WEATHERING OF SIDERITE ($FeCO_3$) FROM LIGNITE OVERBURDEN[1]

by

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Abstract. Acid/base accounting of minesoils and overburden can have substantial errors using current analytical procedures. There is a correlation between the presence of siderite ($FeCO_3$) and errors in determining the neutralization potential and potential acidity of overburden material. The effects of CO_2, O_2, and air on siderite weathering were measured. Unoxidized siderite blocks were placed in containers with H_2SO_4 or potassium hydrogen phthalate (KHP), both at pH 3.0. Carbon dioxide, O_2, or air was bubbled through the solutions. The solutions were changed regularly and aliquots were analyzed by atomic absorption for Fe. Unoxidized siderite and $CaCO_3$ were used in pH-stat titrations to determine reaction rates at pH 3.0. Iron release from siderite was influenced by gaseous environment and decreased in the order: $CO_2 > air > O_2$. Iron release from siderite was slowed by formation of iron oxide coatings on siderite surfaces in H_2SO_4. Siderite in KHP formed no coatings. Siderite reacts slowly with dilute acid at room temperature but will react rapidly at modestly elevated temperatures. This can result in errors in acid/base accounting methods used for overburden and topsoil substitute evaluation when siderite is present.

Additional Key Words: acid/base accounting, reclamation, iron oxides

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[1] Paper presented at the 1989 Symposium Reclamation a Global Perspective, Calgary, Alberta, Canada, August 27-31, 1989.

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*Publication in this proceedings does not preclude the authors from publishing their manuscripts, whole or in part, in other publication outlets.

Proceedings America Society of Mining and Reclamation, 1989 pp 597-606
DOI: 10.21000/JASMR89020597

https://doi.org/10.21000/JASMR89010597

Introduction

Mining for lignite will disturb large areas of land in Texas. It has been estimated that one million acres could be disturbed by surface mining in the state and would require reclamation to restore the land to an acceptable level of productivity (Hossner and O'Shay, I985).

Reclamation of surface mined lands requires the identification and treatment of potentially toxic or acid forming material (AFM) (Department of Interior, 1978; Railroad Commission of Texas, 1983). Acid/base accounting (Grube et al., 1971; Sobek et al., 1978) of overburden is being used. in Texas as a criterium to evaluate the suitability of material for surface placement prior to reclamation. If sampling and chemical analyses are accurate and the acid/base account is positive, the material may be suitable as a topsoil substitute. If the acid/base account is negative, the overburden may not be suitable as topsoil or may require amendments be added prior to its use.

Preliminary work (O'Shay, 1982) indicated a relative abundance of siderite ($FeCO_3$) in Texas overburdens and difficulties in accurately determining acid/base accounting when this mineral was present in the sample. This could result in potentially acidic overburdens having acceptable acid/base accounting values when analyzed in the laboratory.

Acid/base accounting, as used by the Texas Railroad Commission, is the difference between the acidic plus acid forming and basic constituents in the sample. It is determined by subtracting the potential acidity (PA) and exchangeable acidity (EA) from the neutralization potential (NP).

$$\text{A/B Accounting} = NP - (PA + EA) \qquad (1)$$

The NP can be determined by treatment of the sample with acid followed by titration of the excess acid with standard base (Sobek et al., 1978). An alternative procedure for determining NP has been proposed by the Texas Railroad Commission. Neutralization potential is calculated after determining the inorganic carbonate content and the cation exchange capacity (CEC).

$$NP = CaCO_3 + 0.2\ CEC \qquad (2)$$

Inorganic carbon can be determined by the method described in Allison and Moodie (1965) or Bundy and Bremner (1972). The overburden is treated with an excess of acid and $CaCO_3$ calculated from the amount of carbon dioxide evolved.

Potential acidity is normally determined by one of three methods. 1) The total sulfur content of the overburden can be measured by dry combustion in an induction furnace followed by iodometric titration (Sobek et al., 1978). All sulfur is assumed to be due to pyrite so the PA can be calculated based on the stoichiometry of pyrite oxidation; 2) the ASTM (1968) method which is based on non-pyritic Fe and S being extracted with HCl followed by selective dissolution of pyrite with HNO_3. The PA is calculated from the amount of Fe or S associated with the pyrite; and 3) pyrite is determined directly by H_2O_2 oxidation followed by titration of H^+ produced by oxidation of the pyrite to iron oxide and H_2SO_4 (Grube, 1971; O'Shay, 1982). Any carbonates are assumed to be removed by an acid soak.

