# RESEARCH INTO THE USE OF APATITE ROCK FOR ACIDIC DRAINAGE PREVENTION

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ENOXY COAL INC.

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## Laboratory Investigation Procedure and Results (Pyrite Oxidation and Apatite Addition Effects)

Most known or suggested acid preventive techniques for mine overburdens are intended to, in some manner, minimize, prevent, or retard the oxidation of pyrite ($FeS_2$). It is this oxidation which releases sulfuric acid ($H_2SO_4$) and soluble iron oxy/hydroxide compounds. Alternately, an acid drainage prevention method may increase the solubility of the alkaline components of surface mine overburdens, thereby insuring in-situ neutralization of any acid produced. To obtain insights as to the oxidation of pyrite under the influence of different contact solutions, and to assess the effectiveness of apatite rock in preventing acid mine drainage, a system for measuring the oxidation of pyrite in contact with various solutions was developed.

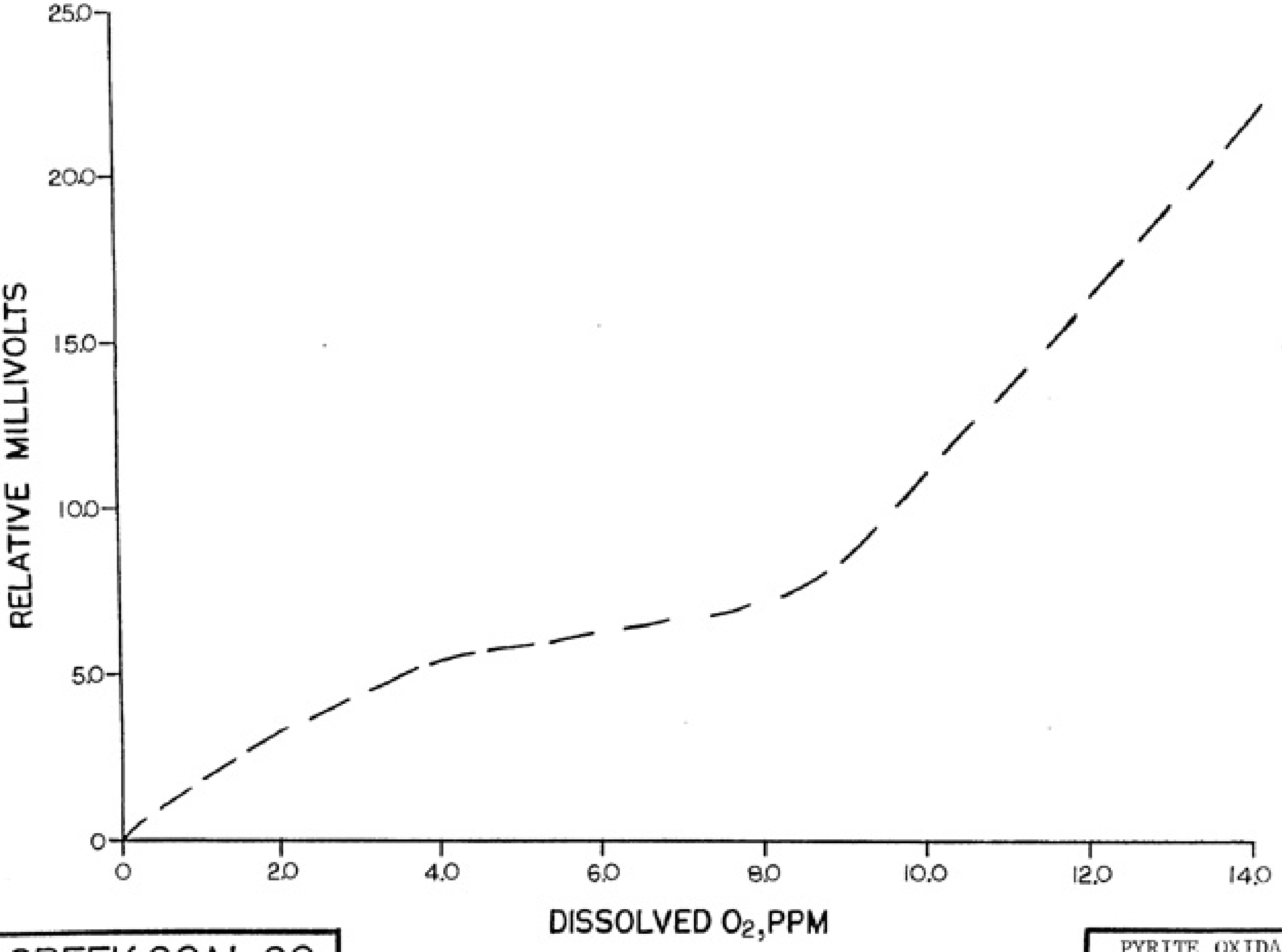
The instrumentation used for making the pyrite oxidation measurements consists of a saturated KC1 calomel reference electrode, a pyrite electrode, and a potentiometer capable of reading in relative millivolts. Since pyrite electrodes are not commercially available, one was constructed by epoxying a crystal of pyrite onto the end of a length of 1/4" glass tubing, with a mercury junction used to connect the pyrite with the wiring going to the potentiometer. When the probes are immersed in a solution, the loss (oxidation) or gain (reduction) of electrons by the pyrite crystal can be measured.

Because of the variations of pyrite morphology, surface area, and crystalline structure, and the degenerative nature of the probe, the oxidation potential measured by the above system cannot be used for quantitative predictions of pyrite oxidation rates. However, a measurement of the loss (positive millivolt reading) or gain (negative millivolt reading) of electrons by the pyrite probe in a solution can be made, and related to that in distilled water (set at 0 millivolts). Therefore, this system can be used to indicate the relative potential, of various anions and cations in solution, to oxidize pyrite. The results of a series of tests are presented graphically by figures included herein, and discussed below.

Figure No. 1 is a plot of pyrite oxidation (expressed as relative millivolts) versus dissolved oxygen. A solution with a dissolved oxygen concentration of zero ppm was obtained by bubbling nitrogen into distilled water. The 14 ppm solution (saturated with dissolved oxygen) was obtained by cooling distilled water to 1' centigrade and achieving saturation by aerating with an air stone. The plot indicates, as expected, that an increase in dissolved oxygen increases the oxidation of pyrite.

Figure No. 2 graphs pyrite oxidation (expressed as relative millivolts) versus solution pH. The solutions were prepared by mixing distilled water with pH 4.0 and pH 10.0 buffer solutions. Minimal amounts of buffers were used so as to produce solutions with stable pH values. Oxygen content of the solutions was kept at ambient level (approximately 3.2 milligrams per liter). The plot indicates that pyrite oxidation is decreased in contact with high pH water, and increased under low pH conditions, relative to distilled water set at 0 millivolts. This was as expected, based on standard reference information (Handbook of Chemistry and Physics, CRC). It has been established that the oxidizing capability of a given concentration of dissolved oxygen in solution is approximately three times greater in the presence of free hydrogen ions (acidic, low pH condition) than in a solution without free hydrogen, ions (neutral).

FIGURE NO. 1



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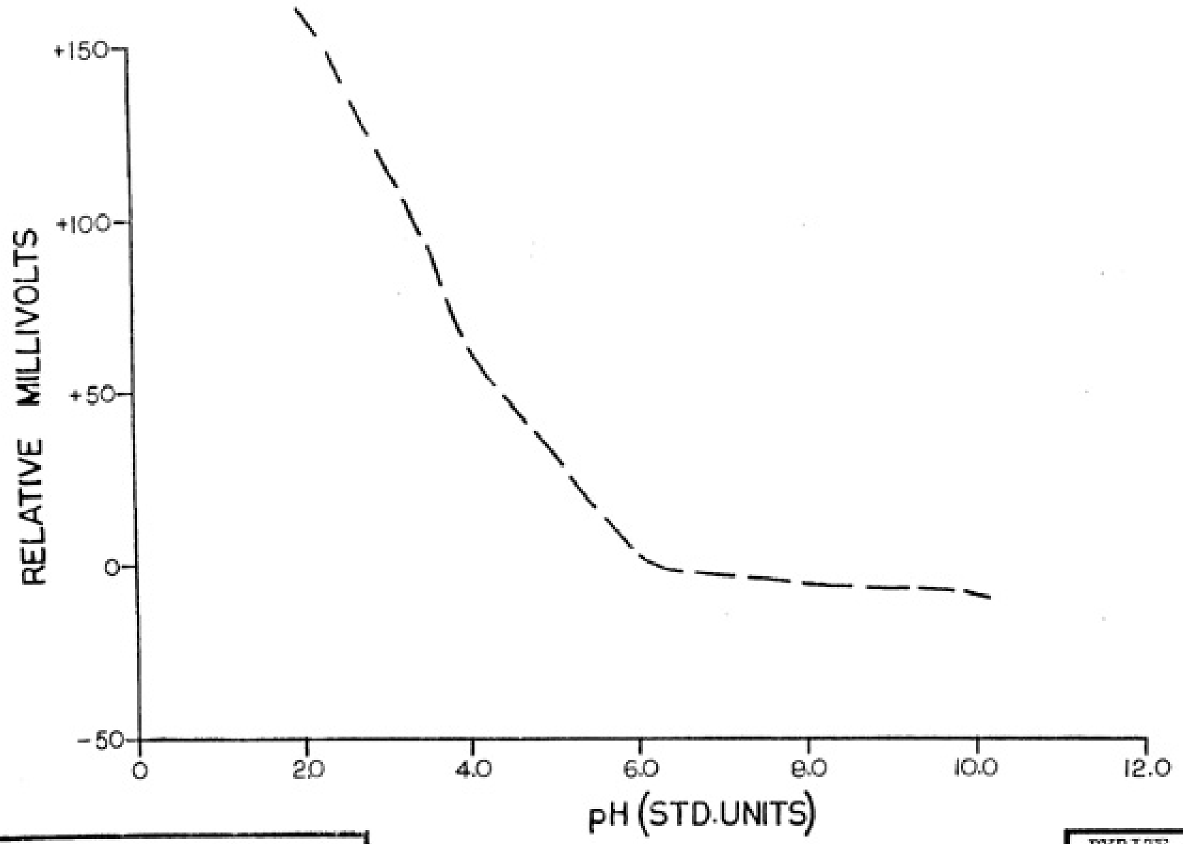
PYRITE OXIDATION IN DISTILLED WATER WITH VARYING DISSOLVED OXYGEN CONTENT.

FIGURE NO. 2



ISLAND CREEK COAL CO.
UPSHUR RESEARCH

PYRITE OXIDATION IN AQUEOUS SOLUTION WITH VARYING pH VALUES; DISSOLVED OXYGEN MAINTAINED AT 3.2 MILLIGRAMS PER LITER.

