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THE USE OF PHOSPHATE MATERIALS AS AMELIORANTS FOR ACID MINE DRAINAGE

Volume 1: The Use of Rock Phosphate (Apatite) for the Ameliorization of Acid Mine Drainage from the Mining of Coal

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FLORIDA INSTITUTE OF PHOSPHATE RESEARCH

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The Use of Rock Phosphate (Apatite) for the Ameliorization of Acid Mine Drainage from the Mining of Coal

FINAL REPORT

VOLUME 1

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PERSPECTIVE

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Acid mine drainage is the primary environmental problem facing the high sulfur coal mining industry in West Virginia, parts of western Pennsylvania, Ohio, western Kentucky and Illinois. In West Virginia alone, nearly 4,000 miles of streams have been effected by acid mine drainage. The estimated cost of reclaiming these streams is more than four billion dollars. In West Virginia there exists approximately 37,500 acres of abandoned mine lands and another 52,000 acres of non-burning waste material from previous mining operations. These areas are typically acid producers and are, for the most part, unvegetated because of surface toxicity. Even in areas that have achieved some degree of success in the handling and treatment of acidic materials, surface revegetation remains a problem because of the physical and chemical shortcomings of the topsoil material placed back on these areas. In many cases, this material is simply crushed sandstone which has a low water and nutrient storage capacity and it could be an acid producing material itself.

Earlier experiments conducted by these investigators have shown that phosphate rock could be used to reduce the acidity of the waste to acceptable levels. Thus, it is believed that addition of phosphatic clays would not only reduce the acidity but also would add phosphate as a plant nutrient. In addition, it would improve the physical and chemical properties of these soils. Therefore, it was the specific objective of this research to systematically evaluate the effectiveness of both rock phosphate and phosphatic clay slurries in ameliorating the acidity produced from waste materials through bench scale and small field scale experiments and to test the effectiveness of phosphatic clays as a topical additive to mine soils.

From the perspective of finding different uses for phosphatic clays, the Institute granted West Virginia University research team funds to conduct an investigation to achieve the above objectives.

The data generated in this study are reported in two volumes. The first volume includes the results of the bench scale and small field experiments investigating the effectiveness of the phosphatic material in ameliorating the acidity of coal mine waste. The second volume involves the results of the vegetation studies. Several conclusions can be drawn of these studies:

1. Apatite is an effective ameliorant for the acid generated from the weathering of iron disulfide minerals when used at an addition schedule of 4-5% by weight and a particle size less than 18 mesh.

2. Phosphatic clays (enriched with -325 mesh apatite) are found to be an extremely effective acid ameliorant.

3. Phosphatic clays have a potential for amending acid minesoils for revegetation purposes.

    a. Crop yields were higher on phosphatic clay treated minesoils than on other minesoils treated with rock phosphate or monocalcium phosphate. Also, these clays are better amendments for unlimed than limed minesoils.

    b. Phosphatic clays improved the uptake of macronutrients of plants grown on both shale and sandstone minesoils. At the same time, they reduced the plant uptake of other elements such as manganese, copper, zinc, iron and aluminum.

    c. These results need to be confirmed in a field experiment before they can be recommended for use in revegetation of mined lands.

The above listed conclusions are of significant importance since they illustrate the effectiveness of phosphatic material in ameliorating the acidity of coal mine drainage. However, still there are several economic questions involving the cost of transportation, the use of phosphatic material from sources other than Florida, etc. Thus, the Institute's staff believe that the results of this project do not present immediate benefits to the state of Florida.

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Executive Summary

Preliminary studies by the authors of acid production from toxic coal mine waste had shown that the addition of phosphate ion to the leachate in synthetic weathering experiments was effective at stopping the production of acid by removing the major oxidizing agent of the iron disulphide minerals, ferric ion, as a totally unsoluble precipitate. Chemical analyses of the materials and leachates involved in the experiments indicated that the effectiveness of the phosphate ion was not stoichiometric but may have been mass transfer controlled.

The original proposal was to investigate whether or not the use of the apatite bearing clay slimes produced as a by product of the phosphate mining industry could be used to ameliorate the acid produced from the waste rock generated by the coal mining industry. The toxic materials chosen for the study consisted of: 1) a "standard" toxic material which was used throughout the study to allow quantitative comparisons to be made, and 2) a suite of rock materials which represented all of the individual potentially toxic rock units associated with the coal to provide the entire range of rock toxicities.

The toxicity of the rock materials was based upon: 1) the total potential acid production and 2) the rate at which acid was produced. The theoretical total potential acid production can be calculated based on the total sulfur content of the material and the accepted stoichiometry of the acid producing reactions. However, the actual total acid load and the range of acid production can only be determined by simulated weathering

experiments which themselves must be verified by controlled large scale field wreathing experiments.

Prior to this study, the authors designed and validated a combination bench scale-small field scale experimental procedure which allowed the accurate determination of both acid production rate and total acid load in time for the entire suite of potentially toxic rock types encountered in the mining of coal. The bench scale experiments utilized 100 gram samples of the rock material top sized at 1/4" and a standard 123mm Soxhlet. The total sulfur content of the rock material had been previously determined using a LECO 1R32 sulfur analyzer. The samples were initially leached for 24 hours to remove any existing acid salts and the leachate collected. Following the initial leach, the sample was reoxidized in a standard 105° C coal drying oven for a period of 2 weeks after which the sample was releached. The oxidation-leach cycle was repeated four times with a leachate collected for each cycle. The leachates were analyzed for sulphate ion as a measure of the original iron disulphide oxidation and subsequent acid production. The process proceeds by psuedo first order reaction kinetics. Based on the sulfate content of the leachate the amount of iron disulphide oxidized was calculated for each cycle. This value was translated into the amount of unreacted iron disulphide remaining in the material at the end of each cycle. The slope of the plot of log unreacted sulfur versus time was the observed reaction rate constant.

The small field scale experiments consisted of placing 300 pounds of the same materials top sized at 1 1/4" into 35 gallon plastic barrels designed as fixed bed plug flow reactors. The sulphur content of the rock material was determined as previously described. The packed barrels were exposed to natural weathering conditions for one calender year. Leachates were collected after every major rain event and snow melt. Analysis of the leachate and the processing of data was the same as that indicated for the bench scale experiments. Again, this was a pseudo first order kinetic reaction process. As a result, the slope of the log unreacted sulphur versus time plot was the reaction rate constant, the bench scale and small field scale reaction rate constants were equated by scaling factors based upon the times required for the system to reduce the sulfur contents of the rock material to equal values of unreacted sulfur. The scaling factors were validated with the results from the weathering of 350 tons field scale pile.

The ameliorative effectiveness of the phosphate materials was demonstrated by the ability of the materials to alter the reaction rate constants as determined by the above outline procedures. The initial studies involved bench scale treatment of the "standard" toxic material and each of the various potentially toxic rock types with various concentration of the clay slime to test the effectiveness of the slime as an acid ameliorant. The initial experiments showed that the slime even when applied at an application schedule equivalent to 5 wt % apatite was not effective presumably because of the extreme diluting effect of the clay matrix. The original experimental design was then expanded to allow the testing of: 1) a range of rock phosphate materials ranging in mean particle size from about 1/4" diameter gravels down to -325 mesh ground apatite and 2) a mixture of the clay slime and -325 mesh ground apatite.

Both bench scale and small field scale experiments were conducted using various combinations of toxic materials and phosphate ameliorants. The bench scale experiments utilized phosphate materials in application schedules from 0 wt. % apatite (controls) up. to 7 wt. % apatite. The small field scale experiments were conducted with application schedules ranging from 0 wt. % (controls) up to 4.8 wt. %. Because early bench scale experiments showed the large sized material to be of limited effectiveness, the small field scale experiments were conducted with materials less than 18 mesh.

The findings of this study are as follows:

1) Rock phosphate (apatite) is an effective ameliorant for the acid generated from the weathering of iron disulphide minerals when used in particle sizes of less than 18 mesh (750 microns) and at application schedules in excess of about 1 wt. % apatite.

2) Maximum ameliorative effectiveness will be achieved using the fine grained rock phosphate at addition schedules of about 4 to 5 wt. %.

3) Below a particle size of 18 mesh, the particle size of rock phosphate becomes less important than the application schedule in

acid reduction.

4) The clay slime enriched with -325 mesh apatite is an extremely effective acid ameliorant.

5) Bench scale experiments can effectively evaluate and predict the response of potentially toxic materials or combinations of toxic materials and ameliorants exposed to atmospheric weathering.

INTRODUCTION

GENERAL INFORMATION

Acid mine drainage (AMD) is one of the most severe pollution problems in the Appalachian region. Acid mine drainage is the aqueous solution of the inorganic salts of sulfuric acid which are leached from the rock surfaces exposed to weathering during coal mining operations. It is not unusual in surface-mine operations to expose ten tons of potentially toxic rock per ton of coal mined. Since West Virginia has an average annual coal production from surface mines of 28 million tons, it is not difficult to appreciate the enormous quantity of overburden rock that is exposed to conditions of chemical weather annually. (App. Reg. Comm., 1969) With the number of surface mine operations increasing each year, it is expected that the acid mine drainage problem will only become worse. In fact, it is safe to say that if the problem of acid production is not solved, a significant percentage of the coal reserves within the northern Appalachian Basin will not be mined because of potential adverse environmental problems. In an attempt to evaluate the environmental damage caused by decades of coal mining in the affected areas, an EPA report concluded that 500 billion gallons of mine drainage wastes, containing 5 to 10 million tons of acid, pollute over 10,000 miles of surface streams and more than 15,000 acres of impounded water annually. (Stiller, 1981.) Since the printing of the EPA report, millions of dollars have been invested in treating and ameliorating acid mine drainage. However, no unequivable treatment has been found which stops AMD production. This situation has been caused, at least in part, by insufficient understanding of two basic phenomena: (1) the chemical mechanism of acid formation and (2) the influence of the physical properties of rocks on the rate of acid production.

Coal is a rock which is interlayered with other types of sedimentary rock. Those most frequently associated with coal are illustrated graphically in Figure 1. During the mining operations these rocks, which may contain up to 8% of disulphide minerals, mostly pyrite, (FeS_2) by weight, are exposed to the atmosphere. Oxygen and water react with FeS_2 producing ferrous sulfate, $FeSO_4.H_2O$, and sulfuric acid, H_2SO_4. These compounds dissolve in the leaching water and produce an acidic solution of low pH with high concentrations of ferrous and sulfate ions. The acid concentration of the affected water makes it unsuitable for human consumption and detrimental to aquatic life. A typical analysis of acid mine drainage water is given in Table 1. (Eldridge, 1942).

Table 1: Typical Composition of Acid Mine Drainage Water

	Content (mg/ml)
Total	5680
Chloride (NaCl)	150
Total Iron (Fe)	710
Sulfate (SO_4^{-2})	2000
Calcium (CaO)	550
Magnesium (MgO)	250

The commonly accepted mechanism for the production of AMD is summarized in the following equations (Singer, et al, 1970):

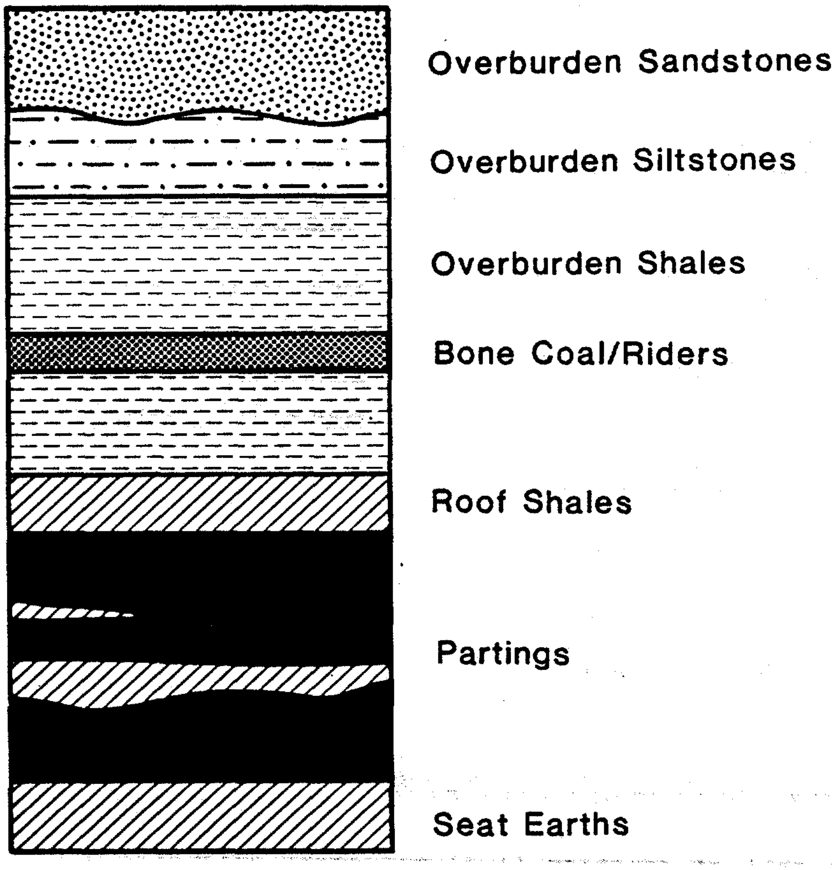

FIGURE 1. Potentially Toxic Lithic Units Associated with Coal

$$FeS_2(s) + 7/2\ O_2 + H_2O \rightarrow Fe^{+2} + 2SO_4^{-2} + 2H^+ \qquad (1.1)$$

$$Fe^{+2} + 1/4\ O_2 + H^+ \rightarrow Fe^{+3} + 1/2\ H_2O \qquad (1.2)$$

$$FeS_2(s) + 14Fe^{+3} + 8H_2O \rightarrow 15Fe^{+2} + 2SO_4^{-2} + 16H^+ \qquad (1.3)$$

$$Fe^{+3} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+ \qquad (1.4)$$

Initially, iron disulfide is oxidized directly by oxygen dissolved in water (Reaction 1.1). A portion of the ferrous ion produced is further oxidized to ferric ion both by chemical and microbiological (bacterial) oxidation. (Reaction 1.2). Ferric ion in turn proceeds to rapidly oxidize iron disulfide generating increased concentrations of hydrogen and sulfate ions along with more ferrous ion (Reaction 1.3). Consequently, the oxidation of iron disulfide is a self-sustaining reaction which terminates only after all of the exposed iron disulfide has been consumed.

Reaction (1.1) is relatively slow and does not contribute significantly to the total amount of acid that is produced from the mechanism over a short period (Singer et al, 1968). The second pathway for iron disulfide, oxidation by the ferric ion (reaction 1.3) not only is much faster than that of reaction (1.1) therefore producing more acid in a short time period but also produces a higher ratio of acid to initial iron disulphide concentration (Singer, et al, 1968). It is obvious that the technique which has the greatest potential to control the production of acid formation will be that which eliminates the ferric ion oxidation of iron disulfide. This can be accomplished in one of two ways: 1) prevent the formation of ferric ion by the oxidation of ferrous ion or 2) eliminate both ferric and ferrous ions from the system by chemical complexation or precipitation (Singer, et al, 1968)

A. $2FeS_2 + 7O_2 + 2H_2O = 2Fe^{+2} + 4SO_4 + 4H^+$

B. $14Fe^{+3} + FeS_2 + 8H_2O = 15Fe^{+2} + 2SO_4^{-2} + 16H^+$

A. Fe^{+2}/SO_4^{-2} ratio = 1/2

H^+/SO_4^{-2} ratio = 1/2

B. Fe^{+2}/SO_4^{-2} ratio = 1/2

H^+/SO_4^{-2} ratio = 8/1

ACID-BASE ACCOUNTING

Up until 1978, no method existed to predict the chemical response of a rock material to produce acid upon exposure to the atmosphere. In 1978, Sobek et al, reported a procedure that was to become known as acid-base accounting, a procedure that was quickly adopted by the industry for environmental evaluations of the acid producing potentials of rock materials.

The acid-base account procedure consists of two basic measurements: 1) the determination of the total sulfur content and 2) the determination of the concentration of hydrochloric acid soluble carbonates. Based on the stoichiometry of pyrite oxidation, the maximum acid producing potential by acid-base accounting is calculated from the total sulfur content and reported in terms of calcium carbonate equivalents. Total sulfur measurements will accurately quantify the total potential acid production of a material acidity only if all sulfur is present in iron disulphide minerals. However, because organic sulfur, sulfate minerals and sulfur in non-acid-producing forms can and often are present in coal associated rocks, the estimate of potential acid production based on total sulfur is generally too high and is therefore considered to be a maximum acid producing potential. Acid-base accounting measures the concentration of potential mineral neutralizers present in the rock sample by subjecting a known mass of sample to a standardized solution of hydrochloric acid followed by a back titration with a standard base. This is considered a neutralization potential and is also expressed in terms of calcium carbonate equivalents. The acid-base accounting procedure assumes that the only hydrochloric acid soluble minerals in the rock are carbonates and that all carbonates will dissolve to provide an alkaline solution. Unfortunately, siderite, a significant component in these rocks, produces a neutral solution upon dissolution. Ignoring this false basic assumption, the neutralization or base potential is numerically balanced against the acidic potential. If the acidic producing potential is greater than the neutralization potential, it is deemed necessary to add neutralizers to the material to ameliorate potential AMD. More specifically, when this deficiency is five or more tons of calcium carbonate equivalents per thousand tons of material, the sample is considered to be toxic. On the contrary, if the neutralization potential is greater than the acid potential, it is assumed that there is an excess of neutralizers in the material and no further treatment is needed. Furthermore, if the neutralization potential is at least five to ten tons of calcium carbonate per thousand tons of material more than the acid potential, the material is considered to be alkaline.

Historically, if the acid-base calculation indicated a need for extra neutralizers, limestone was added as a neutralizer to improve the resultant water quality. The necessary amount of limestone was physically admixed with the toxic overburden during the reclamation process However, due to the fact that acid-base accounting over estimated the acid producing potential, it was not considered necessary to apply the entire amount of limestone calculated to neutralize the total excess potential acidity. Theoretically, this overestimation of acid potential resulted from two sources (Bit. Coal Res., 1971). The first being that pyrite oxidation may occur over a long period of time; and, if the toxic material is quickly covered, the decrease in oxygen and water supply may result in a decrease in pyrite weathering. Secondly, acid-base accounting estimates complete neutralization (to pH 7.0), which is not needed for most purposes. Quite often a pH of 5.5 is adequate for many land uses and will insure non-toxic water. (11)

To compensate for this overestimation, the immediate lime requirement (I.L.R.) concept has been developed (Grube, 1973). The estimate of the immediate lime requirement was made by using the following equation.

$$\text{I.L.R.} = \text{Tons } CaCO_3 \text{ Needed/1000 Tons of Material} - \%S_{\text{Total}} \times 15$$

The derived I.L.R. is about one-half that of the theoretical requirement based on total sulfur content. Five tons of calcium carbonate per acre is considered the maximum recommended dosage for surface application, and if admixing of limestone with toxic waste is used, this figure increases to ten tons per acre (Greenlands, 1979). As with all application techniques, other special considerations such as particle size may pose additional problems (Greenlands, 1979).