Siderite, if present in the sample, can interfere with determination of the acid/base accounting in several ways. Siderite reacts slowly with acids at room temperature to release CO_2. If the acid neutralization method is being used, an error is introduced due to neutralization of the acid by siderite:

$$FeCO_3 + 2HCl = FeCl_2 + H_2O + CO_2 \qquad (3)$$

Carbon dioxide is also given off in this reaction so direct determination of CO_2 to calculate $CaCO_3$ content can be in error.

Pure siderite weathers to form goethite, FeOOH (Dixon et al.,1982). Also formed are amorphous iron oxyhydroxides (Postma, 1983) and hematite, Fe_2O_3 (Seguin, 1966). Siderite oxidizes according to the following equations (Lindsay, 1979).

$$FeCO_3 + 2H^+ = Fe^{2+} + CO_2 + H_2O \qquad (4)$$

$$Fe^{2+} = Fe^{3+} + e^- \qquad (5)$$

$$3H_2O + Fe^{3+} = Fe(OH)_3 + 3H^+ \qquad (6)$$

$$FeCO_3 + 2H_2O = Fe(OH)_3 + CO_2 + H^+ + e^- \qquad (7)$$

The net reaction of siderite oxidation is acidic rather than basic due to oxidation and subsequent hydrolysis of Fe. Therefore, the presence of siderite in samples used for determination of NP for acid/base accounting can result in a substantial error due to the initial reaction (Equation 4). However, in nature where the reaction is allowed to go to completion, the net reaction is expected to be acidic (Equation 6).

Oxidation of Siderite

Seguin (1966) documented the time required for siderite dissociation. A grain size of less than 300 mesh would take approximately 35 years and a grain size between 60 - 100 mesh would take approximately 370 years to dissociate in air at room temperature. Under conditions of temperature and acidity used to determine NP, siderite would be expected to react rapidly and elevate the level of inorganic carbonates detected in the overburden. This would result in a higher NP than actually exists and could lead to the conclusion that the overburden material may have a suitable acid/base account when in reality the account could be negative.

Objective

The objective of this study was to determine siderite weathering as measured by solution Fe when incubated in acid solution under varying gaseous environments.

Materials and Methods

The siderite used in this study was collected from unoxidized surface mine overburden. The fresh siderite was placed in a plastic bag and stored in a freezer until used in this study.

The siderite sample was characterized by X-ray diffraction (XRD) (Figure 1) and chemical analyses. The XRD patterns were evaluated using the Mineral Powder Diffraction File (1980). Based on the XRD pattern, the sample used in this study contained siderite and a small amount of quartz. All of the siderite pieces used in the Fe release study were cut from a single siderite rock. The siderite rock was cut into blocks approximately 1 x 2 x 0.5 cm in size. The blocks were ground to a uniform surface area then freeze dried and weighed.

The rate of iron release was determined by placing freshly prepared blocks into solutions of potassium hydrogen phthalate (KHP), pH 3.0, or H_2SO_4, pH 3.0. Carbon dioxide, O_2, or air was bubbled through the solution to maintain a constant gaseous atmosphere. The solutions were changed regularly to maintain a pH below 4.5. Initially, 100 mls of solution were added to each container. To insure pH values below 4.5 at all times, it was necessary to increase the amount of solution to 200 ml. The H_2SO_4 solutions were changed daily and the KHP solutions were changed every 48 hours and an aliquot was saved for Fe analysis on a Perkin-Elmer Atomic Absorption Spectrometer (model 603). Solution pH was checked every 12 hours for the first 15 days and every 24 hours on all samples after 15 days.

The rate that siderite and $CaCO_3$ neutralized H_2SO_4 was determined by pH-stat titration. A sample of the fresh siderite was crushed and sieved. The sample was freeze dried and stored in a helium purged desiccator until analysis. A 20 mg sample of siderite or $CaCO_3$, crushed finer than 74 um, was titrated with 0.5 *N* H_2SO_4. A Copenhagen Radiometer automatic titrator equipped with an extended time pH-stat unit was used. Nitrogen purge gas was injected above the solution to prevent a build up of CO_2. The gas was first hydrated to reduce evaporation of the sample solution.

