THE USE OF PHOSPHATE MATERIALS AS AMELIORANTS FOR ACID MINE DRAINAGE

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Abstract.--Research has shown that limestone, when used as an acid ameliorant in surface mine reclamation may result in an increase in both the acid production rate and the total acid load. Rock phosphate has been shown to be an effective acid ameliorant based upon its ability to sequester the major oxidizing agent of the iron disulphide minerals, Fe^{+3}, as an insoluble phosphate. A series of coordinated bench scale and small field scale experiments were conducted to evaluate the response of rock phosphate intermixed with toxic rock materials upon exposure to laboratory and real weathering conditions. The experiments utilized rock phosphate from granule size down to -325 mesh at application rates up to 7 wt% apatite. The work showed that rock phosphate in excess of about 1/16" mean diameter was relatively ineffective as an ameliorant. Effectiveness as an ameliorant, however, increased with decreasing particle size and application rate. Most effective was a clay slurry spiked with -325 mesh apatite and hydraulically applied. The results showed that a minimum application rate of about 1 wt% apatite is required for ameliorization to become effective and that reductions of acid production rate and total acid load can be reduced up to 90% over an untreated control at application rates of about 4 to 5 wt% apatite.

INTRODUCTION

In areas producing high sulfur coal (>1 wt% S) such as the Illinois Basin, highly calcareous overburden materials or calcite-rich surficial materials are readily available for reclamation purposes. As a result, acid mine drainage is rarely a problem. However, in high sulfur areas such as the northern Appalachian Basin where calcareous rocks are not generally abundant, limestone has been routinely added to the toxic (sulfur containing) rock materials during reclamation to ameliorate acidity. However, the use of limestone has not always resulted in the elimination of acid waters.

Early in the research of the authors, experimental weathering data indicated that the presence of calcite in sulfur-containing rock materials could actually INCREASE acid production. In initial soxhlet leach experiments designed to evaluate the acid producing potential of various coals and coal-associated rocks, a direct correlation was observed between the calcium content and INCREASING sulfate concentration (used as a measure of originally produced acidity) of the leachates. It was also observed that coals collected for study which did not have exceptionally high sulfur contents but contained iron disulphide minerals in direct contact with calcite invariably would rapidly decompose the cloth collection bags. Acid was obviously being produced at a rate disproportionate to the sulfur content of the coal.

To further investigate the effect of calcite on acid production from toxic rock materials, a series of experiments was conducted which intermixed pure calcite with several rock materials of differing toxic potential at application schedules of 0.50, 1.00, 2.00 and 4.00 wt% calcite. The experiments showed that the addition of calcite in application rates up to about 5 wt% increased acid production over that of the untreated controls (Fig. 1). Acid loads reached a maximum at about 1.0 wt% calcite addition after which acid production dropped. At about 5 wt% $CaCO_3$ addition, the acid production equaled that of the untreated controls. Beyond 5 wt% calcite addition, the acid production decreased relative to the controls, and calcite became an

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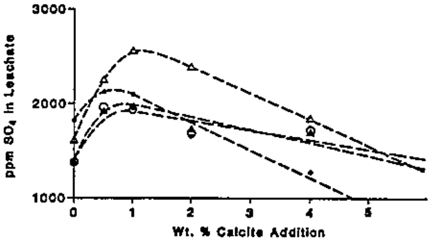


FIGURE 1. Relation Between SO_4^{-2} Production (Acid Production) from Four Typical Toxic Rock Materials Treated with Calcite at 0.5, 1.0, 2.0 and 4.0 Wt. % Addition Rates

effective acid ameliorant.

It is important to note that the use of limestone in surface mine reclamation is usually not intended to eliminate the PRODUCTION of acid from the weathering of rocks containing iron disulphide minerals but rather is meant only to neutralize acidity. It should be pointed out, however, that $CaCO_3$ will inhibit the oxidation of the iron disulphides and subsequent acid production if the application rate is high enough to raise the pH of the system to approximately pH 6-7. At this point, acid production would be reduced both by the precipitation of dissolved iron, the major oxidizing agent, and by the inhibition of iron and sulfur oxidizing bacteria.

Normally, calcite is used simply to neutralize acid already generated. Because the neutralization reaction takes place at the surface of the calcite grains, the calcite grains will eventually become coated with precipitated iron oxy-hydroxides thereby reducing the effective calcite concentration. According to the experimental data presented in Fig. 1, should the effective calcite concentration drop below 5 wt%, the system will once again become a net acid producer. This may explain the frequent lack of success in using limestone as an AMD ameliorant.

With limestone being questioned as a potential ameliorant, a substitute was sought. Our objective was to utilize a natural occurring material so as not to subject the environment to another source of unnatural pollution and preferably to utilize a material that would actually prevent the oxidation of the iron disulphide minerals rather than simply neutralize acidity. Apatite was chosen because it filled all the criteria. Apatite eliminates acid formation by removing Fe^{+3}, the major oxidizer of the iron disulphide minerals, and precipitating it as an insoluble iron phosphate below pH 5.5. In addition, apatite only dissolves when the conditions drop below pH 5.5 (ref. 1). It is therefore a time release material. The purpose of this work was to systematically evaluate the effectiveness of a variety of available phosphatic materials as acid ameliorants.

EXPERIMENTAL MATERIALS

PHOSPHATE MATERIALS: Phosphate materials were categorized for this study into three types: 1) sand to pebble sized rock phosphate, 2) fine grained (less than 150 mesh) rock phosphate and 3) dried phosphate slurry (slime). The sand to pebble sized rock phosphate, composed largely of the mineral apatite, is the material that is presently being used in the Appalachian Basin with varying amounts of success (or lack of success). The fine grained rock phosphate is the larger sized apatite that has been ground into fine particle sizes in order to increase the available reactive surface area. In this research, two sizes of ground apatite were used, one designated CODE 30 that was 95% in the size range from 150 to 250 mesh and a second material designated CODE 31 that was about 65-70% less than 325 mesh. The 150-250 mesh material was considered the finest size that could be used on-site without dust generation problems. The -325 mesh material was primarily considered as an additive to increase the apatite content and subsequent effectiveness of the dried slurry material.