EFFECT OF CALCITE (LIMESTONE) ADDITION UPON ACID PRODUCTION

In areas producing high sulfur coal (>l wt% S) such as in 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 abundant calcareous rocks are not generally available, limestone has been routinely added to the toxic rock materials during reclamation following the previously outlined tenets of acid base accounting to ameliorate the production of acid. In actual practice, however, the use of limestone has not always resulted in the elimination of acid waters.

Early in the research of the authors, experimental data indicated that the presence of calcite in a potentially toxic system could actually

INCREASE acid production. In early 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 (acidity) of the leachates. Further observations had also been made that coals collected for study that did not contain exceptionally high sulfur concentrations but did contain iron disulphide minerals and calcite in direct contact invariably would rapidly decompose the cloth collection bags. Acid was obviously being produced at a rate disproportionate to the sulfur content of the coal. It soon became apparent from experimental data that when $CaCO_3$ was contained within toxic rock material, the rate of acid production during weathering of the toxic material actually INCREASED.

To further investigate the potential effect of calcite on the acid production of potentially toxic rock materials, a series of experiments were conducted which intermixed pure calcite with several rock materials of differing toxic potential at application schedules of 0.25, 0.50, 1.00, 2.00 and 4.00 wt% calcite. These materials were subjected to a bench scale weathering process to be described later in this report. The data are shown in Fig. 2. The experiments showed that the addition of calcite in application schedules up to about 5 wt% had the effect of increasing acid production over that of the untreated controls.

The experiments showed that acid loads from calcite treated samples reached a maximum at about 1 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 effective acid ameliorant.

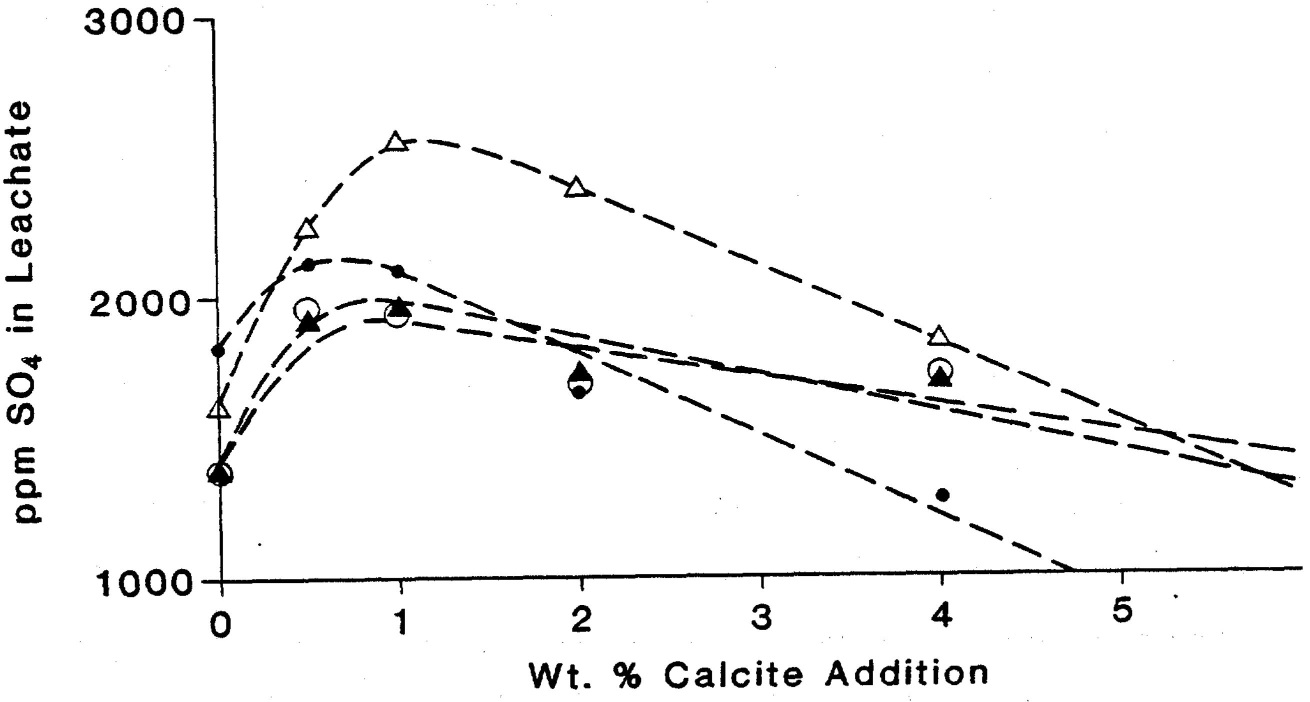

FIGURE 2. Relation Between SO_4^{-2} Production (Acid Production) from Four Typical Toxic Rock Materials Treated with Calcite at 0.5, 1.0, 2.0 and 4.0 Wt. % Addition Rates

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 iron disulphide rich rocks, but rather is meant only to neutralize acid once formed. It should be pointed out, however, that $CaCO_3$ will inhibit the oxidation of the iron disulphides and subsequent acid production if the application schedule is sufficiently large so as 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 and by the inhibition-of iron and sulfur, oxidizing bacteria. This explains the ameliorative effect of high calcium carbonate addition in high sulfur areas such as the Illinois coal basin.

Because the neutralization reaction involving calcite takes place on the surface at 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. 2, should the effective calcite concentration drop below 5 wt%, the system will once again become a net acid producer. This may well explain the frequent initial "success" using limestone as an AMD ameliorant only to be followed by a reversal of the system as the waters turns acid.

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 acid once produced. Apatite was chosen because it filled all the criteria. Apatite eliminates acid formation by removing the major oxidizer of the iron disulphide minerals, Fe^{+3}, by precipitating iron ions as a insoluble iron phosphates. In addition, apatite only dissolves when the conditions become acidic. It is therefore an acid dependent time release material. The purpose of this work was to systematically evaluate the effectiveness of a variety of available phosphate materials as acid ameliorants.

THE CHEMISTRY OF PHOSPHATE AMELIORIZATION OF ACID PRODUCTION

As previously indicated, limestone was used primarily to neutralize the acidic water before it left the mine site either internally within the reclaimed mine site or externally in treatment ponds. In any case, it was meant to neutralize acid already produced by the oxidation of the iron disulphide minerals. It was felt by the authors that a chemical procedure could be developed whichcould actually prevent the acid producing reaction from occurring.

In earlier research by the authors, it has been established from the initial reaction whereby the iron disulphide minerals are oxidized by Fe^{+3} that the ferrous-ferric couple which controls the reaction has an equilibrium voltage of 0.42 (Stiller, 1980). This voltage is important because it represents the lower electrochemical limit of ferric ion which is needed to oxidize pyrite (Stiller, 1981). If the electrode potential of the system can be reduced below 0.42 volts, the oxidation of pyrite can no longer occur. The desired voltage results when the ratio of ferrous to ferric ion concentrations is less than $1:10^{-6}$ (Stiller, 1980). Phosphates are effective in achieving this desired ratio because they can precipitate or coordinate the ferric ion in an insoluble form. Laboratory experiments conducted using $Ca_5(PO_4)_3(OH)$ as the phosphate source showed that when the potential is less than 0.42 volts, the possibility of pyrite oxidation was eliminated.(17) This was also the case even when the samples were rigorously aerated. In addition, it was shown that phosphates precipitated or coordinated the ferrous ion such that it became unavailable for oxidation to ferric ion (Stiller, 1981).

The ferrous ion precipitates as $Fe_3(PO4)_2$ and the ferric ion precipitates as $FePO_4$. The experimental evidence showed that both compounds precipitated on the surface of the pyrite crystals. As the precipitate coating encapsulated the iron disulphide mineral surface, ferrous ion was increasingly unavailable for bacterial oxidation and ferric ion produced by any mechanism was precipitated as an immobile species (Stiller, 1981).

Laboratory experiments showed that even in systems which had been producing acid, the addition of phosphate was effective in eliminating the acid reaction (Stiller, 1980). Once acid production had been eliminated subsequent vigorous aeration of such treated systems did not re-initiate the acid reaction. This implies that toxic materials which are actively producing acid can be treated with $Ca_5(PO_4)_3(OH)$ to halt the acid production.

The results of this initial experimentation showed that PO_4^{-3} acts as a precipitation agent for both iron species, and that iron disulphide minerals cannot be oxidized when the electrode potential is below the equilibrium voltage of the Fe^{+2}/Fe^{+3} cell in the pyrite oxidation system (Stiller, 1980,1981).

EXPERIMENTAL PLAN

The experiments conducted in this work were of two types: 1) bench scale experiments utilizing a synthetic weathering procedure based upon oven oxidation followed by soxhlet leaching of 100 gram samples and 2) small field scale (barrel) experiments which exposed 300 pounds of material to conditions of natural weathering. Both procedures were reported earlier and described in detail by the authors (Renton, et al, 1988). The experimental arrangements for each is shown in figures 3 and 4 respectively.

In preparation for the bench scale experiments, a representative portion of the toxic material was crushed to a top size of 1/4 ". The size limitation was to minimize channeling of the leaching solution within the soxhlet extractor thimble. A representative sample of the prepared toxic material was taken and analyzed for total sulfur by the LECO technique in triplicate. One hundred grams of material were then weighed out into each of three 123 mm cellulose extraction thimbles. A wad of cotton was placed in the thimble covering the sample both to prevent splashing of the leachate and to minimize channeling. The thimble was then placed into the extractor portion of the apparatus. Three hundred milliliters of distilled water was placed in the reservoir and the entire extractor was assembled and brought to temperature. Cyclic leaching of the material was continued for a period of 24 hours. It had been previously established that all of the soluble acid salts had been removed from the most acid of materials within 19 hours of leaching. The 24 hour cycle was chosen for convenience. At the end of the initial 24 hour leaching cycle, the thimble with sample was removed to a 105^{o} C drying oven for a period of 14 days to reoxidize the sample. The leachate was removed from the reservoir, brought to 250 ml volume and

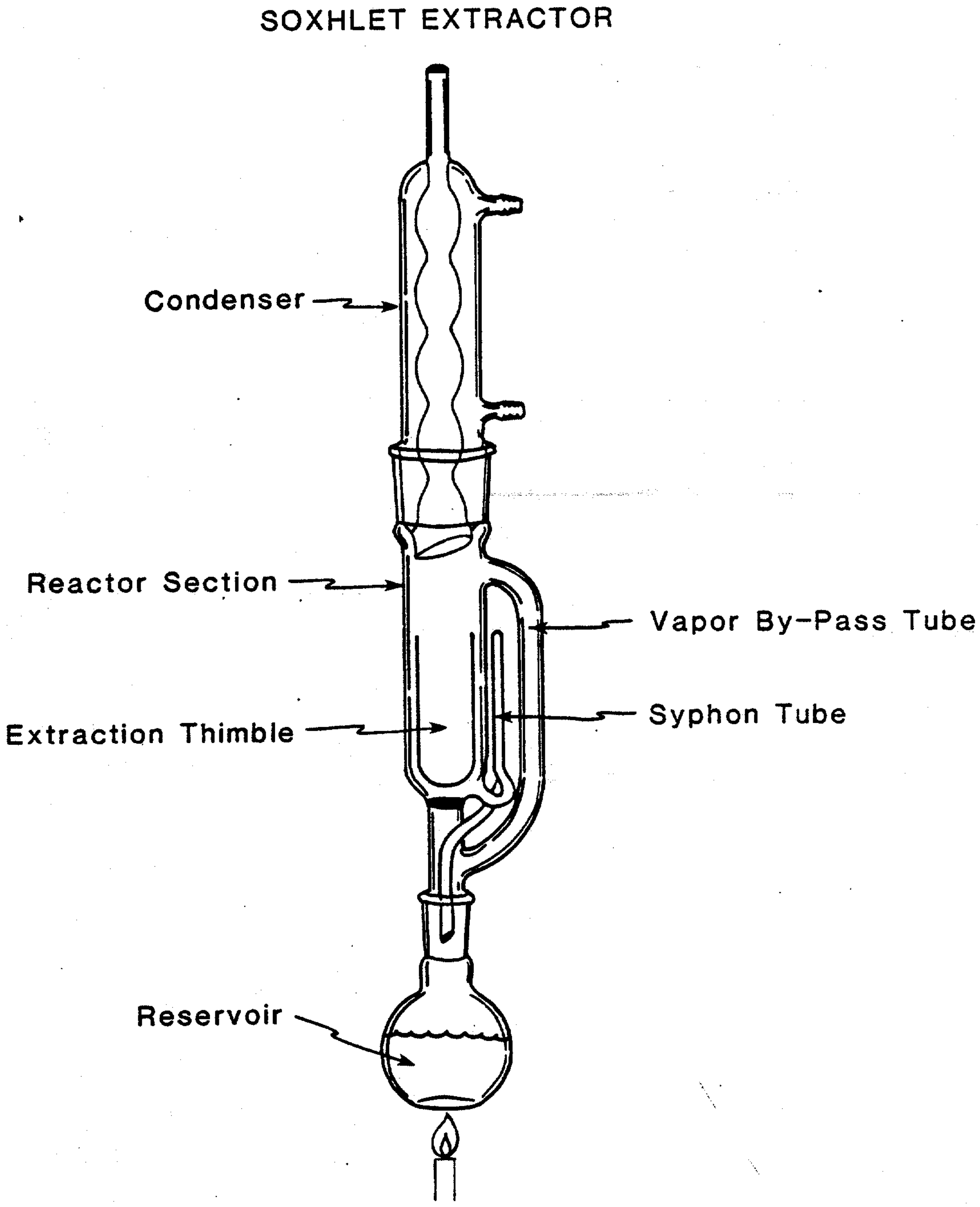

FIGURE 3. Schematic Diagram of Soxhlet Extractor

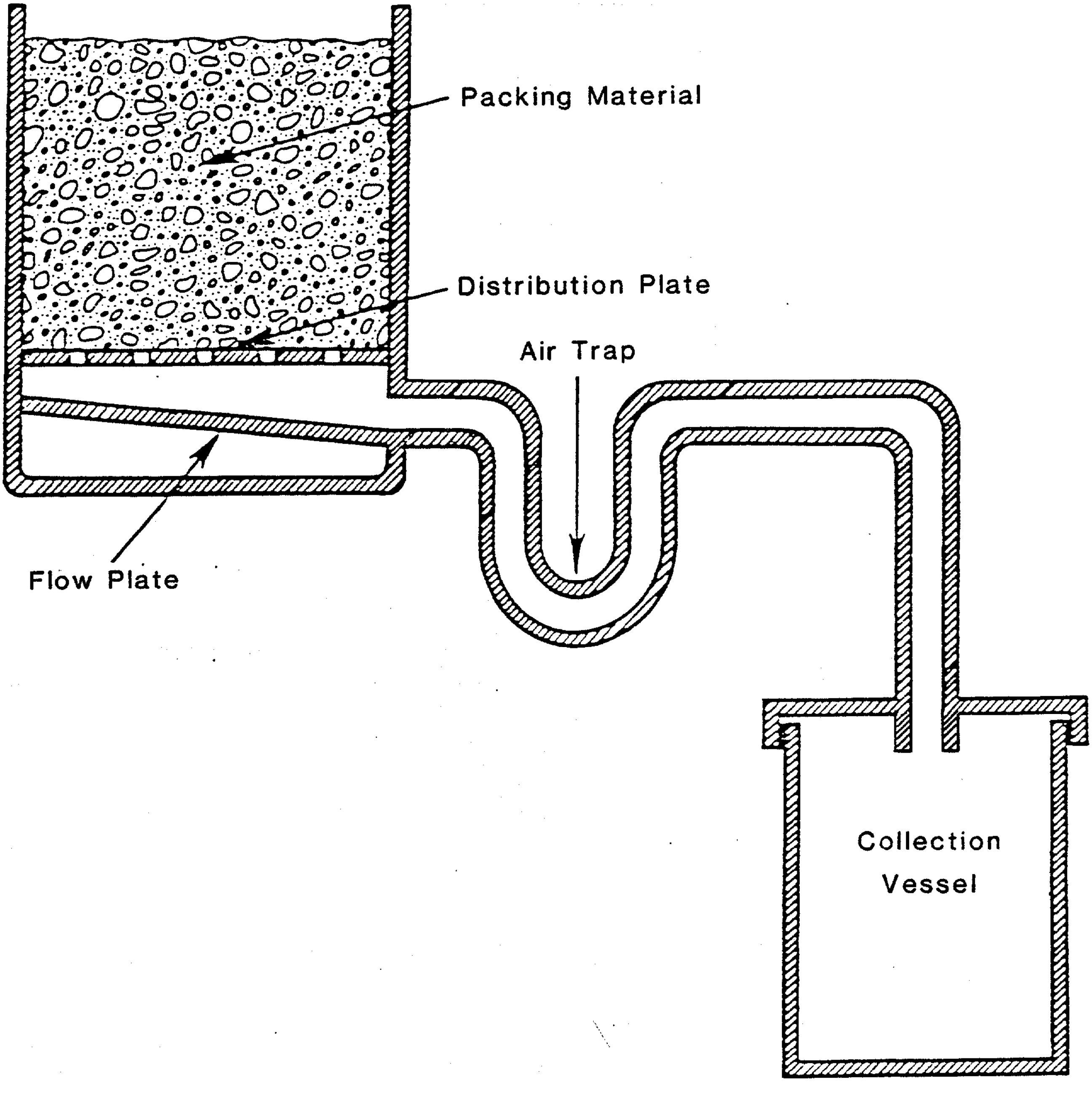

FIGURE 4. **Schematic of Small Field Scale (Barrel) Experiment**

analyzed for sulfate ion by the turbidimetric method.

