FREE ACID IN SOIL MATERIALS EXPOSED BY EXCAVATION FOR HIGHWAYS IN EAST TEXAS

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Summary

Recurring failure of three applications of mulch sod on roadsides of Interstate 20 near Tyler, Texas led to a closer examination of soil material on the face of the cut slopes. The exposed materials on the slopes had pH values ranging from 2.5 to 4.0.[1/]

Material from the surface of the cut slope was more acid than underlying materials. A general positive relationship was found between sulfate content and degree of soil acidity. The acid condition is postulated to arise from the oxidation and hydrolysis of the iron sulfide compounds from in the original sediments. However, the detrimental effect on plants apparently is a result of the low pH which solubilizes iron and aluminum to toxic levels.

Studies are underway to overcome this undesirable soil condition and permit establishment and growth of plants for erosion control on roadsides where these materials occur.

[1/] Soil acidity was measured and lime (agricultural lime, $CaCO_3$) requirements were estimated using potentiometric titration. Lime applications ranging from 0.5 to 22.0 tons per acre were derived. Similar acid soil conditions varying only in degree were found to exist along IH-20 from Van eastward to the state line.

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Cut slopes along Interstate 20 North of Tyler, Texas were left susceptible to erosion when three individual applications of bermudagrass mulch sod grew briefly and then died. Routine soil analyses disclosed pH values as low as 1.8 for soil materials taken from bare areas on the faces of the cut slopes (Figure 1). This study was undertaken to determine the chemical and mineralogical nature of materials in several deep roadcuts in order to make recommendations for the successful establishment of a vegetative cover.

The material exposed by these roadcuts was tentatively identified geologically as the Weches formation (Claiborne Group), a marine and littoral Eocene deposit (4). The Weches formation is essentially a section of glauconite and glauconitic clay, characterized by beds of black and brown iron ore (10). The Queen City sands and Sparta sands, both continental and beach deposits, lie below and above the Weches formation, respectively. The Weches formation outcrops along the middle of the East Texas geosyncline as isolated hills, or along ridges and slopes on the stream divides (10).

The location selected for this study is the roadside along the north side of Interstate 20, four miles east of the interchange with U. S. Highway 69. The cut is fifty feet deep vertically, and the roadsides are finished to a 1:4 slope. The Sparta and Queen City formations are not exposed at this particular location. However, the exposed Weches formation shows a gradation toward coarser material in both the upper and lower areas of the cut. Several layers of ironstone are present, and a dark, carbonaceous deposit occurs in the lower middle portion of the cut. Several areas of pyrite (FeS_2) or chalcopyrite ($CuFeS_2$) are present in the lower middle portion of the cut. The cut contains no visible calcareous marine material.

The sediments exposed in the cut change gradually from a reddish, firm sandy clay loam in the upper area near the original land surface, to a dark olive green, very firm clay loam in the middle area, to a light gray, firable very fine sandy loam in the lower area. Most of the sediments at the exposed surface of the cut have weathered to a reddish orange color with dark mottles.

MATERIALS AND METHODS

Sample holes were dug at intervals of five vertical feet up the center of the slope. Samples of soil material were taken with a bucket auger in six-inch increments to a depth of five feet.

The soil pH was measured using a 1:1 or 1:2 mixture (W/V) of soil with normal potassium chloride (1N KCl). In addition, the amount of soil acidity was measured by the potentiometric titration method, which has been used by many persons working on problems in soil acidity (3, 6, 7, 8). For the potentiometric titration, the soil was mixed with 1N KCl (1:2), and the pH of this mixture was determined following the addition of regular increments of one-tenth normal sodium hydroxide (0.1N NaOH). Reaction time was sufficient to yield pH values which did not change appreciably with time. All samples were titrated to approximately pH 7 in this manner.

Sulfate was determined using a modified turbidimetric method of Chesnin and Yien (2).

In addition to the concerted work on a representative slope, a transect was run along IH-20 from Van,eastward to the state line, a distance of 100 miles. Twenty-six slopes along this route which were bare of vegetation were sampled. Measurements of pH and estimated lime requirements were determined for each sample.