The phosphatic slurry (slime) is a reject material of the phosphate mining industry. The utilization of the dried slurry was considered most important in that it was an attempt to utilize a costly refuse material of the phosphate industry to solve an equally costly problem of the coal industry. The composition of slurry material varys depending upon the geographic source. The dried slurry used in these experiments averaged 25 wt% apatite the remainder being smectite dominated clay minerals. The highly reactive clay-sized apatite content, the ability of the dried material to be reslurried and hydraulically applied, the tendency of the slurry to stick to applied surfaces and the fact that the apatite content could be increased by "spiking" with fine-grained (-325 mesh) apatite were the main attributes of the material.

TOXIC MATERIALS: The toxic materials used in this work were of two varieties. The first was a common toxic "standard" material, a typical coal cleaning plant waste which was used in both bench scale and small field scale experiments. In addition, all phosphatic materials were tested in bench scale experiments against a second suite of toxic materials which represented all of the various rock lithotypes encountered in coal mining. The second suite of rock materials provided the range of sulfur contents and acid producing potentials normally encountered in mining. The data generated by the experiments using this suite of toxic materials allowed the statistical testing of all possible interrelationships between the various phosphate addition rates and individual rock compositional and acid parameters.

EXPERIMENTAL METHODS

The experiments conducted in this work were of two types: 1) bench scale and 2) small field scale (barrel) experiments. The bench scale experiments exposed 100 gram samples of the toxic materials and toxic material/phosphatic material mixtures to the synthetic weathering conditions while the small field scale experiments exposed 300 pounds of the experimental materials to natural weathering conditions. Both procedures were reported earlier and described in detail by the authors (2,3). The experimental arrangements for each is shown in figures 2 and 3 respectively.

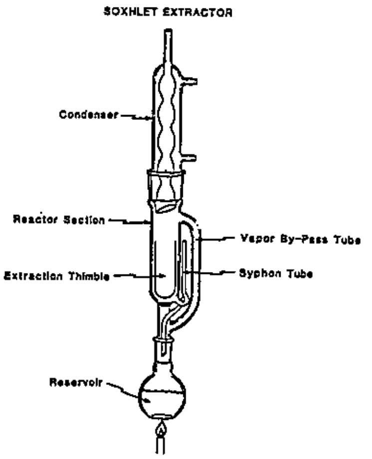


FIGURE 2. Schematic Diagram of Soxhlet Extractor

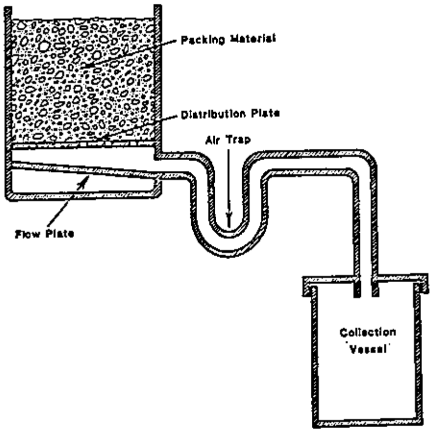


FIGURE 3. Schematic of Small Field Scale (Barrel) Experiment

TABLE 1 EXPERIMENTAL SET #1

CC#	COAL BED ASSOC.	LITHIC TYPE	St	ALPHA	S_{300}	LTA	TREATMENT	TREATMENT CC#
6434	U.FREE	REF.	2.970	-0.0003	2.56	48.00	1/4"-1/8"	5192
116	M.KITT	ROOF SHALE	1.410	-0.0012	7.578	22.495	1/4"-1/8"	5192
114	U.FREE	REF.	2.830	-0.0093	31.159	25.287	1/4"-18"	5192
22	L.KITT	REF.	2.742	-0.0012	10.778	12.405	1/4"-1/8"	5192
6434	U.FREE	REF.	2.970	-0.0003	2.56	48.00	1/8"-1/16"	5191
122	U.FREE	ROOF SHALE	7.771	+0.0075	37.347	23.894	1/8"-1/16"	5191
60	U.FREE	REF.	2.955	-0.0012	7.535	10.467	1/8"-1/16"	5191
53	U.FREE	REF.	6.501	-0.0046	26.600	25.371	1/8"-1/16"	5191
6434	U.FREE	REF.	2.970	-0.0003	2.56	48.00	<1/16"	5190
326	L.KITT	REF.	7.010	-0.0039	33.163	22.314	<1/16"	5190
35	U.FREE	REF.	1.140	-0.0019	9.957	32.649	<1/16"	5190
19	L.KITT	REF.	1.812	-0.0010	2.514	23.103	<1/16"	5190
330	U.FREE	SEAT-EARTH	2.660	-0.0068	20.415	6.263	CODE 30	5168
47	M.KITT	BONE COAL	5.263	-0.0007	19.544	23.957	CODE 30	5168
45	U.FREE	REF.	6.334	-0.0011	20.383	20.158	CODE 30	5168
40	L.KITT	PARTING	4.242	-0.0015	21.252	30.193	CODE 30	5168
6434	U.FREE	REF.	2.970	-0.0003	2.56	46.000	CODE 30	5168
337	L.KITT	REF.	9.113	-0.0051	35.064	21.617	CODE 30	5168
320	U.FREE	REF.	0.535	-0.0535	5.795	25.324	CODE 30	5168
123	U.FREE	REF.	3.156	-0.0080	19.570	16.660	CODE 30	5168
121	U.FREE	ROOF SHALE	9.740	-0.0082	13.737	24.710	CODE 30	5168
63	U.FREE	REF.	4.560	-0.0082	24.22	23.13	CODE 30	5168
55	U.FREE	ROOF SHALE	6.910	-0.0008	9.123	27.71	CODE 30	5168
24	U.FREE	OVERB. SHALE	0.652	-0.0050	4.83	5.00	CODE 30	5168
6434	U.FREE	REF.	2.497	-0.0003	2.56	46.000	AGRICO	5166
5070	U.FREE	REF.	3.150	-0.0050	17.06	56.36	AGRICO	5166
13	U.FREE	REF.	4.550	-0.0052	16.53	17.73	AGRICO	5166
12	L.KITT	ROOF SHALE	1.536	-0.0117	14.64	5.37	AGRICO	5166
19	L.KITT	REF.	1.012	-0.0010	4.777	23.103	AGRICO/C31	8348
26	U.FREE	ROOF SHALE	2.428	-0.0063	20.792	25.676	AGRICO/C31	8348
49	U.FREE	S.S.	1.740	-0.0003	1.359	45.210	AGRICO/C31	8348
62	U.FREE	REF.	5.575	-0.0050	43.102	20.943	AGRICO/C31	8348
64	U.FREE	REF.	3.312	-0.0051	27.847	15.911	AGRICO/C31	8348
119	L.FREE	PARTING	1.940	-0.0033	12.104	12.114	AGRICO/C31	8348

