

The Use of Phosphate Refuse as a Potential AMD Ameliorant ¹

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Abstract

The use of a variety of apatite rock called Code 31 has been evaluated in the laboratory as being a very effective acid mine drainage (AMD) ameliorant. Presently, field studies are being conducted to determine the economic feasibility of using this material to inhibit acid production from 100,000 ton refuse test piles. One drawback to the use of Code 31 is its associated cost and overall expense. A phosphate waste material which contains approximately 25% apatite and is high in calcareous material has been evaluated in the laboratory as either a potential ameliorative material. This material is available at only 10% of the cost of the CODE 31. Functionalization of the cumulative acid load with respect to time and application schedule can be performed to evaluate the cost-economic engineering analysis for the material. It has been shown in laboratory studies that this material is, within certain ranges, an effective ameliorative material and exhibits a synergistic acid neutralization property due to the calcareous material present. In some instances, at higher application rates, however, this material has variable ameliorative and synergistic properties due to the ratio of apatite to calcite present in the phosphate waste tailings.

Additional Key Words: soxhlet extractor.

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Introduction

The potential use of phosphates as AMD ameliorants has been previously reported by Renton (1988). The primary phosphates considered were from North Carolina (Texas Gulf Code 31) and Florida (Florida Institute for Phosphate Research). A Commercial grade product, Texas

Gulf Code 31, was most effective in inhibiting the oxidation of pyrite and improving leachate quality with respect to total acidity. The economics of the use of the Code 31 phosphate are presently under investigation. As a contingency, another phosphate-bearing material (provided by Texas Gulf) referred to as "waste phosphate tailings" was evaluated for potential amelioration. The economics associated with this material are extremely favorable (\$5.00/ton). Therefore, in order for this material to be considered it must exhibit the same consistency and ameliorative properties as the Code 31 material.

General Geology and Mineralogy

Large Miocene phosphorite deposits occur in parts of four states and extend along the Atlantic coastal plain from North Carolina into the center of the Florida Peninsula. The reserves and resources of this large deposit are estimated at several billion tons of phosphate rock. The bulk of the sediments consists of phosphate particles (pellets and other grain types), quartz, and clay minerals. There are locally important and variable amounts of calcite and dolomite with minor amounts of silicates, opal, iron-aluminum phosphates (in weathering zones) and heavy minerals (McClellan 1985).

The observed variations in mineralogy over the region are the result of primary compositional differences as well as post-depositional alteration. The latter includes diagenetic changes that resulted in the formation of authigenic minerals as well as weathering of the deposits to alter the compositions and phases to those that are seen today (McClellan 1985).

Carbonate fluorapatite (francolite) and clay minerals are the two most important constituents from an economic and environmental point of view. Francolite is the only economically important phosphate mineral present; the clays represent a significant source of impurities in the ore and present significant by-product disposal problems. Thus, this brief summary will concentrate on these two groups of minerals (McClellan 1985).

Reactive phosphate rock is an unaltered or low weathered fluorapatite of sedimentary origin in which a high degree of anion and cation substitution, mainly carbonate, has taken place in the lattice structure of the crystal. The predominant mineral of a highly reactive rock is francolite, a carbonate fluorapatite. In francolite, sodium, magnesium, potassium, strontium, zinc, uranium, etc. are substituted for calcium, while carbonate, sulfate, silicate, aluminate, etc. are substituted for phosphates in the crystal lattice (Texas Gulf 1989).

Replacement of calcium by sodium and magnesium in francolite is systematic but limited in the crystal structure. sodium and magnesium are an integral part of the francolite structure and cannot be removed by beneficiation (Texas Gulf 1989).

The waste phosphate tailings, due to the variability of size distribution and general character, were theorized to have a mineralogy different from the materials presented above. The waste phosphate tailings are highly fossiliferous (containing, among other creatures, sharks, teeth and gastropods) and should contain high amounts of carbonaceous minerals with an assortment of cationic replacement. The major mineral, in addition to apatite and calcite, is Kutnahorite (an iron-manganese dolomite). The presence of a weatherable manganese mineral is of primary environmental concern.

The waste phosphate tailing material received by the laboratory was sized and each size

fraction was subjected to x-ray diffraction analysis. The resulting mineralogy can be seen in Tables 1 and 2.

Table 1.

Size Fractions of Waste Phosphate Tailing and Associated Mineralogy

<u>size (mesh)</u>	<u>openings (mm)</u>	<u>mineralogical (table 2)</u> <u>sample id cross-reference</u>		
< 7	> 2.830	1		
7- 14	1.410 - 2.830	2		
14 - 25	0.710 - 1.410	3		
25 - 70	0.210 - 0.710	4		
70 - 100	0.149 - 0.210	5		
100 - 140	0.105 - 0.149	6		
> 140	< 0.105	7		
whole rock batch I waste phosphate tailings		22	23	24
whole rock batch II waste phosphate tailings		25	26	27
Texas Gulf code 31		28	29	30

Table 2.

