

A COMPARISON OF RESULTS FROM ACID-BASE ACCOUNTING VERSUS POTENTIAL
ACIDITY MEASURED BY THE PEROXIDE OXIDATION OF WEATHERED AND
UNWEATHERED SOILS CONTAINING PYRITE¹

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ABSTRACT

Ammons, J. T. (1) and Shelton P. A. (2). ((1) University of Tennessee, Knoxville (2) Southern Illinois University at Carbondale). Fifty samples from weathered disposal area soils and forty-nine samples from unweathered overburden cores were analyzed using two laboratory methods to assess potential acidity. Total sulfur values (percent) were compared with potential acidity values by hydrogen peroxide oxidation (meqH⁺/100g). The percent total sulfur values for the unweathered samples (cores) ranged from 0.006 to 1.32 percent. Potential acidity by hydrogen peroxide oxidation ranged from 3.05 to 67.98 meqH⁺/100g. Total sulfur values for disposal area soil (weathered) ranged from 0.008 to 0.920 percent. Hydrogen peroxide oxidation values ranged from 0. to 52.34 meqH⁺/100g in the weathered disposal area soils. The coefficient of determination (r^2) comparing the two methods is 0.89 for the unweathered samples and 0.71 for the weathered samples. There is a positive correlation between the two methods for the unweathered (fresh) core samples. This relationship is less pronounced for weathered samples from the surface of the disposal areas.

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INTRODUCTION

Laboratory procedures to assess potential acidity problems prior to mining or before major construction have been used in overburden analyses studies by many

investigators (West Virginia University 1971, Smith et al. 1974; Smith et al. 1976; Ammons et al. 1983). These laboratory techniques allow for postmining landuse and post construction landuse planning and decision-making.

Two laboratory procedures have been historically used to estimate the levels of acid-producing materials resulting from mining and construction activities. These procedures are acid-based accounting and determination of potential acidity by peroxide oxidation (Smith et al. 1974). In this study, samples were analyzed to compare these procedures over a wide range of total sulfur values. The samples were selected from fresh overburden cores and disposal areas along the divide section of the Tennessee Tombigbee Waterway in Tishomingo County, MS.

In 1971, West Virginia University compared these procedures using fresh overburden rock samples from surface mines and found a high correlation between the two tests. The same comparison was conducted on old minesoil samples and no consistent relationship was found between the two tests (WVU 1971).

During the excavation of the divide section of the Tennessee Tombigbee Waterway pyritic spoil material was excavated and deposited in the disposal areas. The lower part of the Eutaw formation (Cretaceous) contained lenses of pyrite concentrated in sandy nodules (Ammons et al. 1983).

Corps of Engineers personnel used the peroxide oxidation procedure onsite to access potential acidity of waterway slope soils and requested a comparison of acid-base accounting (as estimated from total sulfur) and the peroxide oxidation procedure (WVU 1971). Although acid-base accounting is less time consuming laboratory facilities are not always available to complete this procedure. This was the impetus to conduct a comparison of the two methods.

MATERIALS AND METHODS

Forty-nine samples from fresh overburden cores (unweathered) and fifty samples of disposal area soils (weathered) were selected for this study. Sulfur values ranged from 0.006 percent to 1.328 percent, representing the range of sulfur values reported the divided section of the waterway.

Total sulfur analyses (as part of acid-base accounting) were completed on all samples using an Automatic Sulfur Analyzer. All samples were ground to 60 mesh for laboratory analyses as described by Sobek et al. (1978).

Potential acidity by hydrogen peroxide was completed according to Smith et al. (1974) except for the following modifications. Blanks were not used because the stabilizer present in the hydrogen peroxide

will not allow the peroxide to decompose upon heating if no sample is present to catalyze the decomposition. This would result in interference from the peroxide (a weak acid) during the titration. Additionally, the carbonates and sulfates were not removed from the samples prior to oxidation. Leaching the samples is a time-consuming process, so the hydrogen peroxide analyses were completed under the same conditions used by Corps of Engineers personnel in the field.