Following reoxidation, the thimble with sample was returned to the soxhlet extractor and leached for another 24 hour period, the leachate collected and the thimble returned to the oven for reoxidation. The acid reoxidation/leach cycle was repeated four times after the initial leach producing a total of five leachates over a period of eight weeks. The original sulfur content of the material and the sulfate content of each leachate were used to calculate the acid producing parameters. The calculations will be discussed in detail in later sections of this report. In experiments designed to test the effect of phosphate addition on acid production, the phosphate material was added to the toxic rock material prior to its placement into the extraction thimble.

The small field scale (barrel) experiments utilized 300 pounds of toxic material topsized at 1 1/4" placed into 35 gallon plastic barrels fitted with distribution plates, air lock drains and enclosed leachate reservoirs. These experiments, run without treatments for controls and with treatments, were exposed to atmosphere weathering for one calendar year. As with the bench scale experiments, representative samples of the toxic material were collected and analyzed to determine the total sulphur content prior to initiation of the experiments. Leachates were collected throughout the year following each major rain event and snow melt. At the time of collection, the date and volume of leachate were recorded. The sulfate content of the leachate was determined turbidimetrically. Treatment of data will be discussed later.

Both the bench scale and small field scale experiments were designed to provide an experimental method for evaluating the acid producing potential of toxic mine waste and to develop an alternative method to acid-base accounting. Both experimental designs were attempts to model the natural weathering process where a toxic material is oxidized upon exposure to the atmosphere followed by the leaching of precipitation and/or percolating ground water. Coordinated experiments were conducted using both of these experimental designs. The combined data were used to formulate an effective mathematical model as described below.

EXPERIMENTAL CALCULATIONS

ALPHA VALUE

The bench scale and small field scale experiments were primarily designed to determine the rate of acid production. The results of the bench and small field scale experiment was to derive a parameter referred to as alpha (α) the parameter alpha quantitatively defined the rate at which the iron disulfide material encapsulated in toxic mine wastes undergoes oxidation and produces sulfate which is in turn proportional to the rate of acid production. The sulfate concentration was used as a measure of original acid produced because once in solution, the sulfate is as difficult to remove while some of the originally produced acid could be internally neutralized.

The intended purpose of any amelioration process is to reduce the rate of pyrite oxidation and thereby to reduce the magnitude of alpha. It is important to note that alpha, as defined, is NOT the absolute oxidation rate of the mineral pyrite, but rather is the oxidation rate of the pyrite as it exists encapsulated within a rock matrix. The alpha value is therefore a property of a pyrite containing rock and as such, the magnitude of alpha can be affected by rock properties such as particle size, porosity, permeability, total % pyritic sulfur, the specific pyrite morphologies contained within the rock, the distribution of pyrite grains within the rock and the presence or absent of associated minerals such as siderite or calcite. The alpha value is the most critical experimental parameter needed to determine the acid producing potential of a specific toxic rock material.

Pyrite oxidation is considered a 'pseudo' first order kinetic chemical reaction process. The term 'pseudo' simply means that higher ordered kinetic processes occur, but the overall reaction behaves as though it is of the first order. Therefore, one can use the standard formulation for a first order reaction when dealing with pyrite oxidation. This reaction is written:

$$S(t) = S_0 e^{-\alpha t} \qquad (2.0)$$

where:

$S_{(t)}$ = the amount of pyritic sulfur remaining in the material after some elapsed time, t

S_0 = the amount of pyritic sulfur originally present in the sample

e = the Natural Log base (2.7182818)

t = time measured in days

α = the ALPHA value

It is preferable to use a version of this generalized equation which deals with percentages of the original amount of pyritic sulfur available. This is done by dividing both sides of the equation by S_0 and multiplying by 100. This revised equation is written:

$$\% S_u = 100 e^{-\alpha t} \qquad (2.1)$$

where:

$\%S_u$ = the PERCENTAGE of the original amount of pyritic sulfur remaining in the material after some elapsed time, t

e = the Natural Log base (2.7182818)

t = time measured in days

α = the ALPHA value

Taking the natural logarithm (ln) of both sides of the equation we obtain:

$$\ln \% S_u = -\alpha t + \ln 100 \qquad (2.2)$$

A plot of the % unreacted sulfur (Su) vs time (t) will be linear with a slope of alpha (α) and a y-intercept of the natural logarithm of 100 which is 4.605.

The mass of the original sample and the weight percent of % total pyritic sulfur present in the toxic material yields the amount of pyritic sulfur present in the sample prior to oxidation. This value combined with the amount of sulfate ion quantified in the leachates during any time interval is used to calculate the percent of pyrite which has oxidized. A simple calculation then determines the amount of sulfur that remains unoxidized, % S_u. A semilog plot of %Su vs time and a least squares linear regression line most representative of the data determines alpha, which is the slope of the line. Alpha therefore measures the rate at which sulfate ion, and acid, are being generated within the system. A check for how reliably the data conform to EQUATION 2.2 is how closely the y-intercept of the line approaches 4.605. A second check on the accuracy of the ALPHA determination is to use a Gaussian-Probability regression technique similar to one used by nuclear physicists to determine the half-life values of radioisotopes (Eadie, 1971). This technique regresses the cumulative probability of the reacted sulfur against time. The alpha value is then calculated from the time corresponding to the 50-th percentile. A computer software package was developed for this project that utilizes the both the Gaussian-Probability as well as the statistical technique of least squares linear regression analysis to determine the slope (ALPHA) and y-intercept values corresponding to the data gathered either in the field or the laboratory. The correlation coefficient is used to determine the reliability of the data in conforming to EQUATION 2.2. All alpha values determined in this study using the two experimental designs showed correlation coefficients greater than 0.97.

In order to illustrate the data treatment, Table 2 was constructed from data obtained from BARREL #63 which was a 'control' barrel (ie no phosphate addition). The collection date, leachate volume, and sulfate concentration are used to calculate the variables days, percent sulfur reacted, and percent sulfur unreacted respectively. Figure 5 is the semilog plot required by EQUATION 2.2 for an alpha determination. The y-intercept, as can be seen from the regression plot is very close to 4.6 and the correlation coefficient is 98%. This calculated alpha value is therefore very significant due to the fact that the regression statistics show the fact that the data conform to EQUATION 2.2. Barrels 61, 62, and 63 are all control barrels and an average alpha value determined from the three barrels was -0.003 day.$^{-1}$

The alpha values for phosphate treated samples were calculated in exactly the same manner. Similar calculations were made using experimental field data obtained from BARREL #27 in which the toxic material was treated with 1.2 parts rock phosphate/100 parts toxic material. The particle size of the phosphate material was between 125 and 250 microns. The alpha value obtained from the semilog plot was -0.001 day.$^{-1}$ The correlation of the plot coefficient was 0.97. These data also conform to EQUATION 2.2. The reduction in the magnitude of alpha from -0.003 to -0.001 day^{-1} is a measure of the ameliorative power of the experimental phosphate addition.

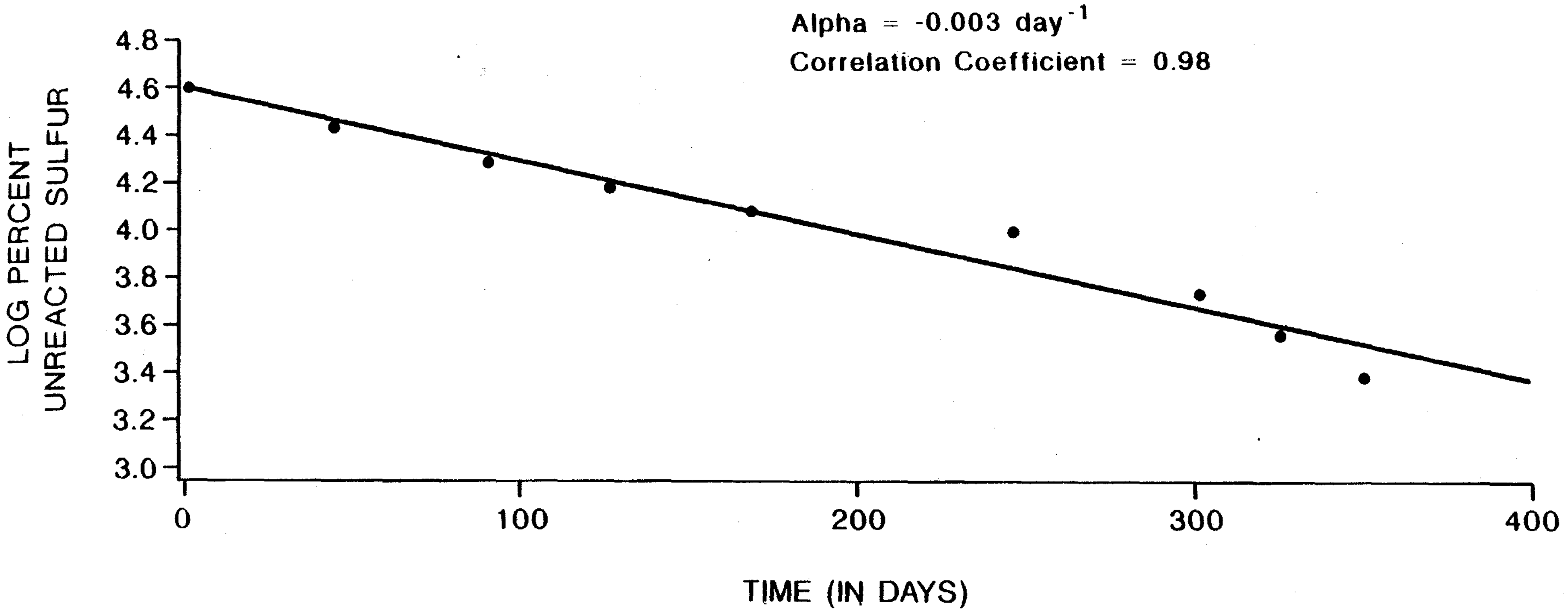

FIGURE 5. **Relationship Between Log Percent Unreacted Sulfur and Time for Control Barrel #63 LOG**

TABLE 2

RAW and TRANSFORMED FIELD DATA FOR BARREL #63 (CONTROL SERIES)

DATE	LEACHATE COLLECTED (liters)	SULFATE (mg/1)	ACIDITY (pH = 7) (mg/l $CaCO_3$)
08-28-86	20.13	31011.9	128100
10-13-86	22.18	20440.8	68250
11-18-86	18.72	15581.1	53730
12-30-86	19.40	11797.0	31250
03-18-87	15.54	13026.9	37230
05-12-87	23.00	21693.3	33250
06-05-87	23.63	11094.2	34600
06-30-87	23.63	9864.3	30430

TRANSFORMED FIELD DATA BARREL 63 (CONTROL SERIES)

TIME (in-days)	CUMULATIVE CONCENTRATION (mg)	% SULFUR UNREACTED	LOG %-UNREACTED SULFUR
0	0	100.00	4.60
44	624467	84.24	4.43
90	1077881	72.80	4.28
126	1369672	65.44	4.18
168	1598642	59.66	4.08
246	1801151	54.55	3.99
301	2300096	41.96	3.73
325	2562323	35.35	3.56
350	2795479	29.46	3.38

The determination of a numerical value for alpha derived from data obtained using the soxhlet oxidation is similar to the method used to calculate alpha from the barrel data with the following differences:

1. the time is measured in soxhlet cycles, rather than real days

2. ALL masses are consistently measured in milligrams.

Semilog plots are constructed and the slope is determined using least squares linear regression statistical methods (see figure 6). The alpha value for the material used in this bench scale study was, -0.0255^{-1}.

Since the alpha values obtained from barrel leachate data in time units, it is necessary to equate real (barrel) days to soxhlet cycles. This time equality can be derived mathematically as follows.

(1) For the barrels: $S_u = 100e^{-\alpha_\beta t}$ (3.0)

where: α_β = alpha for barrels

t = time (days)

(2) For the soxhlets: $S_u = 100e^{-\alpha_s C}$ (3.1)

where: α_s = alpha for soxhlets

C = soxhlet cycles

when:

(3) $(S_u)_{Barrels} = (S_u)_{soxhlets}$

then:

(4) $100e^{-\alpha_\beta t} = 100e^{-\alpha_s C}$ (3.2)

and

(5) $e^{-\alpha_\beta t} = e^{-\alpha_S C}$ (3.3)

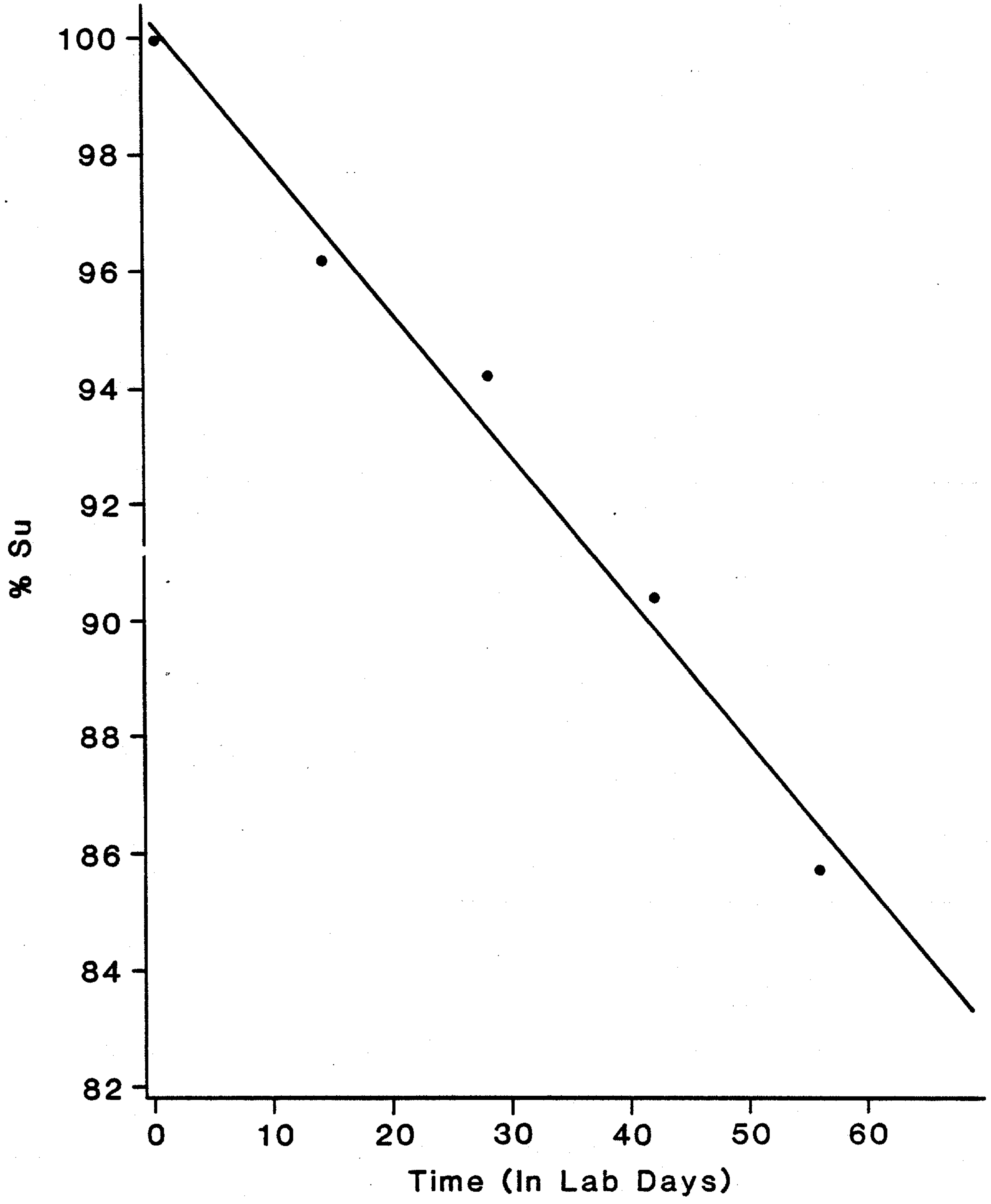

FIGURE 6. Percent Unreacted Sulphur (%Su) Versus Time in Lab Days for Bench Scale Experiments

Taking the Log:

(6) $\log e^{-\alpha_{\beta} t} = \log e^{-\alpha_S C}$ (3.4)

(7) $-\alpha_B t = -\alpha_S C$ (3.5)

(8) $\alpha_B t = \alpha_S C$ (3.6)

(9) $\frac{\alpha_B}{\alpha_S} = \frac{C}{t}$ (3.7)

Therefore the ratio of alpha values obtained from each method gives the "real day" equivalent

This prediction of the mathematical relationship between barrel days and soxhlet cycles is shown in FIGURE 7. The data points used in the construction of FIGURE 7 represent times where the % unreacted sulfur in the barrel materials and the % unreacted sulfur in the soxhlet materials were the same. Barrel days are shown on the vertical axis and soxhlet cycles are shown on the horizonal axis. From equation 3.7 as well as FIGURE 7, it is found that a single soxhlet cycle corresponds to 8.8 barrel (REAL) days. This scaling factor developed for this study is the same as the scaling factor obtained for other similar projects (see Table 3). The 8.8 days per soxhlet cycle is therefore a consistent number.