BENCH SCALE EXPERIMENTS

The bench scale experiments were designed to evaluate the effect of different addition schedules of each of the three basic phosphatic materials on both the rate of acid production and on the ultimmate acid load. Four sets of experiments were conducted.

SET #1:

Table 1 summarizes the first set of bench scale experiments which were conducted to evaluate the effect of intermixing the various kinds of phosphatic materials with a suite of different toxic lithotypes. In each of the experiments, the respective phosphatic material was added in 0.25, 0.50, 1.00 and 2.00 wt% apatite. All data were compared to an untreated control. All experiments were run in triplicate. The table lists the coal bed association, the specific lithotype and the various acid evaluation parameters for each of the toxic materials. The CC#'s are laboratory identification numbers.

The first 12 experiments listed are the sand to pebble sized rock phosphate separated into the indicated categories. As previously indicated, the "CODE 30" material is the rock phosphate in the size range from 150 to 250 mesh and the material indicated "CODE 31" is the same material ground to pass 325 mesh. The CODE 30 and CODE 31 materials were acquired from Texasgulf Sulfur at Aurora, North Carolina. The material termed "AGRICO" is a solar dried slurry (slime) acquired from the AGRICO Mining Co., Mulberry, Florida.

The results of the experiments were compared by plotting percent acid reduction relative to the control versus the wt% apatite addition. The data were extrapolated by computer to 5 wt% apatite addition.

SET #2:

Based upon the success of the initial experiments, a second set of experiments was conducted utilizing the AGRICO slurry material with and without CODE 31 addition intermixed as a water slurry and run against a common toxic material. The experiments are summarized in Table 2. Each wt% apatite addition with the exception of 7.00 wt% apatite was conducted using two different slurry mixtures. All experiments were conducted in triplicate. Based on the results of these experiments, two final sets of experiments were designed.

TABLE 2 EXPERIMENTAL SET #2

	SOLID MIX			SLURRY MIX	
CC#	gm AGRICO	gm CODE 31	ml/H_2O	gm SOLID MIX	WT% APATITE ADDITION
8342	5	0	50	5	0.25
8343	260	13	200	40	2.00
8344	260	13	750	275	1.25, 1.75, 3.25, 3.50, 3.75, 4.00
8345	300	60	300	60	0.75, 2.25, 2.75
8346	300	60	1000	300	2.75, 3.25, 4.00, 4.50
8347	450	225	750	75	0.25, 0.50, 1.00, 1.25, 1.50, 1.75, 2.50
8348	450	225	750	150	0.50, 1.00, 2.00, 2.50, 3.00, 3.50, 5.00
8349	450	225	1500	450	0.75, 1.50, 2.25, 3.00, 3.75, 4.50, 5.00, 7.00

SET #3:

In this set of experiments, slurry CC# 8348, a 1:0.5 blend of dried slurry CODE 31 apatite was intermixed with four different toxic materials at application schedules of 1, 2, 3 and 4 wt% apatite (see Table 3).

TABLE 3 EXPERIMENTAL SET #3

AGRICO VS. 6 DIFFERENT TOXIC MATERIALS

CC#	COAL	ROCK TYP.	St	ALPHA	S300	ETA
26	U.FREE	ROOF SH.	2.418	0.0065	21.325	25.676
62	U.FREE	PREP.REF.	5.525	0.0050	28.397	20.943
64	U.FREE	PREP.REF.	3.312	0.0061	17.741	15.911
119	L.FREE	PARTING	1.940	0.0033	13.976	12.114

CC# 8348 SLURRY
450 gm AGRICO + 225 gm CODE 31
750 ml H_2O + 150 gm MIXTURE

APPLICATION SCHEDULE
CONTROL, 1 wt%, 2 wt%, 3 wt% and 4 wt% APATITE

SET #4:

Initially, the CODE 30 material was tested against a variety of toxic lithotypes. In the fourth set of experiments, the CODE 30 material was intermixed with the previously utilized common toxic lithotype in application schedules ranging from 0.50 wt% to 5.00 wt% at 0.25 wt% intervals.

The entire bench scale experimental effort consisted of a total of 3285 individual experiments with 65,700 analyses. This point is made only to emphasize the fact that the database is sufficiently large to allow a reasonably high statistical reliability to be assigned to any effectivity comparisons that will be made.

SMALL FIELD SCALE (BARREL) EXPERIMENTS

The second phase of this work involved small field scale (BARREL) experiments. The primary objectives of this study were twofold: 1) to determine the effect of phosphate mine waste on acid production from bituminous mine waste rock under natural conditions of weathering and 2) to provide the data needed to calculate conversion factors to allow bench scale data to be related to real weathering situations. The fact that phosphate rock can significantly reduce the production of AMD had already been established by the authors by previous experimentation. However, statistical analysis of the data showed that the effectiveness of phosphate was not directly related to any stoichiometric formulation based on the percentage of pyrite in the rock sample. Therefore, the ameliorative property of phosphate must be mass transfer controlled. This being the case, the sample treated with the smaller particle size, but equal application rate of rock phosphate will be more effective as an ameliorant.

