EVALUATION OF ACID/BASE ACCOUNTING TECHNIQUES USED IN SURFACE-MINE RECLAMATION[1]

by

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Abstract. Surface mine reclamation laws in Texas permit the use of mixed overburden as a topsoil substitute. Overburden material must have a positive acid/base account (AB_a) to remain within 4 feet of the reclaimed surface. Acid/base account is calculated by subtracting potential acidity (PA) plus exchangeable acidity (EA) from the inherent acid neutralization potential (NP) of the material. Material with a negative AB_a may be limed to increase the AB_a value. Two separate research studies were conducted to determine 1) the effects of siderite ($FeCO_3$), a frequently identified mineral in mixed overburden, on NP determination and 2) the long-term pH stability of potentially acidic mixed overburden limed to an AB_a of zero. Siderite stoichiometrically weathers to produce acidity upon complete oxidation and hydrolysis of released ferrous iron. Siderite contributes to NP because of incomplete iron hydrolysis under the conditions used to determine NP in the laboratory. This "siderite error" can lead to a false positive AB_a value when the current NP procedures are used on samples containing significant quantities of PA and siderite. The long-term pH stability of potentially acidic mixed overburden limed with $CaCO_3$ was evaluated using a simulated weathering study. The liming rates ranged from 0 to 125% of the theoretical amount of lime needed to neutralize the measured AB_a deficit. The data showed the addition of $CaCO_3$ significantly slowed the oxidation of FeS_2; however, the dissolution of the applied lime proceeded at a steady rate with each percolating water front. The dissolution of applied lime was measured to be significantly faster than the release of PA in all treatments, thus the AB_a values of all the treatments were found to decrease with time. Treatments which received less than a 50% lime rate became highly acidic within one year. The results indicate that all treatments would eventually become highly acidic.

Additional Key Words: Acid/Base Accounting, Neutralization Potential, Liming, Calcite ($CaCO_3$), Siderite ($FeCO_3$), Pyrite (FeS_2), Iron Sulfide

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Introduction

The native soils associated with near-surface (< 60 m) lignite deposits in Texas generally have very poor chemical and physical properties; therefore, the practice of removing and replacing soil horizons is impractical. Successful surface mine reclamation has been achieved by using mixed overburden as a topsoil substitute. Mixed overburden forms minesoils that have better chemical and physical properties than pre-mine soils (Dixon et al., 1982; Bearden, 1984). When properly managed these minesoils are capable of supporting crop production (Hons et al., 1978). However, some overburden materials have potential acidity (PA) and can become acidic and produce acid drainage after exposure to atmospheric conditions. The main source of this acidity is the oxidation of acid forming materials (AFM). Pyrite (cubic FeS_2) is the major AFM in Texas lignite and associated overburden; however, marcasite (orthorhombic FeS_2) has also been identified (Arora et al., 1978).

The Railroad Commission of Texas (RCT), the state agency which regulates mining and reclamation, allows mixed overburden to form the top four feet of a reclaimed surface if it meets certain criteria. Among the RCT guidelines are requirements that topsoil substitute material 1) have a stable pH between 5.0 and 8.4 and 2) be free of AFM or have an acid/base account (AB_a) of greater than or equal to zero (Railroad Commission of Texas, 1989). The acid/base account of an overburden material is calculated using Eq. [1] where NP is the analytically measured neutralization potential (Sobek et al., 1978), PA is oxadizable FeS_2 (ASTM, 1968; O'Shay et al., 1990), and EA is exchangeable acidity (Thomas, 1982).

$$AB_a = NP - (PA + EA) \qquad [1]$$

Equation [2] is a second equation used by the RCT to asses the acid/base status of an overburden material.

$$AB_b = (CaCO_3 + 0.2CEC) - (PA + EA) \qquad [2]$$

This equation is often referred to as the acid/base balance (AB_b) or reference equation (Askenasy and Severson, 1988). The parameters in this equation are similar to the AB_a equation, except NP is estimated from an overburden's inorganic carbonate content expressed as calcium carbonate equivalence ($CaCO_3$) and cation exchange capacity (CEC). Reclamation guidelines of the RCT allow the acid/base status of a topsoil substitute to be increased through the incorporation of lime.
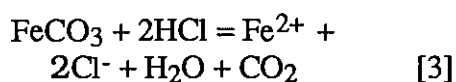
The developmental theory of acid/base accounting is that the pH of minesoil and mine drainage can be predicted based on the PA plus EA and NP of an overburden. If the NP is greater than the PA plus EA, then all acidity released by the overburden would be neutralized. If the PA plus EA is greater than the NP, then acid minesoil and drainage will form. Two assumptions in this theory are; 1) the analytically measured NP and PA will be released under natural weathering conditions and 2) the oxidation of FeS_2 and the dissolution of acid neutralizing material will be simultaneous and at equivalent rates.