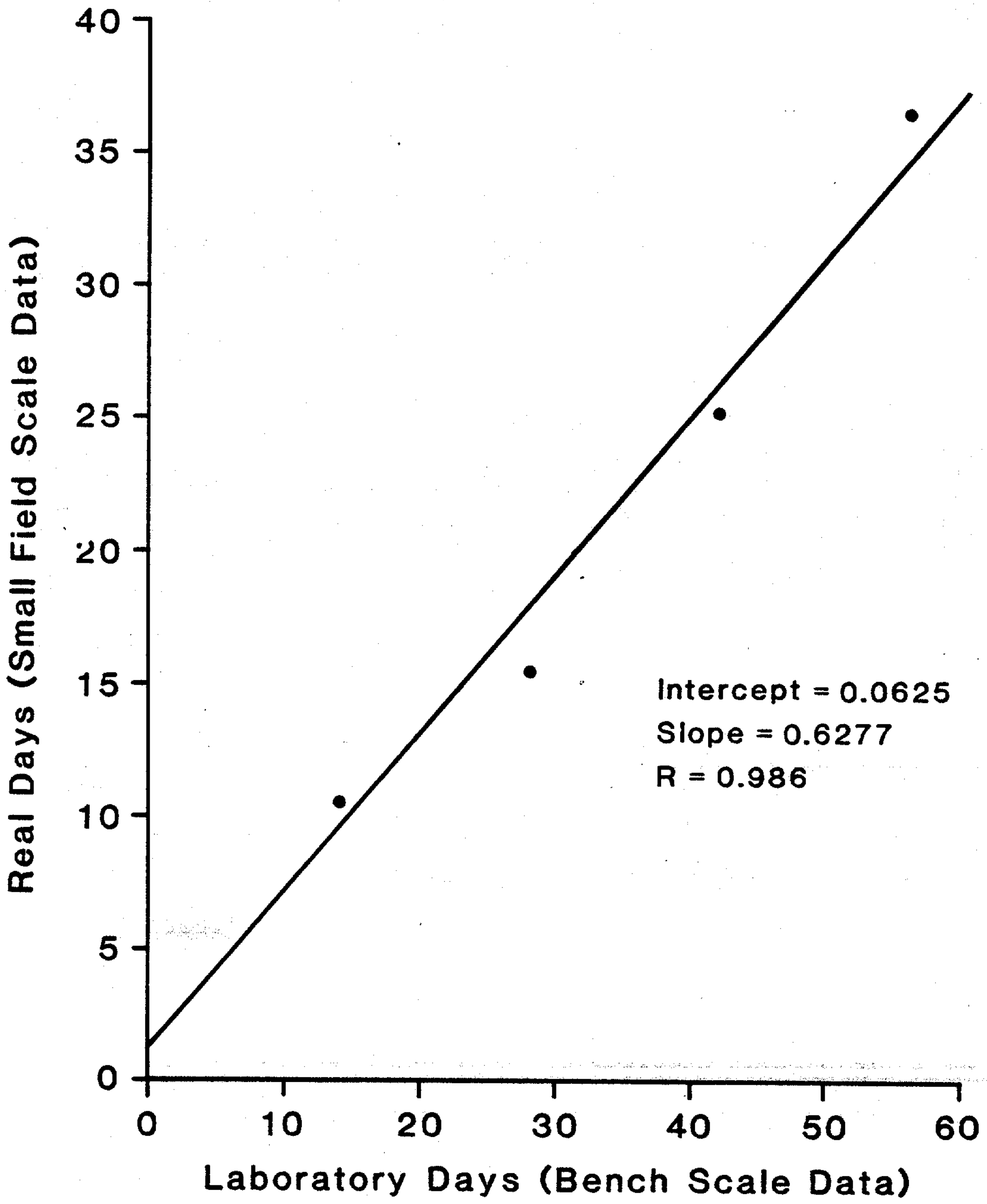

FIGURE 7. Time to Reduce % S to Equal Concentrations of Unreacted Sulphur

TABLE 3

TIME SCALING FACTORS DETERMINED FOR SELECTED BARREL-SOXHLET EXPERIMENTS

PROJECT IDENTIFICATION	CALCULATED SCALING FACTOR (REAL (BARREL DAYS)/SOXHLET CYCLE)
ENERGY RESEARCH CENTER	8.8
BUCKHANNON MINE SITES	8.8
WVU AGRONOMY DEPT.	8.8
FLORIDA INSTITUTE	8.8

SMALL FIELD SCALE EXPERIMENTS:

In both the bench scale and small field scale experiments, the sulfate data were tabulated in cumulative milligrams of sulfate after each collection. Further argument for the conclusion that the experiments followed pseudo first order kinetic rates is the fact that the small field scale experiments (barrels) had, for all practical purposes, ceased appreciable sulfate production (pyrite oxidation) at approximately 300 days (280-325 days), leaving 30% of the sulfur as FeS_2 unreacted. In chemical kinetics, the mean-lifetime, t, of chemical reactions exhibiting first-order behavior is statistically shown to be equal to $1/\alpha$ (Adamson, 1973).

The amount of substance remaining unreacted after this time can be shown to be 37% of:

1) $\bar{t}$ = mean-lifetime and $\bar{t} = 1/\alpha$

2) $\%Su = 100e^{-\alpha t}$

let $t = \bar{t}$

then $\%Su = 100e^{-\alpha\bar{t}}$

since $\bar{t} = 1/\alpha$

then $\%Su = 100e^{-\alpha 1/\alpha}$

then $\%Su = 100e^{-1}$

$\%Su = 37\%$

A substance having an alpha value of -0.003 day^{-1} would have a mean-lifetime of $1/\alpha$ or 330 days. Statistically, at the end of this time, 37% of the material would remain unreacted. The fact that in this study, the small field scale experiments conducted with a rock material having an alpha value of -0.003 day^{-1}, were exhausted after 300 days leaving approximately 30% of the sulfur unreacted lends more credibility to the quantifying of our reasults in terms of 1st order rate kinetics.

A PREDICTIVE EQUATION:

The combined experimental data were used to formulate a mathematical model which calculated the amount of sulfur released into solution as sulfate based upon the original amount of sulfur present in the material, the experimentally determined rate constant, alpha, and time. The slope of the ln %Su versus time plot, α, can also be used to calculate %Su according to the relationship:

$$\% S_u = S_o e^{-\alpha t} \qquad (4.0)$$

where:

S_o = 100% (original % S)

α = the experimentally determined rate constant corrected for real time

t = time in days

The %Su can also be calculated as follows:

$$\%Su = \frac{(M \ -Ms)}{t} \times 100 \qquad (4.1)$$

where:

M = the mass of material in any units

S_t = the sulfur content of the material in Wt%

Ms = the mass of sulfur released into solution (in the same units as for M)

Equating the two relationships for %Su:

$$\frac{(MS_t - Ms)}{MS_t} \times 100 = 100^{e-\alpha t} \qquad (4.2)$$

therfore:

$$Ms = MS_t - MS_t e^{-\alpha t} \qquad (4.3)$$

Using the above imperically derived predictive model, sulfate production was calculated at selected times for a series of the bench scale and small field scale experiments. The calculated and observed sulfate data are summarized and compared in Table 4.

TABLE 4: COMPARISON OF CALCULATED AND OBSERVED SULFATE CONCENTRATIONS

SMALL FIELD SCALE DATE (in Kg SO_4^{-2})

Time In Days	Calc.	Obser.	Diff.
21	3.67	3.36	-8.4%
71	11.40	9.97	-12.5%
160	21.26	23.91	+12.4%
209	25.10	25.13	+ 5.5%
233	26.38	25.44	- 5.5%

AVER. DIFF. = -2.4%

BENCH SCALE DATA (in mg SO_4^{-2})

Time In Days	Calc.	Obser.	Diff.
8.8	4055	3641	-10.2%
17.6	7914	6093	-23.0%
26.4	11583	11714	+ 1.1%
35.1	15030	14948	0.0%

AVER. DIFF. = -8.0%

Another test of the predictive potential of the mathematical equation derived above utilized data from a 350 ton model backfill constructed by Island Creek Coal Co., Buckhannon, WV, as part of an inhouse research project (Meek, 1984). The model consisted of a hydrologically isolated pile of toxic material, 50' x 50' x 4'. All rain which fell on and percolated through the pile was collected by an underlying plastic membrane and was directed through an automatic flow/water sampling device.

Samples of the rock comprising the pile were collected and subjected in triplicate to the bench scale oxidation/leach procedure. The subsequent ln%Su versus time plot showed a slope of -0.00035 days^{-1} with $R=0.987$. The sulfur content of the material was 0.28 wt%. Using the mathematical model derived above, predicted cumulative sulfate data were calculated. These data are tabulated and compared against the observed data in Table 5. A plot of the predicted and observed data is shown in figure 8. Although the mathematical model initially overestimated sulfate production, beyond 230 days the predicted values were within 10% of the observed; at 260 days, the predicted and observed data were equal in magnitude.

TABLE 5 COMPARISON OF ACTUAL AND PREDICTED SULPHATE DATA FOR THE ISLAND CREEK BACKFILL MODEL

$\%S = 0.28\%$, $\alpha = 0.00035$ DAYS $^{-1}$, $R = 0.987$

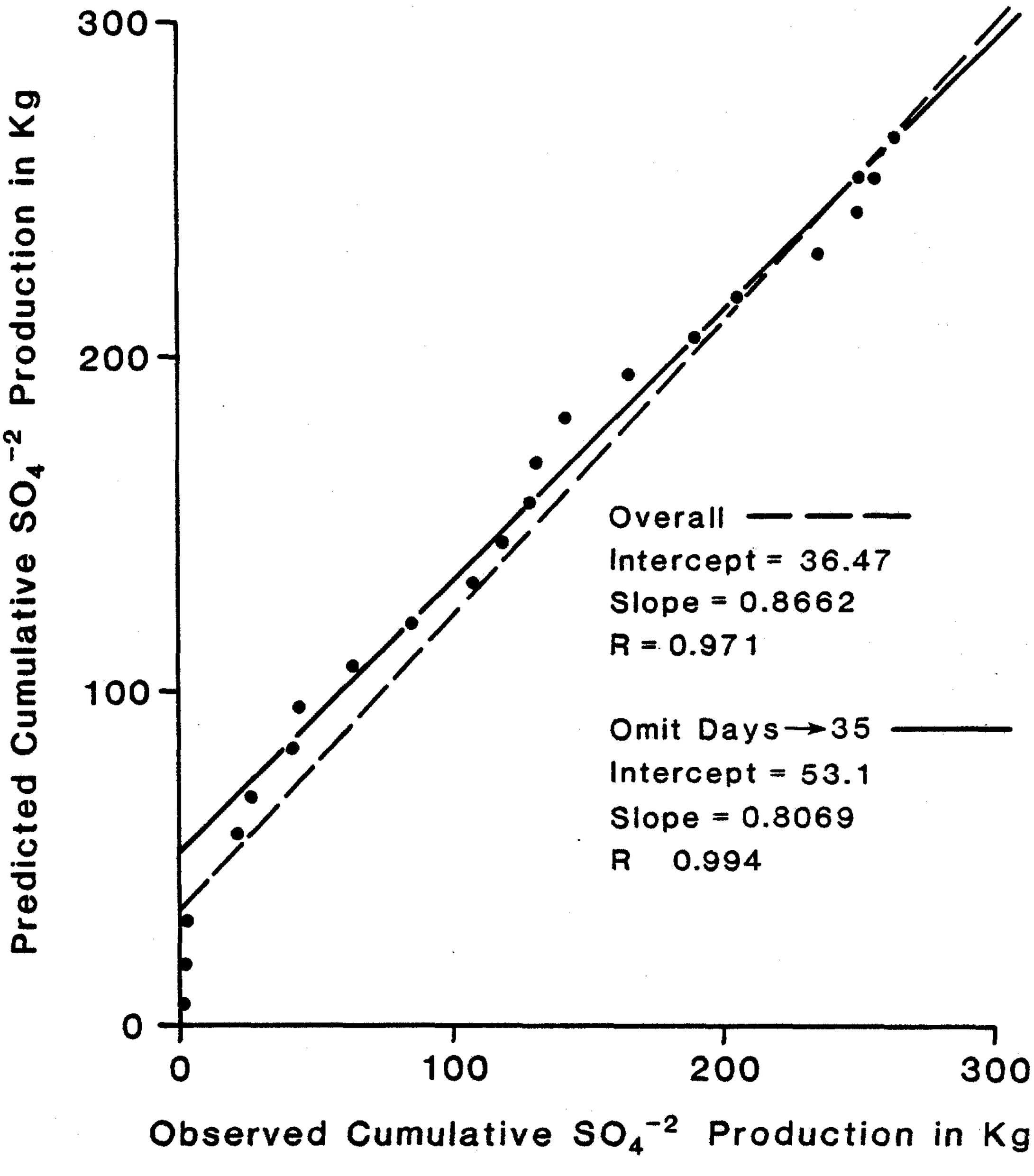

FIGURE 8. Observed Versus Predicted Cumulative $KgSo_4^{-2}$ for Island Creek Coal Co. Backfill Model

OBS	TIME (DAYS)	OBSER. CUM.SO_4^{-2} (in Kg)	PRED. CUM.SO_4^{-2} (in Kg)	%SU
1	0	0	0	100.00
2	8	0.4	7.5	99.98
3	21	0.8	19.0	99.96
4	35	1.4	32.5	99.94
5	63	22.6	58.2	99.15
6	77	27.7	70.9	98.96
7	92	41.2	84.5	98.45
8	105	43.7	96.2	98.36
9	119	64.0	108.8	97.60
10	133	85.6	121.3	96.79
11	148	108.5	134.6	95.93
12	161	118.2	146.1	95.57
13	175	129.7	158.5	95.14
14	189	131.8	170.7	95.06
15	203	142.9	182.9	96.64
16	217	165.4	195.0	93.80
17	231	189.6	207.1	92.89
18	245	205.0	219.2	92.32
19	259	235.8	231.1	91.16
20	273	248.3	243.0	90.69
21	287	255.9	254.9	90.41
22	301	262.4	266.7	90.17

23	315	282.5	278.4	89.51
24	329	282.5	290.1	89.41

It can be concluded from these data that a laboratory procedure and a mathematical model have been devised which allow the rate of sulfate (acid) production and the ultimate acid load to be predicted from any mass of potentially toxic rock materials. The procedure is based upon the total sulfur content of the rock material, an experimentally determined rate constant, α , and the rock mass.

ETA/ACID LOAD

Another experimental parameter, referred to as ETA, was calculated which relates the % total sulfur present in the rock material to its acid load potential. The product of ETA times the % total sulfur of a toxic rock equals the tons of calcium carbonate (limestone) required to neutralize all of the acidity (hydrogen ion) generated by 1000 tons of toxic material. The ETA value is based on the stoichiometric relationships present in the following theoretical reaction scheme:

$$FeS_2 + O\ (aq) \longrightarrow H+(aq) + 2SO_4^{-2}\ (aq) + Fe^{(+2)} \qquad (5.0)$$

$$Fe^{+2}\ (aq) + O_2\ (aq) \longrightarrow Fe^{+3}(aq) + \text{biproducts} \qquad (5.1)$$

$$Fe^{+3}\ (aq) + FeS_2\ (solid) \longrightarrow Fe\ +2(aq) + H+(aq) + 2SO_4^{-2} \qquad (5.2)$$

$$H+(aq) + CaCO_3\ (solid) \longrightarrow H_2CO_3\ (aq) + Ca^{+2}(aq) \qquad (5.3)$$

Since various competing reactions exist which are simultaneously generating or consuming hydrogen ion (acid), it is impossible to predict from such stoichiometic relationships exactly how much of this hydrogen ion (acid) is theoretically possible to exist at any time. Sulfate, on the other hand, presents no such problem because for every one mole of pyrite consumed two moles of sulfate and one mole of aqueous iron ion (ferrous or ferric) are produced. Stoichiometrically, then, we have:

ACID LOAD= tons of $CaCO_3$/1000 tons material =

$$= \frac{\%S \text{ tons Sulfur}}{100 \text{ tons material}} \times \frac{\text{ton moles sulfur}}{32 \text{ tons Sulfur}} \times \frac{\text{ton moles sulfate}}{\text{ton mole Sulfur}} \times$$

$$\frac{(m) \text{ ton moles H+}}{\text{ton mole sulfate}} \times \frac{\text{ton mole CaCO}_3}{2 \text{ ton mole H+}} \times \frac{100 \text{ tons CaCO}_3}{\text{ton mole CaCO}_3} \times \frac{10}{10}$$

$$= \%S\ (m)\ (15.625)$$

where:

m= the stoichiometric mole ratio between sulfate ion and hydrogen ion as determined by SO_4^{-2} and acid titration data respectively.

The ETA value is taken as being equal to the expression 15.625 m, where is evaluated from soxhlet (or barrel) leachate data. Note that acid base accounting method makes the assumption that the stoichiometric ratio between sulfate produced and hydrogen ion generated (m) is equal to 2 and, hence, ETA is equal to 31.25. It has been demonstrated that this assumption is in error (Renton, 1985). The stoichiometric ratio between sulfate and hydrogen ion is quite often less than 2 and as a result the acid base account has either overpredicted the acid load potential or vast amounts of internal neutralization has taken place. Fortunately, in either case no real environmental harm is to be expected. However, if this stoichiometric ratio is greater than 2, the potential for environmental damage reaches greater levels of probability because the acid base account has UNDERPREDICTED the potential acid load.

The unique property of ETA is that, unlike alpha, the magnitude is an inherent rock parameter and is not altered to any significant degree by amelioration. The method for determining alpha values from phosphate treated BARREL samples is identical to the method used for the determination of alpha values from untreated samples. Any potential contamination of the barrel leachate from sulfate that may be present in the phosphate material is minimal due simply to the relative amounts of phosphatic and toxic rock material present in the barrels. On the other hand, because of the small amounts of materials used in the in bench scale experiments, the potential contamination of the leachate by sulfate originally present in the phosphate material was a distinct possibility. Such contamination would yield more sulfate in the leachate than was actually generated by the oxidation of pyrite within the toxic material and would therefore result in falsely high alpha values. As a result, an indirect approach to calculate alpha from soxhlet data was devised taking advantage of the relationships that exist between total percent sulfur, acid produced, and the fact that alpha (rate of pyrite oxidation) is altered by phosphate materials present in the system while eta remains unchanged. The calculation is summarized as follows:

%St = total percent sulfur from laboratory analysis (7.0)

$$Su = \% \text{ sulfur unreacted} = 100\ e^{-\alpha t} \qquad (7.1)$$

$$\text{let } Sr = \% \text{ sulfur reacted} = 100 - Su \qquad (7.2)$$

$$\text{therefore: } Sr = 100 - 100e^{-\alpha t} \qquad (7.3)$$

$$\text{The amount of acid produced } (CaCO_3 \text{ equivalents}) = S_t h = A \qquad (7.4)$$

where:

S_t = % total sulfur

h = eta

A = Acid load

At any time, S_t can be replaced by the expression $S_t \dfrac{Sr}{10}$

Then:

$$\frac{Sr}{S_t(100)}\ h = A \qquad (7.5)$$

$$S_t(1-e^{-\alpha t}) = A \qquad (7.6)$$

$$(1-e^{-\alpha t}) = \frac{A}{S_t} \qquad (7.7)$$

$$-e^{-\alpha t} = \frac{A}{S_t} - 1 \qquad (7.8)$$

$$e^{-\alpha t} = 1 - \frac{A}{S_t} \qquad (7.9)$$

$$-\alpha t = \log \frac{1-A}{S_t} \qquad (7.10)$$

$$\alpha t = -\log (1-A/S_t) \qquad (7.11)$$

therefore:

$$\alpha = -\log \frac{(1-A/S_t)}{t} \qquad (7.12)$$

Therefore, the alpha values for phosphate treated soxhlet samples can be calculated by knowing:

1) %S

2) time

3 A (soxhlet acidity leachate data), and

4 h (derived from soxhlet leachate control data)

THE HALF RATE VALUE

The half-rate value was devised as a means to compare the effectiveness of various phosphate materials as ameliorants. The diversity of toxic lithotypes, phosphate particle sizes, and phosphate materials used in this study generated a wide range of alues for alpha, eta, total % pyritic sulfur values, and acidloads. Since both the toxic materials and phosphate materials vary significantly in degrees of toxicity and ameliorative effectiveness respectively, it is necessary to formulate a parameter which will incorporate all of these critical parameters and allow direct comparisons to be made. Such a parameter is a concept that is termed the HALF-RATE.