The soxhlet experiments tested the effectiveness of surface area and weight percent of phosphate on 100 gram samples of toxic material. Because of the simplicity of this experimental procedure, large numbers of experiments can be run and a large data base can be accumulated. The question that yet remained to be answered was how these soxhlet tests related to actual atmospheric weathering.

The toxic materials used in these experiments were of two types: 1) a cleaning plant waste from Grant County, West Virginia, the toxic "standard" material and 2) a sandstone overburden rock of the Kittanning coal bed in central West Virginia. Compared to many toxic rock wastes studied over the past four years, the cleaning plant waste material is of average toxicity. The Kittanning coal beds are some of the most extensive in the state. As a result, the mining community must frequently contend with the sandstone overburden material. Sixteen tons of each material were obtained and screened to a top size of 1.5" in order to guarantee that when packed into the plastic containers, the water would not channel through the barrels but rather would travel downward in a uniform front.

Identical sets of the samples and corresponding treatments used in the field scale experiments were prepared and evaluated by the soxhlet bench scale procedure experiments to provide the data by which the field scale and bench scale data could be correlated.

Based upon the finding from the bench scale experiments that rock phosphate particle sizes greater than 1/16" showed limited ameliorative effectiveness, only to fine sizes were used in the barrel experiments. For the small field scale experiments, the Code 30 and 31 materials were further sub-sized into four seive size ranges: 1) 18-35 mesh, (750 microns), 2) 36-60 mesh, (375 microns, 3) 60-120 mesh (187 microns), and 4) less than 120 mesh (125 microns).

A total of ninety field scale barrel experiments were prepared (see Table 4). Each experi-

TABLE 4 SMALL FIELD SCALE (BARREL) EXPERIMENTS

MATERIAL	AMELIORANT	PARTICLE MESH SIZE	APPLICATION RATE	REP	EXPER. NUMBER
REFUSE	P-ROCK	18-35	1.20%	1	01
REFUSE	P-ROCK	18-35	1.20%	2	02
REFUSE	P-ROCK	18-35	1.20%	3	03
REFUSE	P-ROCK	18-35	0.40%	1	04
REFUSE	P-ROCK	18-35	0.40%	2	05
REFUSE	P-ROCK	18-35	0.40%	3	06
REFUSE	P-ROCK	18-35	0.13%	1	07
REFUSE	P-ROCK	18-35	0.13%	2	08
REFUSE	P-ROCK	18-35	0.13%	3	09
REFUSE	P-ROCK	18-35	0.04%	1	10
REFUSE	P-ROCK	18-35	0.04%	2	11
REFUSE	P-ROCK	18-35	0.04%	3	12
REFUSE	P-ROCK	35-60	1.20%	1	13
REFUSE	P-ROCK	35-60	1.20%	2	14
REFUSE	P-ROCK	35-60	1.20%	3	15
REFUSE	P-ROCK	35-60	0.40%	1	16
REFUSE	P-ROCK	35-60	0.40%	2	17
REFUSE	P-ROCK	35-60	0.40%	3	18
REFUSE	P-ROCK	35-60	0.13%	1	19
REFUSE	P-ROCK	35-60	0.13%	2	20
REFUSE	P-ROCK	35-60	0.13%	3	21
REFUSE	P-ROCK	35-60	0.04%	1	22
REFUSE	P-ROCK	35-60	0.04%	2	23
REFUSE	P-ROCK	35-60	0.04%	3	24
REFUSE	P-ROCK	60-120	1.20%	1	25
REFUSE	P-ROCK	60-120	1.20%	2	26
REFUSE	P-ROCK	60-120	1.20%	3	27
REFUSE	P-ROCK	60-120	0.40%	1	28
REFUSE	P-ROCK	60-120	0.40%	2	29
REFUSE	P-ROCK	60-120	0.40%	3	30
REFUSE	P-ROCK	60-120	0.13%	1	31
REFUSE	P-ROCK	60-120	0.13%	2	32
REFUSE	P-ROCK	60-120	0.13%	3	33
REFUSE	P-ROCK	60-120	0.04%	1	34
REFUSE	P-ROCK	60-120	0.04%	2	35
REFUSE	P-ROCK	60-120	0.04%	3	36
REFUSE	P-ROCK	LT 120	1.20%	1	37
REFUSE	P-ROCK	LT 120	1.20%	2	38
REFUSE	P-ROCK	LT 120	1.20%	3	39
REFUSE	P-ROCK	LT 120	0.40%	1	40
REFUSE	P-ROCK	LT 120	0.40%	2	41
REFUSE	P-ROCK	LT 120	0.40%	3	42
REFUSE	P-ROCK	LT 120	0.13%	1	43
REFUSE	P-ROCK	LT 120	0.13%	2	44
REFUSE	P-ROCK	LT 120	0.13%	3	45
REFUSE	P-ROCK	LT 120	0.04%	1	46
REFUSE	P-ROCK	LT 120	0.04%	2	47
REFUSE	P-ROCK	LT 120	0.04%	3	48
REFUSE	P-SLURRY	------	4.80%	1	49
REFUSE	P-SLURRY	------	4.80%	2	50
REFUSE	P-SLURRY	------	4.80%	3	51
REFUSE	P-SLURRY	------	1.60%	1	52
REFUSE	P-SLURRY	------	1.60%	2	53
REFUSE	P-SLURRY	------	1.60%	3	54
REFUSE	P-SLURRY	------	0.52%	1	55
REFUSE	P-SLURRY	------	0.52%	2	56
REFUSE	P-SLURRY	------	0.52%	3	57
REFUSE	P-SLURRY	------	0.16%	1	58
REFUSE	P-SLURRY	------	0.16%	2	59
REFUSE	P-SLURRY	------	0.16%	3	60
REFUSE	CONTROL	------	-----	1	61
REFUSE	CONTROL	------	-----	2	62
REFUSE	CONTROL	------	-----	3	63
SANDSTONE	P-ROCK	18-35	0.40%	1	70
SANDSTONE	P-ROCK	18-35	0.40%	2	71
SANDSTONE	P-ROCK	18-35	0.40%	3	72
SANDSTONE	P-ROCK	35-60	0.40%	1	73
SANDSTONE	P-ROCK	35-60	0.40%	2	74
SANDSTONE	P-ROCK	35-60	0.40%	3	75
SANDSTONE	P-ROCK	35-60	0.40%	1	76
SANDSTONE	P-ROCK	35-60	0.40%	2	77
SANDSTONE	P-ROCK	35-60	0.40%	3	78
SANDSTONE	P-ROCK	LT 120	0.40%	1	79
SANDSTONE	P-ROCK	LT 120	0.40%	2	80
SANDSTONE	P-ROCK	LT 120	0.40%	3	81

