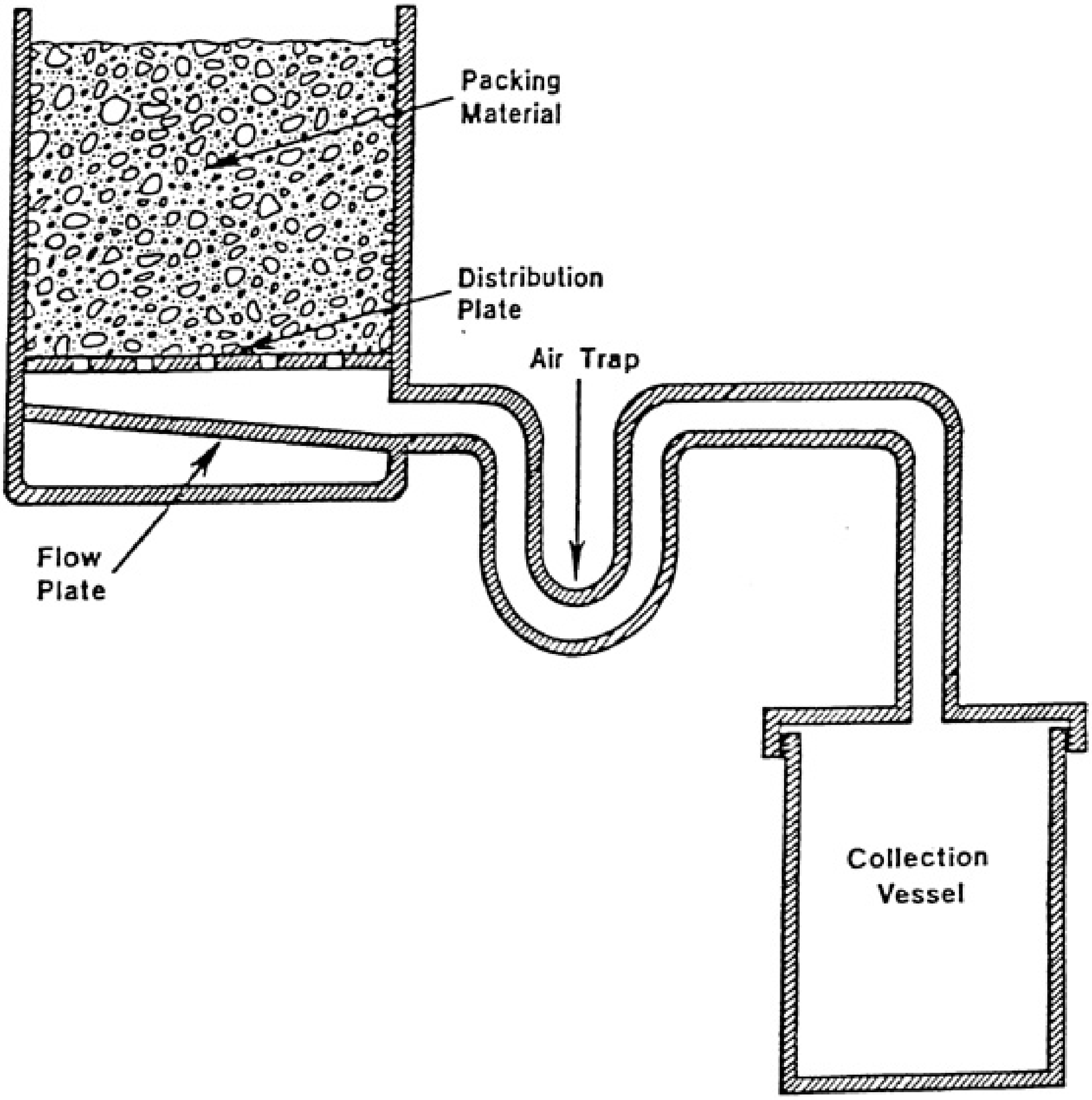


Figure 1. Schematic Diagram of Small Field Scale Experiments

Up to this time, experiments have only been conducted on cleaning plant wastes which constitute a minimum of the material exposed during mining. Tests had to be performed to establish the effect of phosphate rock on acid producing potential of the other lithic units exposed during mining. This first required that the relative acid producing potential of the various lithic units encountered in mining must be evaluated. With these data, the relative ameliorative properties of the various phosphate rich materials available for use would be determined.

METHOD OF ACID PRODUCTION EVALUATION

The method used for the evaluation of acid production and extrapolation to field scale systems was described in detail at this meeting in 1984. Since this paper is a review, it is appropriate to briefly describe this procedure.

It was believed that the typical back fill can be described as a plug flow fixed bed reactor. In other words, the material is not physically moved as the chemical reaction takes place on the weathering rock faces and water flows intermittently over the rocks, washing off the reaction products. In an ideal situation, the weathering reaction occurs independently from leaching. In the development of the model, the first step was to decide on a bench method which duplicated the fixed bed reactor (the soxhlet extractor). The second step was to set up a larger ideal plug flow fixed bed system (the barrel experiments). The third experimental step is to set up a very large pile (a field test) which simulates a plug flow fixed bed reactor. In the bench top system, controlled synthetic weathering determines the acid production rate. In both the barrel study and the field test, natural weathering controls the acid production. A method was then needed to compare acid production by synthetic and natural processes.

In the first step, 100 gm samples was put in porous thimbles, leached for 24 hours in a soxhlet extractor followed by heating in an oven for 2 weeks at 1051C to reoxidize the sample.

The sample was then removed from the oven and releached for 24 hours. This oxidation/leach procedure was repeated four times. Each of the five collected leachates was analyzed for sulfate. Because the only source of sulfate in these materials was the oxidation of pyrite and since the amount of pyrite in the samples was known, these data were represented as percent unreacted pyrite 117S. time. The data plot at % unreacted sulfur verus time is characteristic of a first order decay process. In such cases, when the logarithm of the % unreacted sulfur is plotted against time, the result is a straight line. The slope of this line, referred to as m, is the "reaction rate constant". When this operation was repeated using the controlled weathering experiments, the following equation was developed and can be used to calculate the amount of sulfate produced at any time after a was determined by bench experiments:

$$MSO_4 = 3[MS_t - MS_t e^{\alpha t}]$$

The barrel data show the same characteristic first order decay as the data from the soxhlet extractors. Consequently, an (X value can be experimentally determined by evaluating the slope of the plot of the logarithm of the % unreacted sulfur against time. A scaling factor was determined by plotting the time required for the barrel and soxhlet experiments to reduce the sulfur in the material to the same level of % unreacted sulfur. The scaling factor is a constant which makes the a value from bench top experiments equal to the a value of barrel experiments. The validity of the mathematical model and scaling factor was tested when the acid production from the 350 ton ENOXY -pile was accurately predicted using an m value determined by applying the soxhlet/oven reoxidation Procedure to 100 gms of the material used to construct the pile.

In conclusion, a method of bench top testing has been developed which can be used to accurately predict the acid production from large systems. This method will be used to evaluate the relative acid production of the various lithic units encountered in the mining of coal.

II. ACID PRODUCING POTENTIAL OF VARIOUS LITHIC UNITS ASSOCIATED WITH COAL MINING

The material exposed during mining and used in the Construction of backfills is a combination of seven separate lithic units encountered in the mining of coal including overburden sandstones, overburden siltstones, overburden shales, bone coal, roof shales, partings and seatearths. Simply by observing the different physical properties of these rocks, it is inconceivable that they all would produce acid at the same rate. Consequently it would be equally inconceivable that -phosphate rock would have identical ameliorative effects on the acid production from each rock type. Thus, before apatite can be considered a useful ameliorant, its ameliorative effect on the acid production from these different lithic units must be determined.

The solution to this problem was a multi-step process: (1) The acid producing potential of each of the various lithic units was determined by bench scale experiments, (2)) the results from the bench scale experiment were scaled up to large dimension systems so that extrapolations can be made from bench experiments to the field and (3) different weight percentage of Phosphate were added to selected groups of the lithic units and bench tested. The effect of phosphate addition on acid production was then evaluated against the results of step 1. It is believed that extrapolation can then be made to the field by using the scaleup factors developed in step 2.