RESULTS AND DISCUSSION

The problem of soil acidity is present along IH-20 from Van to the state line. All of the slopes sampled showed varying degrees of acidity ranging from pH 2.6 to 5.9. Only three slopes had a pH of 5.3 or higher. Estimated lime requirements ranged from 0.2 to as much as 22.8 tons per acre. A similar condition has been reported along IH-20 in Louisiana (1). The widespread occurrence of this acid condition suggests that other geologic formations may also be involved.

The materials in the cut slope selected for intensive study are very acid (Table 1). The degree of acidity is related to the type of exposed soil material. For example, exposed carbonaceous materials in the lower middle portion of the cut are more acid than the lighter colored soil materials at the upper and lower portion of the cut. The pH of surface samples, except where remnants of mulch sod were present, ranged from 2.5 to 4.0. These surface samples also required relatively large amounts of base to neutralize the acidity. Samples collected beneath the surface of the cut usually had a higher pH and required less base to neutralize acidity than did surface samples.

Plotting pH change per milliequivalent* (meq) of base added gives a potentiometric titration curve similar to the one shown in Figure 2. This titration measures the exchangeable soil acidity. The initial inflection point or break in the titration curve represents the point at which the titration of exchangeable H^+ and Fe^{3+} is completed and the titration of exchangeable Al^{3+} begins. The second inflection point in the titration curve represents the point at which the titration of exchangeable Al^{+3} is completed. Addition of base past this point to neutrality (pH 7) measures some of the non-exchangeable soil acidity, or that soil acidity due either to organic matter, or to hydroxy iron and aluminum compounds.

Those soil samples that required large amounts of base to neutralize them have large amounts of exchangeable H^+, Fe^{3+} and Al^{3+}. From the potentiometric titration curve, most of the exchangeable acidity present

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* One milliequivalent is the amount of acid or base (in milligrams) which contains or can supply one hydrogen or hydroxyl ion.

was due to Al^{3+}. Those soil samples that required lesser amounts of base to neutralize them showed little or no H^+ and Fe^{3+}, and very small amounts of Al^{3+}. The majority of soil samples contained enough exchangeable Al^{3+} to be detrimental to plant growth.

The lime (agricultural lime, $CaCO_3$) requirement of a soil can be estimated from the exchangeable acidity. Each meq of exchangeable acidity neutralized per 100 g of soil requires 1,000 pounds of lime neutralizing equivalence per acre plow layer[1/] (5). However, due to the lack of total reaction of lime in soils, and additional acidity that may develop with time, the lime requirement determined by titration should be multiplied by a factor of at least two. Applications of from one to twenty-two tons of lime were calculated as needed to neutralize the soil acidity present in the slope.

Sulfate content of the soil material in the slope was very high. A general relationship existed between sulfate contents and amounts of soil acidity.

Eight samples from the slope were oxidized by alternately wetting and drying them at room temperatures over a period of one month. The relationship of changes in acidity and sulfate content between oxidized and

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[1/] A layer of surface soil six inches thick and considered to weigh two million pounds.

non-oxidized soil samples is shown in Table 2. Meq/100 g of Fe^{3+}, H^+, Al^{3+} and acidity (exchangeable acidity) were determined from potentiometric titration curves.

This experiment was conducted several months after the samples were taken. The soil samples readily oxidize at room conditions, therefore the results are not an exact estimate of the change in acidity and sulfate content. However, a general relationship between these two factors still was evident.

Clay mineral analysis was conducted on four soil samples from sites up and down the slope. These samples contained approximately 50% kaolinite, 25% illite and 25% montmorillonite. Degree of clay mineral crystallinity was not noticeably affected by the acid conditions that existed in some of the soil samples used for analysis.

CONCLUSION

Based on the chemical and geological nature of the Weches formation as exposed in the roadcut used for this study, the following theory is proposed for the source and development of the acid conditions on this slope (9).

As the formation was deposited, sulfate-reducing bacteria, under anaerobic conditions and in the presence of sufficient organic matter for bacterial growth, reduced the sulfates of the transgressing sea. The reduced sulfur compounds later reacted with iron compounds in the soil, with the ultimate formation of iron sulfide (FeS_2). This process may have occurred in several formations in East Texas.