Pertinent Mineralogy of Waste Phosphate Tailings.

<u>sample id</u>	<u>% apatite</u>	<u>%Kutnahorite</u>	<u>% calcite</u>	<u>%SiO₂</u>
22	38.2	8.4	42.1	11.3
23	44.7	7.6	34.5	13.2
24	38.0	7.1	42.7	12.2
25	25.1	6.6	44.8	23.5
26	26.8	6.3	40.7	26.2
27	26.8	6.0	43.2	24.0
28	94.7	-	0.8	4.5
29	95.6	-	-	4.4
30	94.5	-	-	5.1
7	5.7	43.8	32.3	18.2
6	5.2	33.0	30.5	31.2
5	11.0	22.0	30.9	36.1
4	10.8	22.0	35.5	31.7
3	10.6	16.3	48.7	24.5
2	24.6	1.2	30.1	44.1
1	28.0	2.3	43.9	25.8

Materials and Methods

Experimental Design

Evaluating the effectiveness of the various forms of phosphate materials in ameliorating acid

mine drainage was done by making use of the soxhlet extraction procedure developed by Renton et al. (1988). The soxhlet extractors are designed to simulate the weathering of mine spoil in the field. A representative sample of mine waste rock was selected from the Island Creek mine in Grant County, West Virginia. samples were dried at room temperature and ground to pass through a seven mesh (2.83 mm opening) ASTM standard sieve tray. This particle size distribution was chosen to ensure that diffusive effects would be present as they are in the field. Phosphate rock samples were similarly selected and dried, but were ground to pass through a 140 mesh (0.105 mm opening) ASTM standard sieve tray. This particle size distribution was chosen to avoid diffusive effects in the phosphate rocks while keeping particle sizes large enough to reduce respiratory irritation. A set of four replicate samples of overburden and phosphate rocks were weighed to 0.1 gram sensitivity. The rocks were combined at a predetermined application schedule and mixed thoroughly. Rock mixture samples were contained in cellulose extraction thimbles and were alternately extracted and oxidized per Renton et al. (1988).

Code 31 phosphate is known to be an effective ameliorant in laboratory studies at application rates of two percent and above (Renton et al., 1988). Due to the differing chemical compositions of the Phosphate tailings wastes, ameliorative effectiveness was expected to vary somewhat from the Code 31 product (as indicated above). The extreme cost advantage afforded by the phosphate tailings wastes would make much greater application rates of these materials economically feasible, if necessary. Consequently, it was decided to apply both the Phosphate waste tailings (and the Code 31, for the sake of reference) at percentages up to double the determined optimum code 31 application rate of two Percent in increments of one-half percent. In addition to the Code 31, two different batches of phosphate waste tailings from the TexasGulf chemicals Aurora, North Carolina mine were applied to the Grant County, WV mine spoil.

Distilled, de-ionized water was used as the solvent in the soxhlet extractors. Leachates were analyzed for pH, neutralization by base to pH's of 7.0 and 8.3, respectively, sulfate content, iron content and manganese content by standard procedures (standard methods for the Examination of water and wastewater) Sulfate content was used by Renton (1988) to indicate acid produced by various overburden types. Analysis of waste tailings compositions showed the presence of sulfates in varying quantities which could lead to inflated estimations of sulfate attributed to the waste rock. Consequently, pH and neutralization by base to pH 7.0 and pH 8.3 were more reliable indicators of ameliorative effectiveness. Iron content was tested against the control to indicate any contribution of the phosphate waste tailings. Manganese is known to be detrimental to human health if present in certain quantities. Manganese content was analyzed to indicate the mobility of this ion which was found to be present in the phosphate waste tailings in the form of Kutnahorite.

A data spreadsheet was set up for each type of waste phosphate and each ion as shown in Table 3.

Table 3 Spreadsheet for data entry

Type of Phosphate Material:
Replicate number:

Percent Phosphate (wt. phosphate/100 g)	weeks				
	2	4	6	8	10
0 (control)					
0.5					
1.0					
1.5					
2.0					
2.5					
3.0					
3.5					
4.0					

Results and Conclusions

The data collected consists of approximately two megabytes and resides on the VAX 780 computer at the WVU College of Engineering. The data were processed on a MICROVAX 3500 Workstation, on a system freely programmed into working architecture by Mr. Paul Sutter, Apple Computer software engineer. All data analyses and graphics were performed by accessing the single database from various subprograms written and developed by the authors.

Data Analysis

The three important aspects of the data analysis involve: (1) Examination of the consistency of the three phosphate types' ameliorative effects with respect to time and application rate (wt phosphate/100 wt refuse material), (2) Functionalization of ameliorative effects with respect to time and application rate, and (3) Evaluation of the functionalized ameliorative effectiveness and cost analysis.