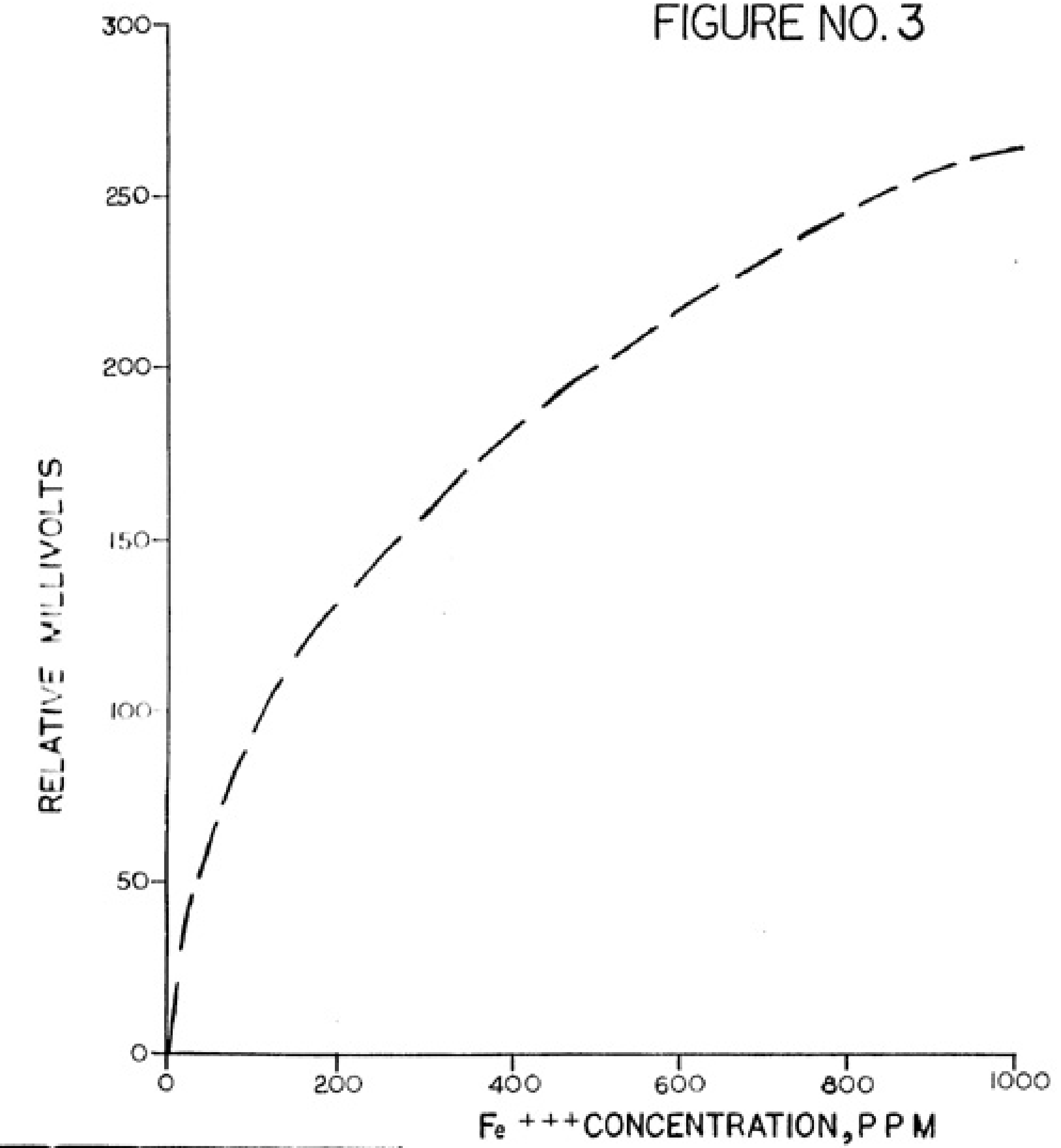
Figures No. 3 and 4 are plots of pyrite oxidation (expressed as relative millivolts) versus ferric and ferrous ion concentrations, expressed in ppm. The solutions were prepared with ferric and ferrous chloride salts and distilled water. The pH of each solution was that created by dissolution of the salts in distilled water. The pH readings were constant for the various concentrations, at 2.5 for the ferric ion solutions, and at 3.0 for the ferrous ion solutions.

It can be concluded from Figure 3 that the oxidation of pyrite increases in relation to increasing concentrations of ferric iron ions in solution.

At first glance, Figure 4 would seem to indicate that increasing solution concentrations of ferrous iron ions decrease pyrite oxidation. While this may be true in part, it is known that the ferrous ions will further oxidize to the ferric form, which will in turn accelerate pyrite oxidation. The millivolt readings recorded on Figure 4 were taken immediately after sample preparation. As time after preparation increased, the millivolt readings also increased to the positive range. This is due to oxidation of the ferrous ions by dissolved 02 to the ferric state, with subsequent oxidation of the pyrite by the ferric ions. Also, it is believed that part of the phenomenon depicted on Figure 4 is directly due to competition by the ferrous ions, with the pyrite, for the available dissolved oxygen.

The information obtained in the above experimentation substantiates previous research 1, 2 which indicates that ferric oxidation of pyrite is the key factor in the formation of acid mine drainage, and that control of ferric iron availability can limit this formation. It is recognized that oxidation of pyrite by oxygen is the initial step, in acid mine drainage formation. However, this process is self-limiting in a backfill due to the limited amount dissolved oxygen that water can contain, and to the relatively low oxidation of pyrite in an oxygen-saturated solution. The acceleration of pyrite oxidation by ferric iron ions is much more significant, and has been shown to be the critical step in perpetuating and accelerating acid production.

FIGURE NO. 3



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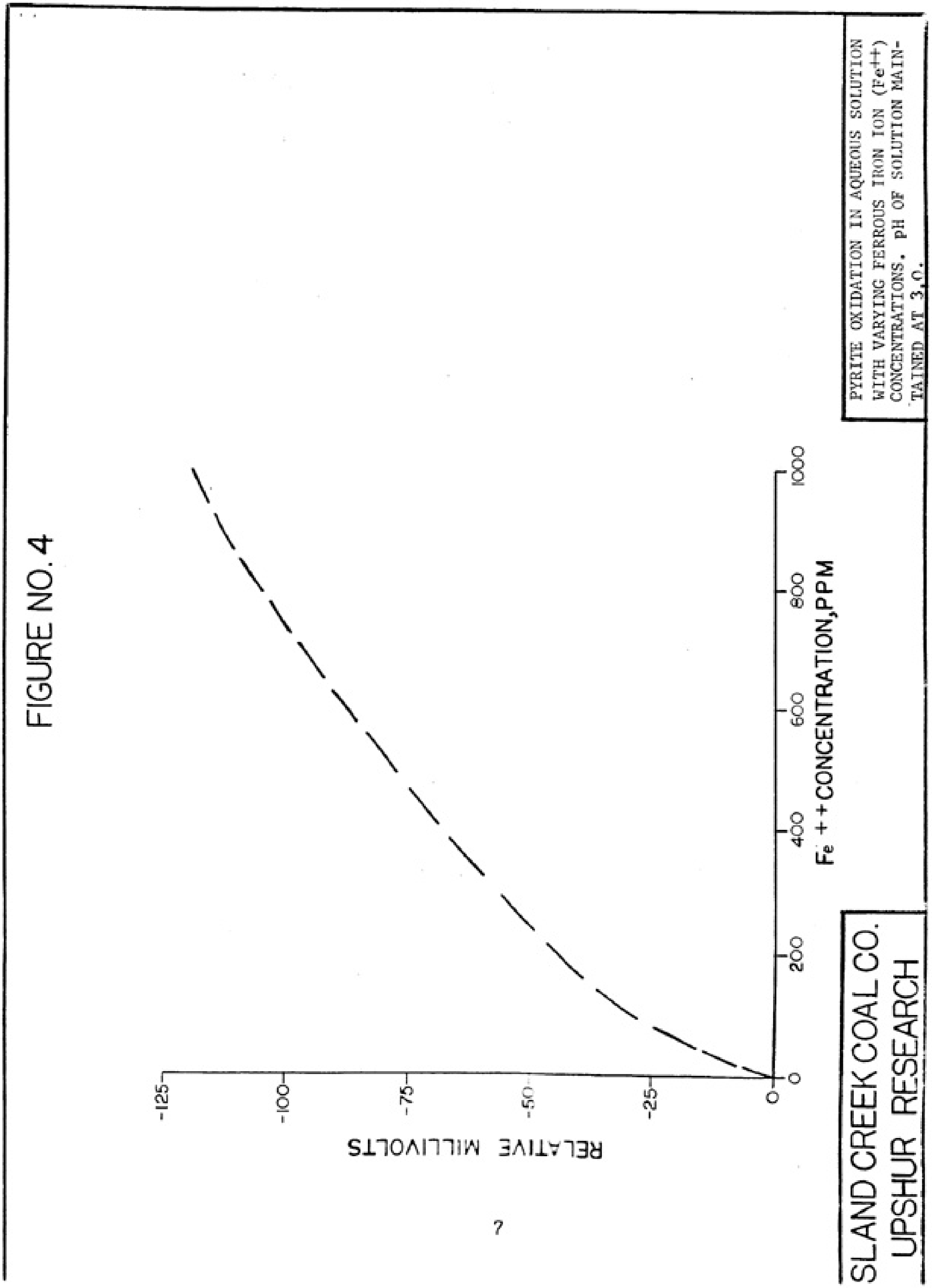
UPSHUR RESEARCH

PYRITE OXIDATION IN AQUEOUS SOLUTION WITH VARYING CONCENTRATIONS OF FERRIC IRON IONS ($Fe^{+++}$). SOLUTION pH MAINTAINED AT 2.5.

FIGURE NO. 4



PYRITE OXIDATION IN AQUEOUS SOLUTION WITH VARYING FERROUS IRON ION ($Fe^{++}$) CONCENTRATIONS. pH OF SOLUTION MAINTAINED AT 3.0.

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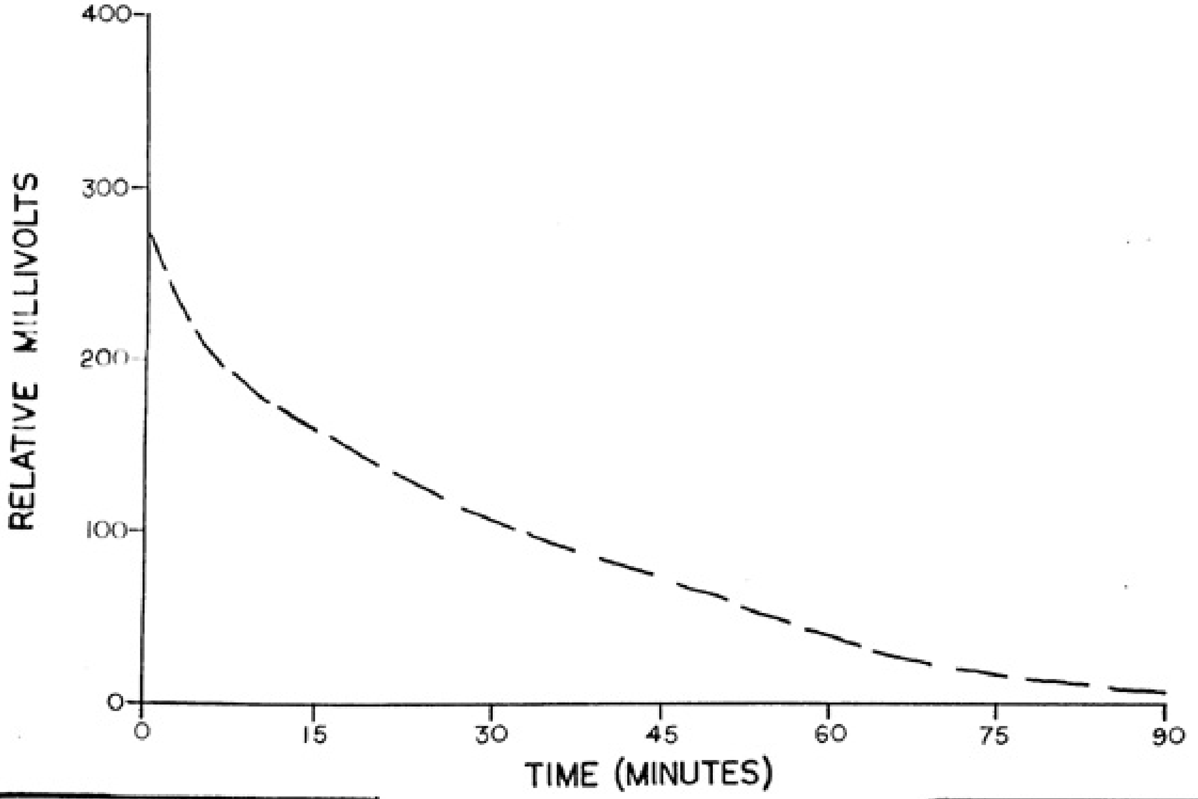
Figure No. 5 exhibits pyrite oxidation (expressed as relative millivolts) in a 1,000 ppm solution of ferric ions, in the presence of phosphate ions generated by addition of phosphoric acid. The phosphoric acid quantity added was stoichiometrically calculated to provide adequate phosphate ions to complex the total 1,000 ppm of ferric ions as Fe $PO_4$.