AMELIORATIVE EFFECTIVENESS

Because the arresting of the acid producing reactions by the use of phosphate materials requires that the phosphate anion come in intimate contact with ferric and ferrous ions, a study was necessary which would establish the mass transfer effectiveness between the phosphate materials and the various lithic units with respect to the specific composition and particle size of the phosphate material. This is complicated because the chemical and physical characteristics of the phosphate materials available for use as ameliorants varies widely. The effect of these chemical/physical variations on acid production from the various lithic units must be established. It might be found, for example, that a relatively low application schedule for -100 mesh apatite rock from one source would be more effective than a higher application schedule of -200 mesh rock from another source. The solution to this phase of the Problem also involved a multi-step process identical to those listed previously. The only modification required was that the last step be repeated with characterized Phosphate materials from the several sources available. Only then could the effects of the various constituents of phosphate rock materials which effect AMD ameliorations be evaluated. The first step in the study was the establishment of the acid producing potential of the various lithic units encountered during coal mining.

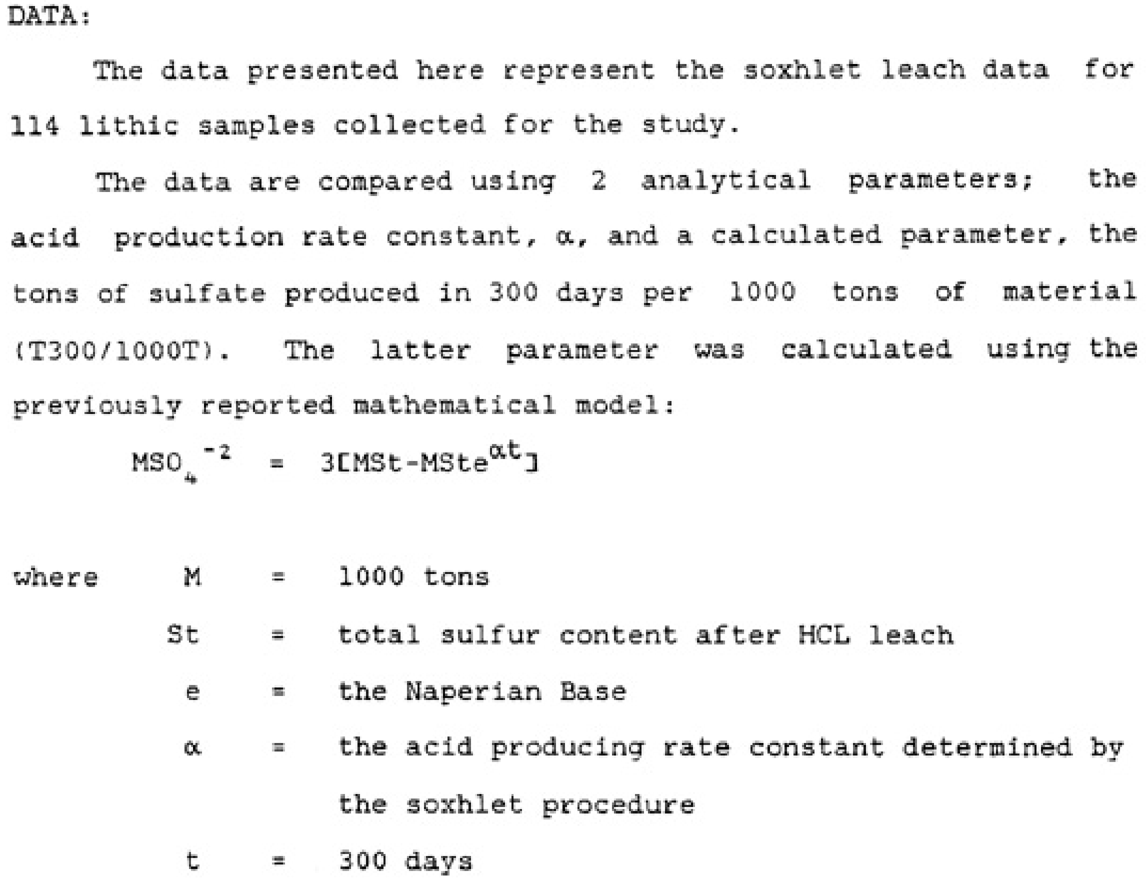
Under a grant from the W.V.U. Water Research Institute (W.R.I.), each of the lithic types previously listed was collected for the Waynesburg, Lower Kittanning, Middle Kittanning, Lower Freeport and Upper Freeport coal beds in eighteen mines over the five county area of Monongalia, Preston, Barbour, Upshur and Tucker. In addition, refuse samples were collected from five coal preparation plants for a total of 129 samples. Each sample was crushed to a top size of 0.25 inch. A representative subsample was removed using a Jones splitter and reduced to -200 mesh with a Spex Mixer-mill.

The -200 mesh samples were analyzed by x-ray diffraction for mineral content and by x-ray fluorescence for elemental composition. Each sample was subjected to total sulfur analyses before and after leaching with 5% HCL to ensure that the sulfur analyses distinguished iron disulphide sulfur. The crushed samples were subjected to the five cycle soxhlet extraction/oven reoxidation procedure previously described to determine the acid production rate constant, a.

DATA:

The data presented here represent the Soxhlet leach data for 114 lithic samples collected for the study.

The data are compared using 2 analytical parameters; the acid production rate constant, a, and a calculated parameter, the tons of sulfate produced in 300 days per 1000 tons of material (T300/1000T). The latter parameter was calculated using the previously reported mathematical model:



DATA:

The data presented here represent the soxhlet leach data for 114 lithic samples collected for the study.

The data are compared using 2 analytical parameters; the acid production rate constant, α, and a calculated parameter, the tons of sulfate produced in 300 days per 1000 tons of material (T300/1000T). The latter parameter was calculated using the previously reported mathematical model:

$$MSO_4^{-2} = 3[MSt - MSte^{\alpha t}]$$

where M = 1000 tons

St = total sulfur content after HCL leach

e = the Naperian Base

α = the acid producing rate constant determined by the soxhlet procedure

t = 300 days

The 300 day interval was arbitrarily chosen, because it represents approximately 2 halflives for the original Dobbin "standard" sample.

The a values and T300/1000T data for the samples are summarized in tables 4 and 5 respectively for the various lithic units and coal beds.

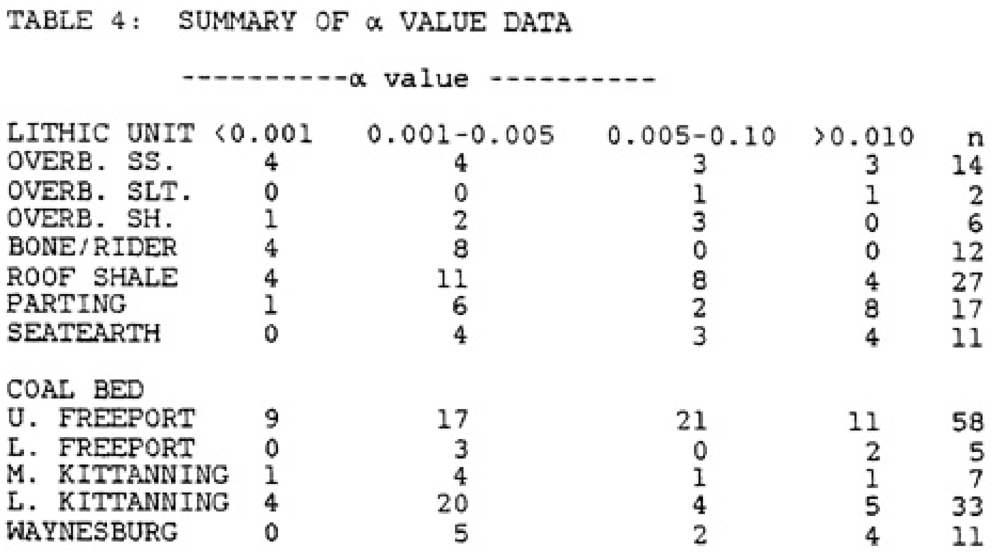


TABLE 4: SUMMARY OF α VALUE DATA

	----------α value ----------				
LITHIC UNIT	<0.001	0.001-0.005	0.005-0.10	>0.010	n
OVERB. SS.	4	4	3	3	14
OVERB. SLT.	0	0	1	1	2
OVERB. SH.	1	2	3	0	6
BONE/RIDER	4	8	0	0	12
ROOF SHALE	4	11	8	4	27
PARTING	1	6	2	8	17
SEATEARTH	0	4	3	4	11
COAL BED					
U. FREEPORT	9	17	21	11	58
L. FREEPORT	0	3	0	2	5
M. KITTANNING	1	4	1	1	7
L. KITTANNING	4	20	4	5	33
WAYNESBURG	0	5	2	4	11