RESULTS AND DISCUSSION

The total sulfur, millequivalents hydrogen per 100 grams of material, and final acid-base account (tons/1000 tons material CaCO_3 equiv.) for overburden core samples are shown in the table 1. Sulfur values ranged from 0.006 to 1.328 percent. Table 2 shows sulfur values ranging from .008 to .920 percent on selected disposal area samples. Sulfur values rarely exceeded 1.0 percent on disposal area soils because of the intense chemical oxidizing environment at the surface immediately after placement.

The results of the comparison between total sulfur and potential acidity by hydrogen peroxide are illustrated in figures 1a-b. The results of the fresh cores samples (fig. 1b) show a significant correlation ($r^2=0.89$) between the two methods. Figure 1a shows the results of the two methods on weathered disposal area samples. The relationship is less pronounced ($r^2=0.71$), suggesting interference in the peroxide procedure from some weathering products (fig. 1a).

Figures 2a-b present the results of the peroxide procedure compared with acid-base accounting. Acid-base accounting is reported in calcium carbonate equivalent (tons/1000 tons material) and includes neutralization potential (amount of bases present).

Table 1.--Total sulfur, milliequivalents of hydrogen by peroxide oxidation, and acid-base account of samples from overburden cores, Tennessee-Tombigbee Waterway.

Sample Number	Percent Sulfur	Meq H ⁺ /100 G	Acid-Base Account CaCO ₃ Equivalent Tons/1,000 Tons Material
895-14	1.3280	67.98	-45.12
895A-11	1.2800	51.40	-23.11
897-22	1.2350	43.33	-57.75
895-23	1.0620	46.61	-24.19
897-21	1.0400	35.96	-43.04
897-34	0.8894	4.97	-28.25
897-36	0.8573	16.36	-16.08
895-26	0.7820	33.45	-21.37
894-30	0.7495	29.82	-24.65
894-5	0.7108	33.16	-25.17
897-51	0.6488	30.62	-30.13
894-33	0.5532	23.91	-19.75
894-19	0.5496	8.80	-22.35
897-23	0.5481	24.47	-23.14
897-41	0.5398	18.01	-24.96
895-35	0.5268	22.73	-19.67
894-6	0.5090	21.97	-22.81
897-20	0.4903	17.13	-18.62
896-42	0.4884	20.38	-15.95
895-38	0.4632	17.28	-12.26
894-14	0.4504	20.48	-14.08
894-38	0.4375	20.05	-17.12
894-34	0.4136	17.43	-14.65
894-44	0.4074	14.64	-14.45
894-3	0.3904	18.92	-13.58
894-36	0.3794	15.98	-8.32
896-34	0.3470	14.07	-11.97
897-13	0.3333	14.73	-9.29
895-10	0.3078	12.95	-10.85
897-47	0.2859	9.24	-8.47
895A-12	0.2749	10.68	-7.21
894-15	0.2623	9.54	-7.06
895A-9	0.2522	11.14	-6.18
894-28	0.2450	8.18	-5.99
895-28	0.2350	9.03	-5.47
896-40	0.2046	8.46	-7.04
897-42	0.1915	7.34	-7.76
897-12	0.1776	7.34	-5.05
895-10	0.1566	6.11	-5.39
897-10	0.1333	4.91	-4.32
895A-5	0.1330	5.74	-2.54
894-12	0.1131	3.88	-2.20
895A-8	0.1046	8.83	-2.99
895A-4	0.0917	4.17	-1.02
895A-13	0.0603	3.05	0.23
897-53	0.0517	7.34	0.40
897-17	0.0283	4.62	0.54
895-26	0.0121	3.14	0.72
896-23	0.0064		

Table--2. Total sulfur, milliequivalents of hydrogen by peroxide oxidation, and acid-base account of samples taken from overburden cores, Tennessee-Tombigbee Waterway.