The results indicate that the pyrite oxidizing capability of ferric ions is dramatically reduced by the introduction of phosphate ions. The phosphate ions preferentially combine with the ferric ions to form Fe $PO_4$. This compound is relatively insoluble. The rate of ferric phosphate formation is pH dependent. Subsequent testing indicated that at a pH of 4.5, the formation of ferric phosphate was almost immediate.

Figure No. 6 is a plot of apatite solubility versus pH. This test indicates that the apatite solubility is pH dependent and is low in neutral or near-neutral pH solutions.

If apatite rock is thoroughly admixed with spoil, it will be exposed to the ambient environment, whether neutral, basic, or acidic. If no acid occurs, the phosphate material would remain relatively dormant within the spoil. However, when, or if, pyrite oxidation (by whatever means) occurs, the acidic condition generated would dissolve the phosphate material (apatite). The released phosphate ions would complex the iron ions, preventing acceleration and perpetuation of acid production, and, in effect, shutting down the acid generation system.

FIGURE NO. 5



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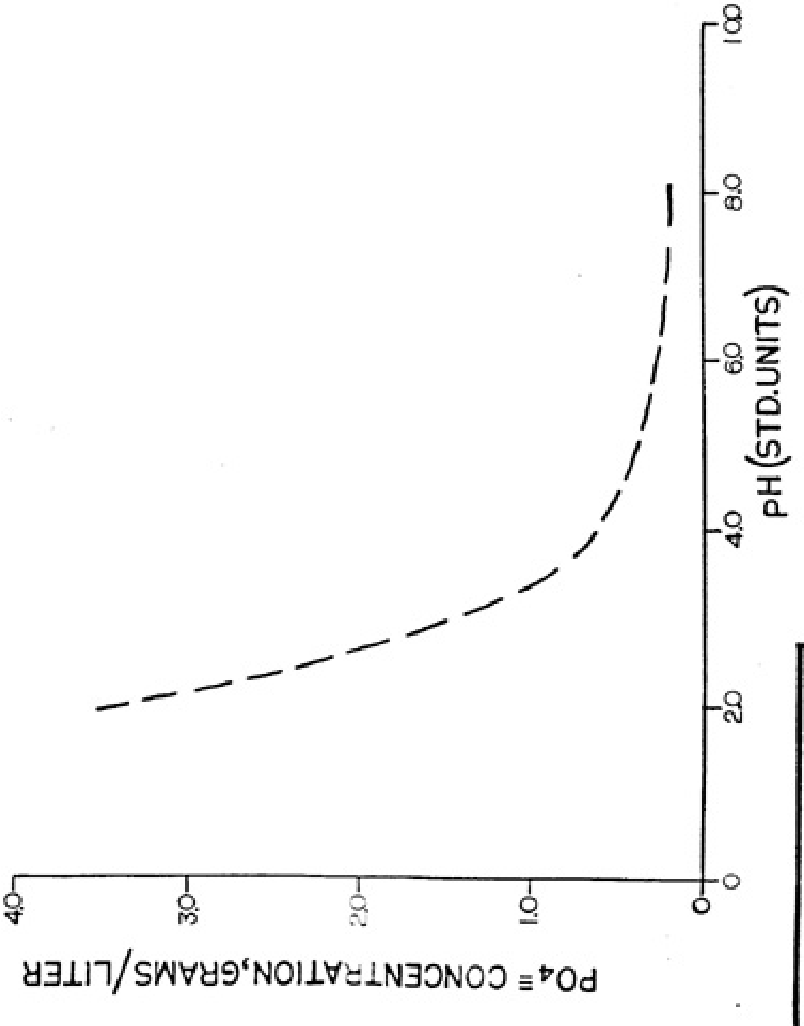
PYRITE OXIDATION IN AQUEOUS SOLUTION CONTAINING 1,000 PPM OF FERRIC IRON ($Fe^{+++}$), PLUS PHOSPHATE ($PO_4^{\equiv}$) IONS. SOLUTION pH MAINTAINED AT 2.5 STANDARD UNITS; RESULTS PLOTTED AGAINST TIME

FIGURE NO. 6



APATITE ROCK SOLUBILITY IN AQUEOUS SOLUTION WITH VARYING pH VALUES. TEST DURATION 24 HOURS AT 25° C.

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We submit, therefore, that use of apatite rock as a phosphate source backfill additive will provide an automatic control of acid production. Also, the low solubility of apatite in a non-acidic environment will provide automatic preservation of the phosphate source, insuring its availability when needed.

## Summary, Laboratory Studies

The laboratory research conducted provides useful insights into the various chemical influences on pyrite oxidation. The chemical mechanisms of pyrite oxidation, and the means by which phosphate addition can control these processes, are now better understood.

Theories established by other researchers have been verified by use of the pyrite probe. The most important result is believed to be confirmation that the activity of ferric ions in oxidation of pyrite is the key factor in acid production. Therefore, control of the ferric ion can prevent acid production. The laboratory research indicates that phosphate ions, supplied by apatite rock, can provide this control.

# OPTIMIZATION OF APATITE ROCK ADDITION, FOR PREVENTING ACIDIC DRAINAGE FROM SURFACE COAL MINES

## Introduction

Several Researchers 1, 2, and 3 have concluded, that the addition of Phosphate Ions ($PO_4^{+++}$) to Iron Disulfide ($FeS_2$) bearing material is successful in minimizing oxidation of Iron Disulfide (Pyritic) Compounds. it is believed, that this preventative method could be used extensively by the surface coal mining industry to prevent acidic drainage from overburdens and coal refuse in areas of potential problems. Current research; however, has not addressed the subject of phosphate application rates to acidic materials, to define the optimum rate. This information is needed, to provide a means to evaluate the method for effectiveness, feasibility and cost, prior to full scale usage by the mining industry.- The following research is intended to define the most cost effective application rate of Apatite Rock ($Ca_{5X} (PO_4)_3$) to acidic mining spoils.

## Background

The concept behind the phosphate addition method is that P04 Ions in solution will combine with ferrous and Ferric Ions, from oxidized and solubilized Pyrite, to produce Iron Phosphate sludges. The Iron Phosphate complex will prevent acid production from the oxidation and hydrolysis of the ferrous Ions, and the sludge produced will coat reactive pyritic surfaces, limiting* further pyrite oxidation.

Various types of phosphate compounds have been proposed for use. The phosphate source considered most likely to be used is phosphate rock, or apatite ($Ca_{5x} (PO_4)_3$).

. x represents the presence of halogen group ions, primarily fluoride, in the Apatite. The solubility of Apatite increases as the pH of the water contacting it decreases. Therefore, the phosphate ions would stay largely inert in the Apatite except when pyrite oxidation occurred with resultant acid production.

It has been felt, that the amount of Apatite added to acidic material should be based on either the total pyritic Iron or Total Iron present in the Acidic material. Thus, providing enough PO Ions to stociometrically combine with the Iron present.

By combining several acidic materials (with different Total and Pyritic Iron Contents) with different application rates of Apatite Rock, the relation of Iron Content, Potential Acidity and the ratio of Apatite to overburden can be evaluated to determine application rates.

## Method

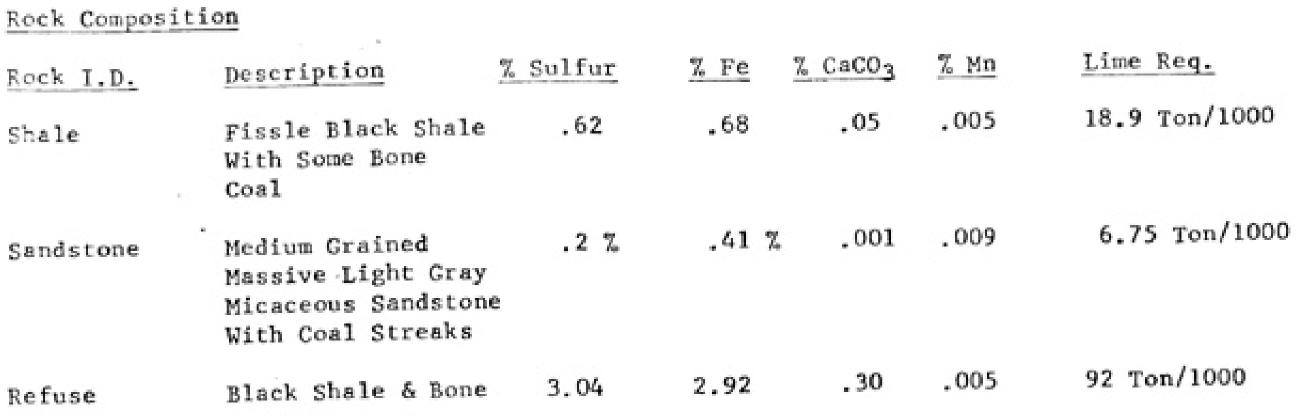
Acid producing shale, sandstone, and coal refuse were obtained for testing purposes. The material was crushed to 1/4" x 0 size and riffled to 16 approximately equal sized samples. one of these samples was further riffled and pulverized to less than 60 mesh for analysis. The chemical characteristic of the rock types are shown -on the following page, The acid producing potential of the materials is as follows: sandstone - slightly acidic; shale -- significantly acidic; and refuse -- extremely acidic.

Leaching columns were constructed from 1 1/2" x 4' P.V.C. pipe, fitted on the bottom with a cap and 1/4" orifice. Inert drainage material was placed in the bottom of the columns. The acidic materials and various application rates of the Apatite Rock were placed in the column. Simulated weathering was achieved by passing air through -the columnes, from the orifice on the bottom, on six day cycles. Every seven days, the columnes were leached with distilled water, drip fed at a constant (5 ml/min) rate (via I. V. drop tube). The leachate was collected and analyzed for pertinent parameters. 13

## Application Rates

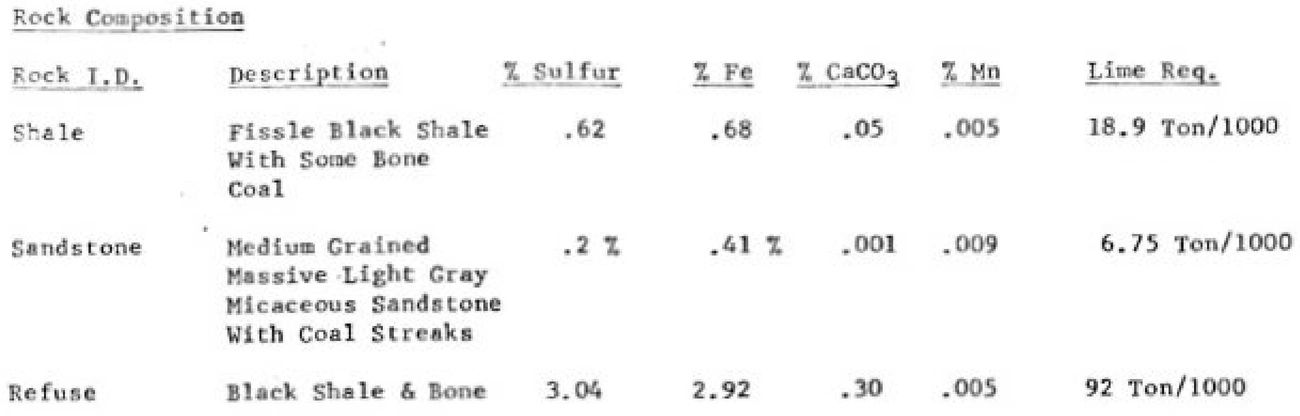
Triplicate columnes of the controls and all application rates were constructed for each material tested to maintain statistical reliability. The apatite application rates were based on the acid producing potenial (pyritic Iron), of the material tested, and range from ".13 x the lime requirement[4] ," to "enough $PO_4^{+++}$ to stociometrically combine with 1/3 the pyritic Iron present in the acid material". Since the three materials tested 'had different acid producing potentials, the ratio of Apatite to overburden varied between materials with the same application rate calculation. The application rates used in this research are as follows:

## Rock Composition



Rock Composition

| Rock I.D. | Description | % Sulfur | % Fe | % $CaCO_3$ | % Mn | Lime Req. |
|---|---|---|---|---|---|---|
| Shale | Fissle Black Shale With Some Bone Coal | .62 | .68 | .05 | .005 | 18.9 Ton/1000 |
| Sandstone | Medium Grained Massive Light Gray Micaceous Sandstone With Coal Streaks | .2 % | .41 % | .001 | .009 | 6.75 Ton/1000 |
| Refuse | Black Shale & Bone | 3.04 | 2.92 | .30 | .005 | 92 Ton/1000 |



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| Sandstone | Medium Grained Massive Light Gray Micaceous Sandstone With Coal Streaks | .2 % | .41 % | .001 | .009 | 6.75 Ton/1000 |
| Refuse | Black Shale & Bone | 3.04 | 2.92 | .30 | .005 | 92 Ton/1000 |

## Shale

1. .13 X Lime Requirement = 2.46 mg/gram
2. Stociometric Equivalent to Complex 1/3 The Pyritic Iron to $Fe_3 (PO_4)_2$ =5.1 mg/gr
3. Stociometric Equivalent to Complex 1/3 The Pyritic Iron to $FePO_4$ = 7.7 mg/gr.

## Test Composition (Shale)

1. Control--Shale; no Apatite
2. Application Rate 1 - 1 mg Apatite/gram of Shale
3. Application Rate 2 -- 2.5 mg Apatite/gram of Shale
4. Application Rate 3 -- 5.0 mg Apatite/gram of Shale
5. Application Rate 4 -- 8.0 mg Apatite/gram of Shale

## Sandstone

1. .13 X Lime Requirement =.88 mg/gram
2. Stociometric Equivalent to Complex 1/3 The Pyritic Iron to $Fe_3(PO_4)_2$=1.65 mg/gram
3. Stociometric Equivalent to Complex 1/3 The Pyritic Iron to FeP04=2.5 mg/gram

## Test Composition (Sandstone)

1. Control--Sandstone; no Apatite
2. Application Rate 1--.5 mg Apatite/gram of Sandstone
3. Application Rate 2--1.0 mg Apatite/gram of Sandstone
4. Application Rate 3--2.0 mg Apatite/gram of Sandstone
5. Application Rate 4--3.0 mg Apatite/gram of Sandstone

## Refuse

1. .13 X Lime Requirement -- 12.35 mg/gr.
2. Stociometric Equivalent to Complex 1/3
   The pyritic Iron to $Fe_3(PO_4)_2$ = 25 mg/gr
3. Stociometric Equivalent to Complex 1/3 The Pyritic Iron to $FePO_4$ = 37.6 mg/gr

## Test Composition (Refuse)

1. Control -- Refuse; no Apatite
2. Application 1 - 12.35 mg Apatite/Gram. of-Refuse
3. Application 2 - 17.0 mg Apatite/Gram, of Refuse
4. Application 3 - 25.0 mg Apatite/Gram of Refuse
5. Application 4 - 37.6 mg Apatite/Gram of Refuse

## Results:

Notes: The columnes were leached for fifteen consecutive weeks. In all rock types tested. The column identification is as follows:

| | |
|---|---|
| Column 1, 2, 3 | --Control |
| Column 4, 5, 6 | --Application Rate one |
| Column 7, 8, 9 | --Application Rate Two |
| Column 10, 11, 12 | --Application Rate Three |
| Column 13, 14, 15 | --Application Rate Four |

## Figures 1, 22 and 3

Figures 1, 2, and 3 show the Acid Loads of the leachate of all columnes tested. Figure one shows that the Application Rates 3 and 4 effectively reduced the acid load of the leachate by 82 and 88.4 % respectively over that produced by the controls. Application Rates I and 2 did not significantly reduce acid loads. Figure No. 2 shows the Acid Load of the Refuse with various Application Rates of Apatite. All application rates effectively reduced the acid load produced by the controls by 96 %.

Figure Number Three shows the acid loads produced from the shale columnes with the different application rates. The effectiveness of the Apatite Application Rates are as follows: Application Rate 1-65 %, Application Rate 2-61 %, Application Rates -- 87.5% and Application Rate 4-92.5 %. The percent reduction in Acid Loads is calculated by averaging the Total Acid Load produced of the three columnes in each application rate and comparing this number to the average of the acid load of the three control

## Figures 4, 5, and 6

Figures 4, 5, and 6 show the Total Iron Loads produced from each rock type with the various applications. Reductions in Total Iron Loads parallel those shown in Figures 1, 2, and 3.

## Figures 7, 8, and 9

A potential problem in using Apatite Rock as and acid preventative treatment is the radioactivity associated with the material. in the production of Phosphate Fertilizers the Apatite is leached with strong acids to liberate the PO-4 present, consequently; Acid Soluble Uranium and Radium present in the Apatite is also liberated. The acidic lixivent is then neutralized with lime. Upon neutralization Calcium Sulfate (Gypsom) is precipitated. Since the Uranium and Radium is acid soluble, upon neutralization, it also precipitates with the calcium sulfate. The radioactive concentration of Apatite Rock is vary low (25 ppm). However, in Phosphate Fertilizer Production, the radioactivity is concentrated in the gypsum sludges. These sludges have caused environmental concern. It is for this reason, that the leachate from this study was also analyzed for pertinent radioactivity concentrations. Figures 7, 8, and 9 summarize the radioactive loads from the various columnes. The figures indicate that the more Apatite present. The less radioactive is the leachant. This seems confusing, since the apatite is the most radioactive constituent of the columnes. However, all rock contains some radioactive compounds. It is felt that since uranium and radium is acid soluble, the reduced acid generation in the columnes containing apatite has resulted in less radioactivity leached. It should be noted that the radioactive concentration in the leachate from all columnes were within or vary close to drinking water standards.

## Summary:

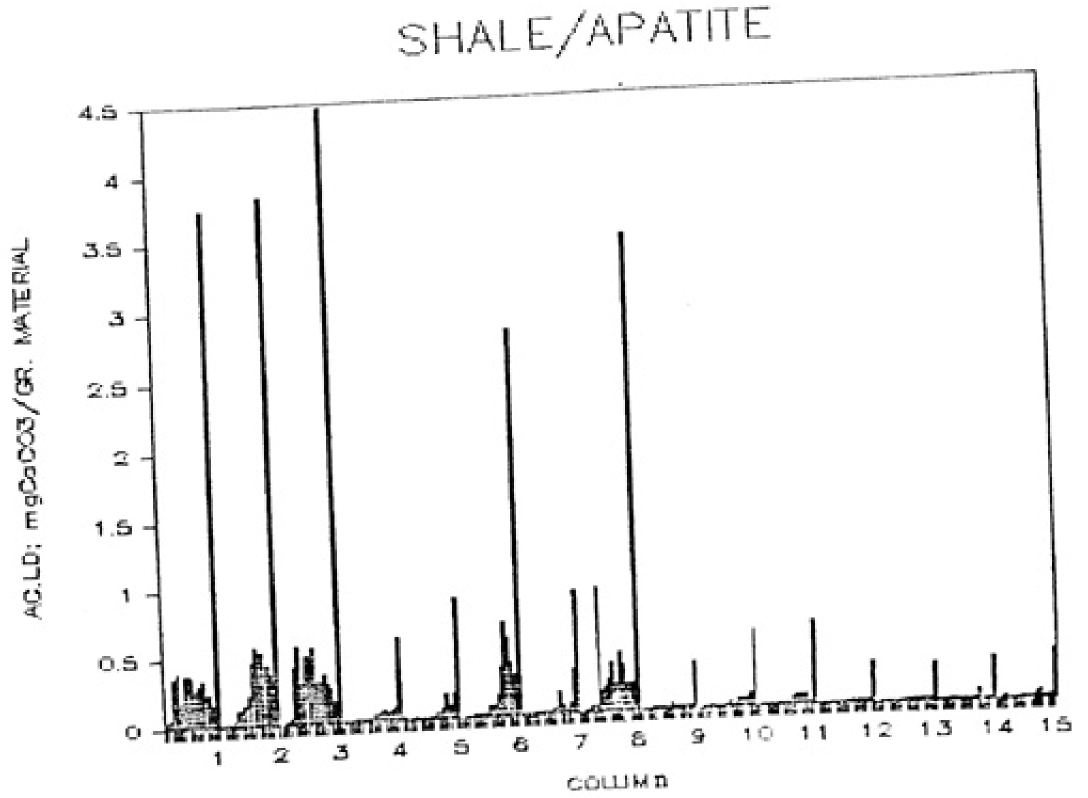
It was originally felt that the application rate of Apatite Rock to Acidic Spoil would be based on the acid producing potential of the spoil to be treated. However, this study has indicated the most important factor which is the percentage of apatite rock present, regardless, of the potential acidity of the rock treated. Figure 10 summarizes the Total Acid Load of all rock types tested at the various concentrations of Apatite Rock present. The information indicates that once the concentration of three tons of apatite per 1000 tons of material is attained, the rate of acid reduction levels off.

Therefore, the most cost effective application rate is three tons of apatite/1000 tons for the three types and sizes of rock tested. It has been well documented that acid production is directly related to the surface area of acidic spoils. Since the surface area of the acidic material tested (1/411 by 0 Mesh) is higher than what would be expected from actual surface mine spoil. The three ton/1000 ton Figure is felt to be conservative.

Note: 1.

1. The Apatite used in this experiment was 64 B.P.L., Northern Florida Phosphate Rock.
2. All Application Rates were thoroughly blended with the acidic spoil.
3. one column of the controls and each application rate were leached for a total of 36 weeks. The results shown in this report have continued to apply.