The consistency with which the material alters the acid production with respect to time and application rate is an important parameter in evaluation of phosphate amelioration. A good ameliorative material is characterized by three properties: (1) the acid load will be inversely proportional to the application rate (2) the cumulative acid load will become asymptotic with time, and (3) the cumulative acid load will not show fluctuations or variability with respect to time and application rate. These properties tend to make curves of acidity versus time and

application rate smooth and continuous for an effective ameliorant. A cost effective ameliorative material will show significantly decreased acid loads with low application rates. To illustrate the first of the properties cited above it is helpful to examine the ameliorative properties of Texas Gulf Code 31 phosphate material with respect to time and application rate. Averaged soxhlet cumulative acidity data are plotted versus time and phosphate application rate in Figure 1. Figure 2 is a grid version of the same data to show trends. Code 31 shows all three properties of a good ameliorative material in that it has an immediate ameliorative effect at low application rates with an increasing ameliorative trend at higher application rates, asymptotic behavior through time, and almost no fluctuations or variation through increased application rates or time. The ameliorative effects are easily functionalized. A plot of data generated from the resulting function can be seen in Figure 3.

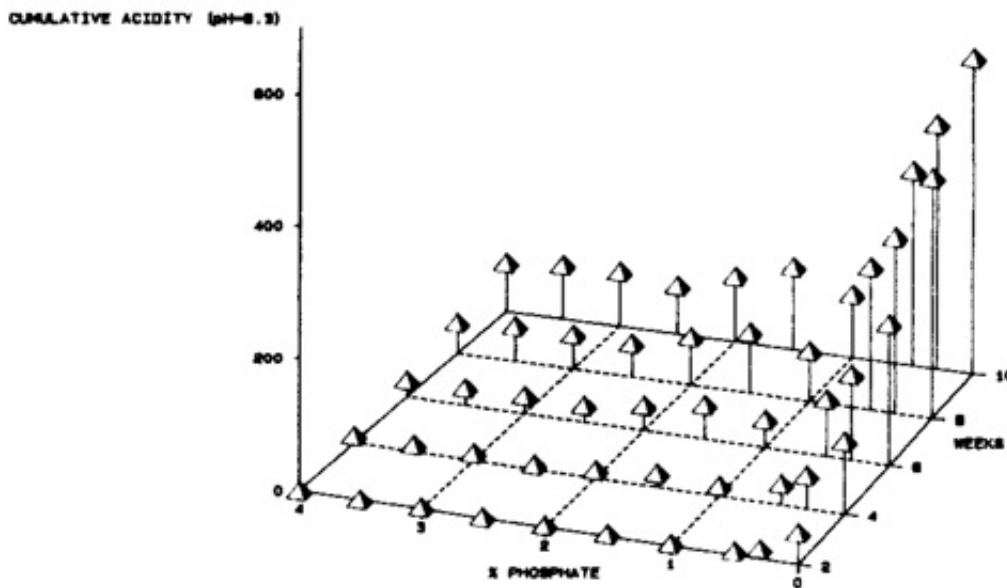


Figure 1

Ameliorative effectiveness of Texas Gulf Code 31 as it relates to weeks in the soxhlet extractors and the percentage of material added to the toxic waste refuse material

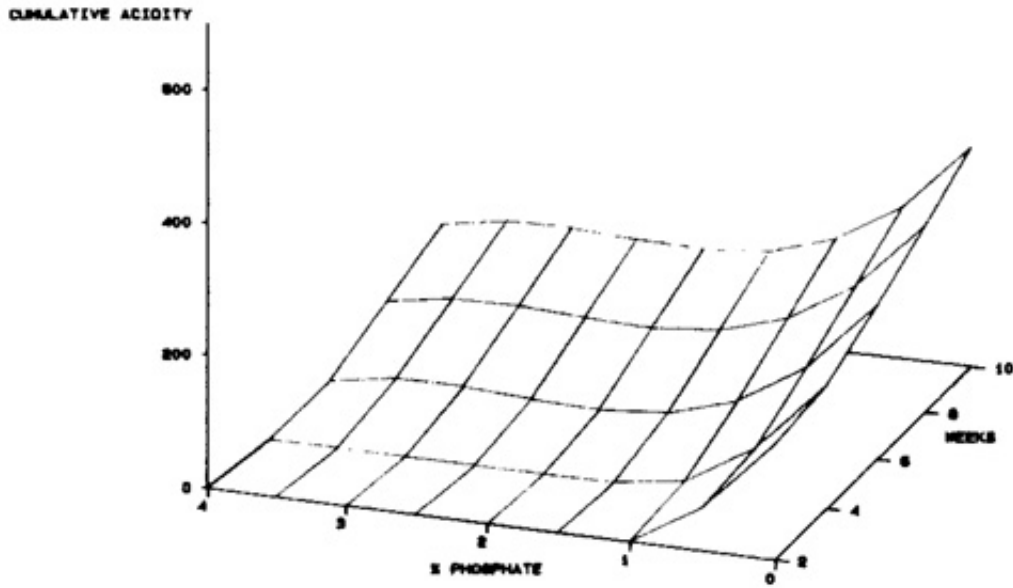


Figure 2.
 Gridded version from Figure 1 data to show contour relationships between ameliorative effectiveness of Texas Gulf Code 31 with respect to weeks and application rate.