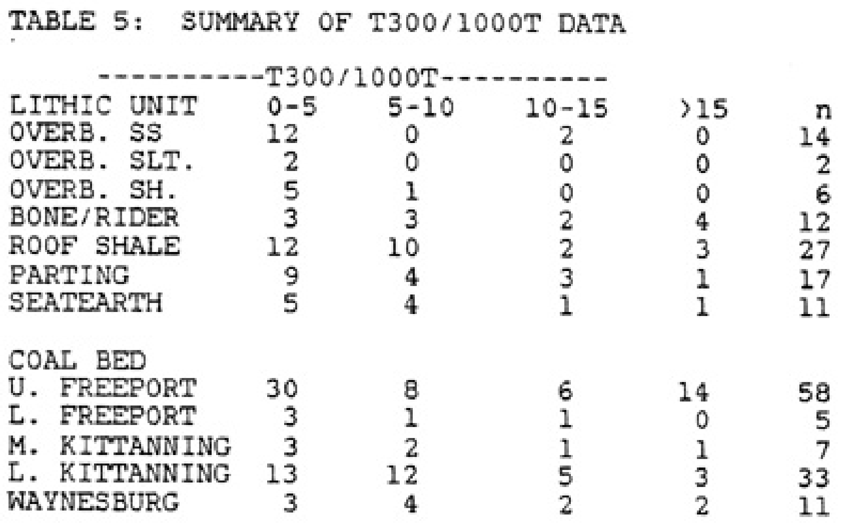


TABLE 5: SUMMARY OF T300/1000T DATA

	----------T300/1000T----------				
LITHIC UNIT	0-5	5-10	10-15	>15	n
OVERB. SS	12	0	2	0	14
OVERB. SLT.	2	0	0	0	2
OVERB. SH.	5	1	0	0	6
BONE/RIDER	3	3	2	4	12
ROOF SHALE	12	10	2	3	27
PARTING	9	4	3	1	17
SEATEARTH	5	4	1	1	11
COAL BED					
U. FREEPORT	30	8	6	14	58
L. FREEPORT	3	1	1	0	5
M. KITTANNING	3	2	1	1	7
L. KITTANNING	13	12	5	3	33
WAYNESBURG	3	4	2	2	11

The average a and T300/1000T values are summarized for the various lithic units in Table 6.

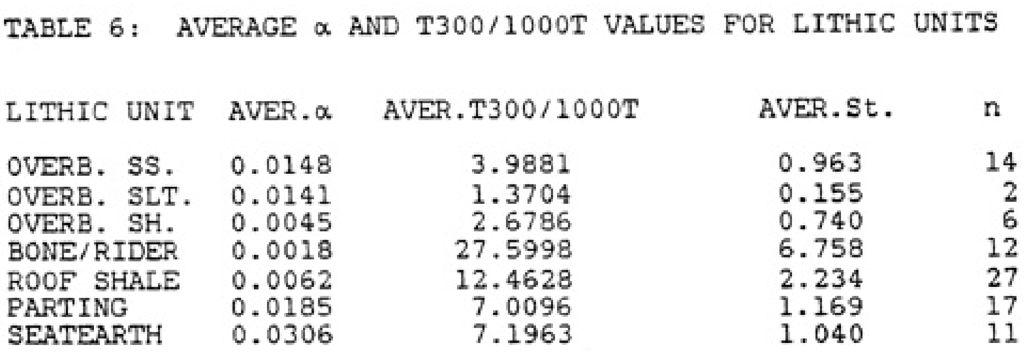


TABLE 6: AVERAGE α AND T300/1000T VALUES FOR LITHIC UNITS

LITHIC UNIT	AVER.α	AVER.T300/1000T	AVER.St.	n
OVERB. SS.	0.0148	3.9881	0.963	14
OVERB. SLT.	0.0141	1.3704	0.155	2
OVERB. SH.	0.0045	2.6786	0.740	6
BONE/RIDER	0.0018	27.5998	6.758	12
ROOF SHALE	0.0062	12.4628	2.234	27
PARTING	0.0185	7.0096	1.169	17
SEATEARTH	0.0306	7.1963	1.040	11

Although these data simply seem to corroborate what has been common knowledge within the industry, the importance of the data is that it actually QUANTIFIES the toxic response of the materials in question and could be accurately extrapolated to large systems by the method described earlier.

It is not surprising, considering our understanding of the origin of the materials, that the lithic units immediately associated with the coal bed, i.e. roof shales, partings and seatearths, have both the highest acid production rates and sulfate production levels. It is also interesting to note that the data substantiate certain field observations. For example, the rocks associated with the Upper Freeport coal show the widest range of potential acid production rates.

DATA PRESENTATION: Several graphic schemes of data presentation have been devised. Figure 2 is a plot of total sulfur after HCL leach versus T300/1000T at various values of a The average T300/1000T data for the individual lithic units and for the original Dobbin "standard" sample are plotted on the diagram. The figure is presented as a "WORKING CHART" from which the T300/1000T data can be determined once St and a. values are known. It can also be used to constantly accumulate data for a specific mine or mining area and can thereby be used as an AMD predictive tool. More samples are currently being evaluated to provide a clear picture of the lithic unit acid contribution.

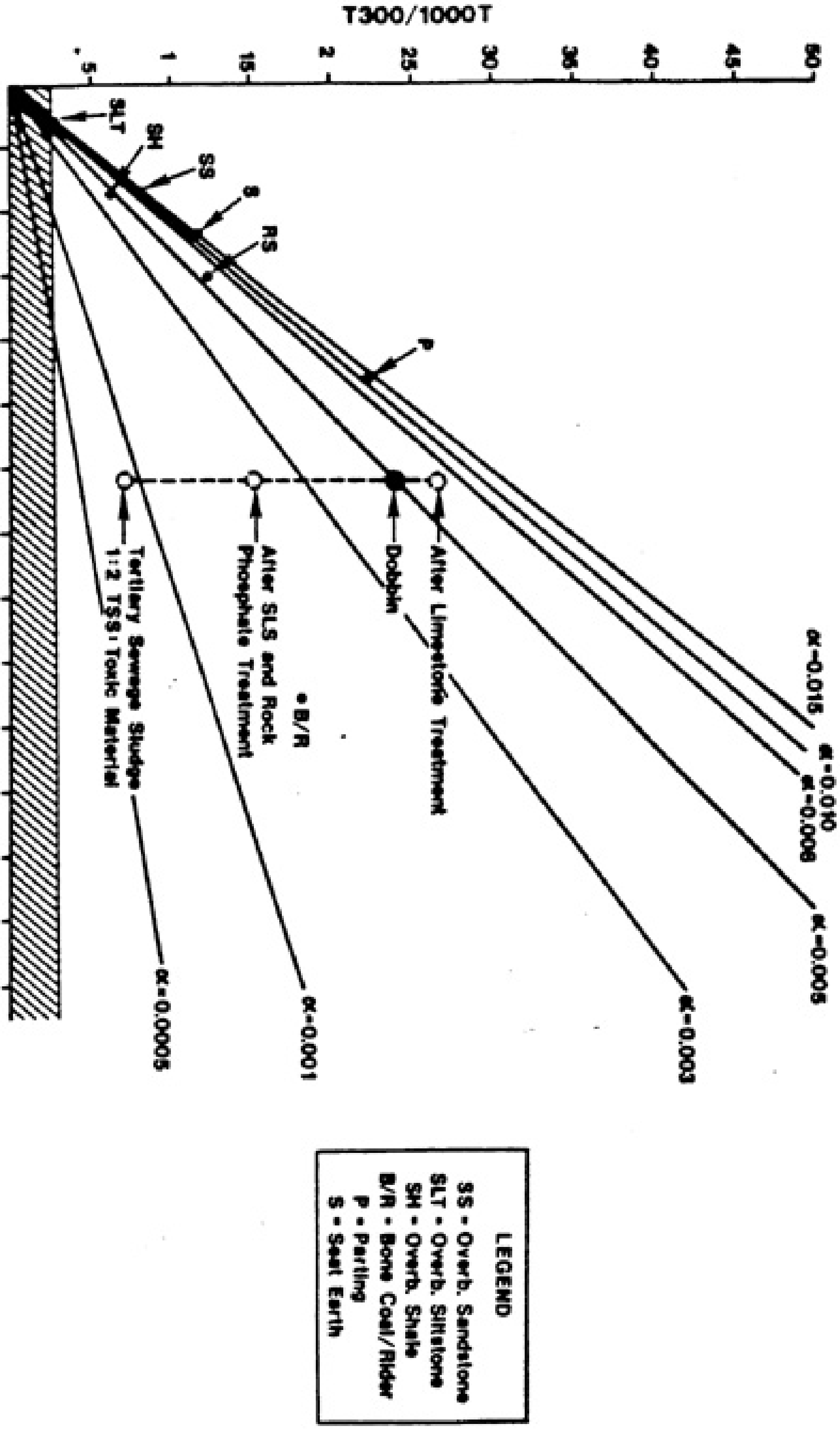


FIGURE 2 Relationship between % Total Sulfur, T300/1000T and α

The chart may also be used to evaluate the effectiveness of ameliorants. The purpose of using a chemical ameliorant such as SLS or rock phosphate or the utilization of the base front concept is to reduce the overall value of a within a reclamation site. In the case of SLS, the reduction in a is brought about by the elimination of bacteria and their subsequent catalytic effect upon disulphide dissolution. In the case of both the use of rock phosphate and the base front concept, the (x value is reduced by the elimination of the main oxidizing agent, the ferric ion. Note that the use of limestone was never intended to reduce acid production but rather was only meant to neutralize the acid once formed.