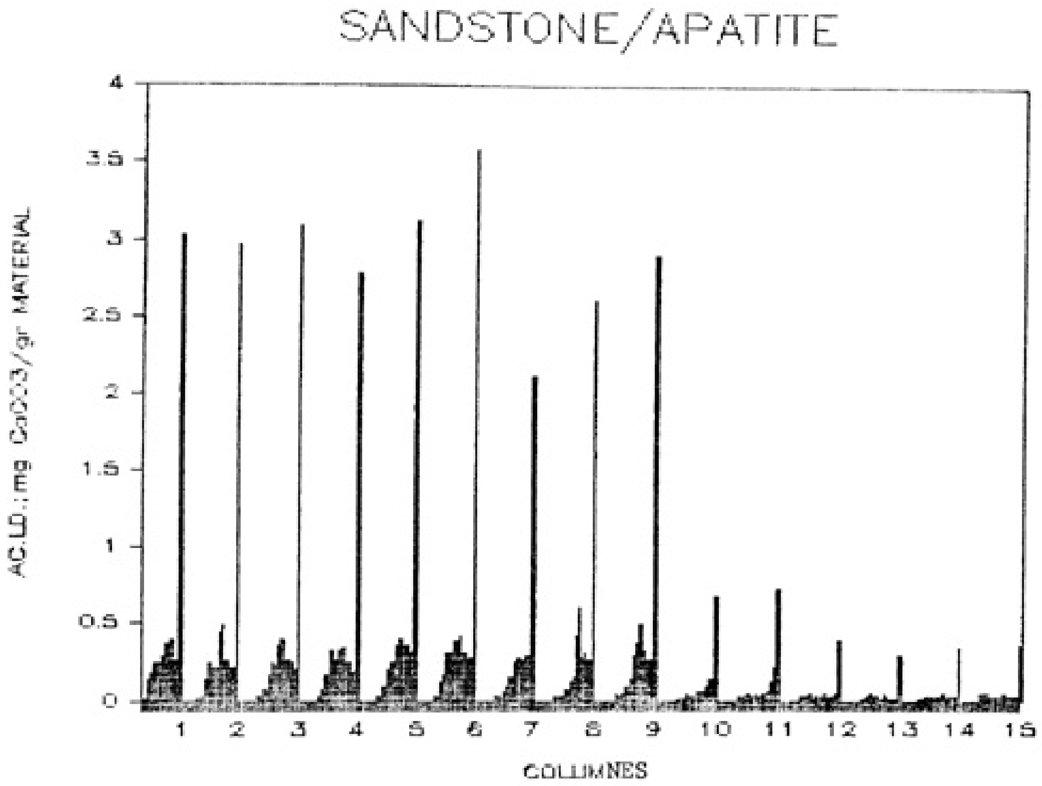
## FIGURE ONE



| Column I.D. | Appl. Rate | Conc. Apatite/Shale |
|---|---|---|
| 1 | Control | 0 |
| 2 | Control | 0 |
| 3 | Control | 0 |
| 4 | 1 | 1 mg/gr |
| 5 | 1 | 1 mg/gr |
| 6 | 1 | 1 mg/gr |
| 7 | 2 | 2.5 mg/gr |
| 8 | 2 | 2.5 mg/gr |
| 9 | 2 | 2.5 mg/gr |
| 10 | 3 | 5 mg/gr |
| 11 | 3 | 5 mg/gr |
| 12 | 3 | 5 mg/gr |
| 13 | 4 | 8.0 mg/gr |
| 14 | 4 | 8.0 mg/gr |
| 15 | 4 | 8.0 mg/gr |

FIGURE TWO

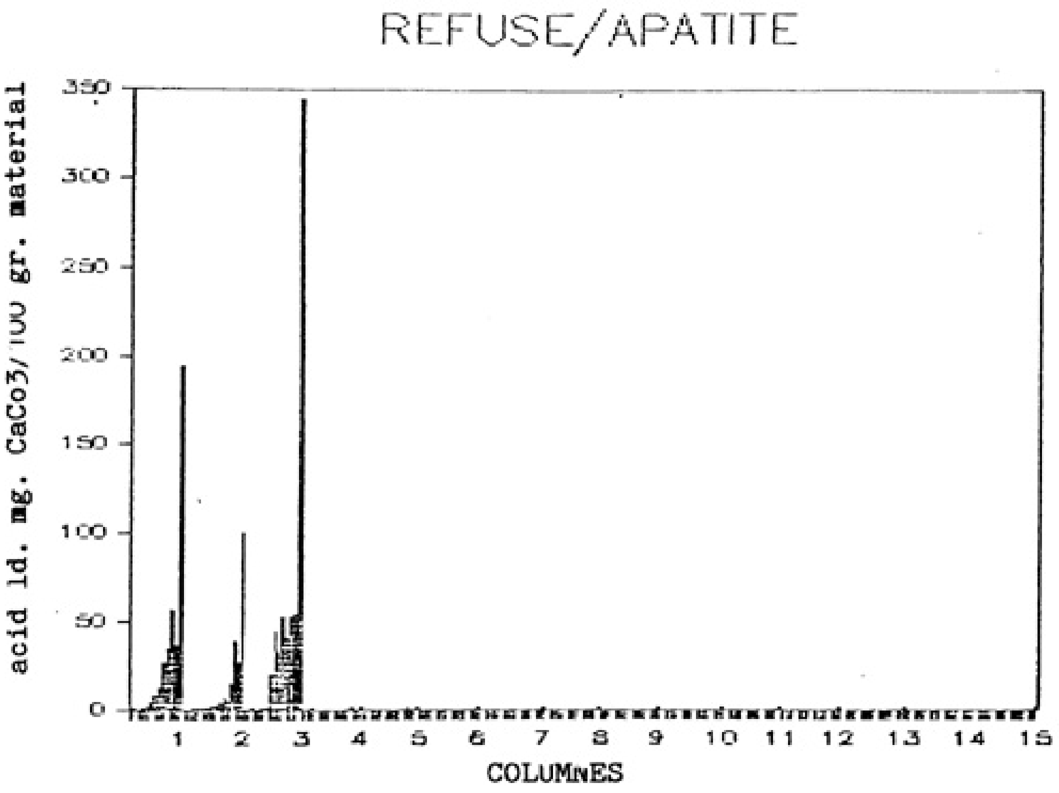
FIGURE TWO



| COLUMN I.D. | APPL. RATE | CONC. APATITE/SANDSTONE |
|---|---|---|
| 1, 2, 3 | CONTROL | 0 |
| 4, 5, 6 | 1 | .5 mg/gr |
| 7, 8, 9 | 2 | 1.0 mg/gr |
| 10, 11, 12 | 3 | 2.0 mg/gr |
| 13, 14, 15 | 4 | 3.0 mg/gr |

**FIGURE THREE**

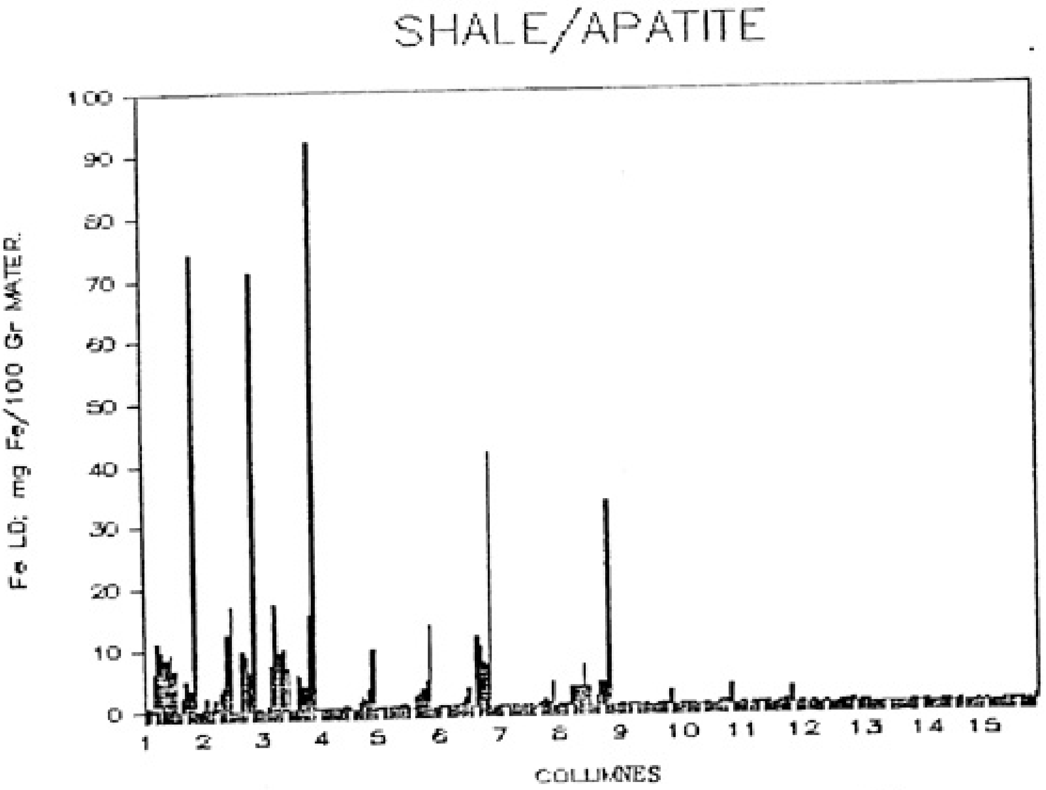
FIGURE THREE



| COLUMN I.D. | APPL. RATE | CONC. APATITE/REFUSE |
|---|---|---|
| 1,2,3 | CONTROL | |
| 4,5,6 | 1 | 12.35 mg/gram |
| 7,8,9 | 2 | 17.0 mg/gr |
| 10,11,12 | 3 | 25 mg/gr |
| 13,14,15 | 4 | 37.6 |

FIGURE FOUR

FIGURE FOUR



| COLUMN I.D. | APPL. RATE | CONC. APATITE/SHALE |
|---|---|---|
| 1 | Control | 0 |
| 2 | Control | 0 |
| 3 | Control | 0 |
| 4 | 1 | 1 mg/gr |
| 5 | 1 | 1 mg/gr |
| 6 | 1 | 1 mg/gr |
| 7 | 2 | 2.5 mg/gr |
| 8 | 2 | 2.5 mg/gr |
| 9 | 2 | 2.5 mg/gr |
| 10, 11, 12 | 3 | 5 mg/gr |
| 13, 14, 15 | 4 | 8.0 mg/gr |