SANDSTONE	P-SLURRY	------	4.80%	1	82
SANDSTONE	P-SLURRY	------	4.80%	2	83
SANDSTONE	P-SLURRY	------	4.80%	3	84
SANDSTONE	P-SLURRY	------	1.60%	1	85
SANDSTONE	P-SLURRY	------	1.60%	2	86
SANDSTONE	P-SLURRY	------	1.60%	3	87
SANDSTONE	P-SLURRY	------	0.52%	1	88
SANDSTONE	P-SLURRY	------	0.52%	2	89
SANDSTONE	P-SLURRY	------	0.52%	3	90
SANDSTONE	P-SLURRY	------	0.16%	1	91
SANDSTONE	P-SLURRY	------	0.16%	2	92
SANDSTONE	P-SLURRY	------	0.16%	3	93
SANDSTONE	CONTROL	------	-----	1	94
SANDSTONE	CONTROL	------	-----	2	95
SANDSTONE	CONTROL	------	-----	3	96

ment consisting of three hundred pounds of toxic material with the appropriate phosphate ameliorant. The barrels were placed on 8 benches, with 12 experiments per bench; the placement of individual experiments was determined by random number generation.

TREATMENT OF THE DATA

The basic data collected from the leachates of both the bench scale and small field scale experiments included pH before and after the addition of hydrogen perioxide, specific conductivity, acidity, the concentrations of Ca, Mg, Na, K, Fe, Mn, Al, Si and sulfate. The sulfate concentration was used as a measure of original acid production and was tabulated in cumulative milligrams of sulfate after each cycle of the bench scale experiments. From these data and the initial sulfur content of the rock material, a percent unreacted sulfur (%Su) remaining within the rock material after each leachate collection was calculated.

Because laboratory leaching and field leaching were conducted under totally different experimental conditions, it was necessary to equate a 14 day soxhlet cycle to the actual field days of the barrel experiments. To accomplish this, the number of field days required to reduce the sulfur content of the rock material to the same percent unreacted sulfur (%Su) for each of the four cycles of the bench scale data were calculated. These data were plotted versus the corresponding times for the bench scale data (figure 4). A regression relationship was used to calculate the real time days required to achieve the corresponding %Su observed in the laboratory experiments. The results showed that one 14-day laboratory cycle was equal to 8.8 real time days. The ratio 8.8/14 was therefore the scaling factor which allowed all subsequent bench scale data to be equated relative to real time.

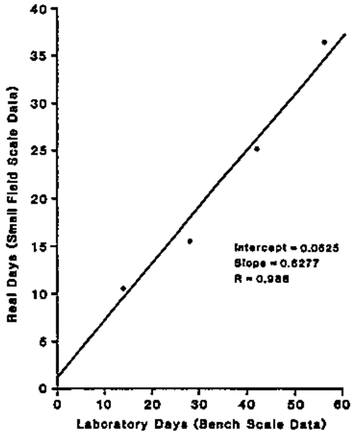


FIGURE 4. Time to Reduce % S to Equal Concentrations of Unreacted Sulphur

EXPERIMENTAL PARAMETERS

Previous research by the authors had established four experimental parameters which were used to evaluate the toxic potential of an acid producing system: 1) an acid production rate constant, ALPHA, which is the slope of the plot of the naturallogarithm of the percent of unreacted sulfur of the toxic material versus real time (see fig. 5) 2) a sulfate production parameter, S300, which is the calculated amount of sulfate produced from 1000 Tons of toxic material in 300 days. This parameter is used as a comparison statistic, 3) the ACID Load which is the equivalent amount of $CaCO_3$ Tons of the toxic material and 4) a parameter ETA, which is calculated by dividing the acid load generated from 1000 Tons of the toxic material by the total sulfur content of the toxic material.

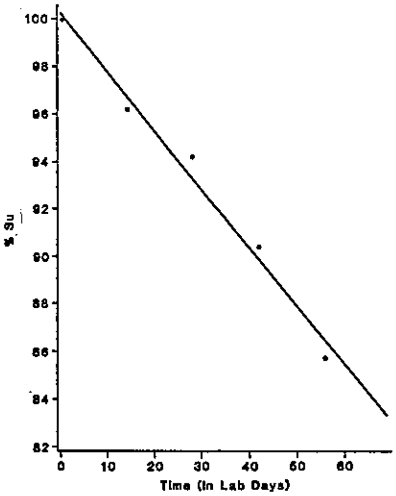


FIGURE 5. Percent Unreacted Sulphur (%Su) Versus Time In Lab Days for Bench Scale Experiments

RESULTS OF THE INVESTIGATION

Bench Scale Experiments

The results of the investigation are quite clear. The effectiveness of the rock phosphate is simply a question of mass transfer; the effectiveness increasing with decreasing particle size and increasing magnitude of the application rate.

The results of experimental SET #1 are illustrated in Figure 6. The toxicity parameters for the rock material used in the individual experiments is indicated on the figure for each particle size experiment. It is significant to note that the sand to pebble-sized material is relative ineffective at acid reduction. Even the -1/16" size does not reduce the acid load by 50% at projected application schedules of 5 wt%.