Results

Iron release from siderite blocks was carried out at ambient laboratory temperature. The temperature in the laboratory was 24 ± 2° C except during the 7 to 13 day period when the temperature increased to about 29° C due to an air conditioning failure. Daily iron release from siderite in the KHP solutions nearly doubled during this period (Figure 2). Iron release from the H_2SO_4 solution increased only slightly.

The siderite blocks incubated in H_2SO_4 solution formed an insoluble Fe^{3+} oxide on the block surface. As the Fe^{2+} released from the siderite weathering

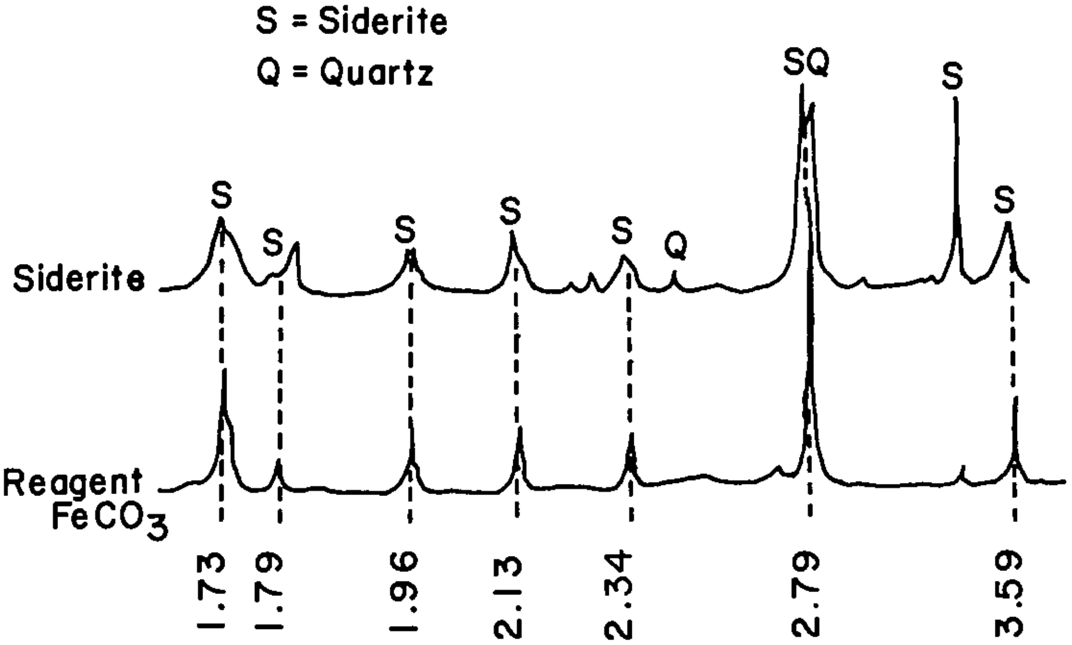

Figure 1. XRD patterns of siderite compared to reagent $FeCO_3$. The d-spacings are given in angstroms.

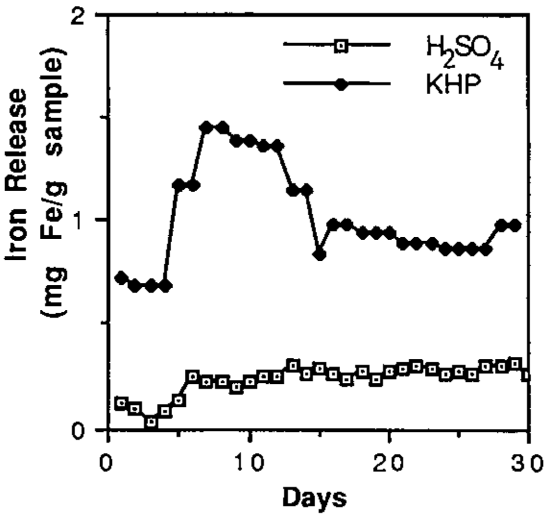

Figure 2. Iron release from siderite over a 30 day period in sulfuric acid or in potassium hydrogen phthalate (KHP) when incubated in air.

comes in contact with an electron accepter; it is oxidized (equation 5). The Fe^{3+} then forms an oxide (equation 6) and precipitates (Schwertman and Taylor, 1977). Siderite blocks incubated under air in H_2SO_4 had a bright red Fe oxide surface coating on the fourth day of the experiment. Based on the color this was assumed to be a coating of hematite. By day 12, siderite blocks under air and O_2 atmospheres in H_2SO_4 were a dark red color. The blocks under CO_2 had a brown coating. Data presented in Table 1 show the samples, treatments, and the color of the surface of the block surface. Munsell colors of the block surface were determined on day 30 of the study. All colors were determined on wet samples.

