

"SIDERITE MASKING" A FACTOR TO CONSIDER IN OVERBURDEN ACID-BASE BALANCING

by

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Introduction

Recent studies, in particular those conducted and reported on by J.L. Morrison, et. al., 1990, drew timely attention to the potentially adverse effects that siderite (FeCO_3), a common iron carbonate to coal bearing strata, can have on neutralization potential (NP) values generated by use of standard acid-base balancing techniques (Sobek, et. al. 1978). More importantly, Morrison's work raised concerns over the accuracy and subsequent adequacy of mining and reclamation plans developed on a siderite influenced NP data base. When siderite is present in the overburden and an insufficient time is given for complete precipitation of ferrous iron (Fe^{++}) during the NP back-titration process of respective sample analyses, erroneously high NP values can be generated. In a sense, the siderite can play a "masking role" in the analytical process and yield misleading NP information. When NP procedures are not modified to account for the influence of siderite, such an analytic oversight can lead ultimately to undesirable environmental water quality impacts and unforeseen costly reclamation obligations.

This paper reports on an abbreviated case study which provides additional documentation to the potentially detrimental role that siderite can play when such a mineralogical factor is not considered in laboratory NP evaluations routinely used in pre-mine overburden characterization work. Focus of the investigation is on a surface coal mine facility located in eastern Tennessee which has recently encountered water problems. The water concerns of the mine site are somewhat surprising in that all pre-mine overburden data at the time of permitting (1987) indicated minimal potential for development of undesirable acid mine drainage (AMD) and/or ferruginous discharge from planned mining activities.

Required re-evaluation of overburden mineralogical and geochemical properties, including the use of a modified NP procedure in acid-base balancing to account for the presence of siderite, has resulted in a re-definition of the acid-potential of the coal-bearing strata. Contrary to the initial pre-mine data and related AMD predictions of a favorable post-mine alkaline scenario, the new modified NPs, when used in conjunction with the acid-base accounting process, disclosed some potentially acid overburden strata not previously identified as problematic in character. Unfortunately for the mine operations, the erroneous NP values and subsequent misleading interpretations of the data resulted in the problematic overburden not receiving adequate handling and treatment during the initial three years of mining. The untimely identification followed by prolonged inadequate handling and/or treatment of such materials are primary contributing factors to the mine's water quality issues. The following discussions briefly summarize the steps taken and the methods used in unraveling the geochemical source mechanisms responsible for the recently observed water

difficulties.

STATEMENT OF PURPOSE

The purpose of this paper is multiple in scope. Primary objectives are to: 1) re-emphasize the importance of considering the influence of siderite on performing acid-base balancing tasks; 2) define modified NP procedures which can be used to compensate for the siderite influence; 3) offer suggested factors or steps to be taken in pre-mine overburden characterization work which can lead to use of appropriate laboratory procedures when siderite strata is encountered; 4) enhance technology transfer within the coal industry in the hopes that all can learn from the experiences of others and that overall gains can be made in the area of cost-effective environmental protection; and lastly, 5) encourage further research in the area of AMD prediction and prevention associated with siderite enriched overburden.

BACKGROUND AND STUDY APPROACH

Geographic Setting The mine site and related coal reserve properties involved with this study are owned and/or controlled by Skyline Coal Company, a subsidiary of AMAX Coal Industries, Inc.. Skyline Coal is a small surface operation (< 1,000,000 tons/year) located in Sequatchie County, approximately 15 miles northwest of Dunlap, Tennessee. Coal reserves at the mine site are developed via the area surface mine method with combinations of dragline stripping and cast-overburden blasting being the primary techniques used in moving the overburden. The surface facility has three permitted reserve areas under different stages of development. Overburden data discussed in this paper have been derived from strata core sampling taken throughout the three reserve areas.

Physiographic and Geologic Setting Skyline Coal's surface operations are located on the southern extension of the Cumberland Plateau through eastern Tennessee. In the area where coal surface mining is on going, the plateau consists of broad and relatively flat uplands capped with resistant Pennsylvanian Age sandstones. Surface elevations of the actual mining sites range from 1700 to 2000 feet above sea level. Mining takes place on upland divides between major drainage systems dissecting the plateau surface. Major streams adjacent to the various mine properties are Glady Fork and Big Brush Creeks.