Separate research studies were conducted to determine 1) the effects of siderite ($FeCO_3$), a frequently identified mineral in Texas lignite overburden (Dixon et al., 1982; Durham, 1982; Arora et al., 1984), on the measurement of NP and 2) the long-term pH stability of liming a potentially acidic overburden material ($AB < 0$) to an AB_a of zero.
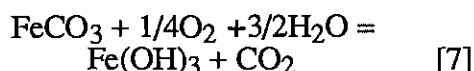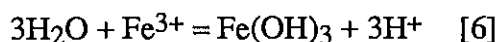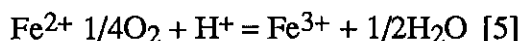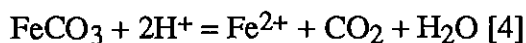
Effects of Siderite on NP Determination

Neutralization potential is the amount of neutralizing bases, including carbonates, contained in an overburden (Sobek et al., 1978). To determine NP for the AB_a equation, the method described in Sobek et al. (1978) is used in Texas. The

overburden sample is treated with acid and heated. This is followed by titration of the excess acid with standard base. Neutralization potential is calculated from the amount of acid consumed by the overburden. Siderite present in an overburden sample can interfere with the determination of NP. The NP measured will be in error due to the neutralization of the acid by siderite:

$$FeCO_3 + 2HCl = Fe^{2+} +$$
$$2Cl^- + H_2O + CO_2 \quad [3]$$

Siderite forms in reducing environments of swamps and basins (Senkayi et al., 1986). Pure siderite weathers to form goethite and FeOOH (Dixon et al., 1982). Also formed are amorphous Fe hydroxides, $Fe(OH)_3$ (Postma., 1983) and hematite, Fe_2O_3 (Seguin, 1966). Siderite weathers under oxidizing conditions according to the following equations (Lindsay, 1979):

$$FeCO_3 + 2H^+ = Fe^{2+} + CO_2 + H_2O \; [4]$$
$$Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2H_2O \; [5]$$
$$\underline{3H_2O + Fe^{3+} = Fe(OH)_3 + 3H^+ \quad [6]}$$

$$FeCO_3 + 1/4O_2 + 3/2H_2O =$$
$$Fe(OH)_3 + CO_2 \quad [7]$$

When the hydrolysis of Fe^{3+} (Eq. [6]) is complete, the net reaction of siderite weathering is acidic. Postma (1983) found the pH of oxidized siderite sediments ranged from 3.5 to 5.5, with an average of 4.5. Seguin (1966) found that the weathering of pure siderite exposed to the atmosphere is a slow process. At room temperature, siderite with a grain size of 48 μm (300 mesh) would take approximately 35 years to dissociate when exposed to the atmosphere. Seguin (1966) also found that siderite dissociation is inhibited by a thin layer of hematite that forms on the crystal surface. Even though the natural dissociation of pure siderite is a slow process, siderite will weather rapidly if exposed to the aqueous and

acidic conditions used in the laboratory to determine NP.

Materials and Methods

The effect of siderite on the NP value used in the AB_a equation was determined. An array of 2 g samples containing overburden with various siderite concentrations was created. Various amounts of siderite (crushed finer than 53 μm or 200 mesh) were added to a base overburden material to obtain 1, 3, 5, and 10 % (w/w) concentrations of siderite. Each sample was analyzed for NP according to the method of Sobek et al. (1978) using two different acid strengths and two different heat treatments. The acid concentrations used were 0.1 M and 0.5 M HCL. The heat treatments were 1) heating on a hotplate just below boiling until any visible signs of reaction had stopped, then boiling for 1 minute, and then cooling to room temperature while covered and 2) sitting at room temperature for 2 hours. Each sample-acid-heat treatment combination was replicated 3 times. All samples were titrated with 0.1 or 0.5 N NaOH to pH 7.0 using an automatic, potentiometric titrator equipped with an automatic sampler.