Table 1. Munsell colors for the the surface of siderite blocks incubated in H_2SO_4 or potassium hydrogen phthalate (KHP) under O_2, CO_2 or air at 30 days.

GAS	SOLUTION	COLOR	MUNSELL
O2	H2SO4	dark reddish brown	5YR3/4
O2	H2SO4	dark reddish brown	5YR3/4
O2	KHP	gray	5Y5/1
O2	KHP	dark gray	5Y4/1
Air	H2SO4	yellowish red	5YR4/6
Air	H2SO4	dark reddish brown	5YR3/4
Air	KHP	dark gray	5Y4/1
Air	KHP	gray	5Y5/1
CO2	H2SO4	dark brown	7.5YR4/4
CO2	H2SO4	strong brown	7.5YR5/6
CO2	KHP	gray	5Y5/1
CO2	KHP	dark gray	5Y4/1

Sample surfaces incubated in KHP were gray to dark gray regardless of incubation atmosphere; this is the color of unoxidized siderite (Mason and Berry, 1968). The KHP is buffered and maintained a pH near 3. In addition, the phthalate ion ($HC_8H_4O_4^-$) is capable of complexing Fe to some degree. Therefore, the Fe remains in solution instead of precipitating as Fe oxides on the siderite surface.

Siderite samples in H_2SO_4 and incubated under a CO_2 atmosphere, had coatings with Munsell colors that corresponded to colors for lepidocrocite, goethite and ferrihydrite (Schwertmann and Taylor, 1977). When Fe^{3+} salts are hydrolyzed rapidly at room temperature, ferrihydrite formation is favored.

The solubility of ferrihydrite increases with decreasing pH and goethite forms from the dissolution of ferrihydrite in increasing amounts with decreasing pH. Lepidocrocite and goethite are polymorphs with goethite having the highest stability. High concentrations of CO_2 favor the formation of goethite over lepidocrocite (Schwertman and Taylor, 1977). Senkayi et al. (1989) found that goethite formed from siderite in a 0.1 *N* H_2SO_4 solution when gaseous mixtures of CO_2 and O_2 were bubbled through a boiling suspension. It is most likely that the blocks incubated under an atmosphere of CO_2 are coated with goethite.

The coatings on the siderite blocks, incubated under air and O_2 environments had Munsell colors that correspond to lepidocrocite and ferrihydrite (Schwertmann and Taylor, 1977). It was concluded that the precipitate coating the blocks was ferrihydrite.

Over time, solution pH values increased less between solution changes so the siderite was remaining in a more acid environment over a longer period of time (Figure 3). The amount of Fe release increased slightly at the lower pH values. This indicates that Fe release from the siderite was being decreased by the iron oxide coating.

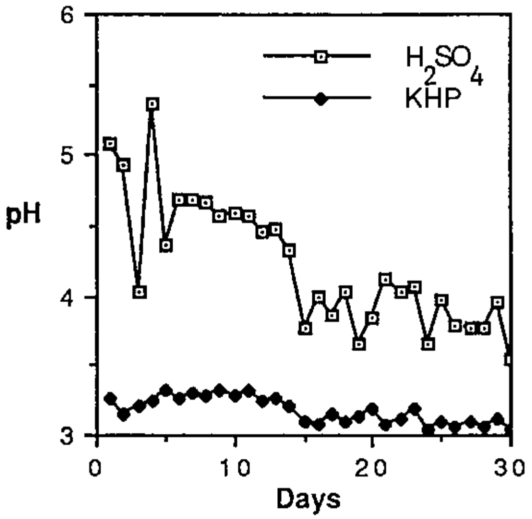

Figure 3. Daily pH of H_2SO_4 and potassium hydrogen phthalate (KHP) solutions containing siderite incubated in air.