If no oxidation occurs the process stops with the formation of iron sulfides. Exposure to the atmosphere results in the oxidation of the iron sulfides and the formation of ferric sulfate and sulfuric acid. In the absence of calcareous material (marl), the sulfuric acid reacts strongly with the clay materials. This yields calcium sulfate, and Al^{+3} becomes the main exchangeable cation on the clay. Very low pH and high amounts of exchangeable acidity develop.

The process may be represented by the following chemical equations:

<u>Oxidation to sulfides to sulfates</u>

$$2\ FeS_2 + 2\ H_2O + 15\ O_2 \longrightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2SO_4$$

<u>Reaction of H_2SO_4 with clays</u>

$$CaSoil + H_2SO_4 \longrightarrow H_2Soil + CaSO_4$$

$$H_2Soil \xrightarrow{Time} Al_{2/3}Soil$$

The results obtained in this study substantiate this theory for the following reasons:

1. The presence of the carbonaceous area in the lower middle portion of the cut indicates that organic matter was present for

anaerobic bacterial growth and reducing conditions existed during deposition.

2. The presence of iron sulfide (pyrite) crystals in the formation indicate that reduction of sulfates in sea water occurred with the ultimate formation of these iron sulfide compounds.
3. The exposed surface of the cut has the lowest pH values and greatest amounts of exchangeable acidity.
4. Subsurface, unexposed samples have higher pH values and less exchangeable acidity, but on exposure to air lower pH values and higher amounts of exchangeable acidity develop.
5. Changes in sulfate content during the oxidation process indicate that the oxidation of sulfides to sulfates occurs with a corresponding increase in exchangeable soil acidity.

Measurement of soil pH gives an indication of the existence of the conditions previously discussed, but does not indicate the amount of soil acidity. Titration of the soil in 1N KCl with NaOH to neutrality gives an indication of the amount of soil acidity. From the amount of base used in the titration, an estimate of the lime requirement can be made.

Measures to overcome excessive acidity of roadside materials and permit establishment of vegetation are under study. The procedures involve neutralization of acidity by incorporation of lime or sealing the acid material from the applied mulch sod using asphalt or other barrier materials.

Addition of lime to neutralize soil acidity would result in the following chemical reactions:

$$CaCO_3 + 2H_2 \longrightarrow Ca(OH)_2 + H_2CO_3$$

$$Al_2Soil + Ca(OH)_2 \longrightarrow CaSoil + 2Al(OH)_3$$

Liming the soil would raise the soil pH to a level favorable for plant growth, and also change the toxic forms of aluminum and iron to non-toxic forms. This should permit the establishment of a protective cover of vegetation. However, the reserve of potential acidity probably indicates periodic applications of lime will be necessary to maintain the established plants.

Figure 1. The dark areas on the backslope are outcroppings of material too acid to support plant growth. Surface drainage on these slope faces kills vegetation to the bottom of the slope and reacts with lime in concrete to cause early deterioration of ditch liners.