Results and Discussion

Siderite influenced the NP of the overburden material used (Fig. 1). Both the heated and room temperature treatments showed a significant increase ($\alpha = 0.5$) in NP with increasing amounts of siderite. The r^2 value for the model NP = %Siderite is 0.995. Therefore, 99.5% of the increase in NP is accounted for by the increase in siderite concentration. The heated treatments showed the same trend as the room temperature treatments, but the heated treatments had a significantly higher magnitude. The 0.5 M HCl treatments (both heated and room temperature) were significantly higher than the 0.1 M HCl treatments. During the titrations, an Fe oxide precipitated. The siderite acted as a base by increasing NP
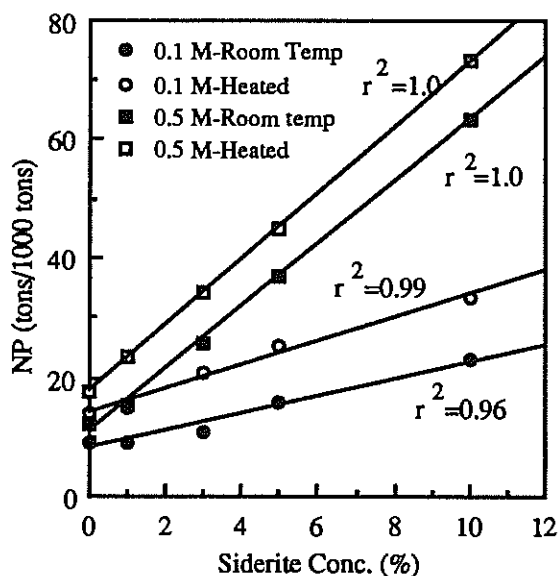
Figure 1. Neutralization potential of an overburden material with increasing amounts of added siderite.

because the Fe^{3+} did not undergo complete hydrolysis (Eq. [6]).

Conclusions

Increasing the percentage of siderite in an overburden material increased the measured NP. This indicates that siderite inflates the NP of an overburden when the current methodology is used. This siderite error can lead to false positive AB_a value when this procedure is used on samples which contain significant quantities of AFM and siderite.

Long-Term pH Stability of Limed Overburden

The long-term pH stability of two potentially acidic overburdens limed with $CaCO_3$ were evaluated using a simulated weathering study.

Materials and Methods

Newly exposed lignite overburden was collected from two strata at an active highwall in Rusk County, Texas. The two materials were lyophilized, crushed to pass a 0.25 mm sieve and characterized (Table 1). Each of the overburdens were divided into six treatments. The treatments were based on the amount of lime (reagent grade $CaCO_3$, $< 53\mu m$) required to theoretically raise the AB_a of the material to 0. The liming rates ranged from 0 to 125% of the measured AB_a deficit (Table 2). The overburden treatments were mixed with 33% sand by weight and packed into polyethylene bottles with holes in the bottom to facilitate drainage. All treatments were inoculated with an active culture of *Thiobacillus ferrooxidans* and stored in an incubation chamber maintained at 30 °C and approximately 100% relative humidity. The treatments were leached with 20 mm of deionized water at 7 day intervals for a total period of 378 days. The rate of FeS_2 oxidation and $CaCO_3$ dissolution were measured during this time period (data not shown) and changes in AB_a and AB_b values were evaluated at the end.

Results and Discussion

The rate of FeS_2 oxidation was found to be source dependent and increase significantly when overburden pH decreased below 4. The addition of $CaCO_3$ increased overburden pH above 7 and significantly decreased FeS_2 oxidation. The dissolution of applied $CaCO_3$, however, was found to be relatively constant and faster than the oxidation of FeS_2 at pH values above 4 (Doolittle, 1991). The added $CaCO_3$ gradually dissolved from the limed treatments with each percolating water front while the FeS_2 remained relatively stable. As the last amounts of lime dissolved from the treatments which received less than 50% AB_a, the pH decreased below 4 and FeS_2 oxidation rapidly increased generating acid drainage (Figs. 2 and 3). The drainage pH from the 50% AB_a treatment of overburden B began to gradually decrease after 200 days. All the other overburden which received 50% AB_a and greater lime treatments maintained a neutral to alkaline pH throughout the study; however, the

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Table 1. Acid/base characteristics of overburden.

Characteristic	Overburden A	Overburden B
FeS_2, %	1.87	4.14
FeS_2 Species	Pyrite/Marcasite	Pyrite/Marcasite
Initial pH (1:1)	6.20	6.20
Potential Acidity[†],cmol kg^{-1}	62.3	138.1
Neutralization Potential[‡], cmol kg^{-1}	7.3	5.8
Exchangeable Acidity[§], cmol kg^{-1}	0.4	0.5
Cation Exchange Capacity [¶], cmol kg^{-1}	6.3	6.8
$CaCO_3$ Equivalent [#], cmol kg^{-1}	3.6	4.1
Acid/Base Account, tons/1000 tons[††]	-28.8	-66.8
Acid/Base Balance, tons/1000 tons	-30.0	-67.0

[†] Method from ASTM, 1968.
[‡] Method from Sobek et al., 1978.
[§] Method from Thomas, 1982.
[¶] Method from Chapman, 1965.
[#] Method from Bundy and Bremner, 1972.
[††] cmol (H^+) kg^{-1} X 0.5 = tons $CaCO_3$ / 1000 tons

Table 2. Lime treatments and projected acid/base values.