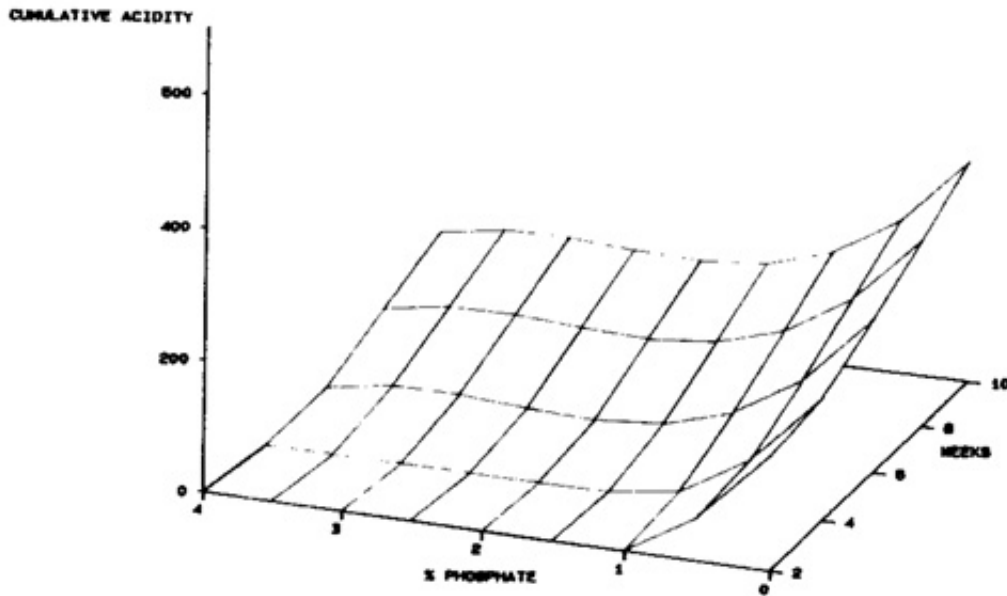


Figure 3.
 Functionalized 3-dimensional relationship between ameliorative effectiveness of Texas Gulf Code 31 with respect to weeks and phosphate application rate. The function is that given by equation 1

Similar treatment can be given to the data for the Batch I and Batch II waste phosphate materials. Batch I plots are seen in Figures 4 to 6 while Batch II plots can be seen in Figures 7 to 9, respectively. Figures 1, 4, and 7 represent actual cumulative acidity data as it relates to time (weeks) and phosphate application rates of each rock type. Figures 2, 5, and 8 show the 3-dimensional grids of the averaged experimental data. Figures 3, 6, and 9 represent the results of functionalization (i.e. cumulative acidity deterministic equation as a function of time (weeks) and phosphate application rates [%phosphate]). Note that the functionalized equations are mathematically smooth.

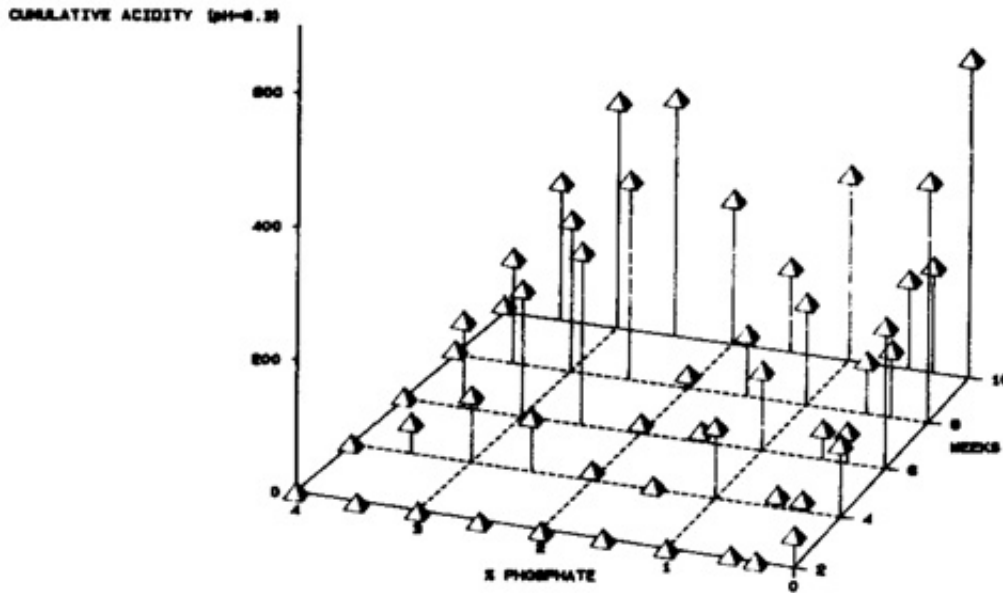


Figure 4.