**FIGURE FIVE**

FIGURE FIVE

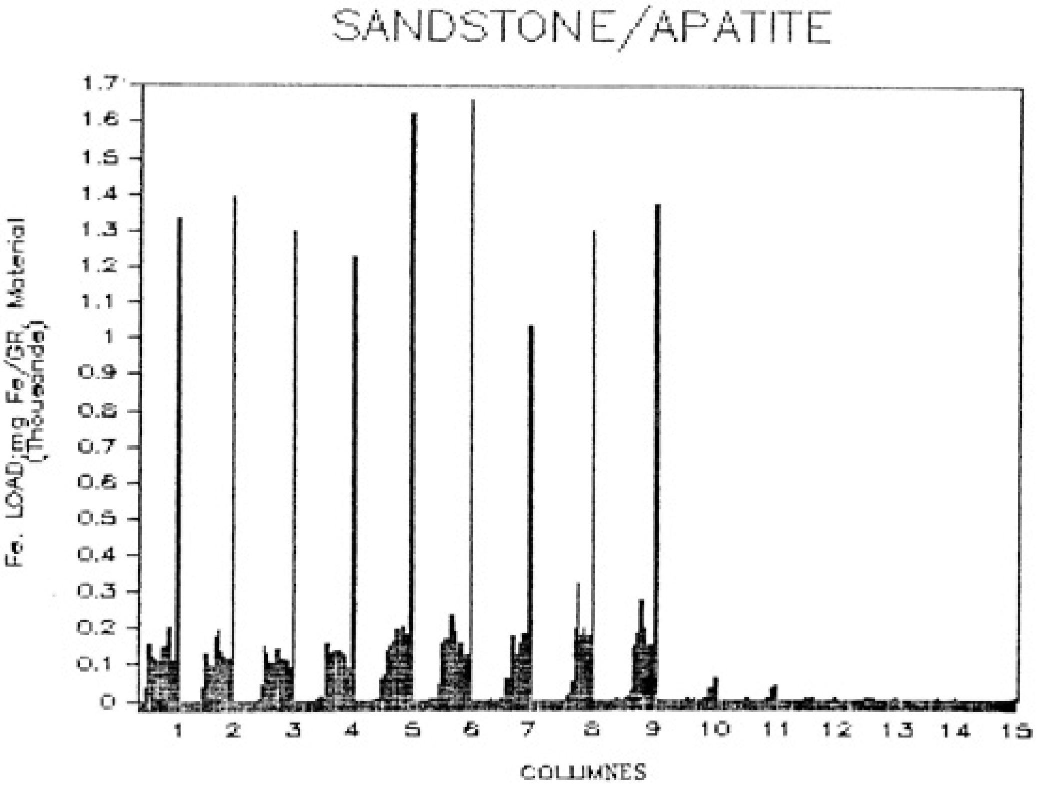
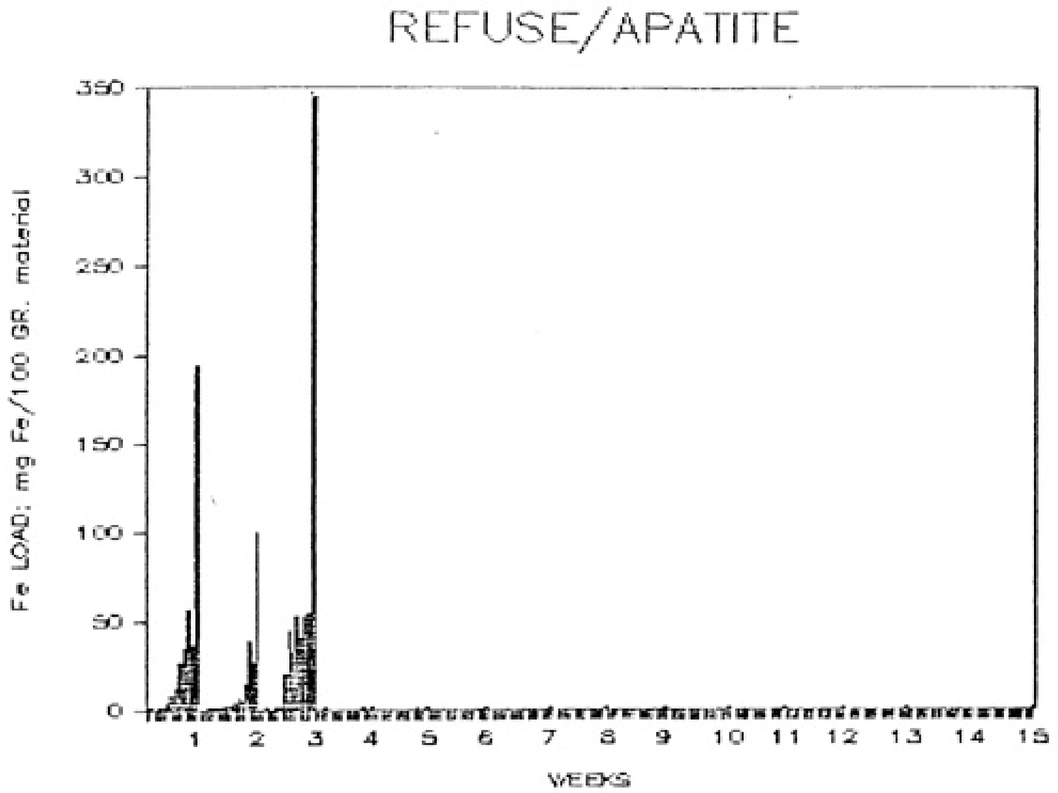


**Figure Six**

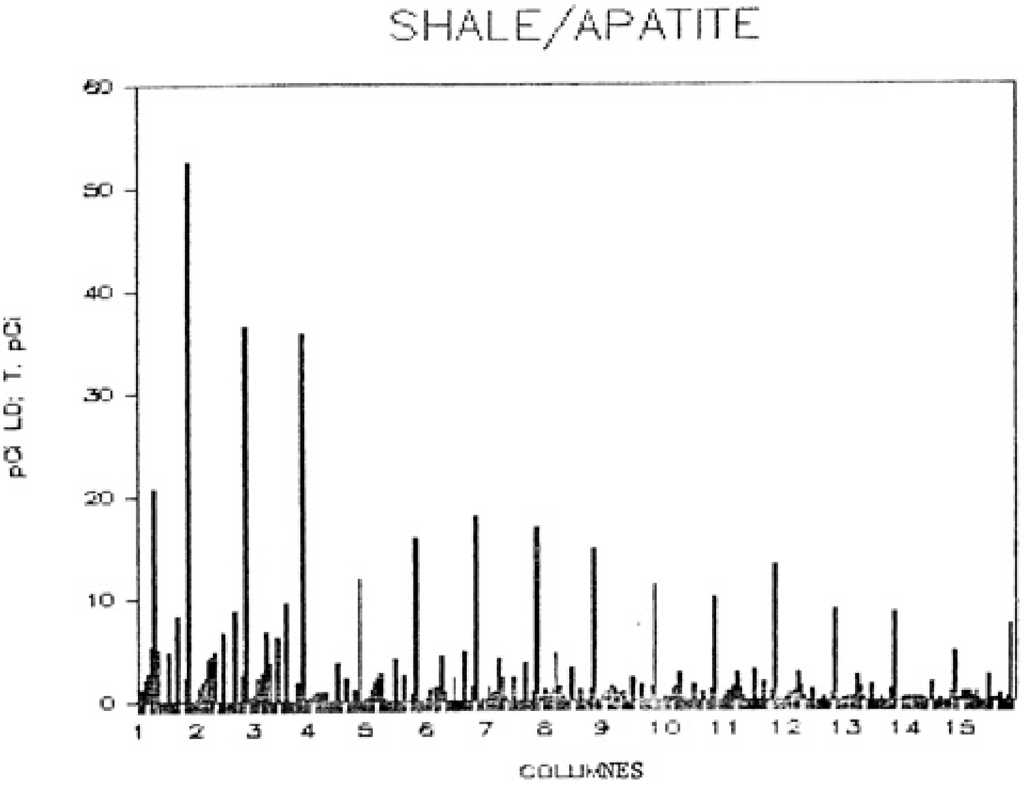
Figure Six



| COLUMN I.D. | APPL. RATE | CONC. APATITE/REFUSE |
|---|---|---|
| 1, 2, 3 | CONTROL | 0 |
| 4, 5, 6 | 1 | 12.35 mg/gram |
| 7, 8, 9 | 2 | 17.0 mg/gr |
| 10, 11, 12 | 3 | 25 mg/gr |
| 13, 14, 15 | 4 | 37.6 |

FIGURE SEVEN

FIGURE SEVEN



| COLUMN I.D. | APPL. RATE | CONC. APATITE/SHALE |
|---|---|---|
| 1 | Control | 0 |
| 2 | Control | 0 |
| 3 | Control | 0 |
| 4 | 1 | 1 mg/gr |
| 5 | 1 | 1 mg/gr |
| 6 | 1 | 1 mg/gr |
| 7 | 2 | 2.5 mg/gr |
| 8 | 2 | 2.5 mg/gr |
| 9 | 2 | 2.5 mg/gr |
| 10, 11, 12 | 3 | 5 mg/gr |
| 13, 14, 15 | 4 | 8.0 mg/gr |