DEFINITION: the HALF-RATE os the application schedule (in parts/100) of phosphate material that is necessary to bring about a reduction in ACIDLOAD of 50%.

$$\frac{dA}{dR} = -\omega A \qquad (8.0)$$

Where:

A = Acidload

R = phosphate addition in parts phosphate per 100 parts rock material

ω = rateconstant

$\frac{dA}{dR}$ = change in acid load with chae in phosphate addition schedule

Therefore:

$$\frac{dA}{A} = -\omega dR \qquad (8.1)$$

Taking the integral:

$$\int_0^A \frac{dA}{A} = -\omega\int_0^R dR \qquad (8.2)$$

At R = 0 the untreated acidload = A_o

Therefore:

$$\log \frac{A}{A_o} = -\omega R \qquad (8.3)$$

$$\frac{A}{A_o} = e^{-\omega R} \qquad (8.4)$$

if $A/A_o = 1/2$, the amount of acid is reducted by 1/2 and R becomes $R_{1/2}$

$$1/2 = e^{-\omega R_{1/2}} \qquad (8.5)$$

$$-\log 2 = -\omega R_{1/2} \qquad (8.6)$$

$$R_{1/2} = \frac{\log 2}{\omega} \qquad (8.7)$$

Using leachate data from soxhlet extraction, acid loads produced at various application schedules combined with either semilog of Gaussian-Probability (Normal) regression techniques yields omega (ω). The HALF-RATE is thus calculated based upon Equation 8.7.

EXPERIMENTAL MATERIALS

PHOSPHARE 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 was 95% in the size range from 150 to 250 mesh and a second material 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 varies 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 previously indicated as being encountered in coal mining. This 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.

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 ultimate acid load. Four sets of-experiments were conducted.

SET #l:

Table 6 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

TABLE 6 EXPERIMENTAL SET #1

CC#	COAL BED ASSOC.	LITHIC TYPE	St	AlPHA	ETA	TREATMENT	TREATMENT CC#
6434	U.FREE	REF.	2.970	-0.0003	48.00	1/4"-1/8"	5192
116	M.KITT	ROOF SHALE	1.410	-0.0012	22.49	1/4"-1/8"	5192
114	U.FREE	REF.	2.830	-0.0093	25.28	1/4"=18"	5192
22	L.KITT	REF.	2.742	-0.0012	12.40	1/4"-1/8"	5192
6434	U.FREE	REF.	2.970	-0.0003	48.00	1/8"-1/16"	5191
122	U.FREE	ROOF SHALE	7.271	-0.0075	23.89	1/8"-1/16"	5191
60	U.FREE	REF.	2.955	-0.0012	10.46	1/8"-1/16"	5191
53	U.FREE	REF.	6.501	-0.0046	25.87	1/8"-1/16"	5191
6434	U.FREE	REF.	2.970	-0.0003	48.00	<1/16"	5190
326	L.KITT	REF.	7.010	-0.0039	22.31	<1/16"	5190
35	U.FREE	REF.	1.140	-0.0019	32.64	<1/16"	5190
19	L.KITT	REF.	1.812	-0.0010	23.10	<1/16"	5190
330	U.FREE	SEAT-EARTH	2.680	-0.0068	6.26	CODE 30	5168
47	M.KITT	BONE COAL	5.263	-0.0007	23.98	CODE 30	5168
45	U.FREE	REF.	6.334	-0.0011	20.15	CODE 30	5168
40	L.KITT	PARTING	4.242	-0.0015	30.19	CODE 30	5168
6434	U.FREE	REF.	2.970	-0.0003	48.00	CODE 30	5168

337	L.KITT	REF.	9.114	-0.0051	21.61	CODE 30	5168
320	U.FREE	REF.	0.535	-0.0535	25.32	CODE 30	5168
123	U.FREE	REF.	3.186	-0.0080	16.66	CODE 30	5168
121	U.FREE	ROOF SHALE	9.740	-0.0082	24.71	CODE 30	5168
63	U.FREE	REF.	4.560	-0.0082	21.13	CODE 30	5168
55	U.FREE	ROOF SHALE	6.910	-0.0008	27.71	CODE 30	5168
24	U.FREE	OVERB. SHALE	0.652	-0.0050	5.00	CODE 30	5168
6434	U.FREE	REF.	2.197	-0.0003	46.00	AGRICO	5166
5070	U.FREE	REF.	3.150	-0.0050	58.36	AGRICO	5166
13	U.FREE	REF.	4.560	-0.0052	17.73	AGRICO	5166
12	L.KITT	ROOF SHALE	1.586	-0.0117	5.37	AGRICO	5166
19	L.KITT	REF.	1.812	-0.0010	23.10	AGRICO/C31	8348
26	U.FREE	ROOF SHALE	2.428	-0.0063	25.67	AGRICO/C31	8348
49	U.FREE	S.S.	1.740	-0.0003	45.21	AGRICO/C31	8348
62	U.FREE	REF.	5.525	-0.0050	20.94	AGRICO/C31	8348
64	U.FREE	REF.	3.312	-0.0061	15.91	AGRICO/C31	8348
119	L.FREE	PARTING	1.940	-0.0033	12.11	AGRICO/C31	8348

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. The rock phosphate in the size range from 150 to 250 mesh was designated "CODE 30", while the material in the -325 mesh size range was designated "CODE 31". 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 7. 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.

SET #3:

In this set of experiments, slurry CC# 8348, a 1:0.5 blend of dried slurry and CODE 31 apatite was intermixed with four different toxic materials at application schedules of 1, 2, 3 and 4 wt% apatite (see Table 8).

SET #4:

Initially, the CODE 30 material was tested against a variety of

TABLE 7 EXPERIMENTAL SET #2

	SOLID MIX			SLURRY MIX	
CC#	gm AGRICO	gm CODE 31	ml/H20	gm SOLID MIX	WT% APATITE ADDITION
8342	5	0	50	5	0.25
8343	260	13	200	40	2.00
8344	260	13	750	225	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

TABLE 8 EXPERIMENTAL SET #3

AGRICO VS. 6 DIFFERENT TOXIC MATERIALS

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

CC# 8348 SLURRY

450 gm AGRICO + 225 gm CODE 31

750 ml H20 + 150 gm MIXTURE

APPLICATION SCHEDULE

CONTROL, 1 wt%, 2 wt%, 3 wt% and 4 wt% APATITE 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 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 the 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) 35 to 60 mesh, (375 microns), 3) 60 to 120 mesh (187 microns), and 4) less than 120 mesh (125 microns).

A total of ninety field scale barrel experiments were prepared (see Table 9). Each experiment 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 peroxide, specific conductivity, acidity, the concentrations of Ca, Mg, Na, K, Fe, Mn, Al, Si and sulfate ion. 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 and after each collection of the small field scale experiments. From these data and the initial sulfur content of the rock material, a percent unreacted sulfur ($\%S_u$) remaining within the rock material after each leachate collection was calculated.

The three previously described experimental parameters were used to evaluate the toxic potential of an each experimental system: 1) the acid production rate constant, ALPHA, 2) the ACID LOAD and 3) a parameter ETA.

RESULTS OF INVESTIGATION

BENCH SCALE EXPERIMENTS

The results of the investigation are quite clear. The effectiveness of the rock phosphate is simply a question of mass

TABLE 9 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

transfer; the effectiveness increasing with decreasing particle size and increasing magnitude of the application rate.

The results of experimental SET #l are illustrated in Figure 9. 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 relatively 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.

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. 10). 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 11 and 12 which plot acid load and alpha reduction versus wt% apatite addition respectively. 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

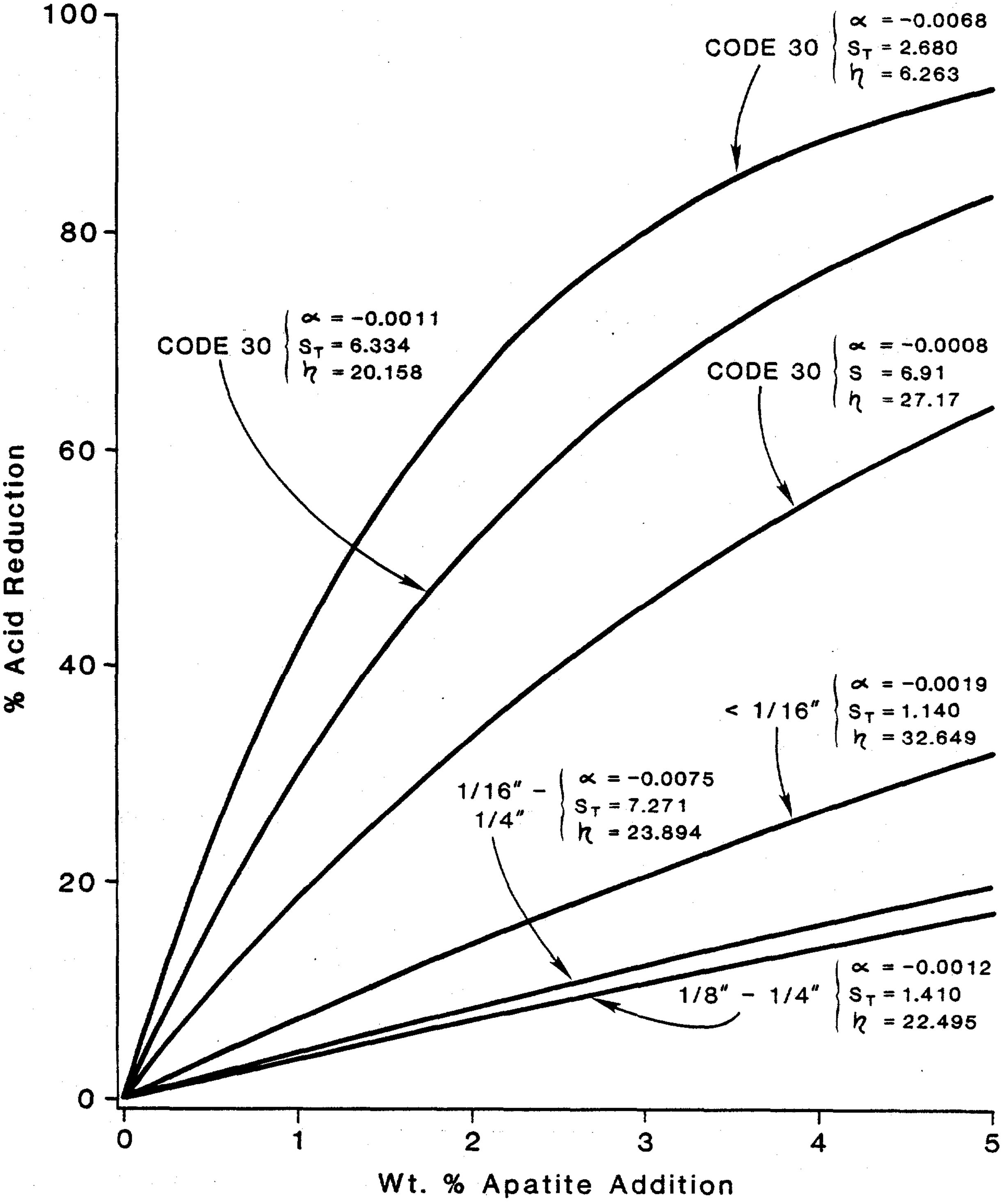

FIGURE 9. Percent Acid Reduction vs. Wt. % Apatite Application for Various Sized Rock Phosphate Materials

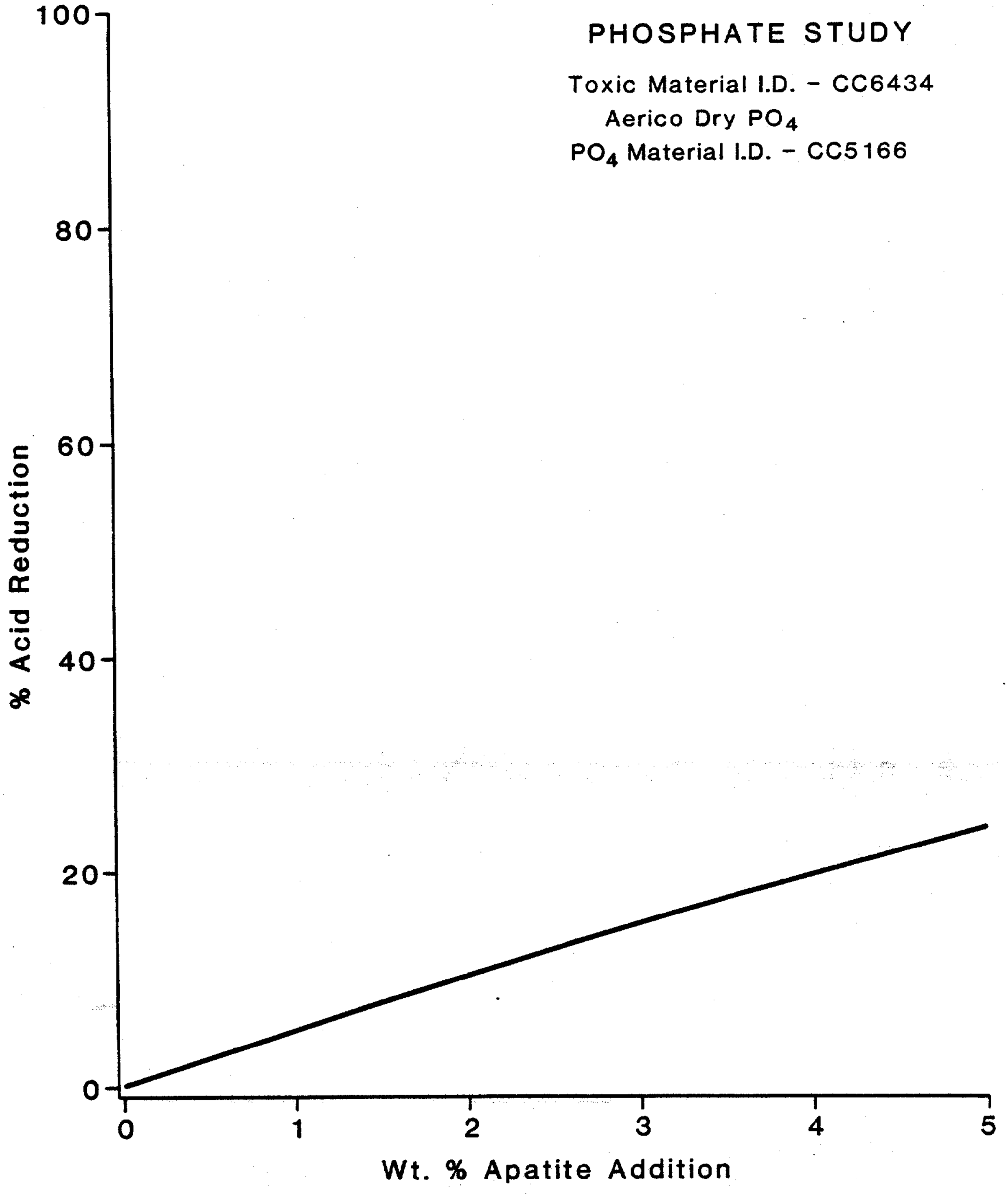

FIGURE 10. Percent Acid Reduction vs. Wt. % Apatite Application for Dried Slurry - No Code 31 Spike

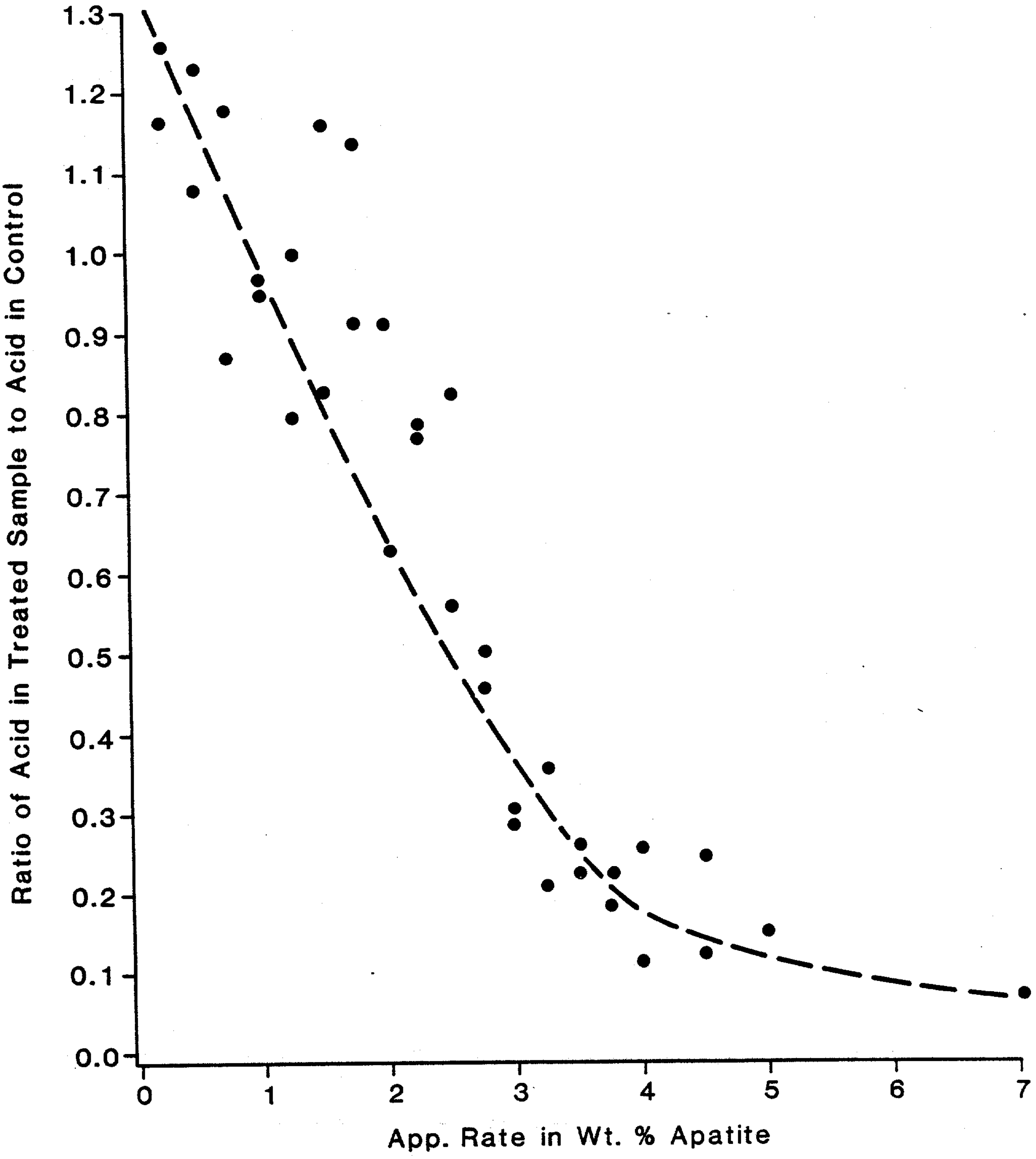

FIGURE 11. Percent Acid Reduction vs. Wt. % Apatite Application for Dried Slurry with Code 31 Spike