Ameliorative effectiveness of Texas Gulf Waste Tailings (batch i) as it relates to weeks in the coxhlet extractors and the percentage of material added to the toxic waste refuse material.

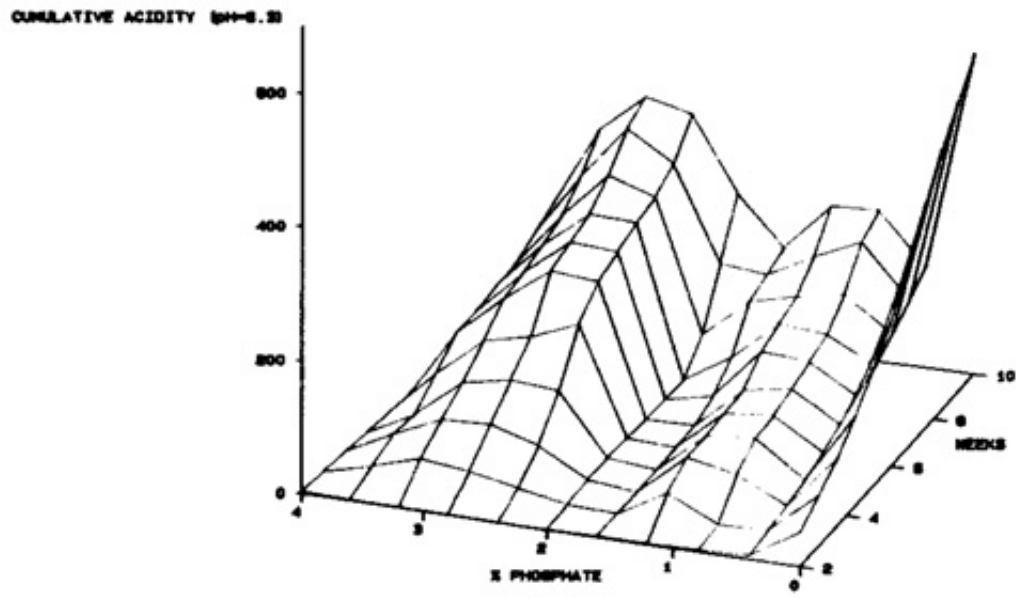


Figure 5.

Gridded version from Figure 4 data to show contour relationships between ameliorative effectiveness of Texas Gulf Waste Tailings (batch I) with respect to weeks and application rate.

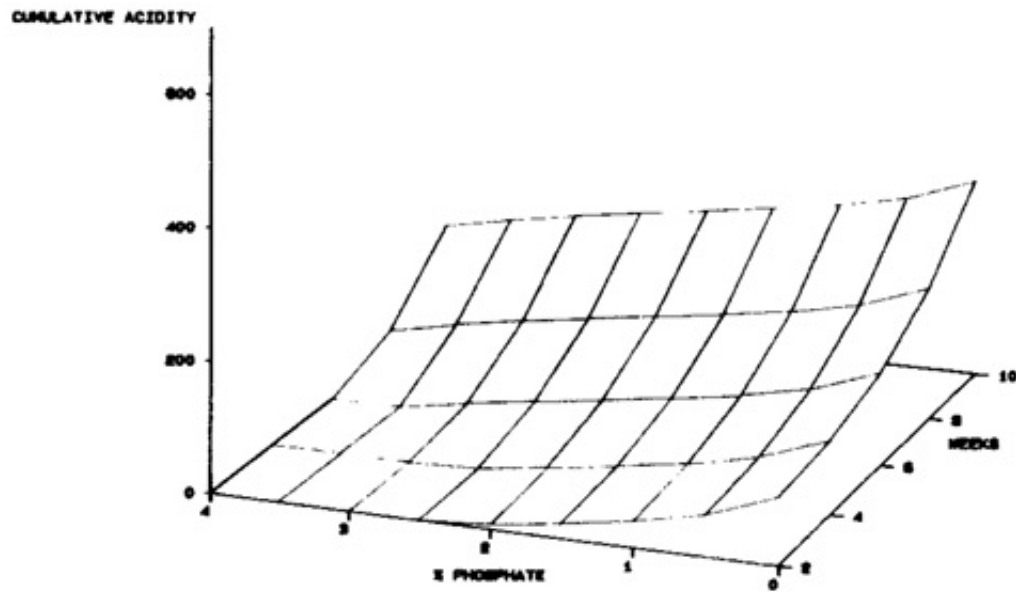


Figure 6.