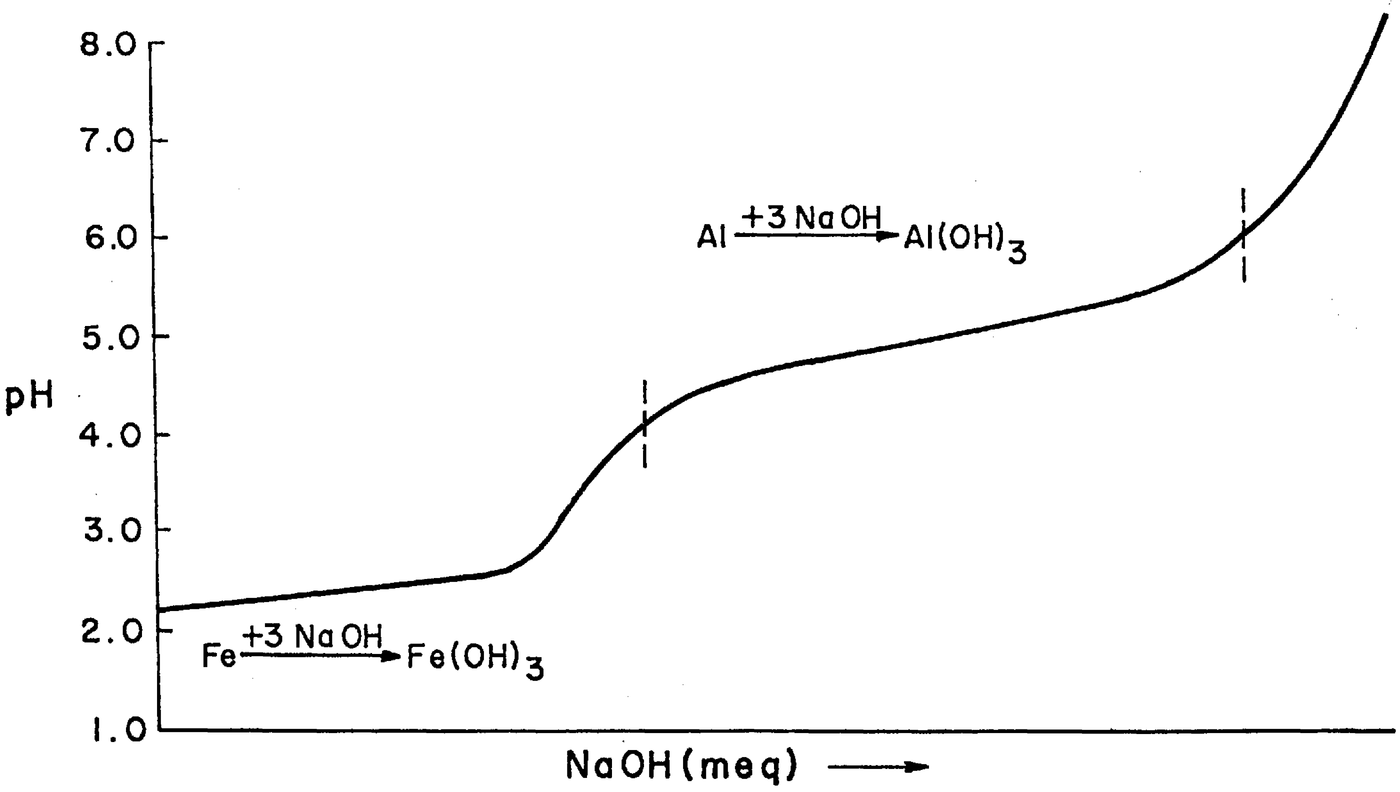

Figure 2. Generalized potentiometric titration curve for determining exchangeable acidity and lime requirements.

TABLE 1. Change in soil acidity with depth.

Position on slope	Depth (ft.)	Initial pH	Meq. NaOH/100 g to pH 7 (Line requirement Tons/Acre)
Upper	0.0 - 0.5	6.0*	0.5
	0.5 - 1.0	3.2	7.0
	1.0 - 2.0	3.7	8.0
	2.0 - 3.0	3.4	10.5
	3.0 - 4.0	3.6	10.0
	4.0 - 5.0	3.6	10.0
Middle	0.0 - 0.5	3.0	24.0
	0.5 - 1.0	3.6	20.0
	1.0 - 2.0	4.3	7.0
	2.0 - 3.0	4.1	7.5
	3.0 - 4.0	4.7	4.5
	4.0 - 5.0	4.5	4.0
Lower	0.0 - 0.5	2.6	8.0
	0.5 - 1.0	3.5	4.0
	1.0 - 2.0	3.7	2.0
	2.0 - 3.0	3.8	2.5
	3.0 - 4.0	3.9	2.0
	4.0 - 5.0	3.8	3.0

* Remnants of mulch sod.

TABLE 2. Change in sulfate content and soil acidity with time.

Position on slope	Treatment	Depth in.	pH	Fe^{3+} and H^+	Al^{3+}	Acidity	SO_4
				meq/100g			
Upper	None	6-12	3.2	2.7	2.3	5.0	0.03
	Oxidized	6-10	3.2	2.5	3.5	6.0	0.09
	None	48-54	3.7	1.2	5.3	6.5	3.12
	Oxidized	48-54	2.6	4.5	8.0	12.5	10.02
Lower	None	0-6	2.6	2.5	3.0	5.0	2.64
	Oxidized	0-6	2.7	4.0	4.4	8.4	3.99
	None	42-48	3.9	---	---	1.5	0.63
	Oxidized	42-48	2.9	1.5	2.0	3.5	3.51

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