Sample Number	Percent Sulfur	Meq H ⁺ /100 G	Acid-Base Account CaCO ₃ Equivalent Tons/1,000 Tons Material
1503-D2	0.9203	52.34	-37.07
501-W1	0.5772	0.00	20.47
1504-PIL2	0.5013	19.23	-22.59
1503-L3	0.4926	24.06	-17.03
1504-K1	0.4633	17.78	-26.94
501-04F5	0.4534	4.76	-13.76
1504-E2	0.4386	16.91	-23.40
1203-02	0.4362	16.40	-19.25
501-J1	0.4153	0.00	203.92
1503-PIL5	0.3786	24.61	-13.21
1503-A2	0.3671	17.28	-19.31
1504-PIL4	0.3390	16.87	-11.05
1704-PIL3	0.3016	12.58	-14.12
1503-PIL4	0.2462	9.28	-11.84
1204-L3	0.2240	9.98	-7.92
1503-PIL4	0.2218	15.27	-8.31
1204-Q1	0.2111	0.82	1.06
1205-05F74	0.1863	2.74	-6.58
1704-PIL1	0.1629	7.92	-11.19
1203-L2	0.1582	6.86	-6.35
1508-04F34	0.1410	1.01	10.76
1503-05F45	0.1345	0.00	23.77
1204-D2	0.1098	5.73	-2.38
1701-07F73	0.1091	0.52	14.45
1504-03F50	0.0999	6.47	-3.12
1503-F1	0.0943	4.13	-2.03
1203-F2	0.0920	7.18	-4.29
1504-B1	0.0889	4.76	-5.95
1504-B2	0.0803	6.08	-4.44
1203-F1	0.0797	0.00	24.27
1203-M1	0.0722	1.37	-1.56
1204-B1	0.0684	0.00	21.11
1203-D1	0.0633	0.00	16.56
1204-L1	0.0597	1.99	0.57
1204-A2	0.0565	3.85	-1.92
1203-B1	0.0503	0.00	14.86
1203-G1	0.0492	0.00	14.86
1203-E1	0.0474	0.16	2.74
501-C1	0.0411	4.03	-1.75
501-E1	0.0373	0.00	9.37
501-E2	0.0350	0.67	-0.85
501-E3	0.0337	1.76	-0.35
1204-SW	0.0318	0.00	3.14
1303-07F86	0.0289	0.00	19.35
1504-Q1	0.0262	2.81	-2.39
1504-L1	0.0210	6.94	-0.20
1501-05F82	0.0194	0.00	11.54
602A-04F2	0.0152	1.01	0.46
1304-SW	0.0102	0.00	1.47
1302A-02F25	0.0078	0.00	1.07

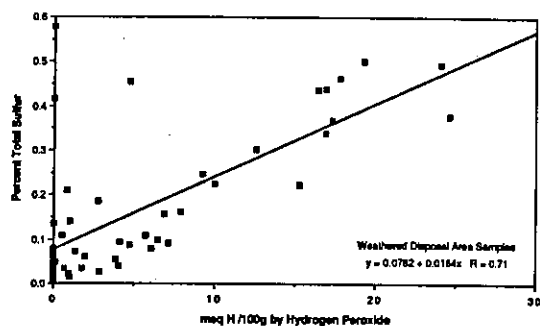


Figure 1a. Weathered disposal area samples.

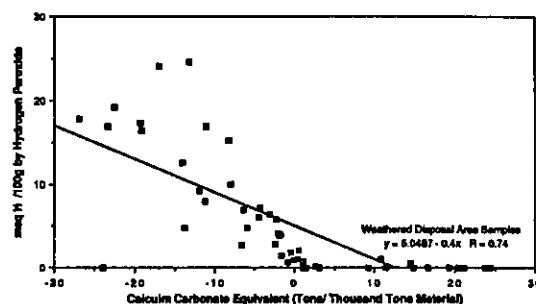


Figure 2a. Weathered disposal area samples.