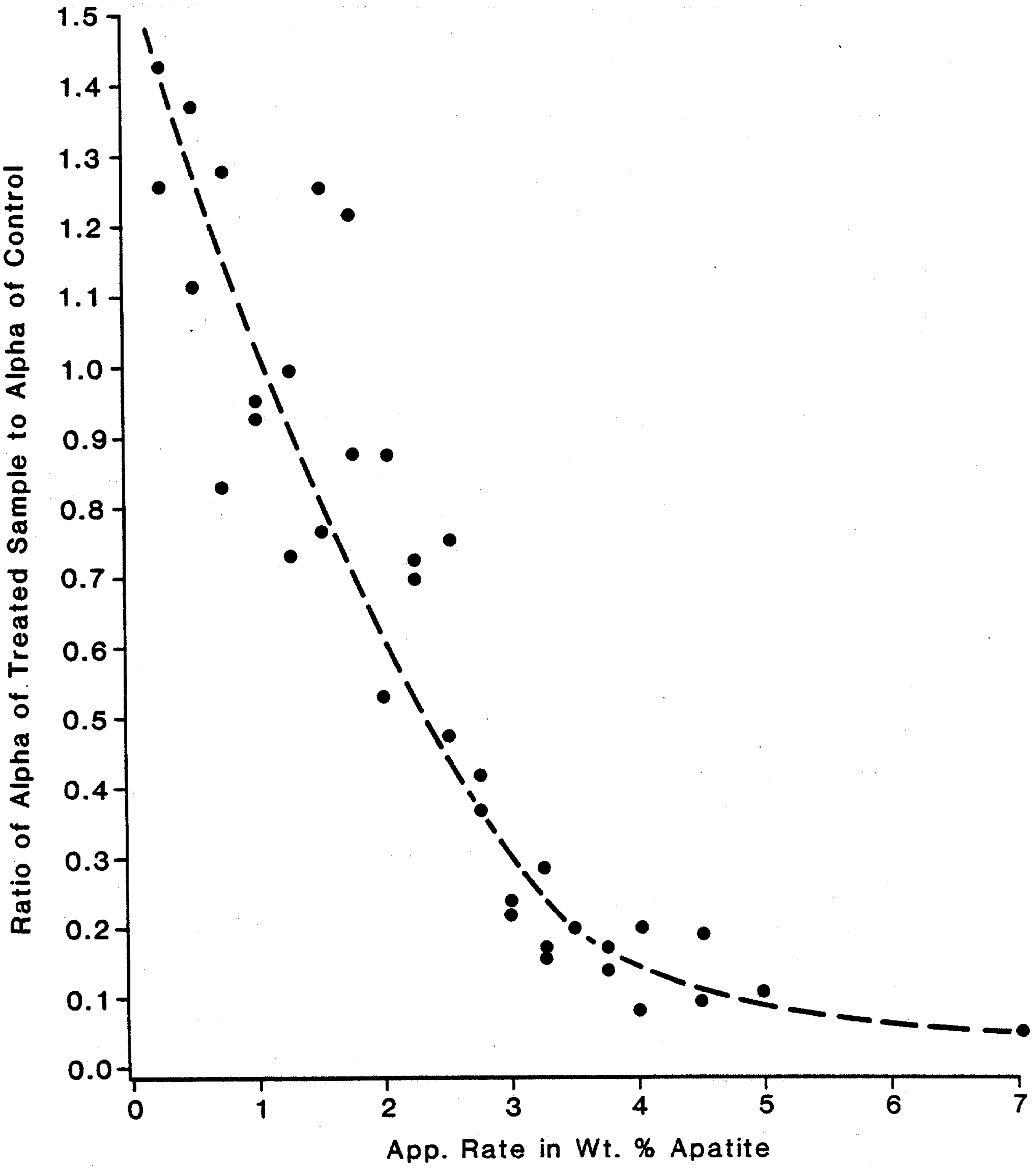

FIGURE 12. Percent Alpha Reduction vs. Wt. % Apatite Application for Dried Slurry with Code 31 Spike

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 13 through 20 and the data from SET #4, the CODE 30 addition to the "standard" prep refuse, are shown in figures 21 and 22. The trends in these data are similar to those of the previous experiments.

SMALL FIELD SCALE EXPERIMENTS

The results of the small field scale experiments are shown in figures 23 through 24A. Similar to the bench sale experiments, the data show the ameliorative effectiveness to increase with decreased particle size. The three dimensional plot in figure 24 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.

CONCLUSIONS

1) Rock phosphate (apatite) is an effective AMD ameliorant

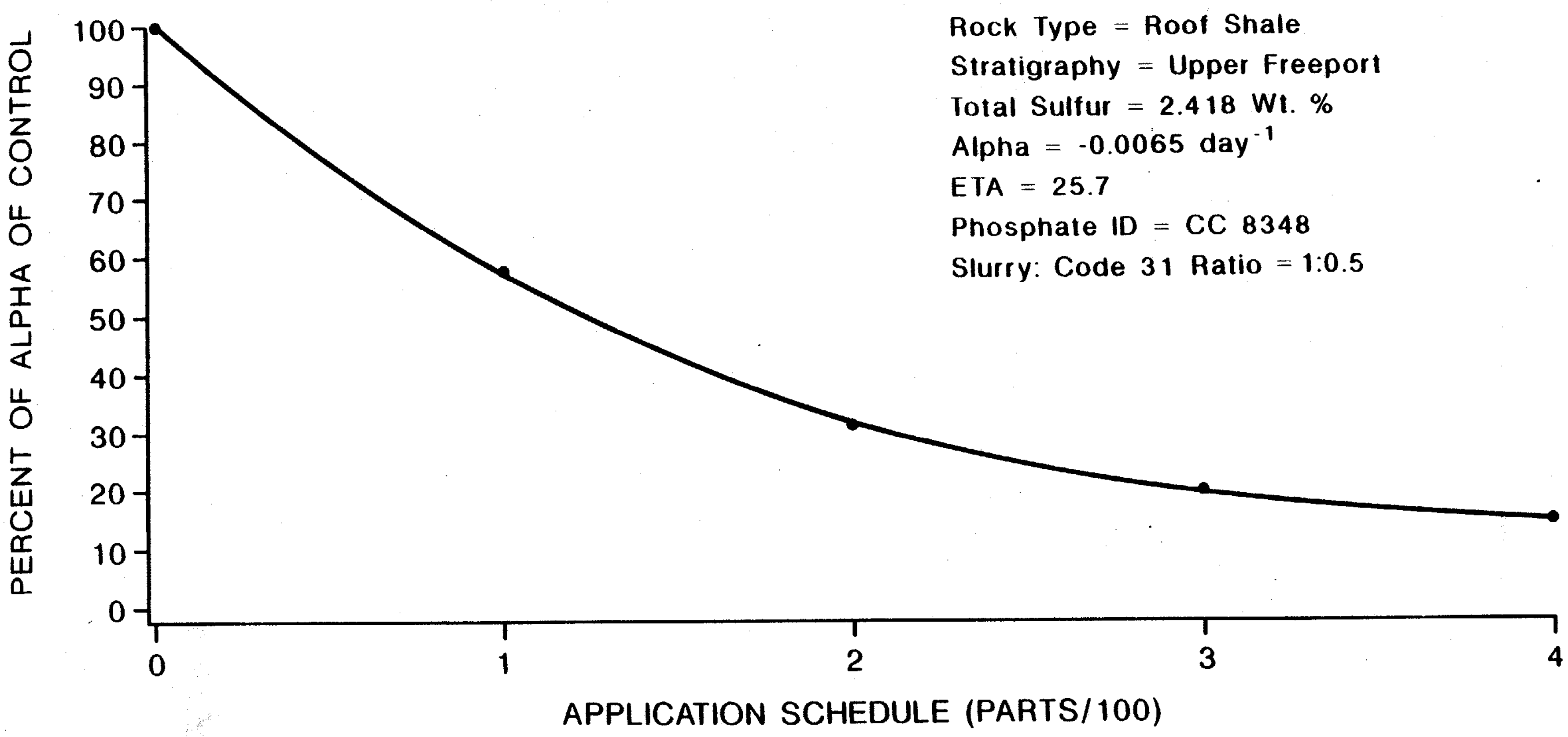

FIGURE 13. Percent of Alpha of Control Versus Apatite Application Schedule for Upper Freeport Roof Shale, St = 2.42 Wt. %

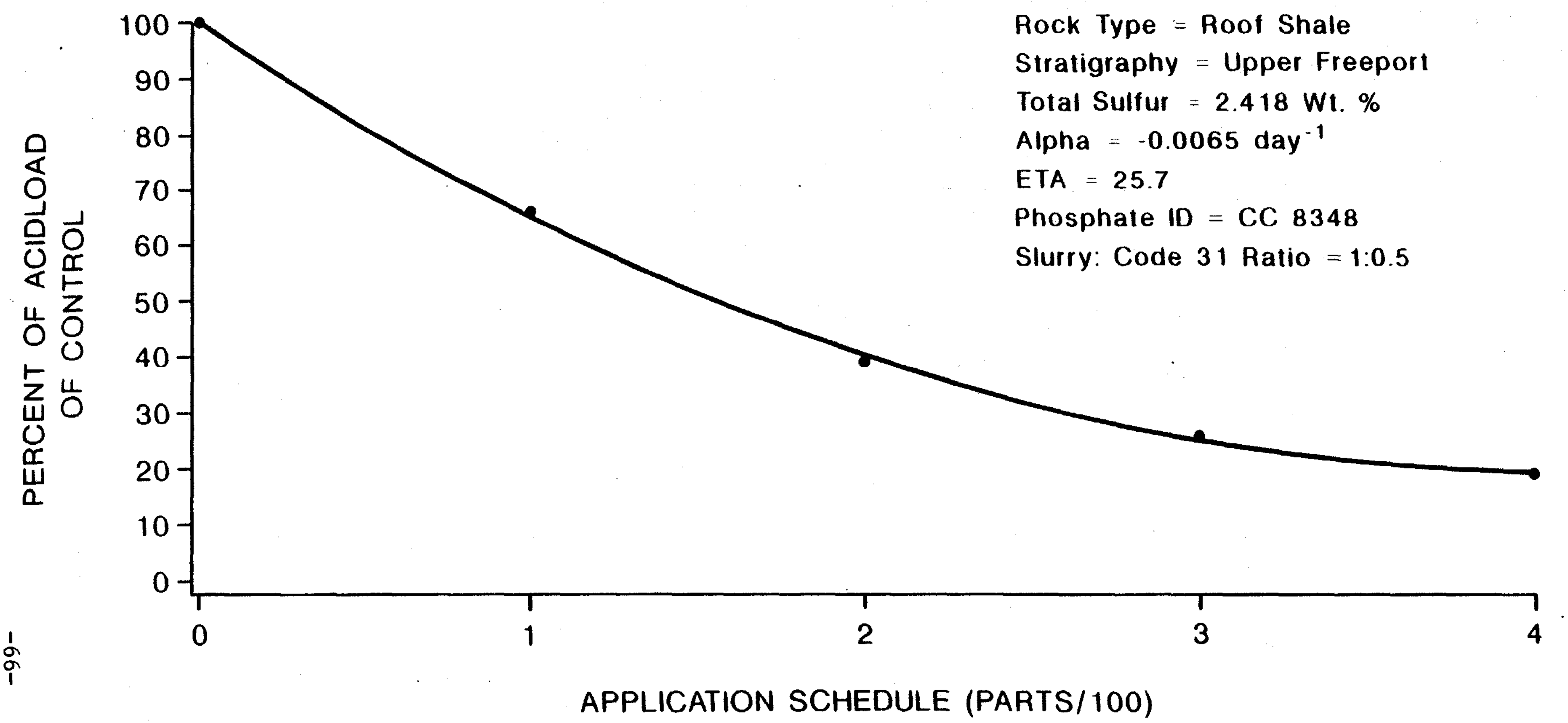

FIGURE 14 Percent of Acidload of Control Versus Apatite Application Schedule for Upper Freeport Roof Shale, St = 2.42 Wt. %

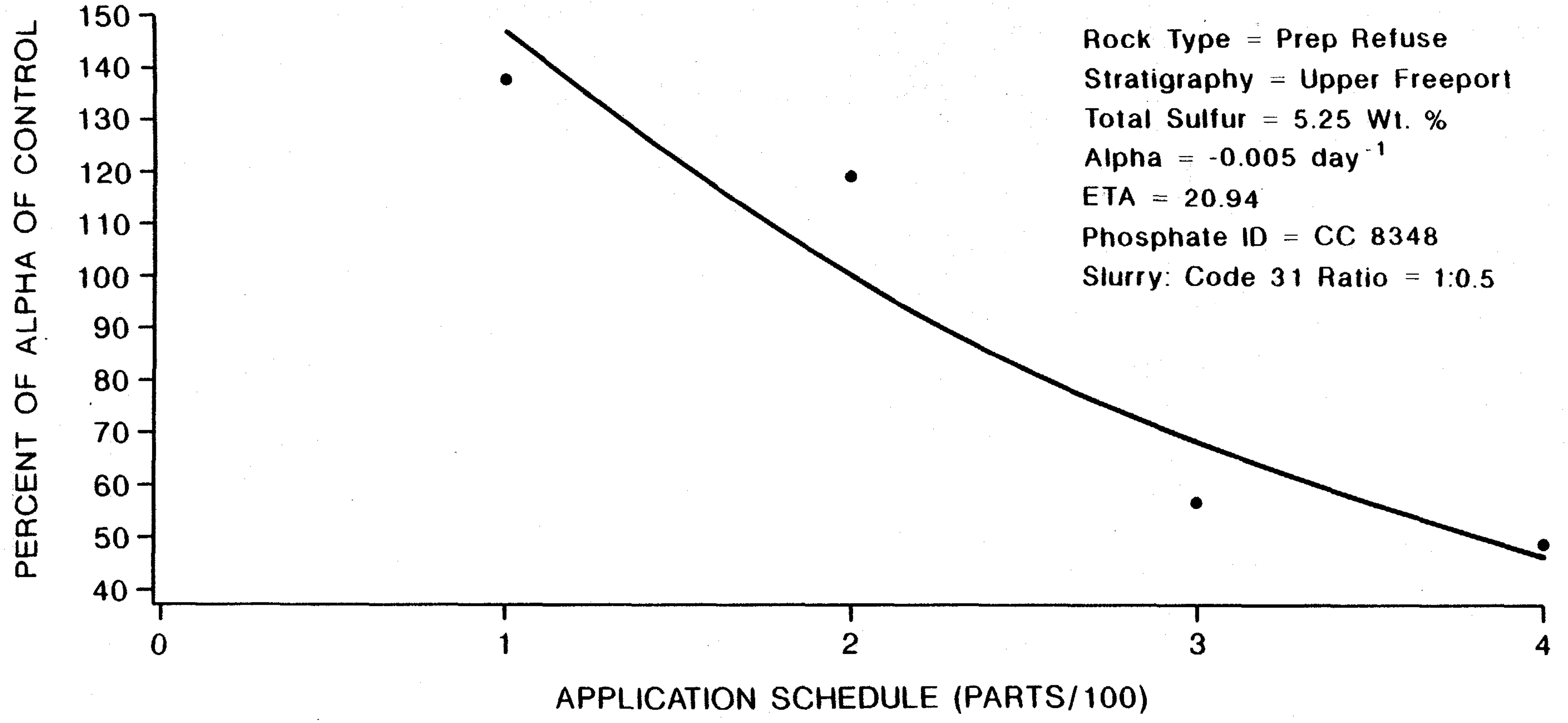

FIGURE 15 Percentof Alpha of Control Versus Apatite Application Schedule for Upper Freeport Prep. Refuse, St = 5.52 Wt. %