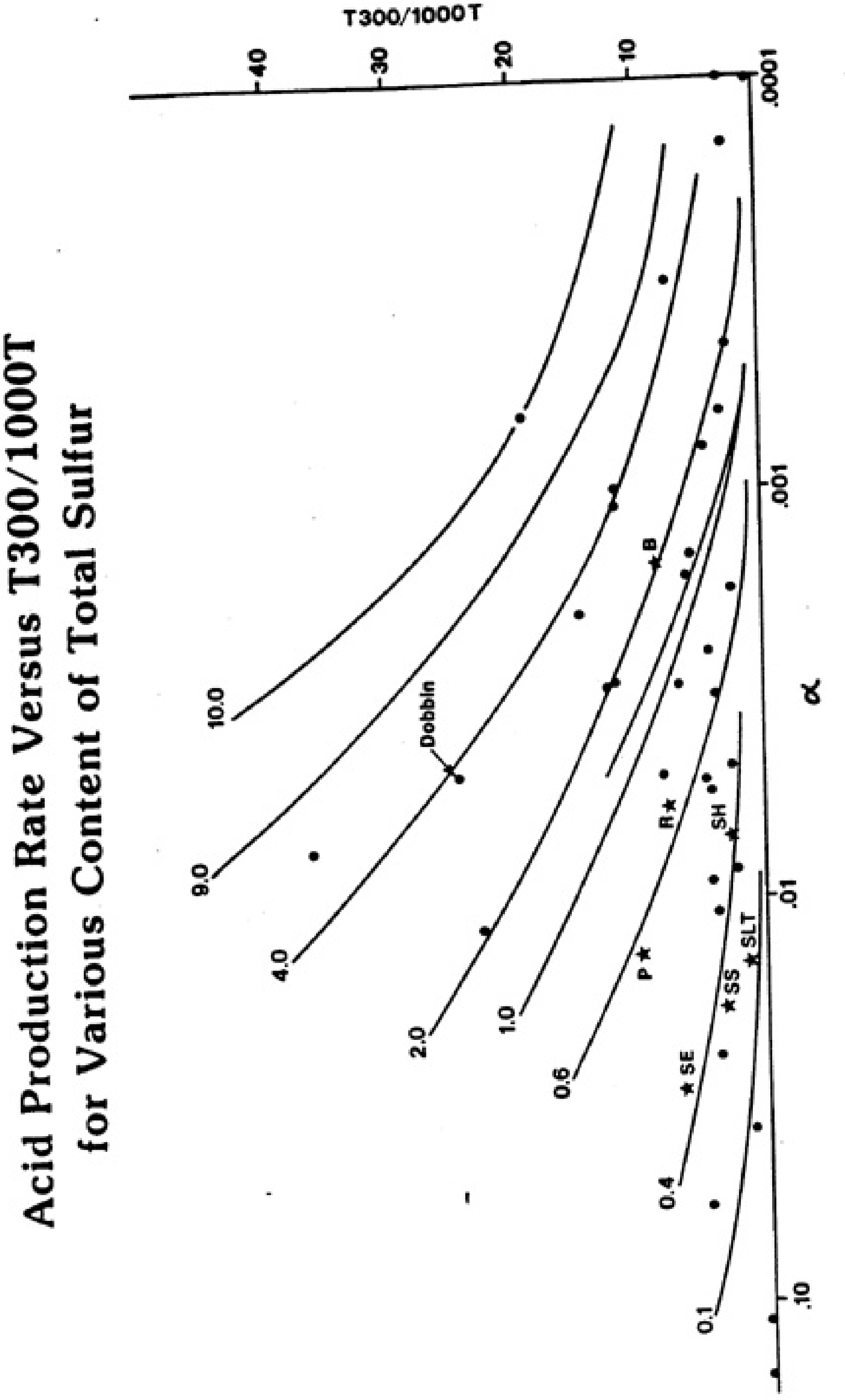
The Dobbin "standard sample" is plotted on the chart at St=3.15 and a = 0.0050 $days^{-1}$. The result of the comparative ameliorant study of Baker (1984) showed that an application of 2 gallons of 2 wt% SLS solution to 300 pounds of Dobbin refuse reduced the a value from 0.0050 $days^{-1}$ to 0.0020 $days^{-1}$. The intermixing of 2.5 pounds of rock phosphate with 300 pounds of Dobbin refuse reduced the a value to a similar level. Note that the addition of 15 pounds of crushed limestone to 300 pounds of Dobbin refuse INCREASED the value of a to 0.0060 days $^{-1}$.

In order for an ameliorant to be successful, the acid production in terms of T300/1000T must be reduced below some level yet to be experimentally determined. A maximum of 2.5 T300/1000T is arbitrarily indicated on the diagram tentatively as the upper limit of a zone within which any acid production would be internally neutralized. The actual upper limit of such a zone must necessarily be experimentally determined and field verified.

A second mode of data presentation is shown in figure 3 where the a value is plotted on a log scale versus T300/1000T. Note, for example, that the samples with the highest values of a (greater than 0.05 days $^{-1}$) are those with the lowest total sulfur contents (less than 0.4 wt%). Note also that the samples group with any level of sulfur content showing a range of a values. Work is now under way to investigate the reason(s) for the observed variation of acid production rates within the limited ranges of sulfur content.

(III) THE EFFECT OF PHOSPHATE MATERIALS ON THE ACID PRODUCTION FROM THE VARIOUS LITHIC UNITS ASSOCIATED WITH COAL

The effectiveness of any ameliorative treatment is a function of three factors: (1) the chemical and physical characteristics of the potentially toxic materials, (2) the chemical and Physical characteristics of the ameliorative material used and (3) the application schedule of the ameliorant. The grant from the W.V.U.



Acid Production Rate Versus T300/1000T for Various Content of Total Sulfur

FIGURE 3

Water Research Institute (W.R.I.) studied the first of the three factors. Although many parameters which affect the level of toxic response of rock materials are as yet not fully evaluated or in some cases are not yet known, it is quite obvious that the mass and chemical response of the individual rock types encountered in mining must be taken into account if any reclamation plan is to be effective.

Within the Past year under grants from the W.Va. Department of Energy and the Florida Institute of Phosphate Research, a study was initiated to examine the second and third factors. A suite of six phosphate materials has been acquired from various sources. Characteristics of the phosphate materials vary widely both physically and mineralogically. The Phosphate materials collected for the amelioration study include: (1) a solar dried slurry refuse material from Florida consisting of approximately 25 wt% apatite with the remainder dominated by smectite dominated clay minerals, (2) a fine grained (-200 mesh) refuse material from North Carolina consisting of approximately a 50/50 mixture of apatite and quartz, (3,4) two fine grained (-200 mesh) high quality rock phosphate from North Carolina and (5,6) two granule to pebble size high grade rock phosphate materials from Florida. In phase three, the W.R.I. lithotype samples and these phosphate materials are being experimentally combined in order to evaluate the relative effectiveness of the various phosphate materials to reduce the acid Production from rocks of varying toxicity. The results from twelve such experiments are reported here.

EXPERIMENTAL DESIGN: For the initial experiments, three of the collected rock phosphate materials were chosen; the Florida solar dried slurry (CC 1770) and two fine grained high quality materials from North Carolina (CC 5168 and CC 5169). The W.R.I. samples assigned to each treatment with their pertinent data are listed in Table 7.