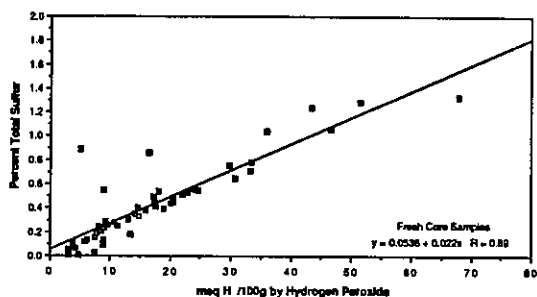


Figure 1b. Fresh core samples.

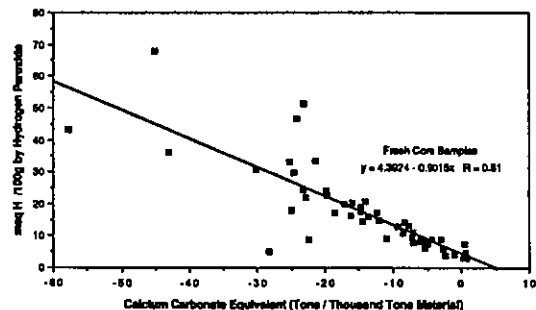


Figure 2b. Fresh core samples.

Figures 1a-b. Comparison of total sulfur (auto analyzer) and potential acidity on weathered disposal area samples and fresh core samples on the divide section - Tennessee-Tombigbee Waterway.

Figure 2a-b. Comparison of potential acidity and calcium carbonate equivalent on weathered disposal area samples and fresh core samples on the divide section - Tennessee-Tombigbee Waterway.

Results from the comparison of the acid-base accounting on the fresh core samples are illustrated in figure 2b. There is high correlation between these methods ($r^2=0.81$). However, the same comparison on weathered disposal area soils shows a poor relationship between the two methods ($r^2=0.42$). Again, this suggests that weathering products may be interfering with the peroxide procedure.

CONCLUSIONS

A strong relationship exists between results obtained using peroxide oxidation and total sulfur by autoanalyzer for unweathered overburden core samples. This relationship was less pronounced on samples that have weathered following placement in disposal areas. Previous research has shown that in material that has been weathering for long periods of time, no relationship exists between the peroxide procedure and total sulfur by autoanalyzer (WVU 1971). When pyrite begins to weather in disturbed soil, various weathering products evolve. These weathering products interfere with the peroxide procedure for potential acidity in soil.

It was not within the scope of this study to examine the sources of error in the peroxide oxidation procedures; however, future research could be directed toward identification of the interfering compounds and development of methods to reduce or eliminate these interferences. Based on the peroxide procedure be limited to fresh, unweathered samples.

LITERATURE CITED

West Virginia University, 1971. Mine spoil potentials for water quality and controlled erosion. Water Pollution Control Research Series. 14010 ESE 12/71 US-EPA. Washington, DC, pp.206.

Smith, R. M., W. E. Grube, Jr., T. Arkle, A. Sobek, 1974. Mine spoil potentials for soil and water quality. EPA-670-12-74-070. US-EPA. Cincinnati, OH, pp.303.

Smith, R. M., A. Sobek, T. Arkle, Jr., J. C. Sencidiver, 1976. Extensive overburden potentials for soil and water quality-EPA-600/2-76-184. US-EPA, Cincinnati, OH, pp. 311.

Ammons, J. T., P. A. Shelton, and G. G. Davis, 1983. A detailed study of five overburden cores and six disposal areas along the divide section of the Tennessee-Tombigbee Waterway. U.S. Army Corps of Engineers, Nashville District, Nashville, TN. pp. 352.

Sobek, A., W. Schuller, J. Freeman and R. Smith. 1978. Field and Laboratory methods applicable to overburdens and minesoils. EPA-600/2-78-OS4. US-EPA, Cincinnati, OH, pp. 204.