Functionalized 3-dimensional relationship between ameliorative effectiveness of Texas Gulf Waste Tailings (Batch 1) with respect to weeks and phosphate application rate. The function is that given by equation 2

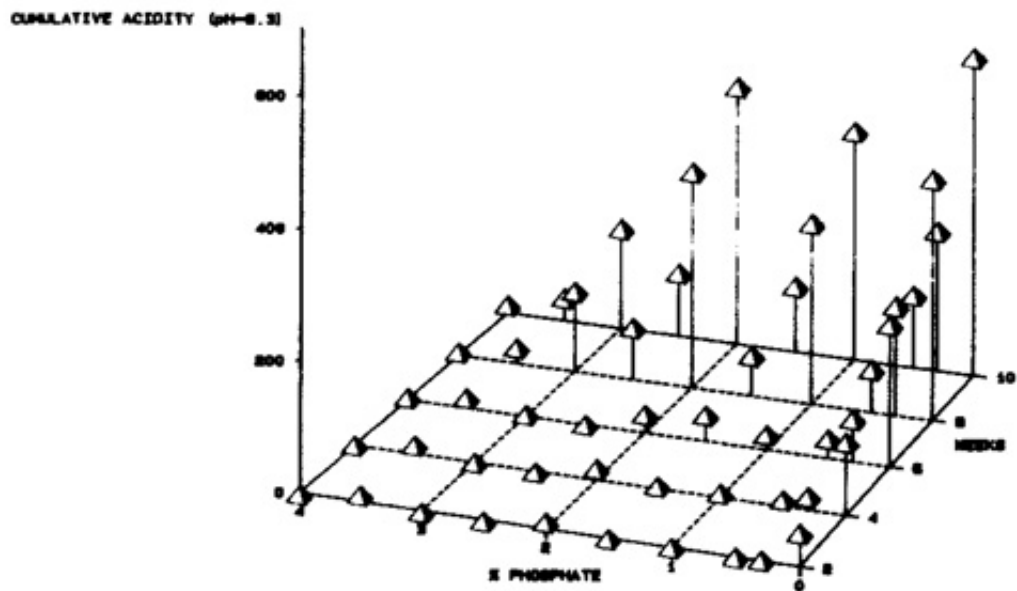


Figure 7.

Ameliorative effectiveness of Texas Gulf Waste Tailings (batch II) as it relates to weeks in the Soxhlet extractors and the percentage of material added to the toxic waste refuse material.

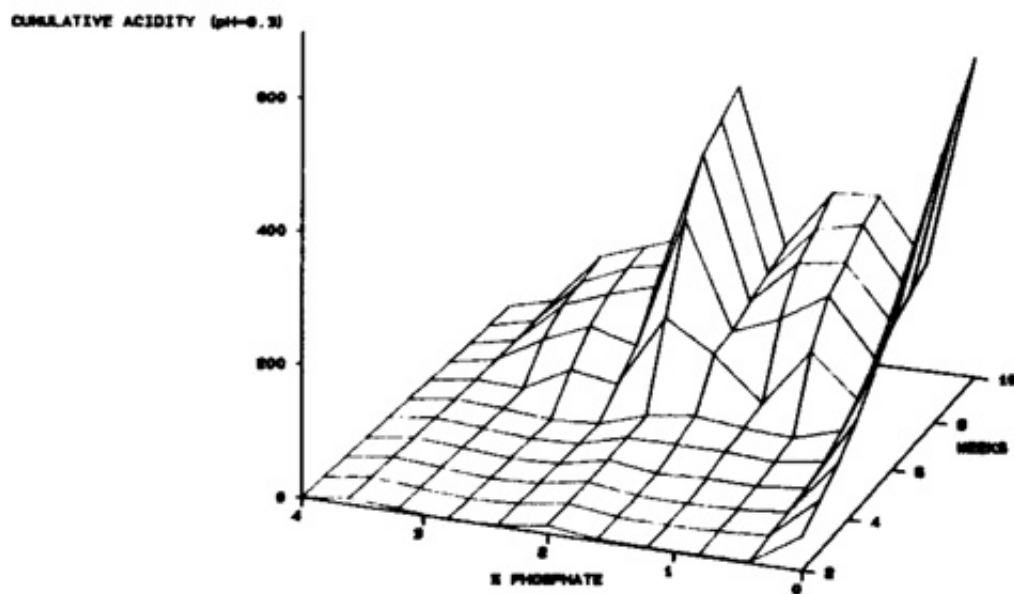


Figure 8

Gridded version from Figure 7 data to show contour relationships between ameliorative effectiveness of Texas Gulf Waste Tailings (batch II) with respect to weeks and application rate.

