

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 ¹

by

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Abstract. CO₂ coulometry is a rapid, highly accurate technique which can be used to determine the carbonate carbon contents of coals and associated overburdens. The rate at which the CO₂ is evolved during the acid digestion process is a function of which carbonate phases are present. Calcite and dolomite reaction times are approximately six to eight minutes under the conditions described herein, with the maximum change in reaction rates occurring between two and four minutes. Siderite requires a lengthy 10 to 15 minutes to completely react with the maximum change in reaction rate occurring between six and eight minutes. The determination of neutralization potential (NP) in the coal-bearing overburdens of the eastern United States is inaccurate when siderite is present because of the slow conversion of Fe²⁺ to Fe³⁺. To alleviate the effects of siderite on NP, a 30 wt. % H₂O₂ Solution can be used to accelerate the conversion of Fe²⁺ to Fe³⁺ during the titration process. The addition of H₂O₂ increases both the accuracy and precision of the NP determination. Despite the addition of H₂O₂, many siderite-bearing overburdens still possess NP. This is interpreted as being the result of: 1) the incomplete oxidation of Fe²⁺ to Fe³⁺ and the incomplete precipitation of iron hydroxide, and/or 2) the presence of Ca and/or Mg occurring in solid solution in the siderite.

Additional key words: fizz rating, hydrogen peroxide, ferrous and ferric iron, carbonate carbon, CO₂ coulometry, x-ray diffraction, microprobe analysis.

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Introduction

Prediction of acidic mine drainage is based in part on the ability to accurately characterize overburdens with respect to sulfur and carbonate. The acid/base accounting method is the most frequently used type of overburden characterization. The acid/base accounting method is composed of two determinations: 1) total sulfur, and 2) neutralization potential. Total sulfur contents are then multiplied by 31.25 to calculate potential acidity. Total sulfur determinations are relatively rapid and accurate. Neutralization potential is determined by digesting the overburden in HCl, back titrating with NaOH to an endpoint of pH = 7 which is held for 30 seconds (Noll, Bergstresser, and Woodcock 1988). This determination was originally used to find the neutralization equivalence of limestone (Jackson 1964). when applied to determining the neutralization potential of overburdens, this method is less accurate when siderite is present. Siderite, a common constituent in overburdens, is believed not to have the same neutralization capabilities as other carbonates (Williams et al. 1982; Palmer 1973). Siderite (FeCO_3) is at least partially digested in the HCl digestion step of the NP determination and will ultimately affect the stability of the titration endpoint because of the slow and incomplete conversion of Fe^{2+} to Fe^{3+} . This instability affects both the accuracy and precision of the NP determination.

Because the differentiation of the various carbonate phases is essential in the prediction of acidic mine drainages, several studies have attempted to differentiate and quantify the various carbonate phases present in coal-bearing strata. The most conventional method used to ascertain variations in carbonate mineralogy is quantitative x-ray diffraction (QXRD) (Despard 1988; Morrison 1988). The primary difficulty with this technique is the lower detection limit of one to two percent. Less conventional methods of carbonate characterization include evolved gas analysis (Hammack 1987) and automated pressure cells (Evangelou, Roberts, and Szekeres 1985).

This paper will present an alternative method of carbonate characterization known as CO_2 coulometry (Huffman 1977). CO_2 coulometry is an analytical technique which is routinely used to determine carbon (both total and carbonate). It is a two-step process in which total carbon is determined by measuring the amount of CO_2 evolved when the sample is heated to 1000°C . Carbonate carbon is determined by digesting the sample in hot perchloric acid and measuring the amount of CO_2 evolved during the digestion. organic carbon is then determined by difference.

Because calcite, dolomite, and siderite exhibit different rates of dissolution in acids

(Evangelou, Roberts, and Szekeres 1985) the CO₂ coulometer was used to measure the evolution Of CO₂ with respect to time. To augment the CO₂ coulometry data, x-ray diffraction was used for carbonate phase identification.

Materials and Methods

CO₂ coulometry is a relatively rapid analytical technique which can accurately determine the carbonate carbon content of a given sample. The schematic of the CO₂ coulometer apparatus is shown in Figure 1.

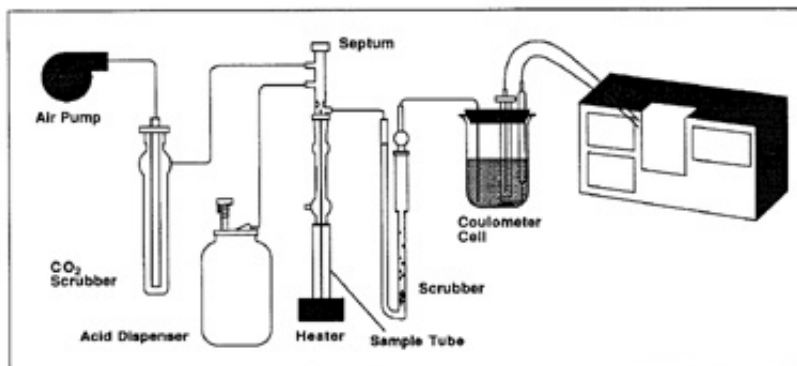


Figure 1: Schematic of CO₂ coulometer.