The coal-bearing sequence under development at Skyline are Pennsylvanian Age rocks of the Crab Orchard Group. The overburden strata consists of the Newton Sandstone and Whitwell Shale Formations of the Group. The primary coal seam being mined is the Sewanee Coal Member of the Whitwell Shale Formation. A typical mining section within any given permit area will consist of 40-60 feet of Newton Sandstone overlying 30 to 40 feet of Whitwell Shale. Average overburden thickness is 95.5 feet. The Newton Sandstone is an extremely indurated, ortho-quartzitic sandstone. The Whitwell Shale consist of a medium to dark-gray to brownish gray, thinly bedded shale. Lenticular silty/sandy shale facies changes are common with the Whitwell shale unit. Historically, the Whitwell shale is known for its siderite content. Siderite occurs in the shale in the form of both nodules and thin lamina or bands.

Definition of Water Quality Problem Development in mid- 1990, Skyline Coal began experiencing water problems at both its Glady Fork and Pine Ridge Mine properties. The water concerns were in the form of offsite seepage emanating from the mine sites into

adjacent streams. The seepage consisted of slightly acidic to alkaline, manganese(Mn) enriched, ferruginous waters. Flow was from mine disturbance areas through fracture systems or other stratigraphic flow paths established in the stream buffer zone and stream bed itself. Although the overall impacts of the seepage to the adjoining streams were limited to aesthetics (red staining) and temporary benthic aquatic habitat concerns (iron sediment coatings), the discharge was defined as a pollution source to waters of the State and therefore implementation of remedial action plans were required to eliminate or minimize degradation potentials.

The range in primary water quality parameters of the seepage discharges at the time of seep discovery were as follows: pH = 3.4 to 7.5; alkalinity = 0 to 121 mg/l; acidity = -2 to -212 mg/l; total iron (Fe) = 4.8 to 48.6 mg/l; total manganese (Mn) = 2.3 to 34 mg/l; and, sulfate (SO₄) = 8 to 812 mg/l.

Approach to Problem Solving To develop and subsequently abate the seepage problems, a two prong investigative approach was pursued. The two stage approach involved: 1) development of mitigative plans to stop or significantly reduce seepage flow from the backfill to adjacent creeks; and, 2) identification of the mineralogical and stratigraphic sources of the acid and metal-loading of the seeps emanating from the backfill with the ultimate objective was to develop and subsequently implement a pollution abatement plan in the mining and reclamation phase of the mining process that will prevent or significantly minimize backfill groundwater deterioration.

In order to eliminate the seeps as quickly as feasible, an in-depth hydro-geologic inquiry was undertaken to define the backfill groundwater hydrology relationships with geology of the surrounding buffer zone areas and the associated streams. Construction of detailed geologic cross-sections, preparation of necessary structure maps, combined with groundwater data gathering (i.e. installation of observation wells in backfill areas) provided necessary insight to the understanding of backfill hydrologic flow-paths and hydrologic head relationships between spoil backfill areas and respective seeps. Once the hydrologic character of each seep was better understood, mitigative plans were subsequently developed and implemented to reduce the groundwater hydrostatic forces driving theseepage flows and/or to re-direct the flows of groundwater sources away from the seepage areas.

The following sections of this paper address in more detail the results of second phase of the study involved with the identification of mineralogical and stratigraphic sources of acidity/alkalinity loading and metal (Fe & Mn) enrichment of backfill groundwater.