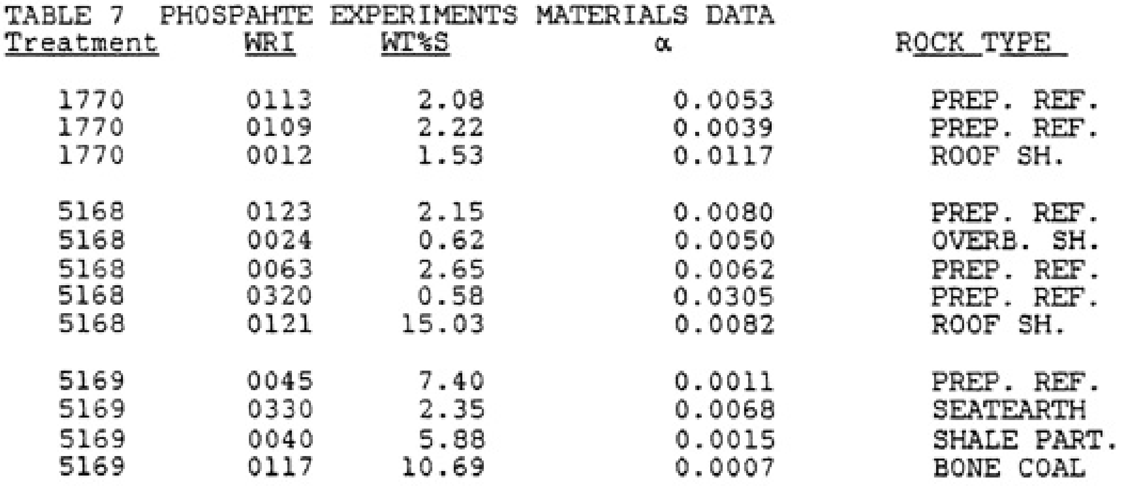


TABLE 7 PHOSPAHTE EXPERIMENTS MATERIALS DATA

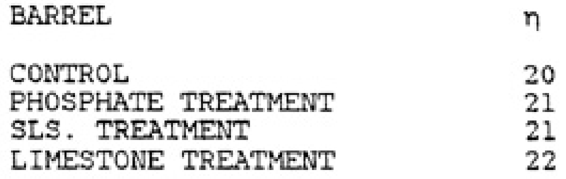
Treatment	WRI	WT%S	α	ROCK TYPE
1770	0113	2.08	0.0053	PREP. REF.
1770	0109	2.22	0.0039	PREP. REF.
1770	0012	1.53	0.0117	ROOF SH.
5168	0123	2.15	0.0080	PREP. REF.
5168	0024	0.62	0.0050	OVERB. SH.
5168	0063	2.65	0.0062	PREP. REF.
5168	0320	0.58	0.0305	PREP. REF.
5168	0121	15.03	0.0082	ROOF SH.
5169	0045	7.40	0.0011	PREP. REF.
5169	0330	2.35	0.0068	SEATEARTH
5169	0040	5.88	0.0015	SHALE PART.
5169	0117	10.69	0.0007	BONE COAL

DETERMINATION OF ETA(n):

In previously reported experiments, a parameter, a, was experimentally determined which measured the rate of acid production from a potentially toxic material. This was determined from the rate at which sulfate ion was released into solution. The direct calculation of a values for phosphate treated experiments is not possible because of the presence of acid soluble sulfate minerals in most of the phosphate materials. Because of the presence of sulfate minerals, the leachate sulfate content cannot be used to calculate the amount of iron disulphides that have reacted in the experiment. An indirect method had therefore to be devised to evaluate a second parameter related to acid production for experiments employing phosphate ameliorants. This parameter is referred to as eta (n). Eta relates the cumulative acid load generated in these experiments to the percent sulfur consumed in the untreated control. The parameter T) is calculated by dividing the cumulative acid load expressed in mg

$CaCO_3$ /100 grams of sample or in Tons $CaCO_3$ /1000 Tons sample by the product of the total sulfur content of the material and the percent sulfur reacted as calculated from the leachate sulfur concentration. For example, in a particular experiment with a toxic material containing 2 wt% sulfur, if at the end of a leach cycle the sulfate content of the leachate indicates that 25% of the sulfur content has been reacted, then the T) value would be calculated by dividing the cumulative acidity by the product 2.00 x 0.25. Values of n calculated for the individual leach cycles of the original Dobbin barrel experiments showed a marked consistency (see Table 8)

TABLE 8 ETA VALUES FOR BARREL EXPERIMENTS



BARREL	η
CONTROL	20
PHOSPHATE TREATMENT	21
SLS. TREATMENT	21
LIMESTONE TREATMENT	22

The reported n values are obtained by using the percent reacted sulfur values from the control experiments to calculate the n values for the equivalent soxhlet cycles of the phosphate experiments. In this way the n values of the phosphate treated samples are calculated relative to the untreated controls. For each experiment., an average n value is calculated from the n values of the three replicates. It should be pointed out that the 31.25 constant in the acid-base account procedure is in fact the N value assuming that 100% of all the sulfur in the sample is in the form of iron disulphides and that all the iron disulphides react to form acid. A histogram of the calculated N values for the 114 W.R.I. lithotype samples is illustrated in Figure 4. Note that the data are highly Gaussian and indicated that for most samples, the acid-base accounting procedure would over-estimate the actual acid load as would be expected. It is perhaps significant to note that in a few cases, the acid-base accounting would underestimate the acid load. In this data set, it is perhaps equally significant that the samples with n values in excess of 31.25 were associated with the Upper Freeport and Lower Kittanning coal beds.

The control and treatment data for the twelve experiments reported in the paper are tabulated in Table 9. An 'n ratio is calculated for each phosphate treatment by dividing the -n value of the treatment by the 'n value of the untreated control. The magnitude of this ratio is the percent of the untreated acid load -produced by the treated system. It is significant to note that at a 2 wt% apatite addition schedule, the acid load of eight of the twelve samples was reduced from 47% to 77% relative to that of the corresponding untreated control. Of the remaining four samples, two of the low acid reduction rates were obviously due to exceptionally high total sulfur contents of 10.69% and 15.03% in the rock materials. It would not be economically feasible to eliminate acid production from such materials by chemical treatment. One of the samples that showed only a 39% reduction in acid load had only 0.62 wt% sulfur. The low ameliorative reaction of such a sample is Probably due to the inherent chemical non-reactivity of the euhedral iron disulphides which characterize this sample. The low acid load reduction (14%) of sample CC 0063 is the only one that is not readily explainable. The sample has a sulfur content of 2.65 wt% and a value of 0.0082 days^{-1} and would have been expected to show a larger acid load reduction. It is however, from this kind of sample response that more information is likely to be learned relative to the major chemical controls of phosphate ameliorization than from those that responded predictably.