Cumulative Fe release from siderite as influenced by incubation solution and gaseous environment is shown in Figure 4 for KHP and in Figure 5 for H_2SO_4. The siderite samples in KHP had greater loss of Fe compared to H_2SO_4. Of the three gas treatments, siderite in KHP under a CO_2 atmosphere had the highest release of Fe. Siderite under O_2 in H_2SO_4 had the lowest Fe release.

The Fe oxide coating formed on the surface of siderite in the H_2SO_4 solutions appears to slow the rate of Fe release compared to the uncoated KHP samples. Solution pH values in air and O_2 treatments were similar. Siderite in air developed an Fe oxide coating before siderite in O_2 followed by siderite in CO_2.

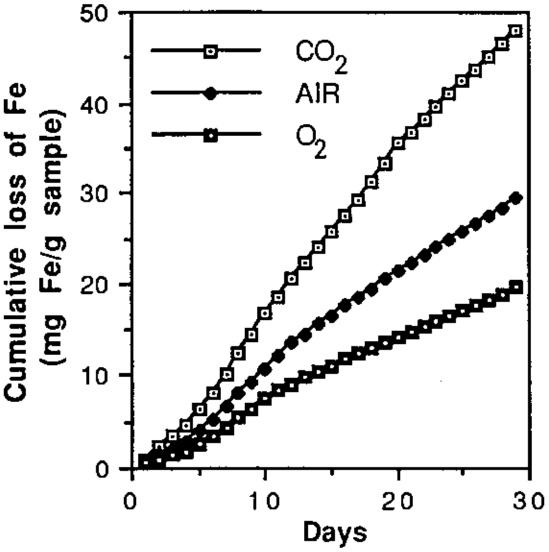

Figure 4. Cumulative iron loss from siderite incubated for 30 days in potassium hydrogen phthalate (KHP) solution under CO_2, air or O_2.

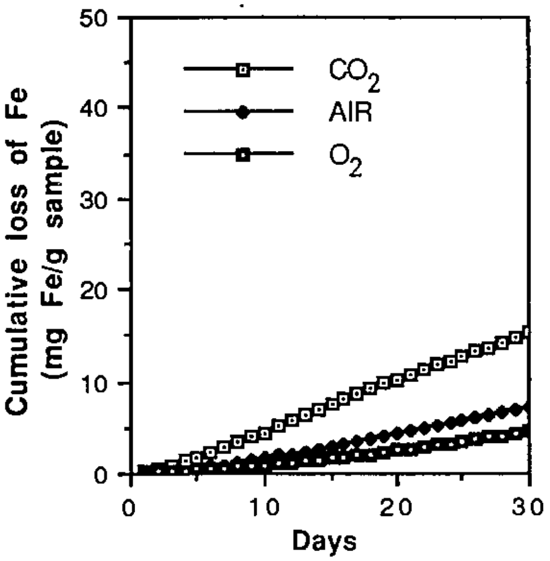

Figure 5. Cumulative iron loss from siderite incubated for 30 days in H_2SO_4 solution under CO_2, air or O_2.

The higher rate of Fe release from siderite under CO_2 is apparently due to the production of carbonic acid (HCO_3) and greater buffering capacity of the solution.

$$CO_2 + H_2O = H_2CO_3 \qquad (8)$$

$$FeCO_3 + H_2CO_3 = Fe^{2+} + 2HCO_3^- \qquad (9)$$

Reaction of < 74 um $CaCO_3$ and siderite at pH 3.0 is presented in Figure 6. All of the $CaCO_3$ was neutralized in about 30 minutes It took over 28 hours for the pH-stat titration of 20 mg siderite to approach 50 % completion.

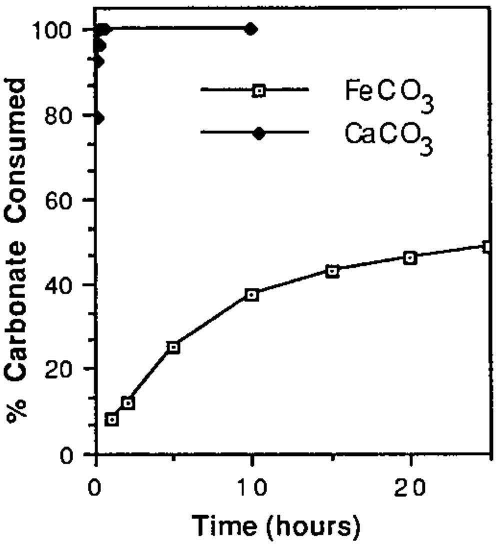

Figure 6. Percent carbonate consumed during the pH-stat titration of < 74 um siderite and calcium carbonate at pH 3.0.