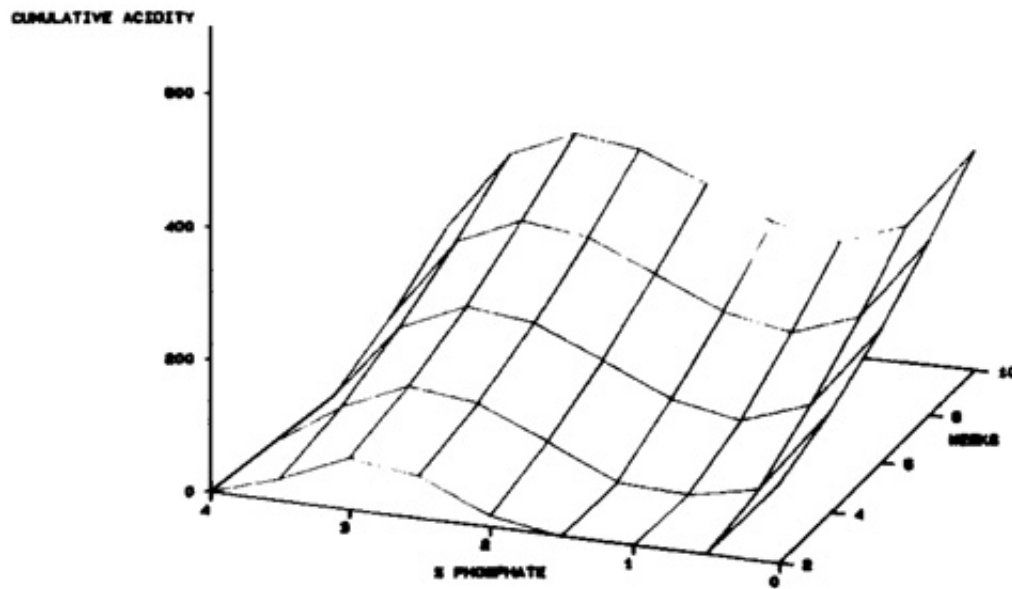


Figure 9.

Functionalized 3-dimensional relationship between ameliorative effectiveness of Texas Gulf Waste Tailings (Batch II) with respect to weeks and phosphate application rate. The function is that given by equation 3.

Manipulation of the three deterministic equations relating the cumulative acidity (for each phosphate type) yields information not obvious from the graphical representations of Figures 1 through 9. The deterministic equation for each Phosphate type is given below:

Code 31:

$$A_{31} = -0.0095 \times t^3 + 0.065 \times t^2 + 33.26 \times t - 13.24 \times p^3 + 104.77 \times p^2 - 261.27 p + 206.26 (1/t) \quad (1)$$

Waste Phosphate Batch I:

$$A_1 = -0.10 \times t^3 + 3.49 \times t^2 - 136.60 \times p^3 + 207.48 \times p^2 - 273.39 p + 102.32 e^{-p} \quad (2)$$

Waste Phosphate Batch II:

$$A_2 = 0.21 \times t^3 - 0.65 \times p^3 - 11.20 p + 98.67 (1/p) \quad (3)$$

where:

- A_i = cumulative acidity for phosphate material, i
- p = phosphate application rate (parts/100 parts overburden)
- t = weeks in soxhlet reactor simulator

A more general function can alternatively be developed using

$$A(r) = A_0 e^{-wr} \quad (4)$$

where:

$A(r)$ = the cumulative acid load as a function of application rate, r

r = application rate for phosphate addition

A_0 = the maximum potential acid load

w = constant

Economics of Phosphate Amelioration

The generation of functions to estimate the milligrams of calcium carbonate required to neutralize the Sulfate effluent from the soxhlets makes it Possible to compare the cost effectiveness of the Phosphate rock types based oil costs of materials and to estimate material costs on a field scale. The total materials cost associated with phosphate amelioration includes both the cost of the Phosphate rock and the cost of the neutralizing material. The phosphate is applied only once and thus represents an initial cost. Neutralizing material must be applied until the acid load is below some specified value which may be determined by regulation. The cost for each material at any time can be found by multiplying the amount of material used by the unit price of the material. Thus, the total cost at time t can be written

$$\$_{T,i} (p_i, t) = U_{p,i} p_i + U_B A_i (p_i, t) \quad (5)$$

where $\$_{T,i}$ = Total cost (dollars)

$U_{p,i}$ = Unit price of phosphate i (dollars per gram)

p_i = Phosphate amount (grams per hundred grams
overburden)

U_B = Unit price of base neutralizer (dollars per
milligram)

A_i = Base neutralizer amount (milligrams)

This function for total cost is valid over the same range as A_i , but extrapolation is only as good as the function used to fit the curve.

With Equation 5, costs can be generated for an infinite number of combinations of phosphate types, phosphate application rates, and times. Therefore, a time, t_0 , which produces a fair comparison among phosphate types must be used. Since the maximum allowable acidity may vary in different areas, the time it takes for a system to approach any such value may be of limited general interest, and it is useful to find a less arbitrary time period. Unameliorated systems will eventually approach a non-zero, but nearly constant level of acid production. Any useful ameliorant should stabilize the system long before this time is reached. The appropriate time is found when the change in A_i with respect to time is very small, or

$$d A / d t |_{p=0} \implies 0 \quad (6)$$

Note that the "i" subscript is unnecessary since zero percent phosphate is the control for all cases. For practical purposes the time, t_0 , can be taken when the derivative function attains some predetermined tolerance, limit about zero. The derivatives can be calculated numerically from finite differences between values generated from the function $A (p=0, t)$.