FIGURE 4

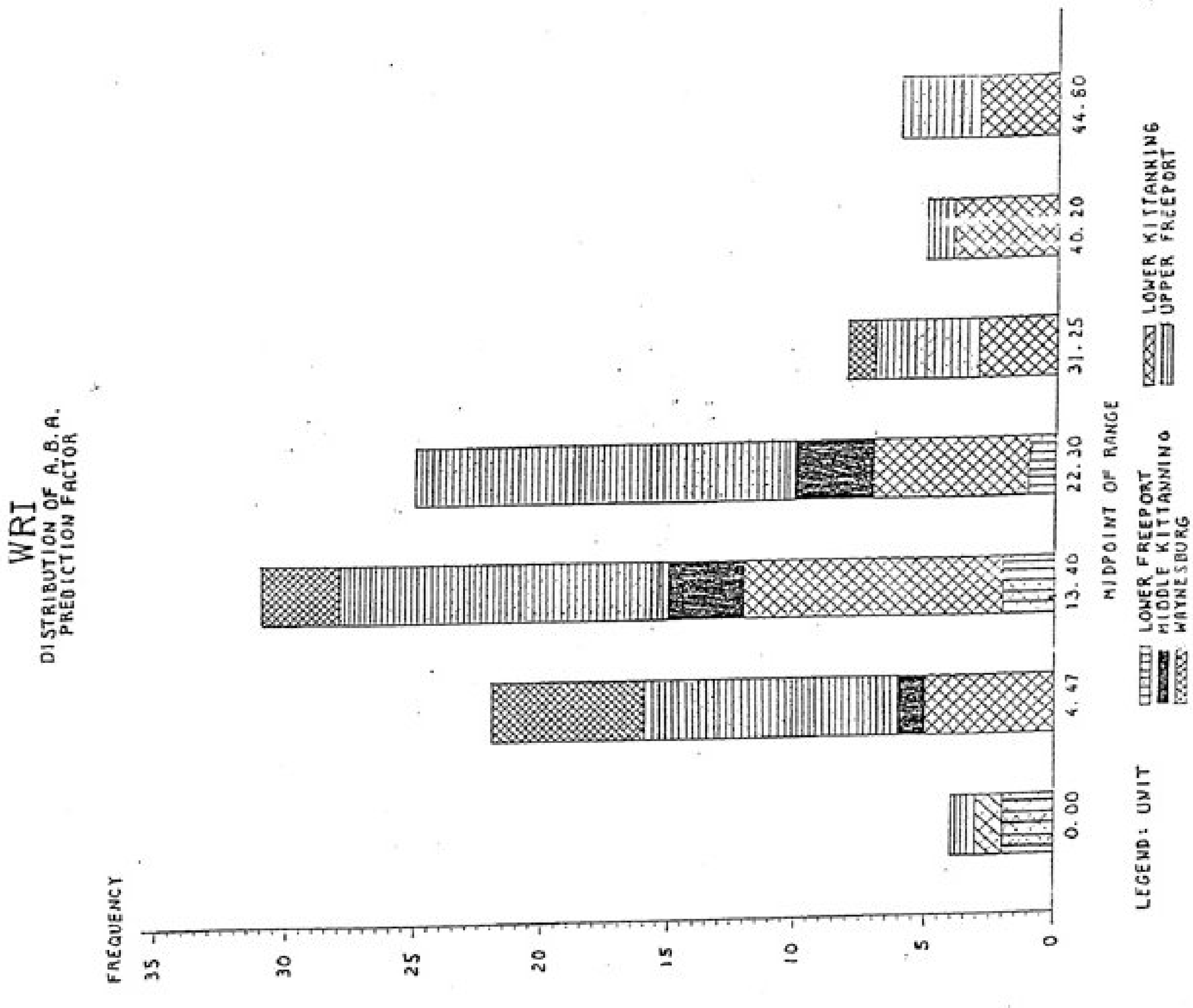


TABLE 9 ETA VALUES AND ETA RATIOS FOR PHOSPHATE STUDY

PHOSPHATE CC NUMBER	WRI CC NUMBER	TOTAL SULFUR	APPLICATION SCHEDULE	ETA	TREATED TO CONTROL ETA RATIO
5168	320	0.58	0.000	36.2140	1.0000
5168	320	0.58	0.250	24.6649	0.6811
5168	320	0.58	0.500	17.3332	0.4786
5168	320	0.58	1.000	16.1284	0.4454
5168	320	0.58	2.000	11.8178	0.3263
5168	24	0.62	0.000	8.9696	1.0000
5168	24	0.62	0.250	6.1220	0.6825
5168	24	0.62	0.500	7.3373	0.8180
5168	24	0.62	1.000	7.4973	0.8359
5168	24	0.62	2.000	5.4652	0.6093
1770	12	1.53	0.000	8.5983	1.0000
1770	12	1.53	0.250	6.9891	0.8129
1770	12	1.53	0.500	6.0287	0.7012
1770	12	1.53	1.000	4.2359	0.4926
1770	12	1.53	2.000	3.3216	0.3863
1770	113	2.08	0.000	56.7320	1.0000
1770	113	2.08	0.250	51.4279	0.9065
1770	113	2.08	0.500	36.6955	0.6468
1770	113	2.08	1.000	30.8109	0.5431
1770	113	2.08	2.000	20.8664	0.3678
5168	123	2.15	0.000	59.1344	1.0000
5168	123	2.15	0.250	50.8804	0.8604
5168	123	2.15	0.500	42.9549	0.7264
5168	123	2.15	1.000	39.2816	0.6643
5168	123	2.15	2.000	31.2557	0.5286
1770	109	2.22	0.000	14.4494	1.0000
1770	109	2.22	0.250	11.7955	0.8163
1770	109	2.22	0.500	20.2931	1.4044
1770	109	2.22	1.000	7.8696	0.5446
1770	109	2.22	2.000	4.0591	0.2809
5169	330	2.35	0.000	18.3493	1.0000