Conclusions

1. Iron release from siderite in acid solutions was influenced by gaseous atmosphere and

decreased in the following order: $CO_2 > \text{air} > O_2$.

2. Iron oxide coatings formed on the surface of siderite when incubated in H_2SO_4 solutions initially at pH 3.0 under atmospheres of air, O_2 and CO_2.

3. Iron oxide coatings did not form on siderite incubated in solutions of KHP buffered at pH 3.0.

4. Iron release from siderite in H_2SO_4 solution was slowed by formation of Fe oxide coatings.

5. Reaction of siderite with dilute acid is slow at room temperature but rapid at elevated temperatures resulting in errors in acid/base accounting methods used for topsoil substitute evaluation.

Literature Cited

ASTM. 1968. Standard method of testing for forms of sulfur in coal. American Society of Testing and Materials, Annual Book of Standards. D2492-68:323-327.

Allison, L.E. and C.D. Moodie. 1965. Carbonate. *In* C.A. Black et al. (ed.) Methods of soil analysis, Part 2. American Society of Agronomy, Madison, WI

Bundy, L.G. and J.M. Bremner. 1972. A simple titrimetric method for determination of inorganic carbon in soils. Soil Sci. Soc. Am. Proc. 36:273-275.

Department of Interior. 1978. Permanent Regulatory Program. Surface Mining Reclamation and Enforcement. Federal Register. Vol. 43, No. 21, Thursday, January 31, 1978.

Dixon, J.B., L.R. Hossner, A.L. Senkayi and K. Egashira. 1982. Mineralogical properties of lignite overburden as they relate to mine spoil reclamation. *In* J. Kittrick et al. (eds.) Acid sulfate weathering. Spec. Pub. 10. Soil Science Society of America. Madison, WI.

Grube, W.E., Jr., E.M. Jencks, R.N. Singh, R.M. Smith, and H.A. Wilson. 1971. Mine spoil potentials for water quality and controlled erosion. E.P.A., O.W.R. Project No. 14010 E.J.E., West Virginia University.

Hossner, L.R. and T.A. O'Shay. 1985. Lignite distribution in the gulf coast region and associated precipitation and temperature. P. 1-7. *In* R. Bitterli (ed.) Lignite surface mine reclamation of the southern gulf coast region. Southern Cooperative Series Bull No. 294. Fayetteville, Arkansas.

http://dx.doi.org/10.2136/sssaj1972.03615995003600020021x

Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley & Sons, New York.

Mason, B. and L.G. Berry. 1968. Elements of mineralogy. W.H. Freeman and Company. San Francisco.

Mineral Powder Diffraction File Data Book. 1980. Compiled by the Joint Committee on Powder Diffraction Standards. JCPDS. Swathmore, PA.

O'Shay, T.A. 1982. The determination of potential acidity in overburden sediments. Master of Science Thesis. Texas A&M University, College Station, TX

Postma, D. 1983. Pyrite and siderite oxidation in swamp sediments. Jour. Soil Sci. 34:163-182.
http://dx.doi.org/10.1111/j.1365-2389.1983.tb00821.x

Railroad Commission of Texas. 1983. Coal Mining Regulations. Surface Mining and Reclamation Division. Austin, Texas.

Schwertmann, U. and R.M. Taylor. 1977. Iron oxides. p. 145-193. *In* J.B. Dixon, et al. (eds.). Minerals in soil environments. SSSA. Madison, WI

Seguin, M. 1966. Instability of $FeCO_3$ in air. Am Jour. Sci. 264:562-568.
http://dx.doi.org/10.2475/ajs.264.7.562

Senkayi, A.B., J.B. Dixon, and L.R. Hossner. 1989. Hydrothermal transformations of siderite to hematite and goethite. Soil Sci. (Submitted for publication).

Sobek, A.A., W.A. Schuller, J.R. Freeman and R.M. Smith. 1978. Field and laboratory methods applicable to overburdens and minesoils. USEPA- 600/2-78-054.