Overburden	% AB_a					
	0	25	50	75	100	125
	Lime Rate g $CaCO_3$ kg^{-1}					
A	0	7.2	14.4	21.6	28.9	36.1
B	0	16.7	33.4	50.1	66.8	83.6
	AB_a tons/1000 tons					
A	-28.8	-21.6	-14.4	-7.2	0	7.2
B	-66.8	-50.1	-33.4	-16.7	0	16.8
	AB_b tons/1000 tons					
A	-30.0	-22.8	-15.6	-8.4	-1.2	6.1
B	-67.0	-50.3	-33.6	-16.9	-0.2	16.6

Figure 2. The pH of drainage from overburden A, which was treated with calcium carbonate to neutralize 0 to 125% of its AB account deficit, plotted as a function of time.
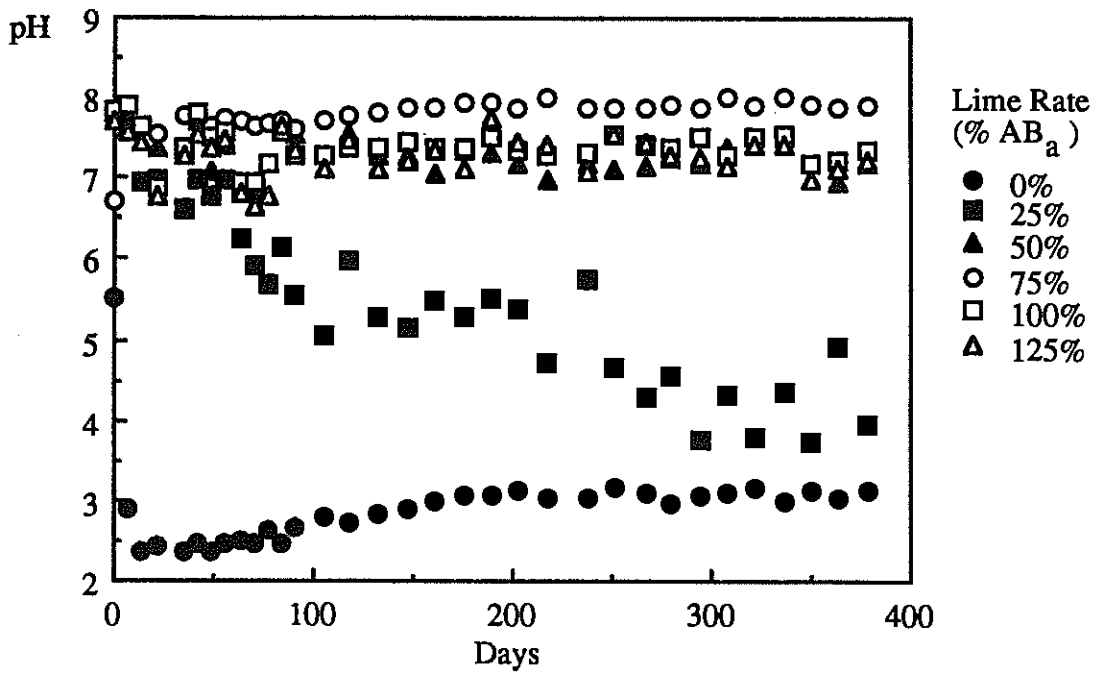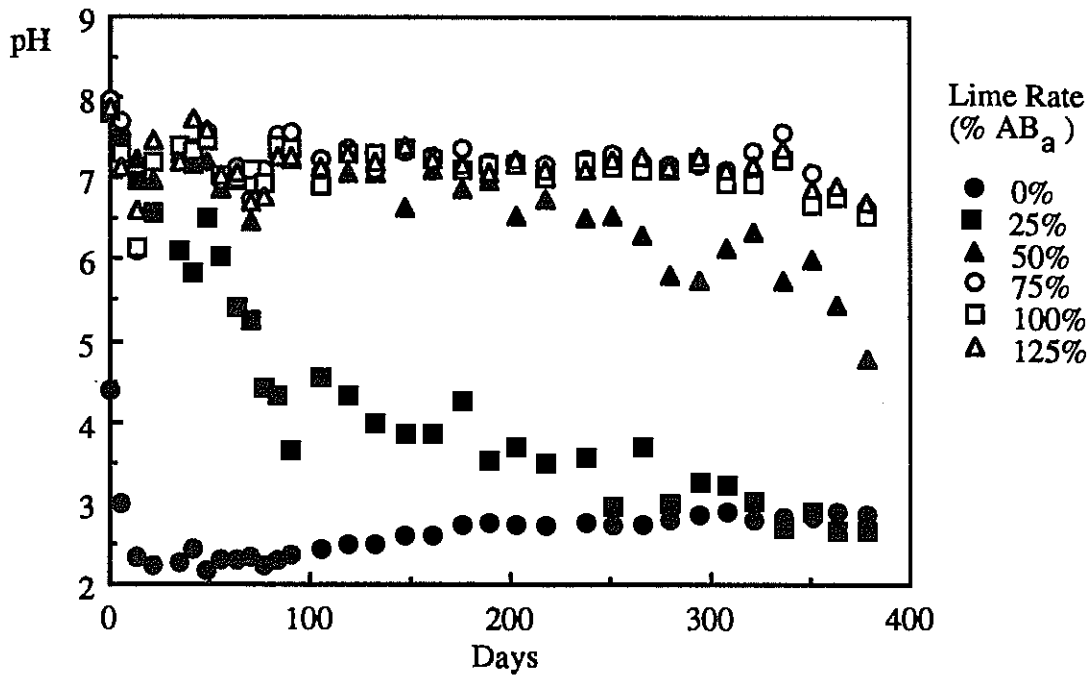