With the value of t_0 determined, values of total cost, $\$_{T,i}$, can be generated for the various phosphate types at different application schedules. For each phosphate type, the total cost can be minimized with respect to percent phosphate applied by satisfying the following conditions:

$$d \$_{T,i} / d p_i |_{t=t_0} \implies 0 \quad (7)$$

$$d^2 \$_{T,i} / d p_i^2 |_{t=t_0} > 0 \quad (8)$$

This can be done numerically analogously to the acidity (A_i) derivative above. With the minimum total cost known for each phosphate type, the optimum choice among the three types is simply the low-cost option.

Determination of Long-Term System Stability

As mentioned above, good ameliorants should make cumulative acid load asymptotic with time without much fluctuation or variability. Laboratory soxhlet testing is an excellent predictor of acid producing potential for the times corresponding to the actual times the soxhlets were run (Renton 1988). Extrapolation is not difficult since the systems are well-behaved and stabilize quickly. For ameliorated systems, behavior of the system depends on the type of ameliorant. Some materials tested as ameliorants have actually had an accelerant effect on acid production (McConaghy 1985). As indicated above, the waste phosphates tested here are not pure apatite, and other components present may diminish effectiveness. Accelerants increase acid production and might be expected to delay or inhibit stabilization of the system since the change in acidity with time may not approach zero or a constant value. Exhibition of this behavior may indicate that all accelerant is present in the waste phosphate to a significant extent. At a minimum, it indicates that the system cannot be accurately predicted without a longer testing period. The apatite/calcite ratios shown in Tables 1 and 2 could demonstrate this.

The final result of the economic analysis can be seen in Figure 10. This shows the total cost of ameliorant (including treatment), the cost of water treatment chemicals, and the cost of phosphate ameliorant material. The vertical line indicates the optimum (minimized) total cost. In this case the phosphate application rate corresponds to 2.5 wt percent phosphate. The toxic rock in question contains 2% total sulfur and the graphical output corresponds to a mass of 200 million tons of this toxic material for which treatment is demanded.

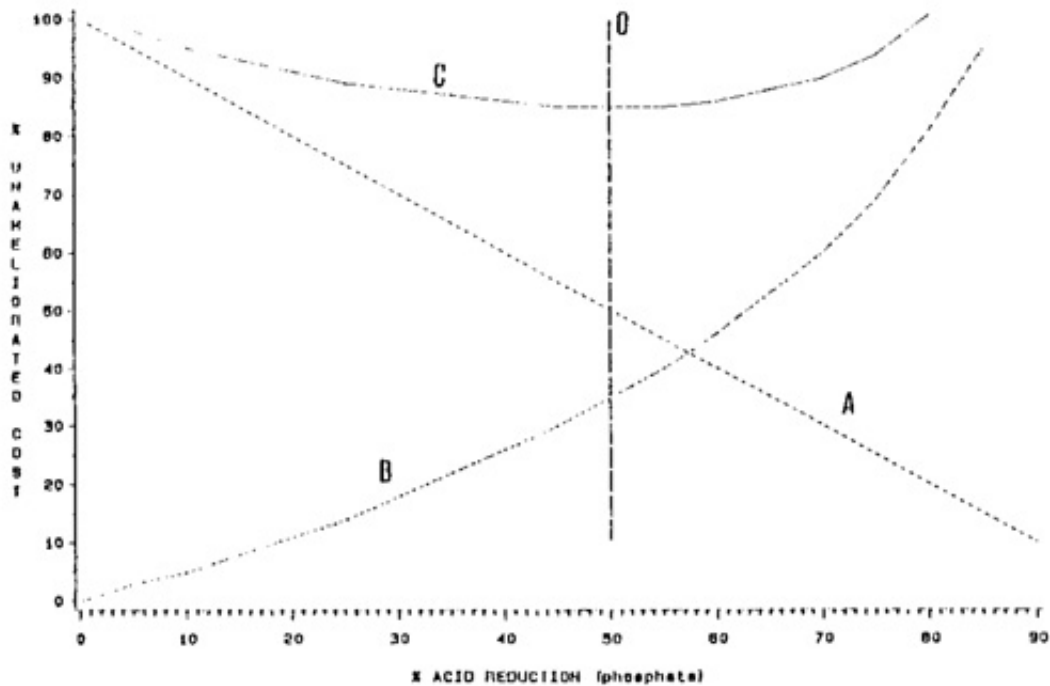


Figure 10.

Cost curves showing the total treatment cost using a combination of water effluent treatment and phosphate amelioration. Curve "A" represents the cost of effluent treatment using standard treatment chemicals (NaOH or CaO). Curve "B" represents the cost of phosphate amelioration material (Code 31). Curve "C" represents total cost of the combination phosphate amelioration material and effluent treatment chemicals. The line "O" represents the optimum level of phosphate treatment with respect to total cost. All costs are expressed as a percentage of the cost of water effluent treatment using phosphate amelioration.

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