IDENTIFICATION OF THE MINERALOGICAL SOURCE(S) OF ACID-LOADING AND METAL Fe & Mn) ENRICHMENT IN BACKFILL GROUNDWATER

To accomplish the mineralogical and stratigraphic source(s) identifications objective of the second part of the study, the overburden and mine spoil was subjected to a barrage of analytical evaluations. Principal techniques and/or analytical tools used to characterize the mineral constituents of the overburden materials included: 1) XRD analysis; 2) Mossbauer spectroscopy; 3) CO₂ coulometry analyses; and, 4) petrographic analyses. Results of the Mossbauer spectroscopy and XRD analyses of both fresh spoil and weathered graded cast identified the mineralogical sources of both acid and/or metal loading to be (listed in relative

order of abundance): 1) siderite (FeCO_3); 2) szomolnokite (an acid, ferrous hydrated sulphate salt resulting from weathering of pyrite); 3) pyrite (FeS_2); and, 4) iron-bearing clays (illite and/or chlorite). CO_2 coulometry data disclosed the dominant carbonate phase within the Whitwell shale to be siderite.

Of the iron-bearing minerals identified in the overburden rocks, the pyritic constituent and its subsequent weathered by-products, in particular szomolnokite, are the principal source of acid-loading associated with the overburden. Dissolution of szomolnokite in the backfill in response to normal precipitation wetting events yields pH 2 water. Acid scouring by such pore-space water as a result of movement through the backfill disrupts the geochemical stability field of both siderite and the iron-bearing clay minerals. Certainly the acid generated from prolonged exposure of pyritic materials exacerbates the dissolution siderite. Subsequent dissolution of the siderite yields further acid and metal (Fe & Mn) loading to backfill hydrology resource. Re-evaluation of total sulfur values of the overburden to define pyritic fractions coupled with petrographic characterization of elevated pyritic sulfur zones provided added confidence levels to newly defined acid-producing horizons in the overburden. Where increased pyritic sulfurs were observed in the overburden, the predominant pyritic types present were reactive microscopic crystalline and/or framboids.

Although siderite was identified as the predominant carbonate phase in the Whitwell shale overburden sequence, the broad peaks of the X-ray diffractograms depicting siderite's presence suggest that the siderite constituents are impure having some admixtures of Ca^{++} , Mg^{++} , and Mn^{++} . In short, the siderite present may very well be solid-solution combination of both siderite and ankerite ($\text{CaCO}_3 \cdot (\text{Mg,Fe,Mn})\text{CO}_3$)' Modified NP data showing remaining neutralization potentials following siderite compensation in the laboratory process coupled with continued monitoring of alkalinity/acidity ratios greater than 1 in the backfill groundwater and the majority of the original seeps support the conclusion that the backfill is getting some inherent neutralization benefits from the dissolution of the siderite bearing strata. Such field and laboratory evidence is contrary to the common belief that siderite when present in the overburden has no net effect on the consumption of acidity and thus must therefore be totally discounted when evaluation acid-overburden potentials prior to mining.

Findings and conclusions drawn from the above analytical efforts were subsequently used in defining additional overburden characterization needed to delineate the stratigraphic source(s) of the metal loading in the coal-bearing strata. Because siderite was identified as a Fe-loading source in the overburden, analytic procedures involved with routine acid-base balance evaluations were changed to account for siderite's known influence on NP determinations. "Simulated weathering" studies coupled with the use of the modified NP analyses were used to identify potential acid-producing and metal-loading horizons in the overburden.

RE-EVALUATION OF STRATIGRAPHIC ACID-PRODUCING POTENTIALS WITH USE OF MODIFIED NEUTRALIZATION POTENTIAL PROCEDURES

Introduction of Modified NP Procedures To compensate for the "masking influence" of siderite on defining neutralization potentials (NP) of the overburden, a 30% hydrogen peroxide (H_2O_2)

additive was introduced into the routine NP procedures (J.L. Morrison, per communications 1990). After the normal acid digestion of the overburden sample and before titration, 5 ml. of H_2O_2 was added to the sample admixture and reboiled for a 5 minute period prior to the normal NaOH titration of the NP process.

Incorporation of the hydrogen peroxide additive into the routine NP process and resulting "modified NP" values differed sharply where siderite was known to exist in the overburden strata. The overall impact to the overburden acid-potential picture for the Skyline properties was a substantial reduction in inherent neutralization potentials compared to original permit data. For the first time, with the use of the modified NP information specific acid-producing horizons began to reveal themselves in the overburden sequence. Although considerable NP reductions occurred, it is important to emphasize here that the majority of the Whitwell shale overburden remained alkaline in character as originally projected by pre-mine data. The following table (Table 1) provides a comparison of NP values generated by the Standard and Modified NP procedures. As can be seen, reductions in assumed available neutralization potentials is significant for some strata, in particular, the siderite -bearing Whitwell shale and siderite conglomeritic sandstone occasionally found at the base of the Newton Sandstone.