Figure 3. The pH of drainage from overburden B, which was treated with calcium carbonate to neutralize 0 to 125% of its AB account deficit, plotted as a function of time.

difference between $CaCO_3$ dissolution and FeS_2 oxidation was expressed by a decrease in AB_a and AB_b values at the end of the study (Table 3). These results indicate that all the limed overburdens would eventually become acidic. The data in Table 3 may be misleading for the 0 and 25% AB_a treatments. Essentially all of the FeS_2 oxidized within these treatments and they produced acid drainage before the end of the study. The AB_a and AB_b values increased due to leaching of the released acidity.

A prediction of the time it would take for the greater than 50% AB_a treatments to lose all of their applied $CaCO_3$ and the time for complete FeS_2 oxidation is given in Table 4. These predictions are based on the amount of $CaCO_3$ and FeS_2 remaining in the treatments and the rates of $CaCO_3$ dissolution and FeS_2 oxidation measured at the end of the study. The added lime in the both of the 125% AB_a treatments would dissolve in 9 to 10 years. This is 3 to 13 years shorter than the time required for complete FeS_2 oxidation; therefore, acid minesoil would eventually form.

Conclusions

Liming overburden containing significant quantities of FeS_2 to an AB_a of zero may not be the best long-term solution for surface mine reclamation in temperate regions with significant rainfall. Under the conditions of this experiment, dissolution of the applied lime occured at a rate faster than the release of potential acidity indicating that acid minesoil would eventually form.

Table 3. Initial and final acid/base values for overburden treatments.

Overburden Material	Lime Rate	AB_a (0 d)	AB_a (378 d)	AB_b (0 d)	AB_b (378 d)
	%AB_a	———————— tons/1000 tons ————————			
A	0	-19.6	-3.8	-27.9	-5.6
	25	-16.6	-10.8	-24.5	-18.4
	50	-11.2	-12.4	-21.0	-22.4
	75	-5.8	-7.3	-12.6	-15.8
	100	-1.9	-3.1	-5.1	-9.5
	125	2.6	1.3	1.1	-3.2
B	0	-44.0	-7.4	-61.4	-7.9
	25	-35.2	-11.4	-53.9	-8.0
	50	-18.3	-28.9	-40.0	-44.5
	75	-16.2	-18.3	-26.4	-29.5
	100	-6.0	-9.9	-14.2	-19.3
	125	3.7	1.6	5.8	-1.0

Table 4. Extrapolation of residual FeS_2 and $CaCO_3$ based on respective oxidation and dissolution rates measured at the termination of the experiment.

Overburden Material	Lime Rate	Time to Zero Concentration	
		FeS_2	$CaCO_3$
	% AB_a	——————— yr ———————	
A	50	29.3	3.0
	75	29.3	5.4
	100	29.3	7.6
	125	29.3	9.9
B	50	12.0	1.4
	75	12.0	5.0
	100	12.0	7.2
	125	12.0	9.2

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