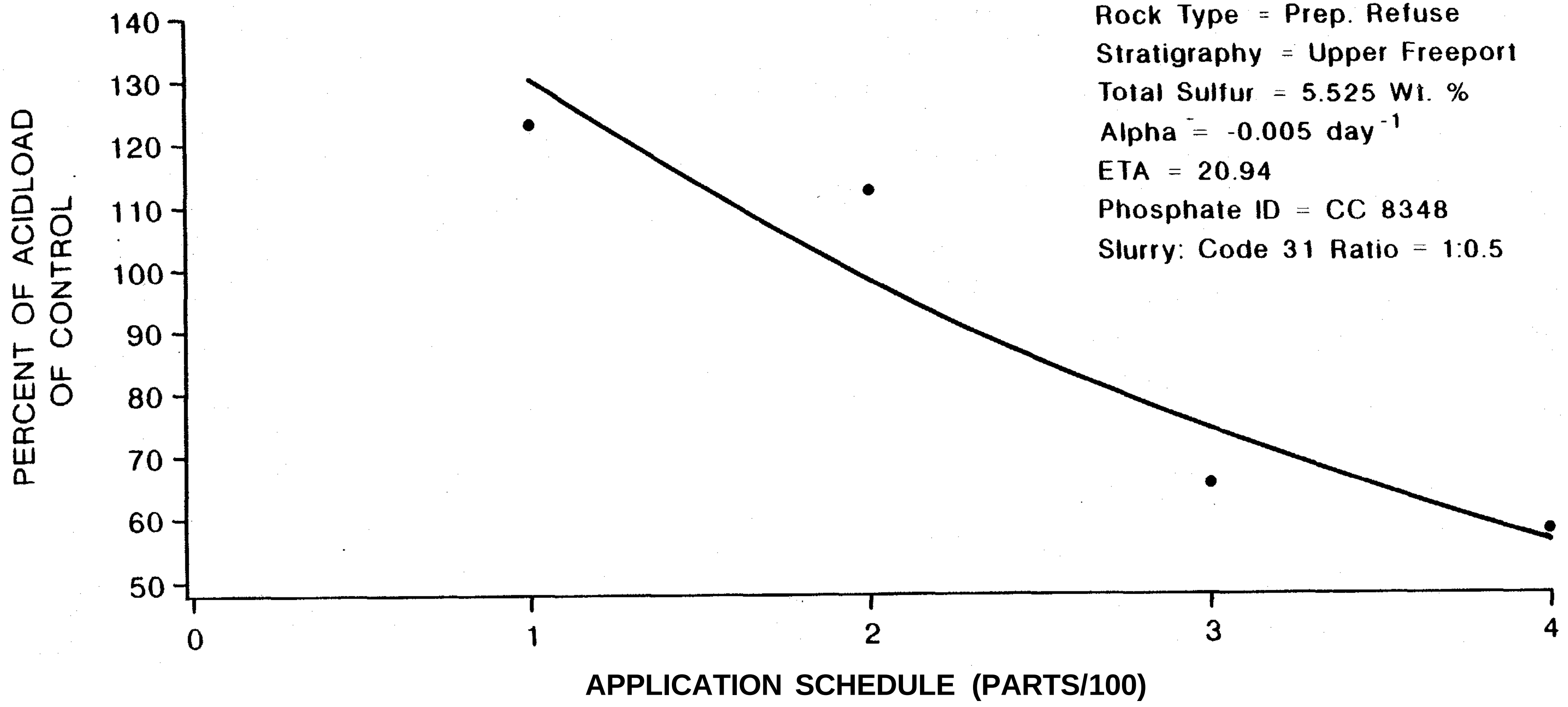

FIGURE 16. Percent of Acidload of Control Versus Apatite Application Schedule for Upper Freeport Prep. Refuse, St = 5.52 Wt. %

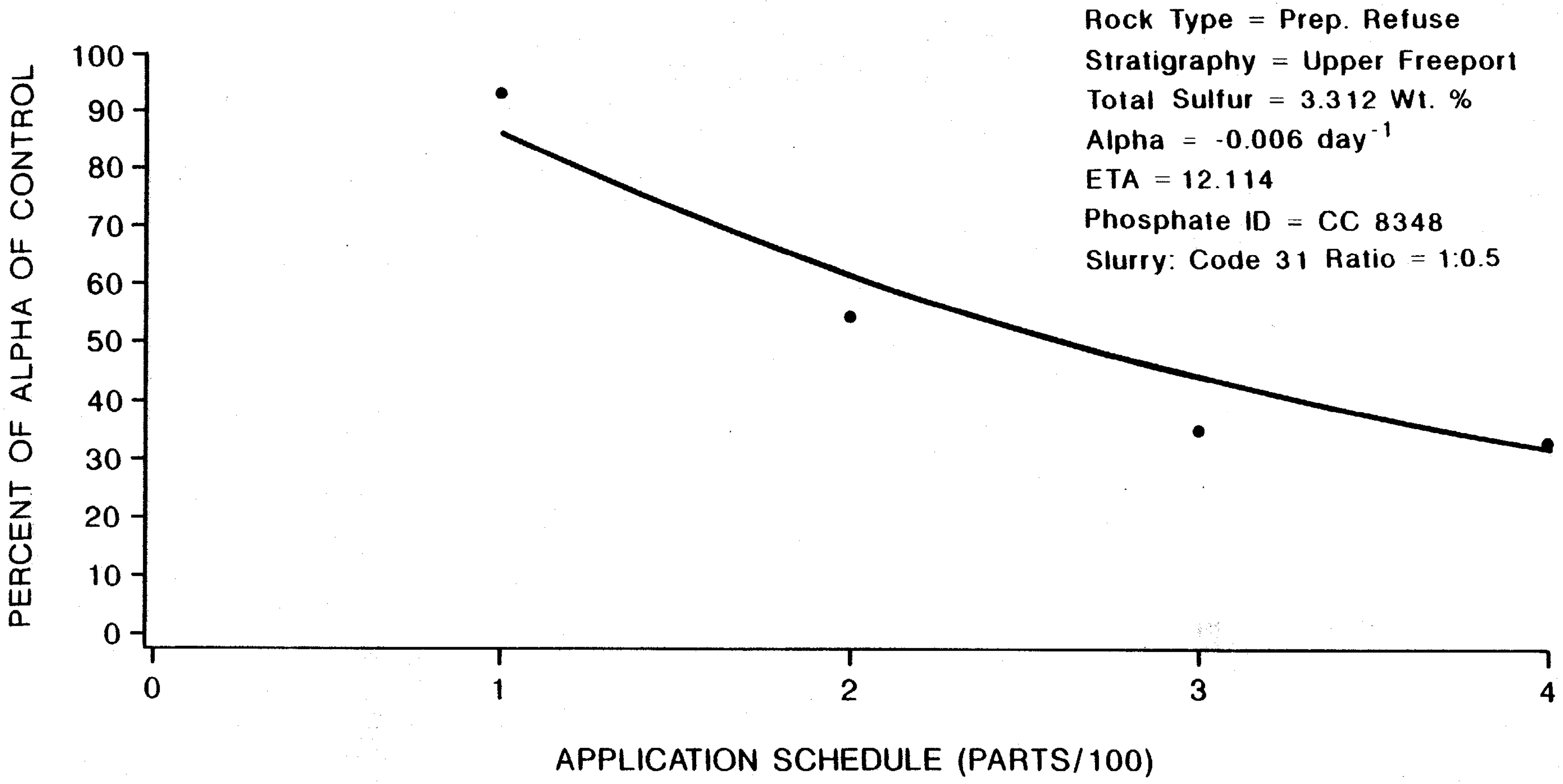

FIGURE 17 Percent of Alpha of Control Versus Apatite Application Schedule for Upper Freeport Prep. Refuse, St = 3.31 Wt. %

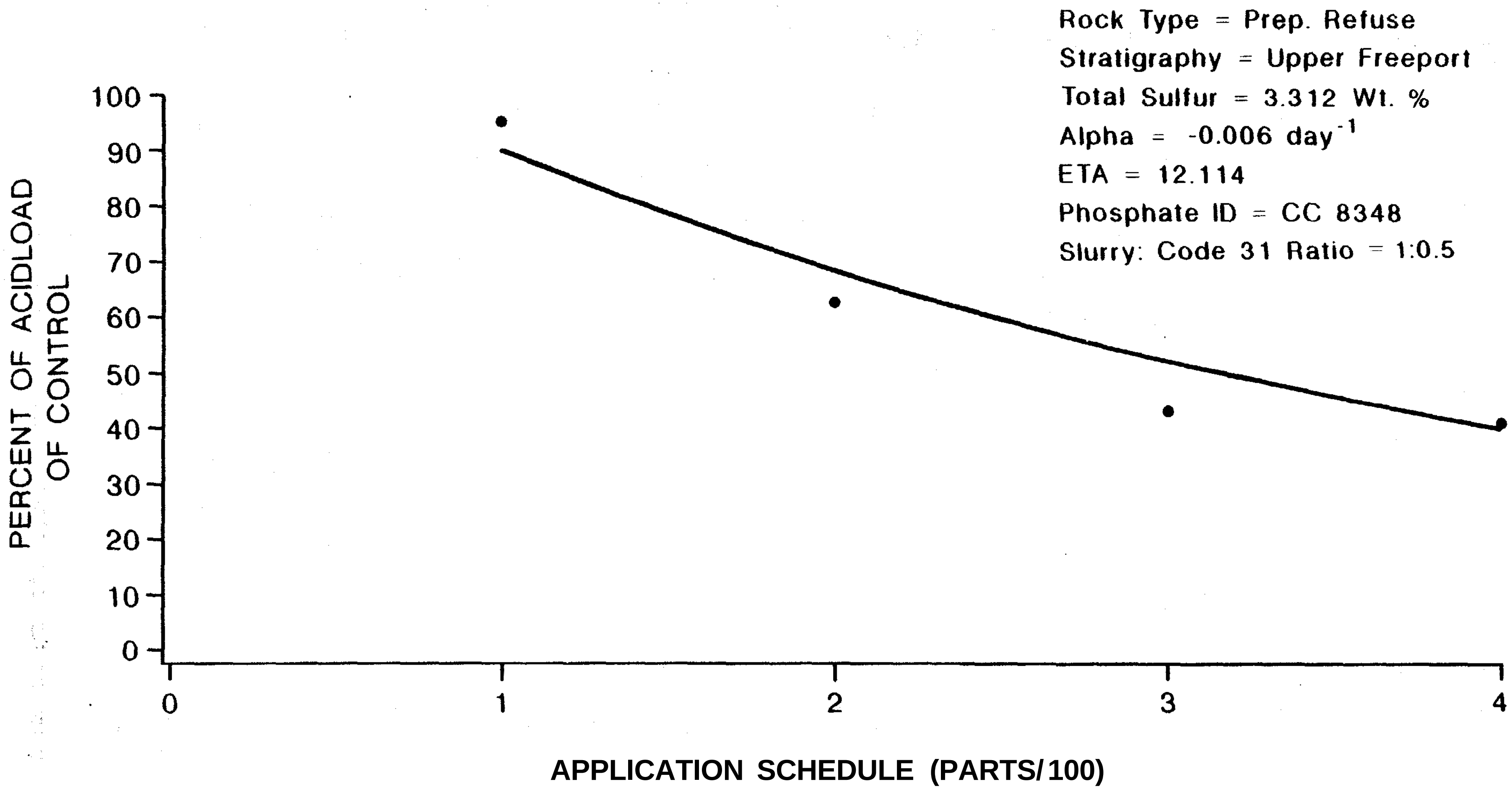

FIGURE 18 Percent of Acidload of Control Versus Apatite Application Schedule for Upper Freeport Prep. Refuse, St = 3.31 Wt. %

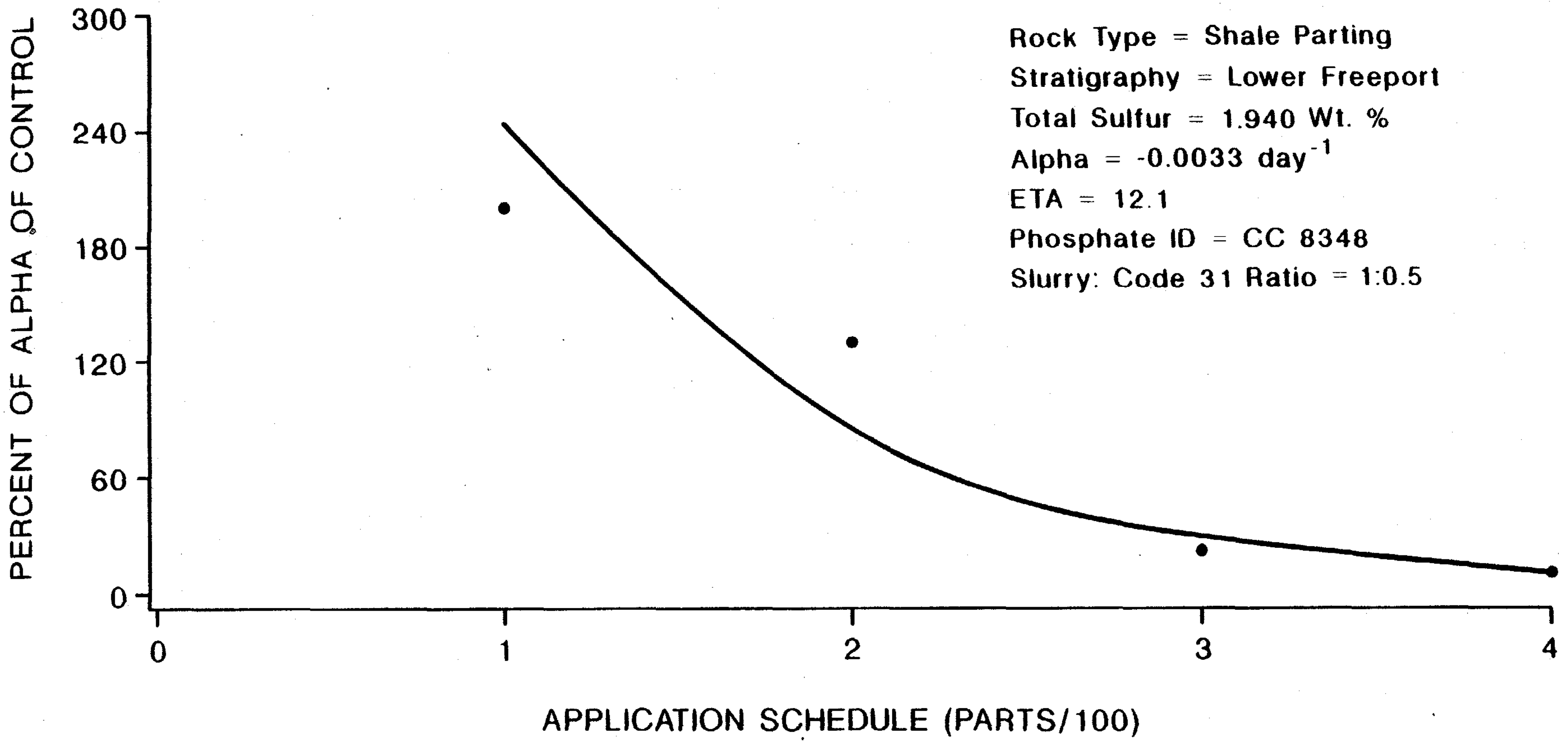

FIGURE 19 Percent of Alpha of Control Versus Apatite Application Schedule for Lower Freeport Shale Parting, St = 1.94 Wt. %

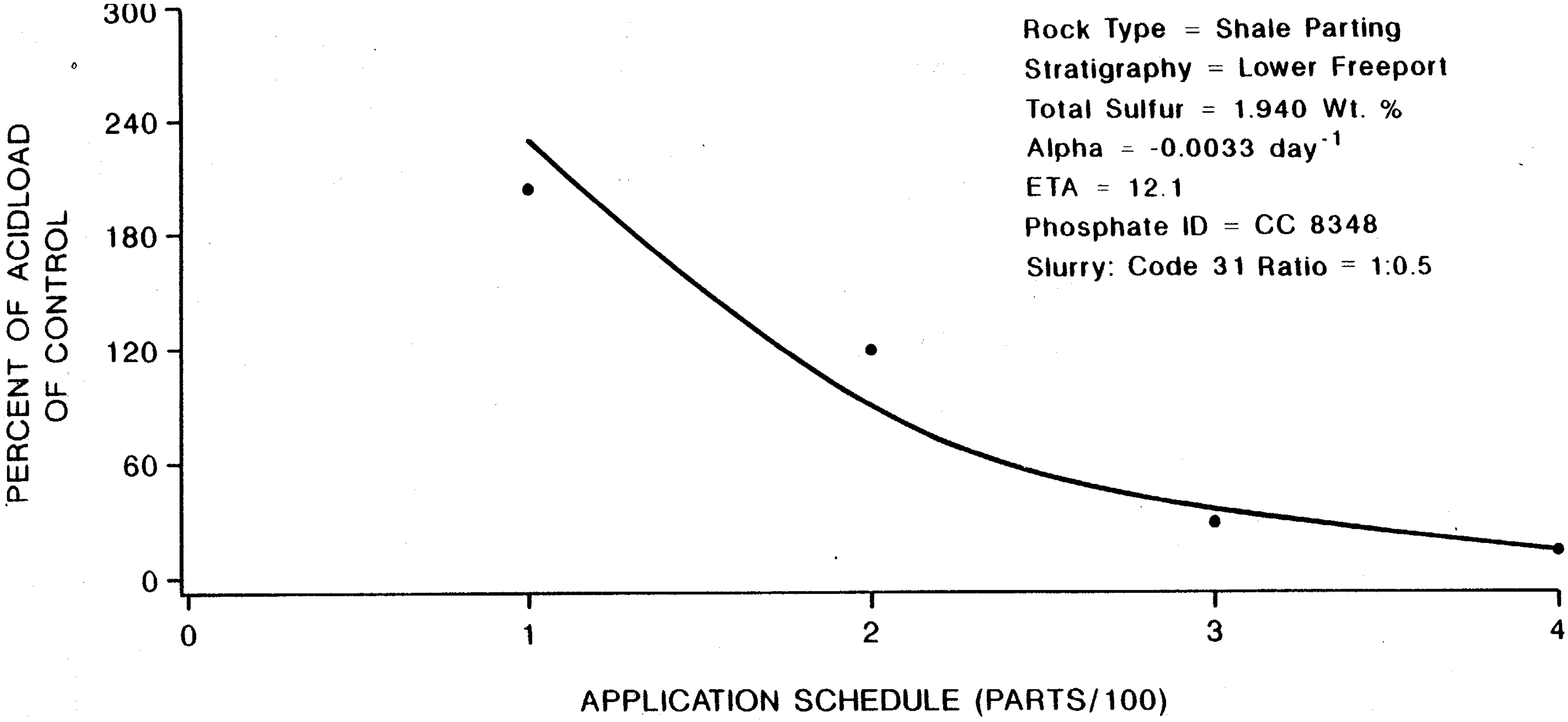

FIGURE 20. Percent of Acidload of Control Versus Apatite Application Schedule for Lower Freeport Shale Parting, St = 1.94 Wt. %