Because of the expedient nature of the study to unravel the sources of acid and/or metal loading to the backfill groundwater resources and based on current technology available at the time to develop an understanding of what geochemical mechanisms were on-going in the backfill, the modified NP procedures outlined above were immediately adopted and the data has subsequently been incorporated into development of mitigation plans. However, it is important to emphasize here that the procedures used in the modified NP process have yet to be officially approved and agreed upon as standard methods to be followed when dealing with siderite-bearing strata.

TABLE 1

SKYLINE COAL COMPANY - SEWANEE COAL OVERBURDEN

Table 1 - Range Comparison of Modified and Standard Net Neutralization Potential Results

Rock Type	Fizz Rate	Pyritic Sulfur	Standard Net Neut. Potential	Modified Net Neut. Potential	Typical Differences
		%	t/1000t*	t/1000t*	t/1000t*
Newton Sandstone					
Upper	0	0.01 to 0.05	-2.1 to 24.4	-8.8 to 6.9	-6.7 to -17.5
Middle	0	0.01 to 0.08	0.6 to 26	-4.3 to 19.6	-4.9 to -6.4
Lower	0 - 2	0.01 to 0.08	2.4 to 227	1.6 to 226.1	-0.8 to -0.9
Whitwell Shale					
Upper	0 - 1	0.02 to 1.1	-8.7 to 29.0	-12.0 to 18.7	-3.3 to -10.3
Middle	0 - 1	0.02 to 0.68	-6.0 to 38.4	-4.0 to 18.5	2.0 to -19.9
Lower	0	0.01 to 0.13	17.2 to 44.1	4.4 to 31.9	-13 to -12.2
Underclay	0	0.03 to 0.25	13.0 to 24.4	-4.0 to 20.8	-17 to -3.6

* tons of calcium carbonate equivalent/1000 tons of material

It still is the opinion of the author that the findings of the modified NP procedure is ultra conservative because the natural weathering process will not totally oxidize all pyritic materials in the backfill. The introduction of the H₂O₂ results in instantaneous oxidation of the remaining pyrite in the previous HCL digest. Therefore, it appears that the modified NP procedure and the normal empirical/arithmetic potential acidity calculations involved in the normal acid-base balancing process result in some "double-dip" accounting of the true acid potential picture of the situation. To make the modified procedure more realistic in approach, it is the author's thinking that the decant liquid of the initial HCL digest should be treated with H₂O₂ before back-titrating to pH of 7.0 in lieu of treating the total admixture. Because there remains some concerns about the validity of the modified NP process in general, university research is needed to investigate and standardize the NP procedures for siderite bearing overburden.

Identification of Potential Acid-Producing Horizons in the Sewanee Coal Overburden Sequence

Having adjusted NP values with the newly derived modified data, potentially acid-producing strata began to show-up. To improve overall confidence in the newly derived data, select overburden strata were submitted to "simulated weathering" tests to assess actual acid-yielding potential under humidity influenced weathering. Primary results of the weathering studies mirror imaged the predictions of the newly derived acid-base assessment using the modified procedures. Overburden samples showing a net deficiency of NP did show acidity and metal generating potentials. Those samples having positive NP values displayed alkaline character and reduced metal loading as projected with the modified acid-base accounting procedure.

The combined data generated from the modified NP procedures and the "simulated weathering" tests identified four (4) strata of potential acid-producing character in the Sewanee Coal overburden sequence. The four horizons are (listed in descending order): 1) the Upper Whitwell shale contact zone (2-5 feet) with the overlying Newton Sandstone; 2) a lenticular sandy shale/shaly sandstone horizon (0-20 feet) within the Whitwell shale interval above the coal seam; 3) the Sewanee Coal cleanings (residual coal materials left in the pit following coal extraction); and, 4) the pavement underclay/shale materials (sporadic in occurrence).