## FIGURE EIGHT

FIGURE EIGHT

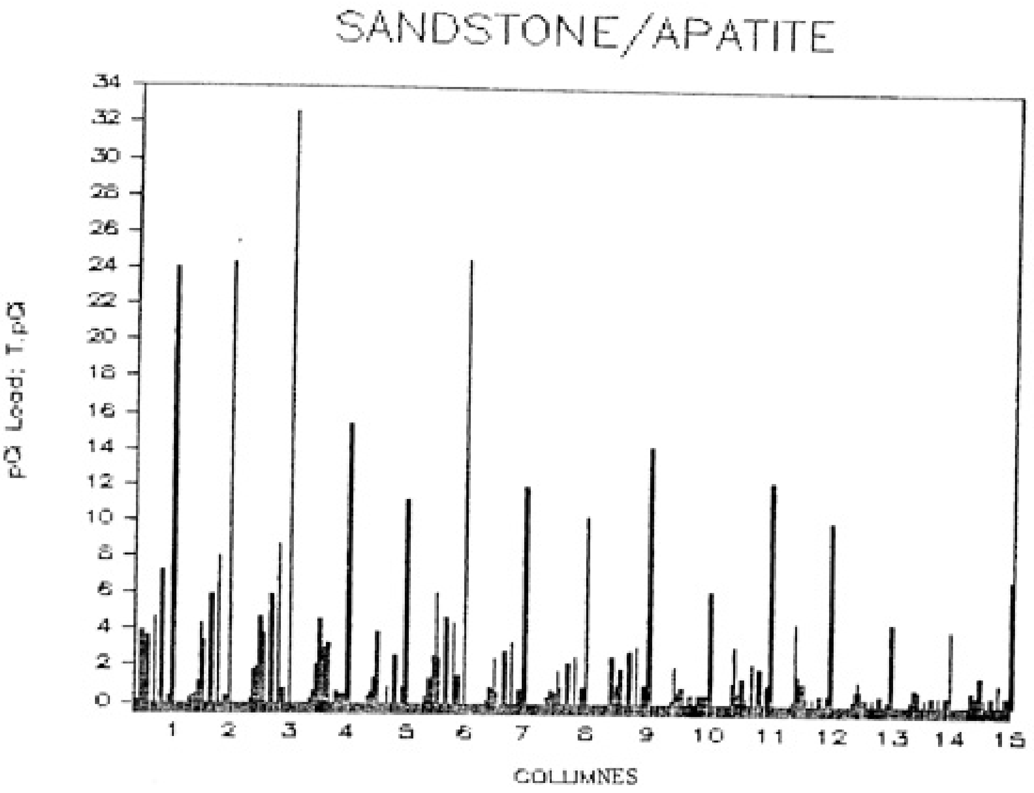


FIGURE NINE

FIGURE NINE

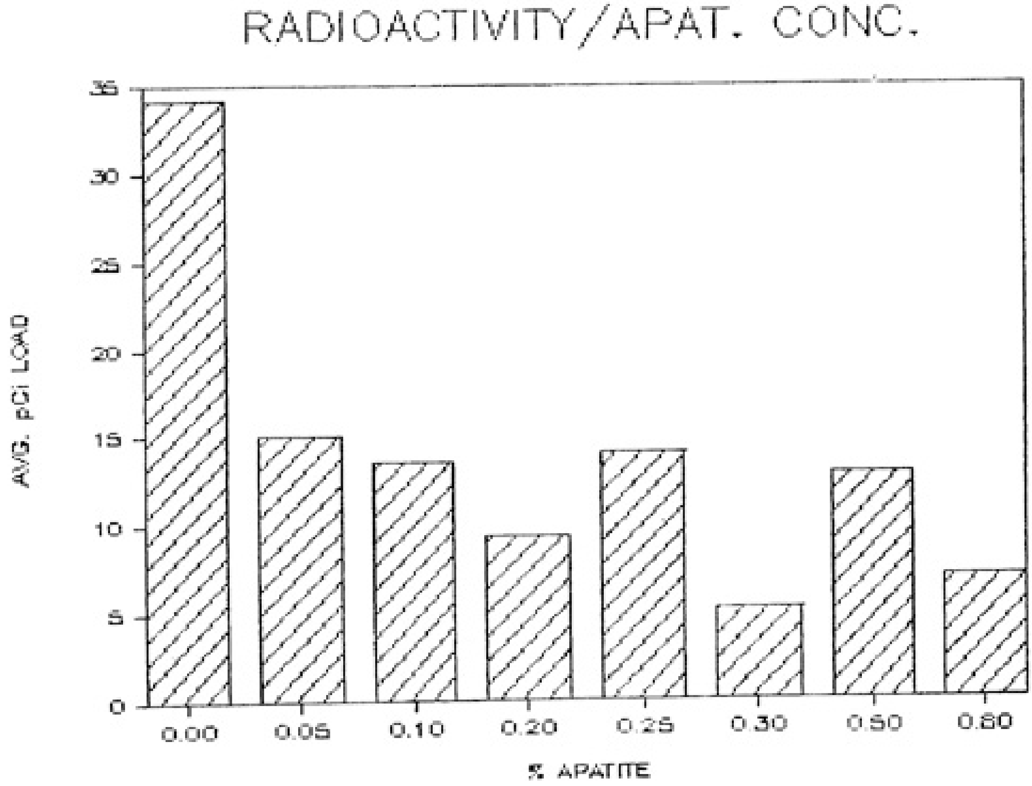
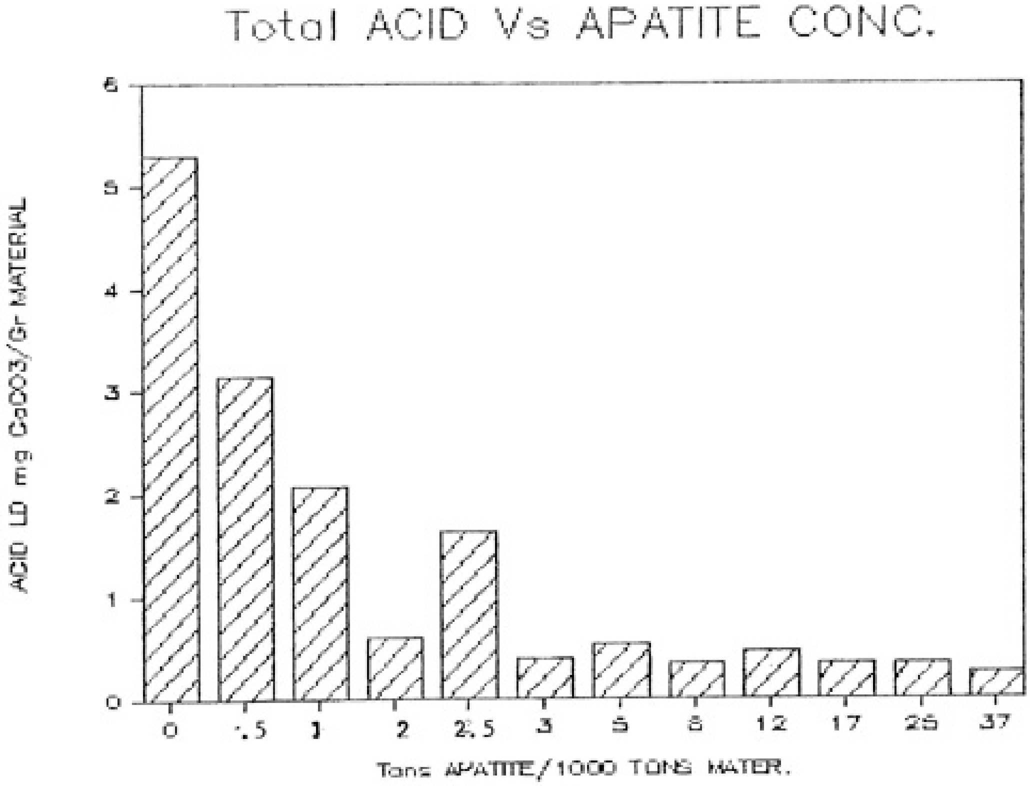


Figure Ten

Figure Ten



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2. Stiller A.H. 1989. A Method for Prevention of Acid Mine Drainage. Paper presented at the Third West Virginia Surface Mine Drainage Task Force Symposium, Clarksburg, W.Va. May, 1982
3. Meek, F.A. 1982, STUDIES in Prediction and Prevention of Acidic Surface Mine Drainage. Island Creek Coal Distribution only.

## Field Scale Research

Field scale research plots were constructed to assess the effectiveness of apatite rock in preventing acid mine drainage under actual field conditions. 50' x 50' x 5' miniature representations of mine backfills were constructed (see Drawing #1). Acidic shale and boney coal material (partings) were used in the tests. This material was analyzed by acid-base accounting methods. To minimize variability amongst fills in the size consist of the overburden, the material was crushed to 6" x 1/2" gradation prior to placement in the test fills. Truck scales were used to obtain the weight of material placed into each fill.

In order to assure that only water percolating through or running off the test fills would be monitored, the fill sites were graded, and external diversions were provided. A 50' x 50' x 20 mil thick pvc underliner, and a fifty foot section of perforated plastic pipe, were installed to provide a leachate containment system. The leachate collection and monitoring system for each site consists of a 1" parshall flume in conjunction with an ISCO automatic sampler and flow meter. The samplers were calibrated to collect and store a 120 milliliter sample for each 10 gallons of leachate and/or runoff flowing from the fills. The resulting samples are flow proportioned composites. The leachate samples were analyzed to identify acid-base reactions occurring in the overburden under actual field exposure conditions. A description of the pertinent fills follows:

Fill #2 - 366 Tons of shale/coal (parting) material

Fill #6 - 367 Tons of shale/coal material with 1.14 tons of apatite rock added

Fill #7 - 368 Tons of shale/coal material with .55 tons of apatite rock added

Once the fills were completed, a vertical column sample (core) was obtained from each of the fills. The samples were analyzed to verify initial acid-base accounting results. In addition, total mineralogy and elemental makeup tests were conducted. The results of the second acid-base accounting tests were very similar to the original .

Fills Number 6 and 7 had apatite rock added in 3 lifts during construction. The application rate for Number Six was that calculated to provide enough phosphate ions to complex one third of the iron associated with the pyrite in the material. Fill Number 7 contains one-sixth of this stoichiometric equivalent.

## Results (Field Scale Research)

The total effectiveness of the apatite addition technique was assessed by comparing the pH of the drainage (Figure 7),the net alkalinity/acidity (Figures 8 and 9), and the pyrite oxidation rate (Figure 10), amongst the fills. The net alkalinities of the sites treated with apatite rock are consistently much higher than 60 ppm. This is an interesting point, in that it has been previously established by researchers [3,4] that alkalinities from $CaCO_3$ cannot exceed approximately 60 ppm with the $CO_2$ concentration present under atmospheric conditions. Further laboratory investigation showed that the unexpected excess alkalinity was most likely due to the siderite ($FeCO_3$) present in the overburden, as affected by the phosphate ions. In the absence of phosphate ions, the reactions involving siderite are as follows:

$FeCO_3 \longrightarrow Fe^{++} + CO_3^{-2}$

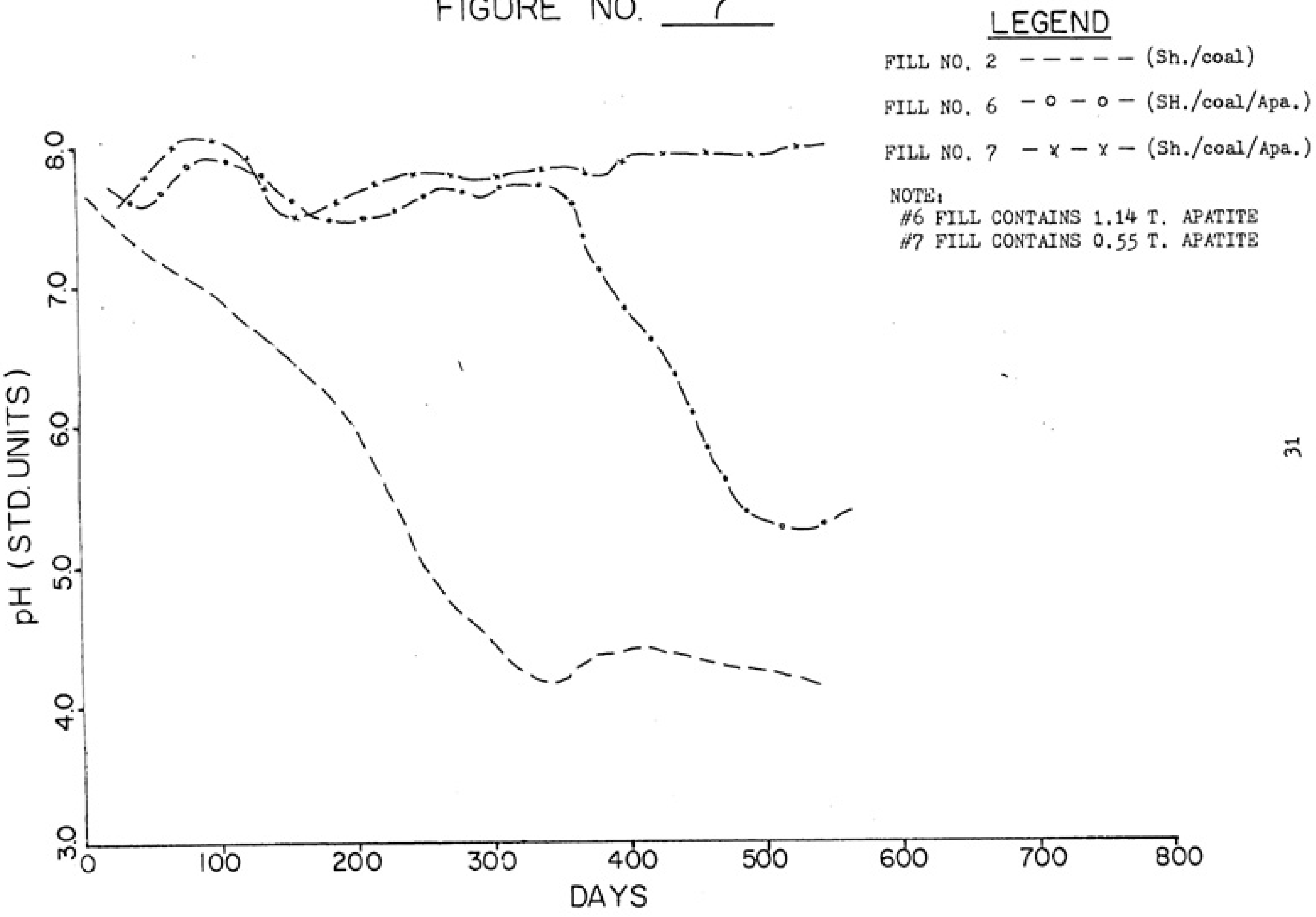
$CO_3^{-2} + 2H^+ \longrightarrow H_2CO_3$