The CODE 30 material, as would be expected was significantly more effective with 8 out of 12 experiments resulting in a 50% acid reduction with an average application schedule of about 2.2 wt% apatite. Of the remaining 4 experiments which showed relatively low response, the sulfur content of the toxic material in two of the experiments was in excess of 9 wt%, thereby explaining the limited response.

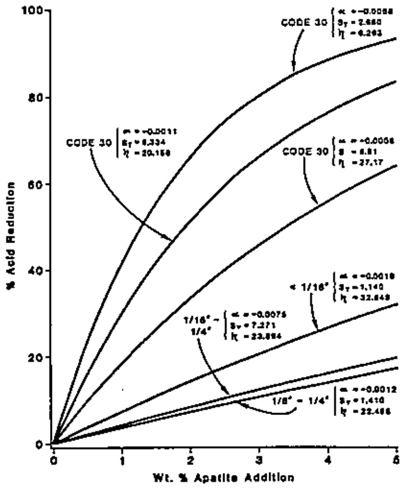


FIGURE 6. Percent Acid Reduction vs. Wt. % Apatite Application for Various Sized Rock Phosphate Materials

Most encouraging, however, were the results of experiment SETS #2 and #3 which utilized the dried slurry material. Because the material contained only about 25% by weight apatite, the effectiveness of the material used without any apatite addition was limited (fig. 7). However, with the addition of CODE 31 material, the slurry material showed significant improvement in performance. The results of experimental SET #2 are summarized in figures 8 and 9 which plot acid load and alpha reduction versus wt% apatite addition respectively.

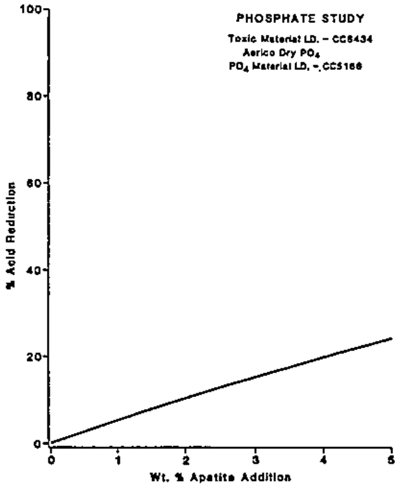


FIGURE 7. Percent Acid Reduction vs. Wt. % Apatite Application for Dried Slurry - No Code 31 Spike

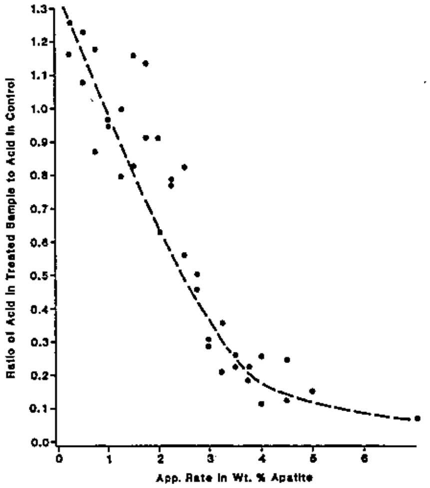


FIGURE 8. Percent Acid Reduction vs. Wt. % Apatite Application for Dried Slurry with Code 31 Spike

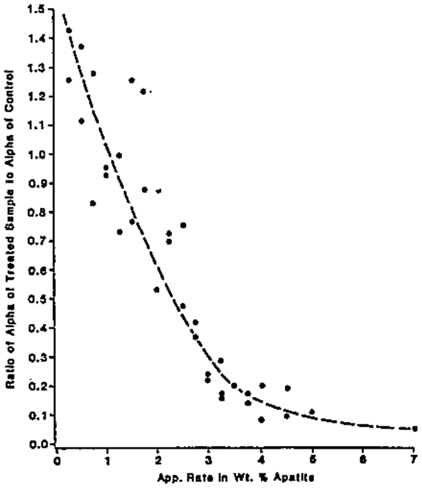


FIGURE 9. Percent Alpha Reduction vs. Wt. % Apatite Application for Dried Slurry with Code 31 Spike

The data show that approximately 0.9 wt% apatite must be added before acid reduction is initiated. Below 0.9 wt% apatite addition, the chemical effect of calcium on the system is apparently the same as observed for calcite addition, namely, it results in an increase in acid production. Between 0.9 wt% and 4.0 wt% apatite addition, however, reduction in acid production is rapid. Note that on the average, an application schedule of 5 wt% apatite reduced both acid load and the rate of acid production by more than 90% relative to the untreated control. As previously shown, calcite must be added at a 5 wt% addition schedule simply to INITIATE positive acid reduction.

The results from the slurry-CODE 31 mixtures of experiment SET #3 are illustrated in figures 10 through 17 and the data from SET #4, the CODE 30 addition to the "standard" prep refuse, are shown in figures 18 and 19. The trends in these data are similar to those of the previous experiments.

FIGURE 10

ROCK TYPE = ROOF SHALE
STRATIGRAPHY = UPPER FREEPORT
TOTAL SULFUR = 2.418
ALPHA = 0.0068
ETA = 25.7
PHOSPHATE ID = CC 8348
SLURRY: CODE31 RATIO 1:0.5

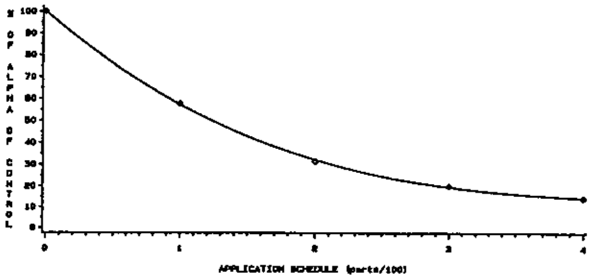


FIGURE 11

ROCK TYPE = ROOF SHALE
STRATIGRAPHY = UPPER FREEPORT
TOTAL SULFUR = 2.418
ALPHA = 0.0068
ETA = 25.7
PHOSPHATE ID = CC 8348
SLURRY: CODE31 RATIO 1:0.5