CONCLUSIONS AND RECOMMENDATIONS

The following are primary conclusions and recommendations that can be made as a result of the in-depth study of the Sewanee Coal overburden sequence.

Conclusions

1. The Whitwell Shale overburden associated with the Sewanee Coal seam is laden with siderite carbonates. Although the siderite constituents are not necessarily mineralogically pure (i.e. admixture of calcium, magnesium, and manganese carbonates), they need to be taken into consideration when conducting routine acid-overburden evaluations and predicting post-mine water quality characteristics.
2. Modified NP procedures need to be followed when evaluating neutralization potentials of siderite -bearing overburden. Comparisons of standard NP data with data generated using the modified NP procedures show a significant reduction in available neutralization capabilities of siderite enriched strata.
3. Positive NP(excess neutralization potential) data generated from use of the modified NP procedures can be assumed available for inherent neutralization in the backfill. Both "simulated weathering" results and data generated from backfill groundwater quality support the position that such materials due add natural alkalinity to the backfill.
4. Primary acid-forming and metal-loading contributors associated with the Whitwell shale overburden sequence can be attributed to oxidation of pyrite and subsequent dissolution of siderite.
5. A combination of simple field observations and analytical techniques can be used to identify the presence of siderite in the overburden prior to advancing to NP evaluations. Close scrutiny of strata cores during initial pre-mine investigations coupled with routine fizz testing can give direction to the analytical path to be followed in acid-base accounting. Visual observations of siderite nodules and/or banding is a definite clue. Dark colored shale materials with low fizz ratings should be suspect. XRD analysis coupled with CO₂ coulometry evaluations on select samples are extremely helpful in delineating the carbonate phases of the overburden.
6. Use of the modified NP procedures followed by select "simulated weathering" testing are important analytic steps to be taken in order to increase the confidence level of post-mine water predictions made from siderite -bearing overburden.
7. Select horizons within the Whitwell shale overburden sequence associated with the Sewanee Coal seam in eastern Tennessee have the potential for creating ferruginous, and in some cases, slightly acidic post-mine drainage conditions. When such strata are not properly identified and properly handled during stripping, the strata can lead to the development of undesired environmental impacts and costly reclamation clean-up.

Recommendations

1. It is extremely important that university research investigate the reactions further and establish standard overburden assessment procedures to be followed when attempting to evaluate and improve overall success at predicting post-mine drainage of siderite-laden overburden.
2. A better understanding is needed regarding the neutralizing potential of siderite, at least the impure phase of the mineral. Contrary to current belief that siderite has no net effect on the consumption of acidity, this particular study suggests otherwise. Backfill alkalinities associated with siderite enriched Whitwell shale support the contention that the carbonate component of the siderite has neutralizing potential. Consideration needs to be given for crediting some neutralization potential values to calcium, magnesium bearing siderite constituents.
3. Most importantly, further AMD work needs to focus on development of mitigative reclamation tools to combat the inevitable dissolution of siderite when such materials co-exist with pyrite-bearing strata. In particular, remedial steps need to be defined that can improve the geochemical stability field of siderite in the backfill. Development of cost-effective reclamation techniques which will enhance the stability field of siderite is needed.

REFERENCES

Caruccio, F.T. and W. Bradham. 1991. Skyline Coal Company Overburden Quality Assessments.

Hammach, R. W. 1990. USBM (Communications) Re: Mossbauer Spectroscopy Findings of Whitwell Shale.

Morrison, J.L., S. Atkinson, A. Davis, B. Schmertz. "The Use of CO₂ Coulometry in Differentiating and Quantifying the Carbonate Phases in the Coal-Bearing Strata of Western Pennsylvania: its Applicability in Interpreting and Modifying Neutralization Potential (NP) Measurements," Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Vol. 1, pp. 243248, 1990.

Sobek, A.A., W. A. Schuller, J.R. Freeman, and R.M. Smith. 1978. Field and Laboratory Methods Applicable to Overburden and Minesoils. U.S.E.P.A. Report EPA-600/2-78-054.

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