$H_2CO_3 \longrightarrow H_2O + CO_2$

$Fe^{++} + 1/4\ O_2 + H^+ \longrightarrow Fe^{+++} + 1/2\ H_2O$

$Fe^{+++} + 3\ H_2O \longrightarrow Fe\ (OH)_3 + 3H^+$

FIGURE NO. 7



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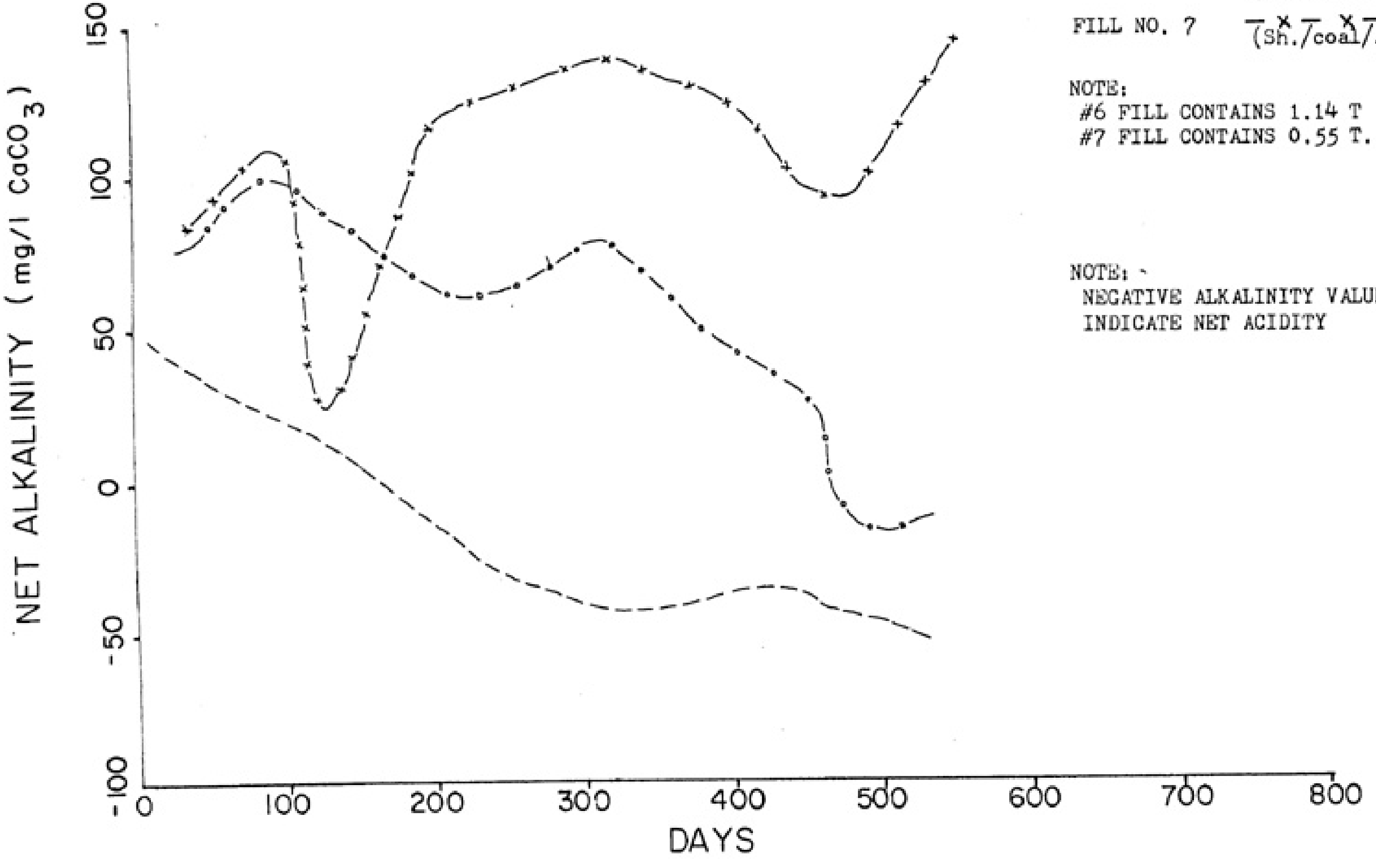
TEST FILL DATA: pH OF EFFLUENT VERSUS TIME

FIGURE NO. 8



LEGEND

FILL NO. 2 (Sh./coal)

FILL NO. 6 (Sh./coal/Apatite)

FILL NO. 7 (Sh./coal/Apatite)

NOTE:
#6 FILL CONTAINS 1.14 T .APATITE
#7 FILL CONTAINS 0.55 T. APATITE

NOTE: -
NEGATIVE ALKALINITY VALUES
INDICATE NET ACIDITY

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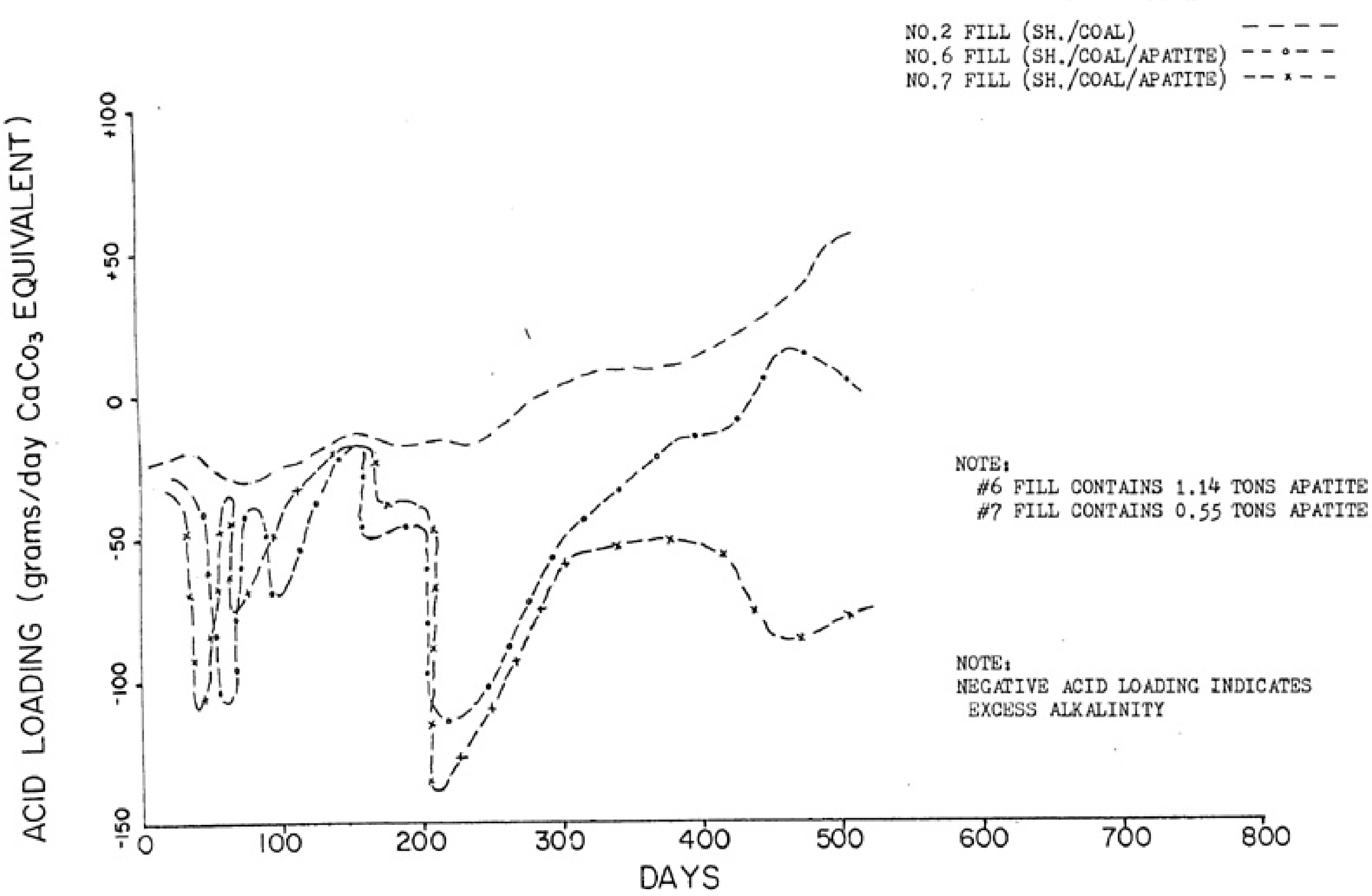
TEST FILL DATA: NET ALKALINITY VERSUS TIME

FIGURE NO. 9



NOTE:
#6 FILL CONTAINS 1.14 TONS APATITE
#7 FILL CONTAINS 0.55 TONS APATITE

NOTE:
NEGATIVE ACID LOADING INDICATES EXCESS ALKALINITY

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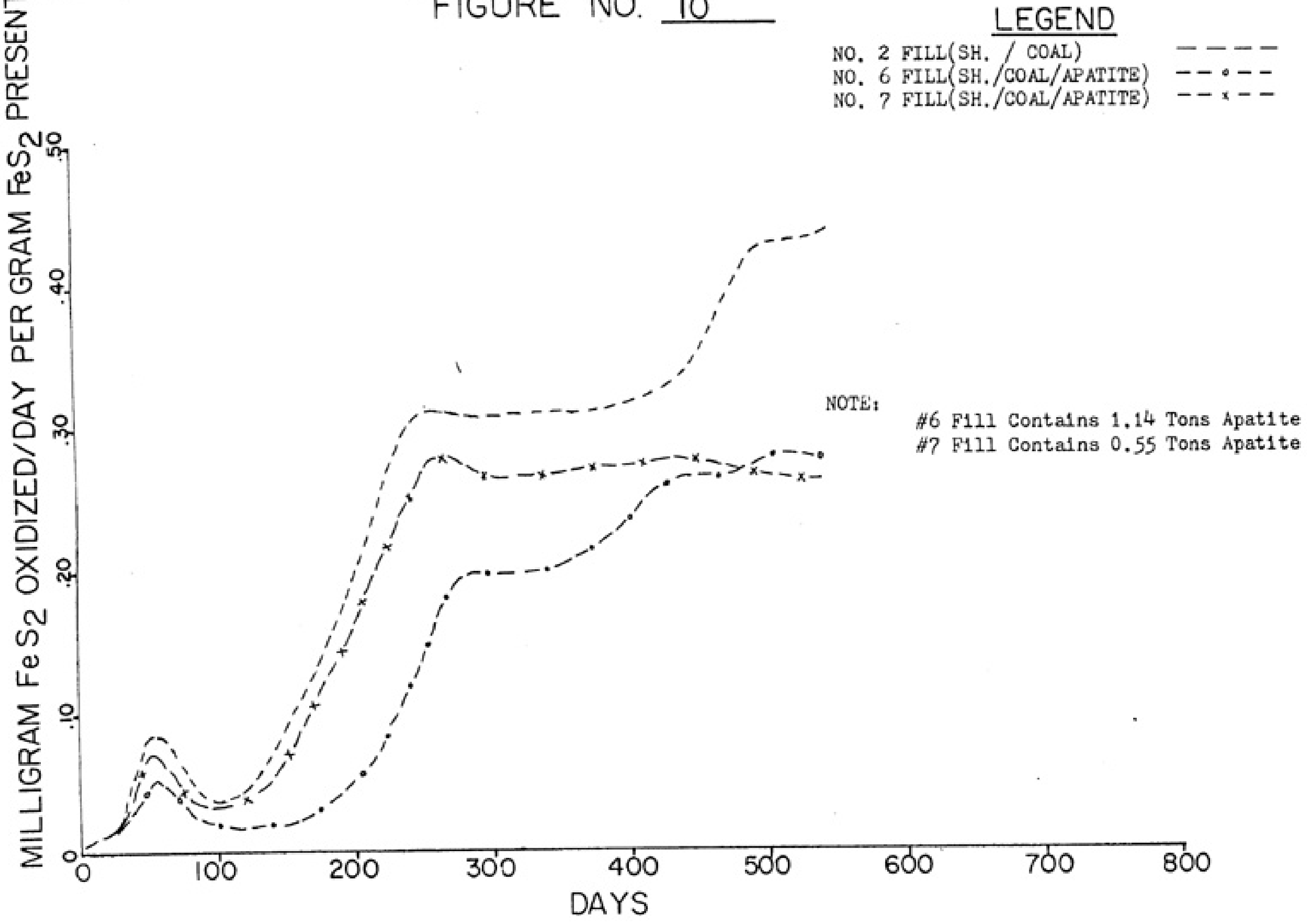
TEST FILL DATA: ACID LOADING VERSUS TIME

# FIGURE NO. 10



NOTE:
#6 Fill Contains 1.14 Tons Apatite
#7 Fill Contains 0.55 Tons Apatite

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TEST FILL DATA; PYRITE OXIDATION RATE Vs.TIME

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3. Caruccio, F. T., G. Geidel. CARGEID, 1981. An Evaluation of the Proposed Holly Grove Mine (Canaan, W.V.) to Impact the Little Kanawha River with Acid Waters. Report to U. S. Environmental Protection Agency.
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