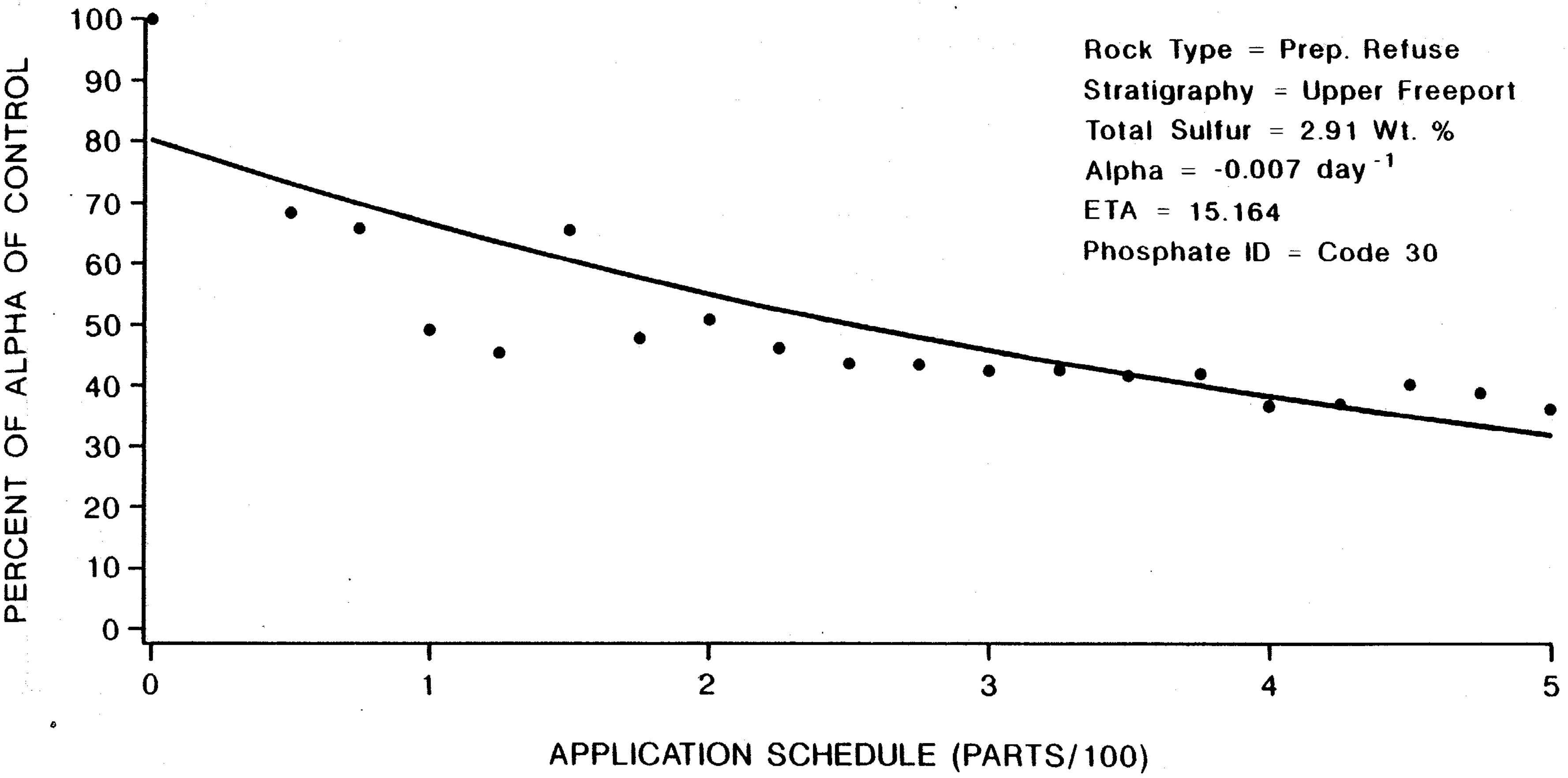

FIGURE 21 Percent of Alpha of Control Versus Apatite Application Schedule for Upper Freeport Prep. Refuse, St = 2.91 Wt. %

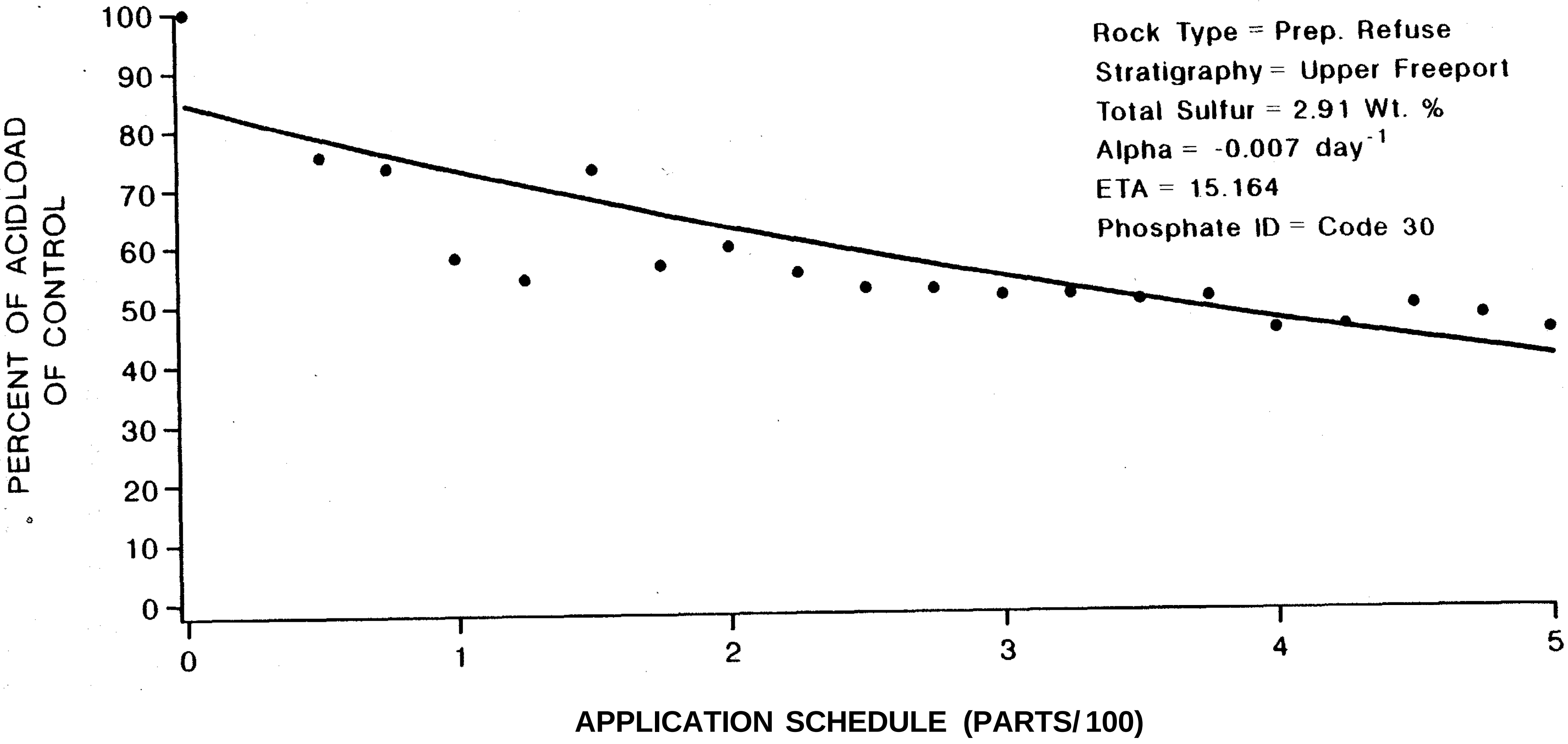

FIGURE 22. Percent of Acidload of Control Versus Apatite Application Schedule for Upper Freeport Prep. Refuse, St = 2.91 wt. %

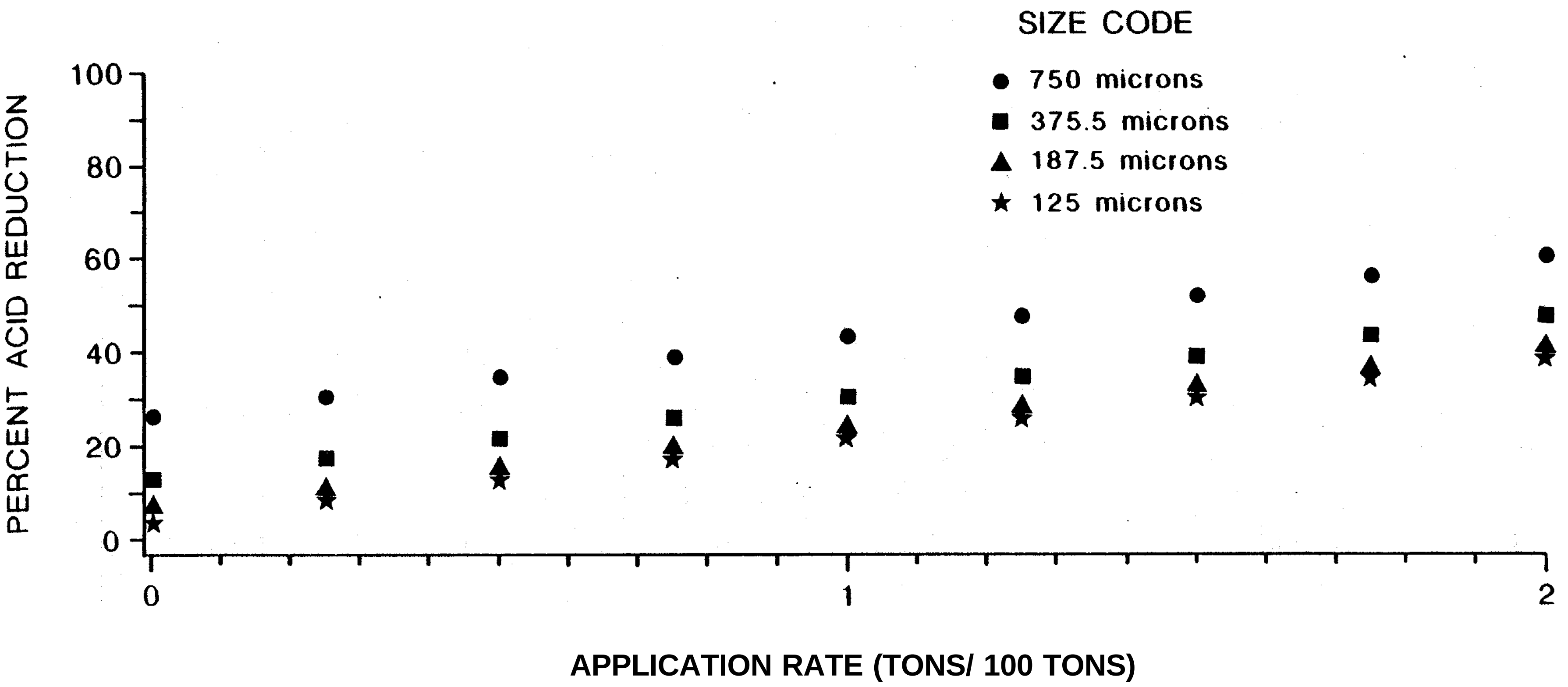

FIGURE 23. **The Effect of Various Rock Phosphate Particle Sizes on Acid Production from a Single Toxic Material**

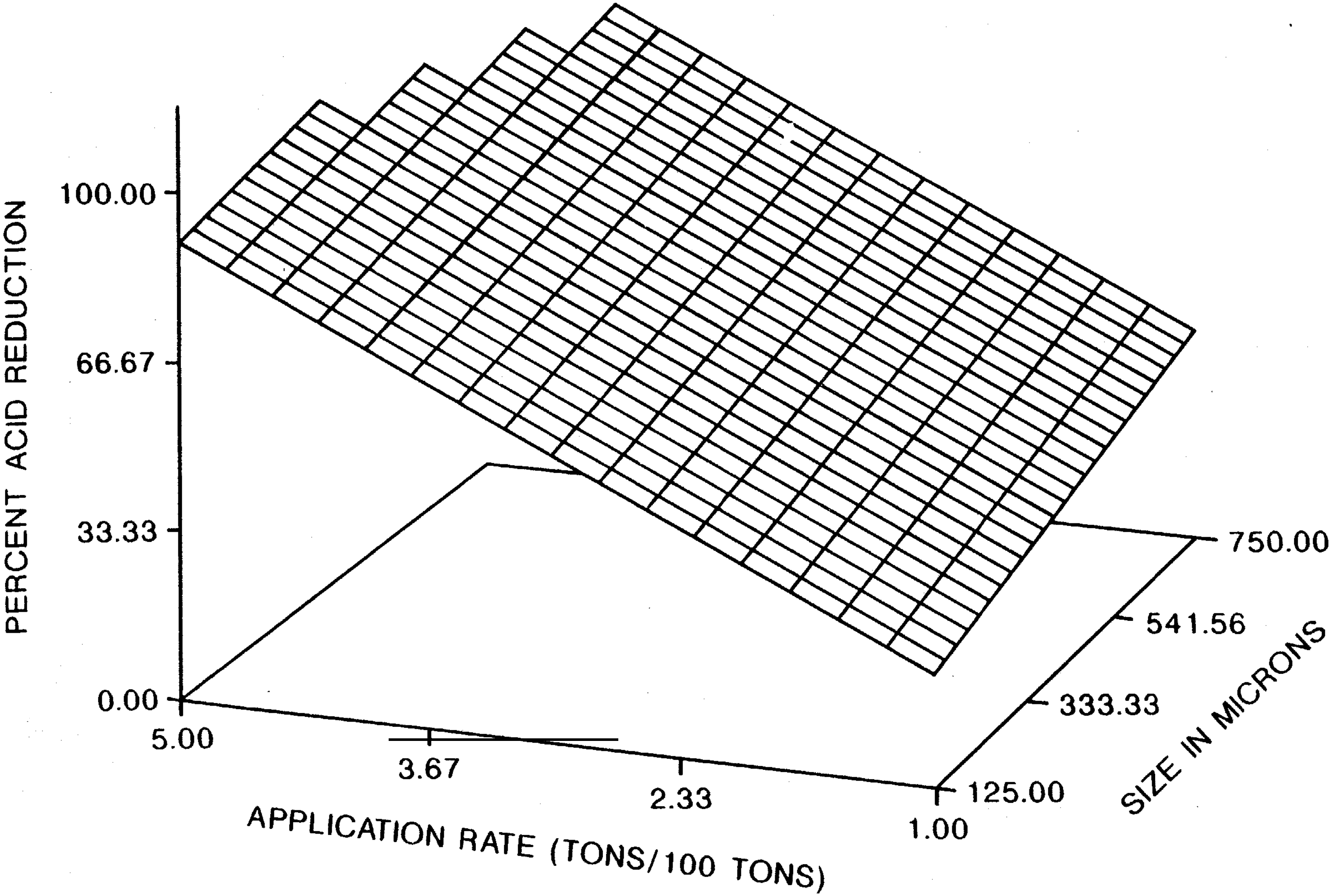

FIGURE 24 Surface Showing Relation of Particle Size and Application Schedule with Acid Production Showing Relation

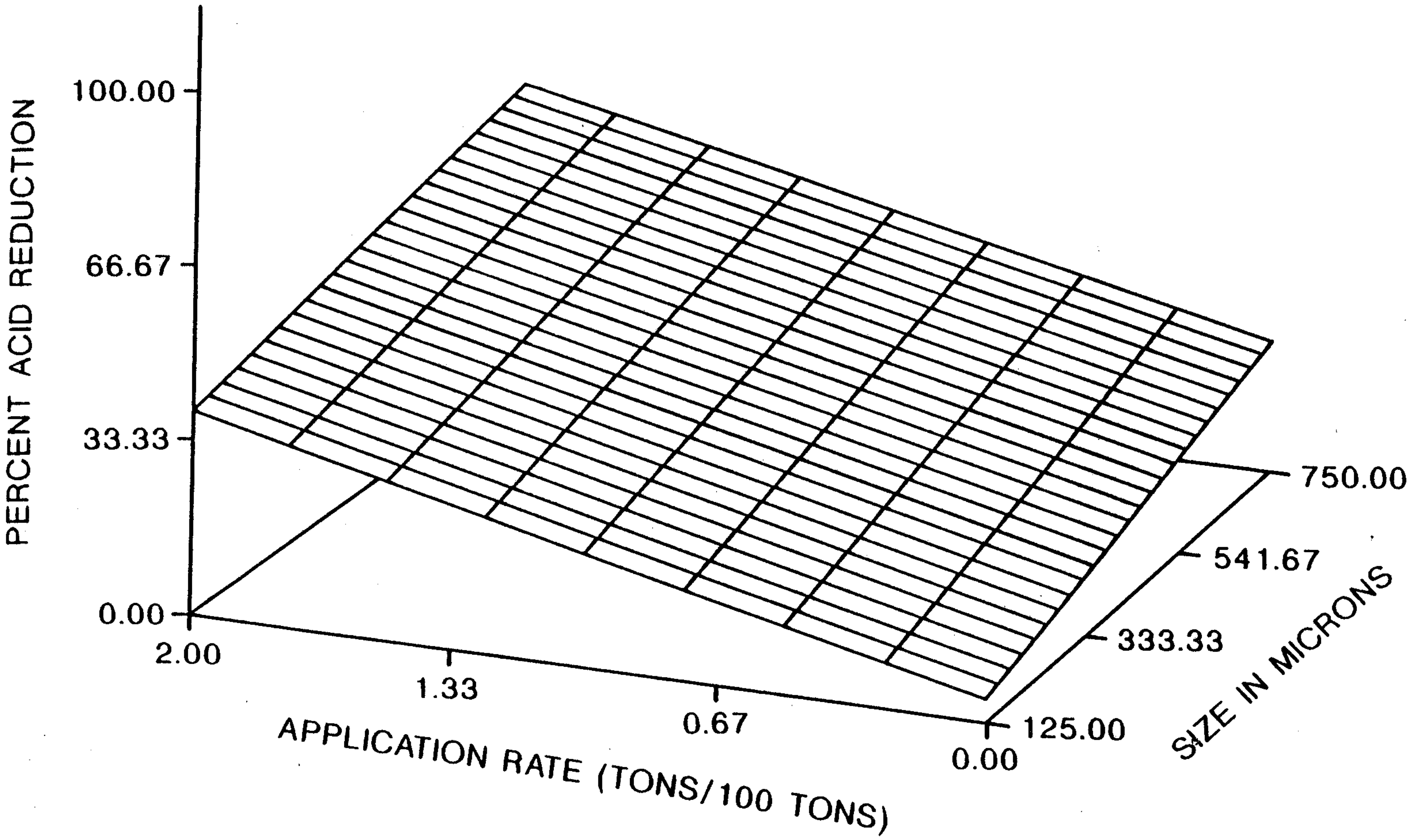

FIGURE 24A Surface Showing Relation of Particle Size and Application Schedule with Acid Production when used in particle sizes less than 18 mesh (750 microns) and with application rates in excess of about 1 wt%.

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 -325 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.

ACKNOWLEDGEMENTS:

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