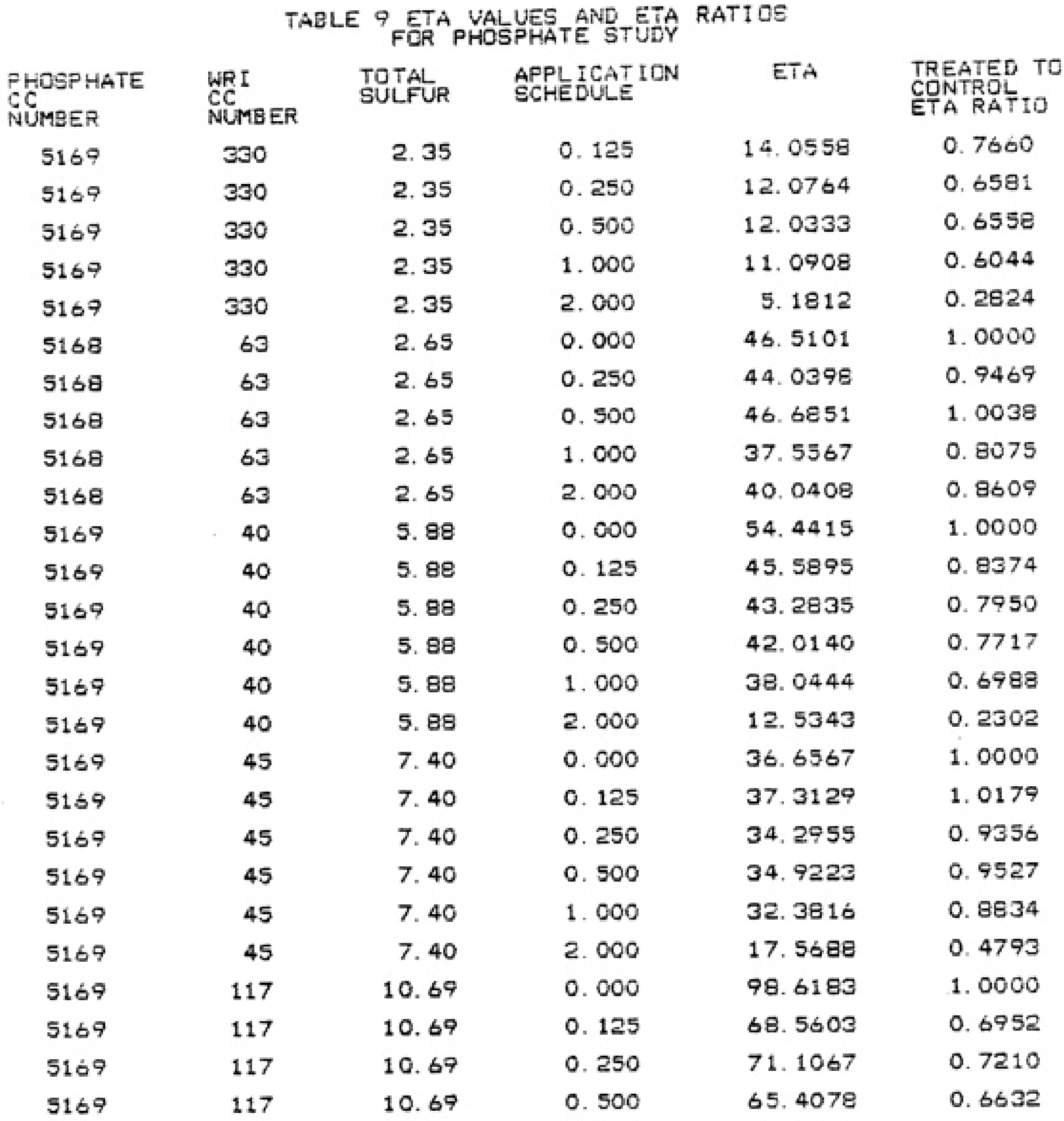


TABLE 9 ETA VALUES AND ETA RATIOS
FOR PHOSPHATE STUDY

PHOSPHATE CC NUMBER	WRI CC NUMBER	TOTAL SULFUR	APPLICATION SCHEDULE	ETA	TREATED TO CONTROL ETA RATIO
5169	330	2.35	0.125	14.0558	0.7660
5169	330	2.35	0.250	12.0764	0.6581
5169	330	2.35	0.500	12.0333	0.6558
5169	330	2.35	1.000	11.0908	0.6044
5169	330	2.35	2.000	5.1812	0.2824
5168	63	2.65	0.000	46.5101	1.0000
5168	63	2.65	0.250	44.0398	0.9469
5168	63	2.65	0.500	46.6851	1.0038
5168	63	2.65	1.000	37.5567	0.8075
5168	63	2.65	2.000	40.0408	0.8609
5169	40	5.88	0.000	54.4415	1.0000
5169	40	5.88	0.125	45.5895	0.8374
5169	40	5.88	0.250	43.2835	0.7950
5169	40	5.88	0.500	42.0140	0.7717
5169	40	5.88	1.000	38.0444	0.6988
5169	40	5.88	2.000	12.5343	0.2302
5169	45	7.40	0.000	36.6567	1.0000
5169	45	7.40	0.125	37.3129	1.0179
5169	45	7.40	0.250	34.2955	0.9356
5169	45	7.40	0.500	34.9223	0.9527
5169	45	7.40	1.000	32.3816	0.8834
5169	45	7.40	2.000	17.5688	0.4793
5169	117	10.69	0.000	98.6183	1.0000
5169	117	10.69	0.125	68.5603	0.6952
5169	117	10.69	0.250	71.1067	0.7210
5169	117	10.69	0.500	65.4078	0.6632

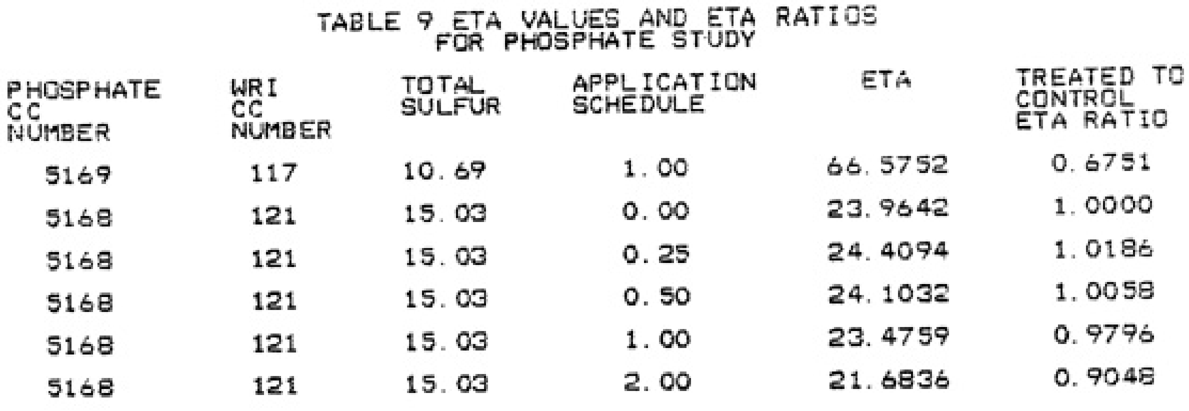


TABLE 9 ETA VALUES AND ETA RATIOS
FOR PHOSPHATE STUDY

PHOSPHATE CC NUMBER	WRI CC NUMBER	TOTAL SULFUR	APPLICATION SCHEDULE	ETA	TREATED TO CONTROL ETA RATIO
5169	117	10.69	1.00	66.5752	0.6751
5168	121	15.03	0.00	23.9642	1.0000
5168	121	15.03	0.25	24.4094	1.0186
5168	121	15.03	0.50	24.1032	1.0058
5168	121	15.03	1.00	23.4759	0.9796
5168	121	15.03	2.00	21.6836	0.9048

Plots of n ratio versus wt% apatite addition in most of the samples illustrate a exponential relationship (i.e. the % reduction in n is exponentially related to the apatite wt%). (See figure 5 through 7). It must be pointed out however that as was the case in the original study, comparable data from the small field scale (barrel) experiments are yet needed to allow the mathematical relationships devised from the bench scale experiments to be scaled up to actual field conditions. The necessary field experiments are now being Prepared and should be in place by April.

FUTURE WORK: The work planned for the future includes detailed investigations into all samples that exhibit unusual responses such as those indicated above. From the work completed to date and reported in part here, it is quite obvious that, although the various kinds of phosphate materials have potentially different ameliorative responses, apatite is an effective AMD ameliorant. Future experiments will further investigate the ameliorative properties of the varieties of phosphate materials available. Experiments are now in progress to investigate the effect of rock phosphate particle size and of possible effects of other phosphate associated minerals in acid ameliorization.

