

## MODIFIED NP TESTING FOR LIGNITE OVERBURDEN SAMPLES IN TEXAS

by

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**Abstract.** Neutralization potential (NP) measures easily weatherable minerals, including carbonates, present in an overburden. Siderite ( $\text{FeCO}_3$ ) is present in Texas overburden and can cause false positive NP values when present and result in acid drainage and long-term reclamation problems. The effects of  $\text{KMnO}_4$ ,  $\text{K}_2\text{S}_2\text{O}_8$ , and  $\text{H}_2\text{O}_2$  on the neutralization potentials of mixed overburden samples from Texas lignite mines were examined. Neutralization potential was determined on the samples before and after the addition of the oxidizing agents using EPA method 600 / 2-78-054 3.2.3. Addition of the oxidizing agents significantly reduced the NP of samples containing.

Additional Key Words: siderite, acid base account

### Introduction

Texas has 21.2 billion metric tons of near-surface lignite resources (Doolittle, 1991). The lignite formations in Texas are overlaid by the Claypan and East Texas Timberlands land resource areas. Due to the nature of the native soils existing over near surface lignite resources in Texas, present reclamation procedures allow for the use of mixed overburden as a topsoil substitute. Mixed overburden materials in east Texas generally have a moderate pH and a high base status making them more suitable for plant growth than native soils (Senkayi et al., 1988). The mixing of overburden and subsequent reclamation produces soils that possess superior physical and chemical properties compared to native soils (Doolittle et. al., 1992).

Selected overburden may be used to replace topsoil if it is determined that the overburden is of equal or better quality than the original topsoil and is the best available material to support revegetation. Determination of a suitable topsoil substitute is based on chemical and physical analyses of the overburden and topsoil. Care must be taken to prevent undesirable chemical effects (i.e. acid drainage) due to the oxidation of acid-forming materials (AFM), which are commonly found in association with lignite seams. To assess residual soil acidity and the possibility of acid drainage, the acid-base account (ABA) for overburden samples is determined using Eq. (1) where NP is the neutralization potential, PA is the potential acidity, and EA is the exchangeable acidity.

$$\text{ABA} = \text{NP} - (\text{PA} + \text{EA}) \quad (1)$$

When the ABA is positive, the acidity produced by the soil constituents is predicted to be neutralized. If the ABA is negative, the overburden may produce residual acidity and should be buried more than 4 feet below the surface or, if necessary, may be treated to neutralize acidity to prevent formation of acid soils.

Neutralization potential measures the amount of easily weatherable minerals, including carbonates, present in an overburden by treating the sample with a known amount of hydrochloric acid as described by Sobek et al. (1978). The sample and the acid are heated to ensure that reaction between bases and acids goes to completion. The NP of the sample is obtained by determining the amount of acid neutralized by titrating excess acid with standardized NaOH.

Siderite ( $\text{FeCO}_3$ ) is present in Texas overburden and can cause interference in NP testing methodology when present in overburden samples. Under acidic testing conditions,  $\text{FeCO}_3$  reacts to neutralize acid, which contributes to the NP. However, continued weathering of  $\text{FeCO}_3$  produces a neutral to slightly acidic solution. Doolittle et al. (1992) concluded that  $\text{FeCO}_3$  affected NP because the  $\text{Fe}^{2+}$  did not undergo complete oxidation and hydrolysis.

We studied the effects of the oxidants;  $\text{KMnO}_4$ ,  $\text{K}_2\text{S}_2\text{O}_8$ , and  $\text{H}_2\text{O}_2$ , and pH adjustment on the neutralization potentials of mixed overburden samples containing  $\text{FeCO}_3$ . Our objective was to evaluate how  $\text{KMnO}_4$ ,  $\text{K}_2\text{S}_2\text{O}_8$ , and  $\text{H}_2\text{O}_2$  affected the measured NP of overburden samples.