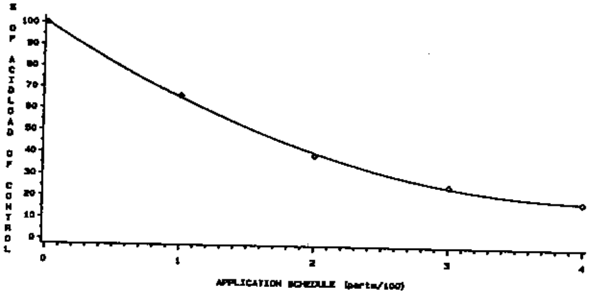


FIGURE 12

ROCK TYPE = PREP REFUSE
STRATIGRAPHY = UPPER FREEPORT
TOTAL SULFUR = 5.825
ALPHA = 0.005
ETA = 20.94
PHOSPHATE ID = CC 8348
SLURRY: CODE31 RATIO 1:0.5

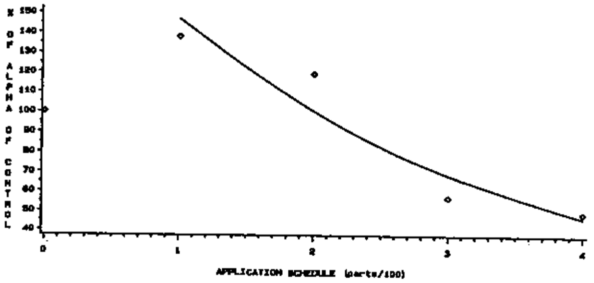


FIGURE 13

ROCK TYPE = PREP REFUSE
STRATIGRAPHY = UPPER FREEPORT
TOTAL SULFUR = 5.825
ALPHA = 0.005
ETA = 20.94
PHOSPHATE ID = CC 8348
SLURRY: CODE31 RATIO 1:0.5

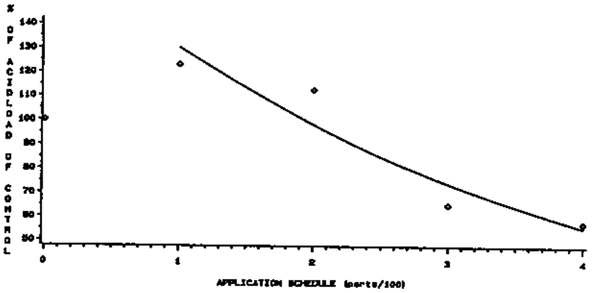


FIGURE 14

ROCK TYPE = PREP REFUSE
STRATIGRAPHY = UPPER FREEPORT
TOTAL SULFUR = 3.312
ALPHA = 0.008
ETA = 12.114
PHOSPHATE ID = CC 8348
SLURRY: CODE31 RATIO 1:0.5

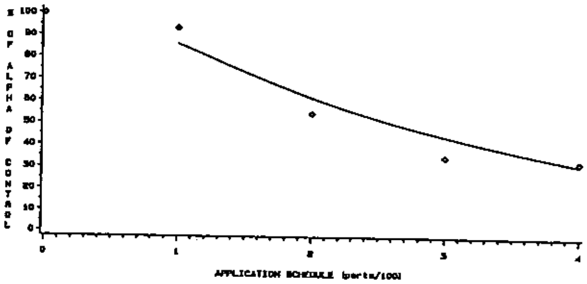


FIGURE 15

ROCK TYPE = PREP REFUSE
STRATIGRAPHY = UPPER FREEPORT
TOTAL SULFUR = 3.312
ALPHA = 0.008
ETA = 12.114
PHOSPHATE ID = CC 8348
SLURRY: CODE31 RATIO 1:0.5

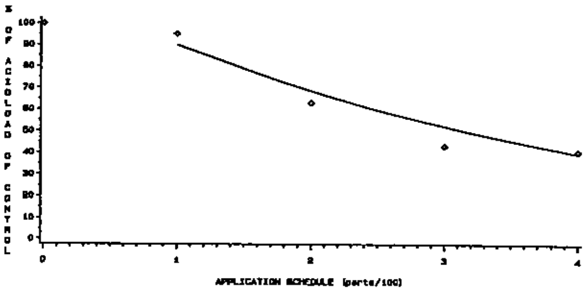


FIGURE 16

ROCK TYPE = SHALE PARTING
STRATIGRAPHY = LOWER FREEPORT
TOTAL SULFUR = 1.940
ALPHA = 0.0033
ETA = 12.1
PHOSPHATE ID = CC 8348
SLURRY: CODE31 RATIO 1:0.5

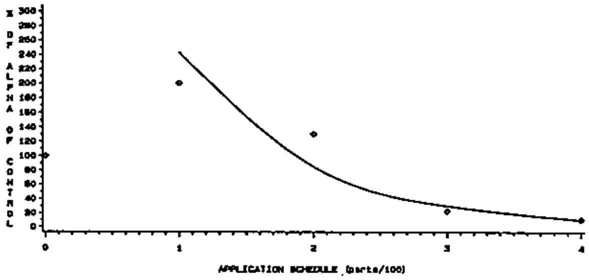


FIGURE 17

ROCK TYPE = SHALE PARTING
STRATIGRAPHY = LOWER FREEPORT
TOTAL SULFUR = 1.940
ALPHA = 0.0033
ETA = 12.1
PHOSPHATE ID = CC 8348
SLURRY: CODE31 RATIO 1:0.5