FIGURE 5

PHOSPHATE TREATMENT

FOR CC NUMBER 0012

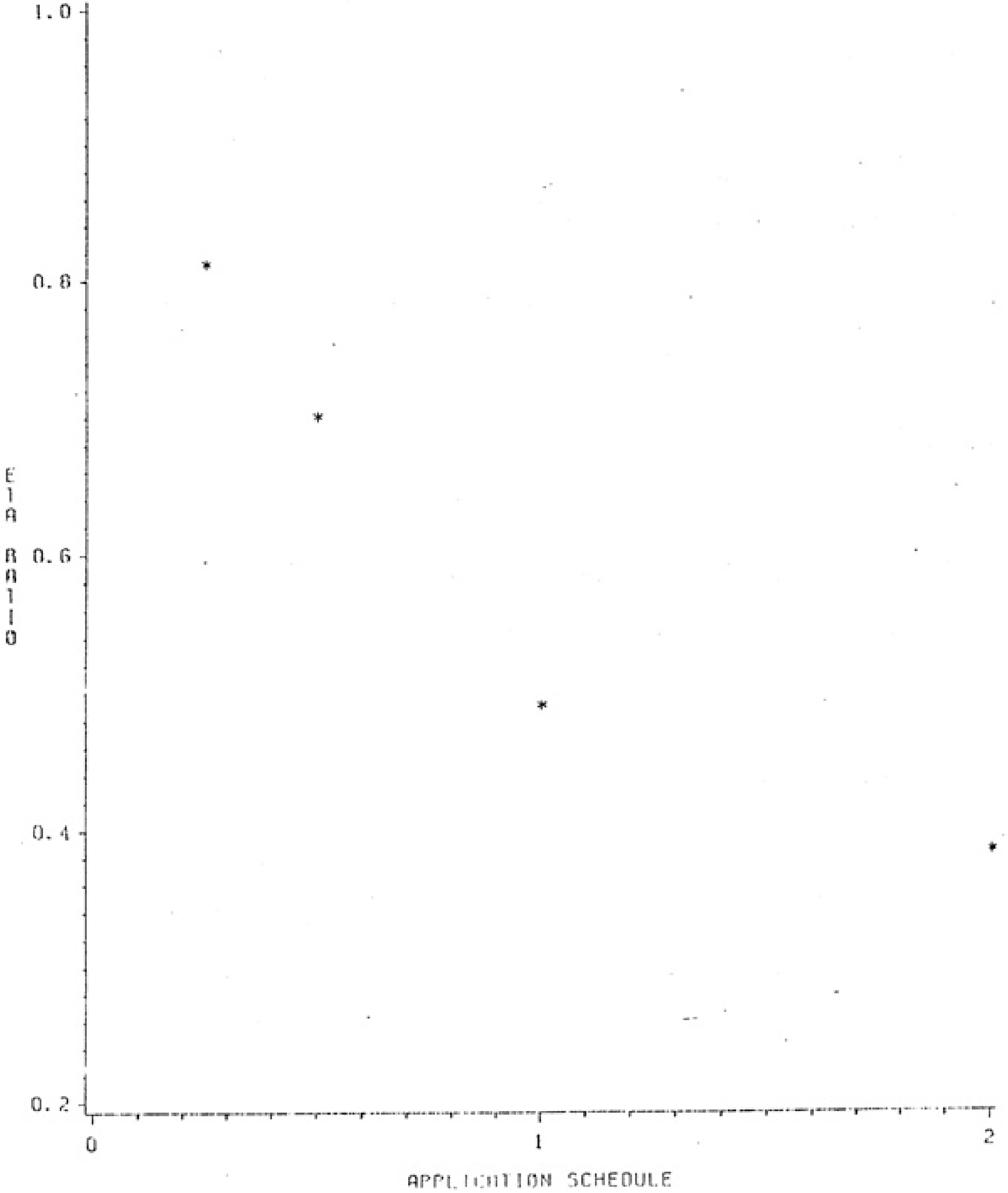


FIGURE 6

PHOSPHATE TREATMENT

FOR CC NUMBER 113

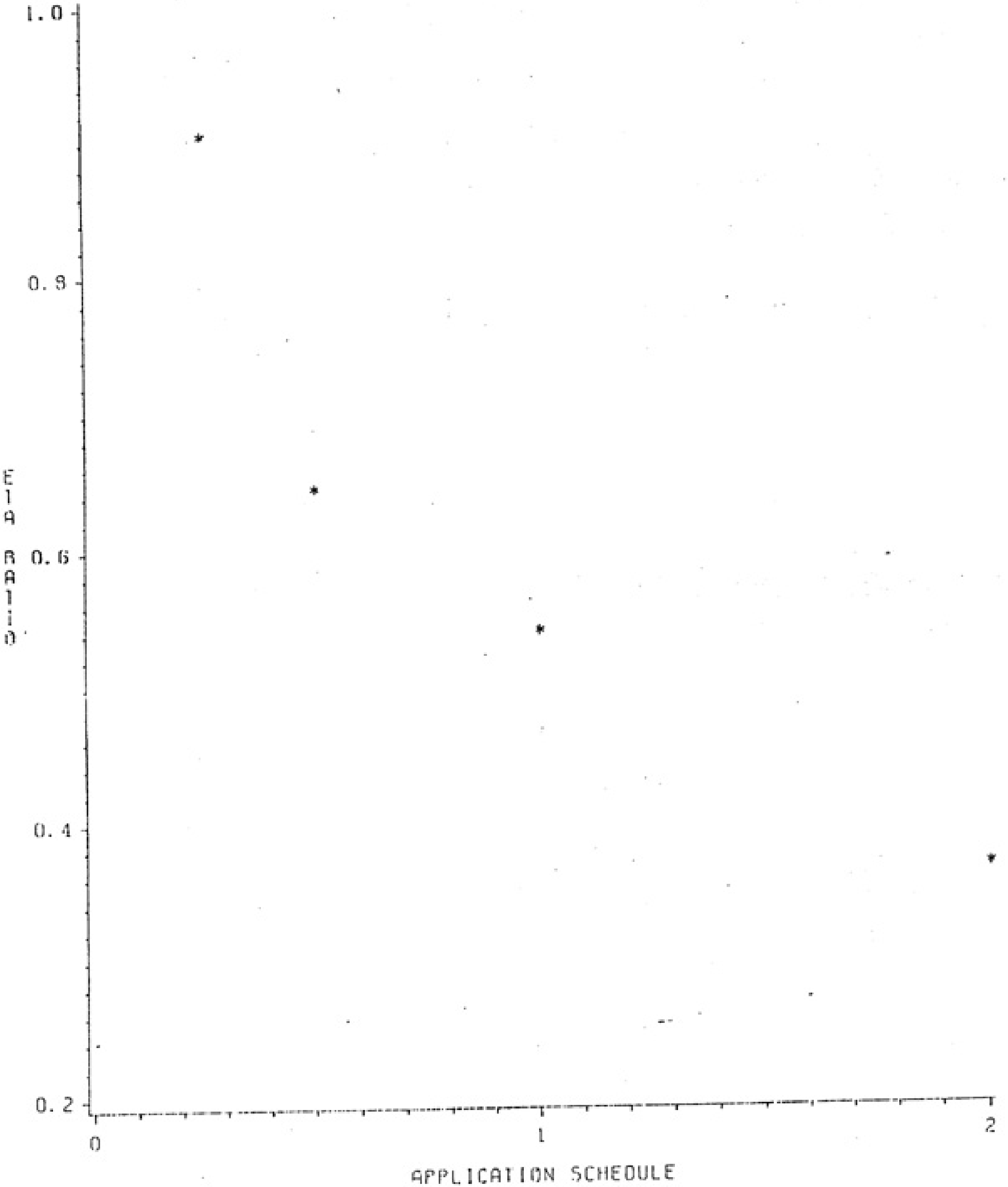
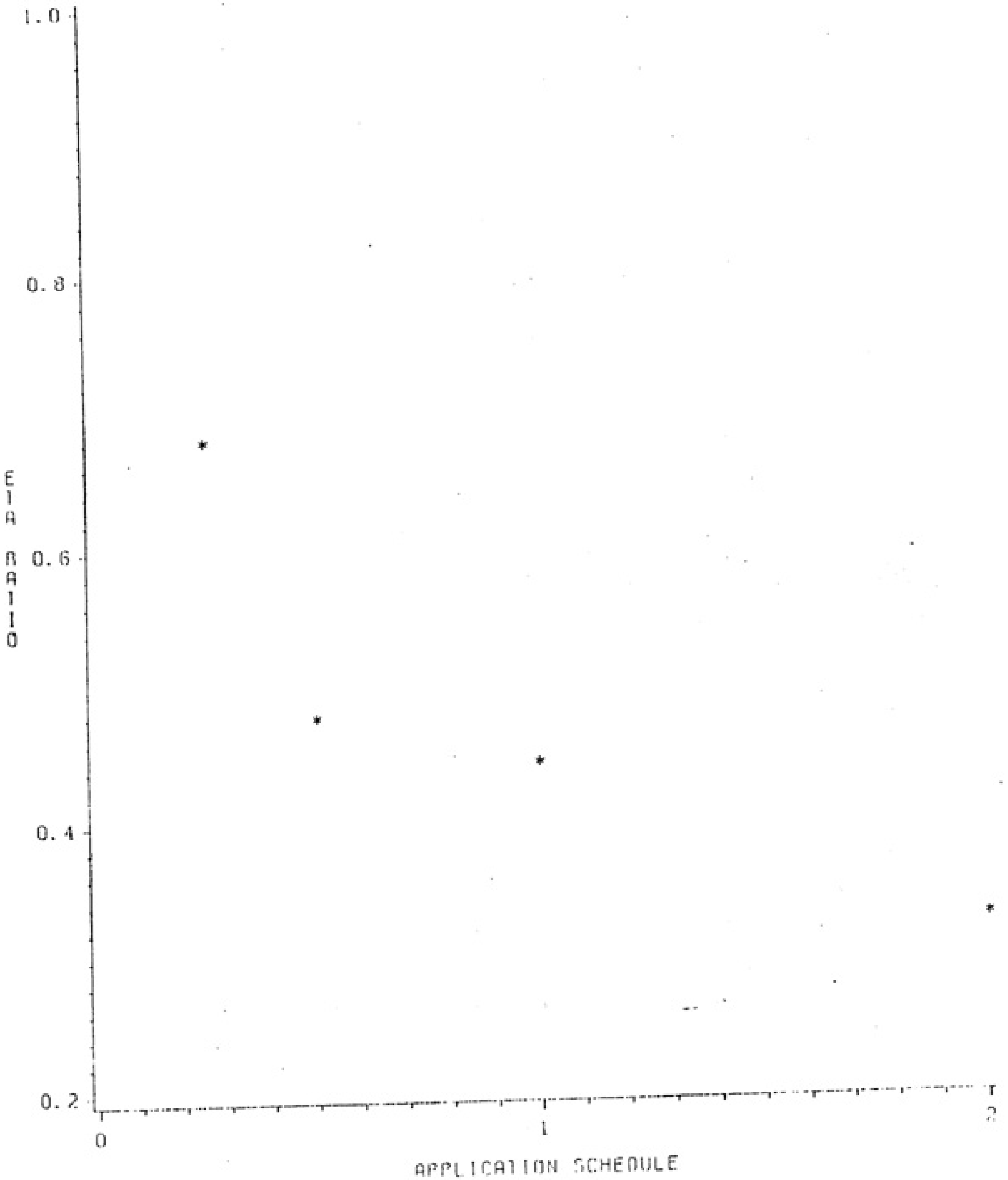


FIGURE 7

PHOSPHATE TREATMENT

FOR CC NUMBER 320



In addition to the data referred to here, a large database exists consisting of additional compositional data characterizing the toxic materials, the phosphate materials and the experimental leachates. Data are available, for example, evaluating the production of heavy metals from the various lithic materials and the potential of the phosphate ion for their removal. All of these data will be analyzed by multivariate statistics. The results of these data syntheses will hopefully contribute to a better understanding of the chemistry of acid formation and its controls and of the chemistry of phosphate ameliorization. It is further anticipated that the work will allow the attainment of the ultimate goal of this work namely, the formulation of a mathematical model which will determine the optimum application schedule for any particular phosphate material to reduce the rate of acid production from any toxic material to such a low level so as to be internally neutralized within the system.