## Materials and Methods

Twenty-two overburden samples were selected based on NP values determined by the method outlined by Sobek et al. (1978). The samples selected had high NP values and a fizz rating of "none". If the sample showed no effervescence upon addition of HCl and had a high NP, there was high probability of the presence of FeCO<sub>3</sub>. Samples were previously ground to pass through a 60-mesh sieve (<2mm). An additional bulk sample of overburden and a representative sample of FeCO<sub>3</sub> rock was obtained and ground to pass a 250 μm sieve. The ground FeCO<sub>3</sub> was added to the bulk sample so that composite samples contained 2.50%, 5.00%, and 10.00% FeCO<sub>3</sub> by weight. The NP was determined on the samples before and after the addition of KMnO<sub>4</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and H<sub>2</sub>O<sub>2</sub> using EPA method 600 / 2-78-054 3.2.3 (Sobek et. al., 1978). All samples were digested with 0.5 N HCl and filtered before oxidation treatments.

**KMnO<sub>4</sub> oxidation.** Potassium permanganate (KMnO<sub>4</sub>) was added to the filtrate until a pink color formed, indicating an excess of KMnO<sub>4</sub>. Samples were then titrated with NaOH to pH 7.

**H<sub>2</sub>O<sub>2</sub> oxidation.** 7 – 8 ml. of 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was added to the filtrate then boiled for 5 and 15 minutes. Samples were titrated to pH 7 with NaOH.

**K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> oxidation.** 0.5 g. of potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) was added to the filtrate. Samples were gently boiled for 1 hour before titration with NaOH to pH 7.

## Results and Discussion

Treatment of samples containing FeCO<sub>3</sub> with oxidizing agents reduced NP values proportionate to the amount of acidity produced by the oxidation and hydrolysis of Fe<sup>2+</sup>. The data in Fig. 1 show a strong correlation between theoretical NP values for 2.5%, 5.0%, and 10% siderite obtained by stoichiometry and experimental NP values. The reaction of Fe<sup>2+</sup> with KMnO<sub>4</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and H<sub>2</sub>O<sub>2</sub>, will produce 1.4, 3, and 2 moles H<sup>+</sup>, respectively. The amount of acidity produced from oxidation and hydrolysis of Fe by each oxidant must be taken into account when calculating NP (tons of CaCO<sub>3</sub>/1000 tons of material).

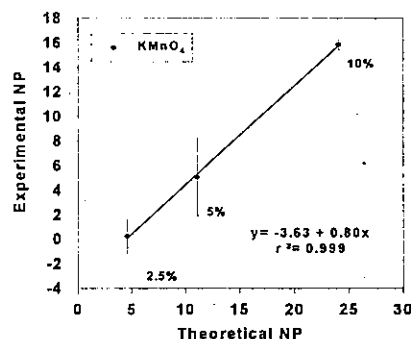


Figure 1. Neutralization potential: theoretical vs experimental.

Skousen et al. (1997) found that the addition of H<sub>2</sub>O<sub>2</sub> decreased the NP of the overburden samples. However, the NP values we obtained when using H<sub>2</sub>O<sub>2</sub> were highly variable, apparently due to incomplete removal of H<sub>2</sub>O<sub>2</sub> during boiling.

## Literature Cited

- Doolittle, J.J., N.M. Frisbee, and L.R. Hossner. 1992. Evaluation of acid-base accounting techniques used in surface-mine reclamation, In Proc. 1992 Meeting of the American Society for Surface Mining and Reclamation, Duluth, Minnesota, June 14-18. <https://doi.org/10.21000/JASMR92010068>
- Doolittle, J. J. 1991. The Kinetics of Iron Sulfide Oxidation in Lignite Overburden as Influenced by Calcium Carbonate. M.S. thesis. Texas A&M University, College Station.
- Senkayi, A.L. and J.B. Dixon. 1988. Mineralogical Consideration in Reclamation of Surface-Mined Lands p.105- 124. In Hossner, L.R. (ed.) Reclamation of Surface Mined Lands, Vol. 1. CRC Press, Inc. Boca Raton, FL.
- Skousen, J.J. Renton, H. Brown, P. Evans, B. Leavitt, K. Brady, L. Cohen, and P. Ziemkiewicz. 1997. Neutralization potential of overburden samples containing siderite. Journal of Environmental Quality, 26(3):673-681. <https://doi.org/10.2134/jeq1997.00472425002600030012x>
- Sobek, A.A., W.A. Schuller, J.R. Freeman, and R.M. Smith. 1978. Field and laboratory methods applicable to overburdens and minesoils. Industrial Environmental Research Laboratory. Office of Research and Development. U. S. Environmental Protection Agency. EPA-600/2-78-054. Cincinnati, OH.