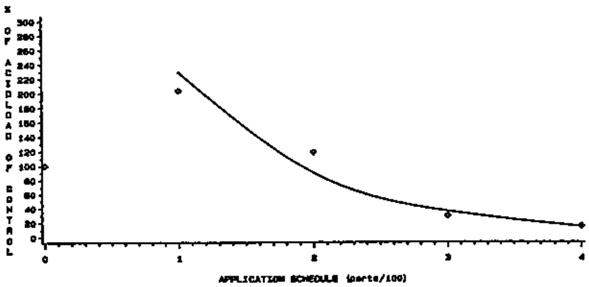


FIGURE 18

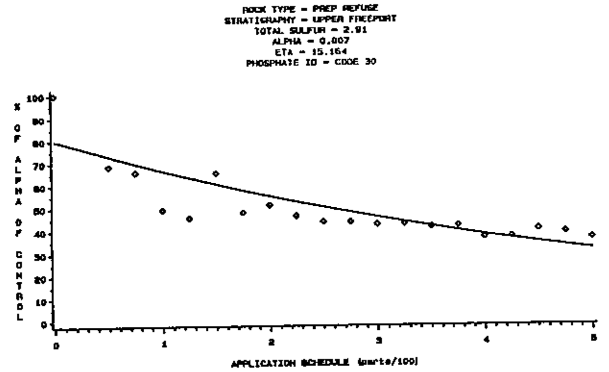
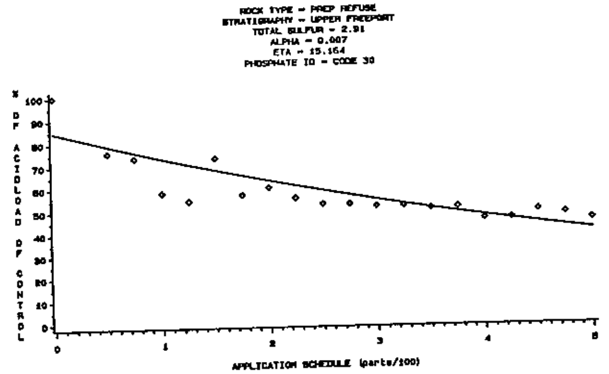


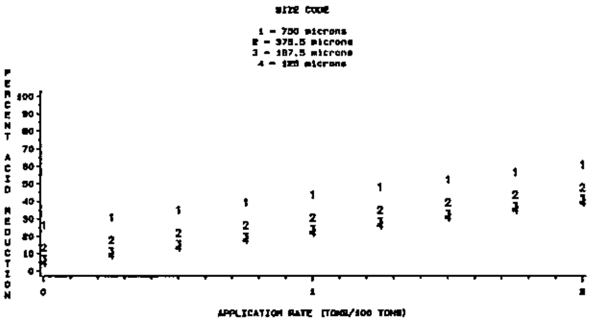
FIGURE 19



SMALL FIELD SCALE EXPERIMENTS

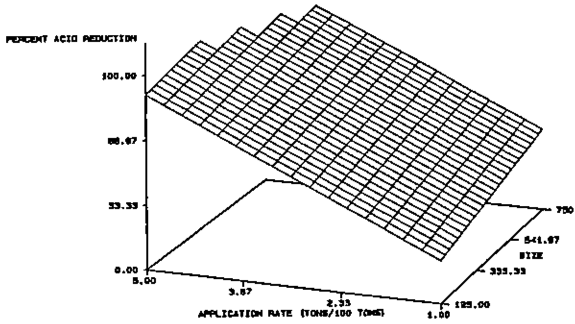
The results of the small field scale experiments are shown in figures 20 through 21A. Similar to the bench scale experiments, the data show the ameliorative effectiveness to increase with decreased particle size. The three dimensional plot in figure 21 shows however, that when dealing with fine particle sizes, the application schedule is more influential on ameliorative effectiveness than is particle size. Statistically, the ameliorative reaction of all the fine sizes tested was similar. Most significant is that both the bench scale and field scale sets of experiments show that maximum ameliorative effectiveness of rock phosphate is achieved at about 4 wt% apatite addition.

FIGURE 20



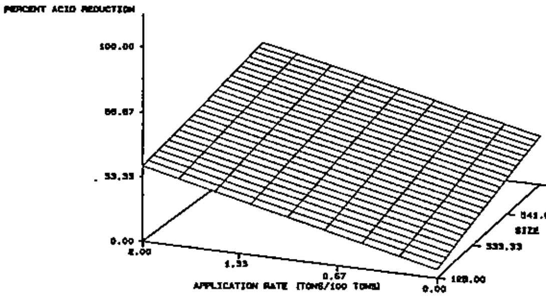
VARIOUS PHOSPHATE PARTICLE SIZE EFFECTS ON ACID PRODUCTION OF A SINGLE TOXIC MATERIAL

FIGURE 21



SURFACE SHOWING RELATION OF PARTICLE SIZE AND APPLICATION SCHEDULE WITH ACID PRODUCTION

FIGURE 21-A



SURFACE SHOWING RELATION OF PARTICLE SIZE AND APPLICATION SCHEDULE WITH ACID PRODUCTION

CONCLUSIONS

1) Rock phosphate (apatite) is an effective AMD ameliorant when used in particle sizes less than 18 mesh (750 microns) and with application rates in excess of about 1wt%.
2) Maximum ameliorative effectiveness will be achieved using fine ground rock phosphate at an addition rate of about 4 or 5 wt%.
3) Below a particle size of 18 mesh, the particle size of rock phosphate becomes less important than the application rate in acid reduction.
4) The clay slurry spiked with -375 mesh apatite is an extremely effective AMD ameliorant.
5) Bench scale experiments can effectively evaluate and predict the response of toxic materials or combinations of toxic materials and ameliorants exposed to atmosphere weathering.

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REFERENCES

Stumm, W. and Morgan, J.J., 1970, Aquatic Chemistry, Wiley Interscience, John Wiley and Sons, N.Y., p. 522.

Stiller, A.H., Renton, J.J., and Rymer, T.E., 1984, A Mathematical Hypothesis for Determination of Mine Effluent Behavior, Proc. Surface Mining and Water Quality, 5th Annual West Virginia Surface Mine Drainage Symposium, Morgantown, WV, March 1984.

Renton, J.J., Stiller, A.H., and Rymer, T.E., 1985, Relationships of Various Lithologies and Geologic Strata for Acid Producing Potential, Proc. Surface Mining and Water Quality, 6th Annual West Virginia Surface Mine Drainage Symposium, Morgantown, WV, April 1985.