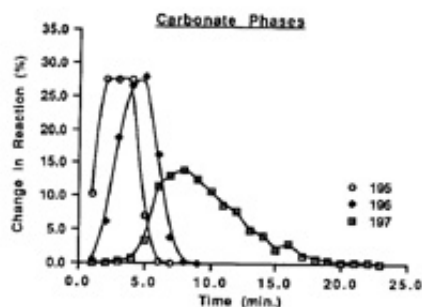
The overburden sample was accurately weighed (20 to 25 mg) in a ceramic weighing boat and then placed in the sample tube housing shown in Figure 1. The side of the sample housing was rinsed with one mL of deionized water to ensure that any particles adhering to the side of the sample housing would be rinsed down to the zone in which the acid will be introduced. This rinse was kept constant at one mL to prevent creating subtle variations in the normality of the perchloric acid which might have an impact on the rate of digestion. The sample housing was then closed and the system degassed for approximately two minutes to remove the atmospheric CO₂ introduced into the system when the sample was placed in the sample housing. After degassing, the analysis is commenced by the addition of 2 mL of 2 N perchloric acid. The CO₂ evolved during the hot perchloric acid digestion is carried to the CO₂ coulometer cell where it is electrochemically titrated. Results are expressed as wt% carbonate carbon and reported to the nearest 0.01%.

Calcite, dolomite, and siderite standards were analyzed on the CO₂ coulometer. Calcite and dolomite standards were provided by Bellefonte Lime of Bellefonte, Pennsylvania and are reported as being 97.73% and 98.85% in purity, respectively. Sample (195) is a high quality limestone (Valentine member of the Linden Hall Fm. collected from Bellefonte, PA) and sample (196) is a high quality dolomite (Ledger dolomite member collected in southeast PA near Devault, PA) in which the atomic ratio of Ca/Mg is nearly one. Siderite standards are more difficult to obtain. The siderite standard (197) is an in-house standard.

Results and Discussions

Figure 2 summarizes the CO₂ coulometry profiles and the measured NP values for the various

standards described above. When viewing the CO₂ coulometry profiles in Figure 2, the following observations should be noted: 1) the time for 100% reaction, 2) the time at which the maximum change in reaction occurs, and 3) the overall geometry of the profile. The calcite (195) and dolomite (196) profiles are characterized by relatively short reaction times over which the rate of the reaction is relatively rapid. In contrast to this, the siderite (197) profile is characterized by a much longer reaction time and a more sluggish reaction rate as evidenced by a much broader profile. It is important to note that siderite did not generate any CO₂ until the two to three minute reading.



Sample	Description	Carbonate Carbon	Theoretical Carbonate Carbon for Pure Sample	Time (min) for 100% Reaction	Neutralization Potential
195	High Calcium Ls	11.685	12.000	7	971.58
196	Dolomite	12.952	13.026	9	1054.66
197	Siderite	10.573	10.367	23	37.10

Figure 2: CO₂ coulometry profiles for calcite, dolomite, and siderite standards.

Figure 3 illustrates the CO₂ coulometry profiles for three overburden samples with wide ranging NP's, fizz ratings, carbonate carbon contents, and lithologies.

Figure 3A is a CO₂ coulometry profile for a dark gray shale and appears to be very similar to the siderite standard. This profile is characterized as being relatively broad with the maximum rate of reaction occurring at the six minute mark. In addition, CO₂ is undetectable until the two to three minute mark. X-ray diffraction analysis found siderite to be the only detectable carbonate phase. Multiplying the carbonate carbon content (1.30) by FeCO₃/C ratio determines there is 12.54% siderite present.

In Figure 3B, the CO₂ coulometry profile for a siderite concretion (sample 71) is illustrated. Again, the CO₂ profile is relatively broad and the rate of reaction is slow. Unlike the previous CO₂ profile, however, there is the indication of a slight reaction having occurred at the one to two time interval. X-ray diffraction analysis found siderite to be the only detectable carbonate phase present. Microprobe analysis of this sample determined 3.52 +/- 0.93 wt% Ca present in the siderite (Morrison, Atkinson, and Scheetz 1990). This presence of Ca in the siderite may explain the slight reaction encountered during the one to two minute reaction time. Assuming that all the carbonate present is in the siderite phase, the carbonate content of 7.11 translates into 68.58% siderite.

In Figure 3C, the CO₂ coulometry profile for an Upper Freeport limestone is presented. This profile is very different from the previous two profiles (173 and 71). This profile is characterized by a rapid reaction rate but requires a relatively long time (13 mins.) to react completely. Although the two minute mark for reaction time is similar to that of calcite, the lengthy time for 100% reaction indicates that other carbonate phases are present. X-ray diffraction identified abundant calcite and ankerite. The presence of ankerite is interpreted as being responsible for the lengthy reaction time. Despite this, multiplying the carbonate carbon (7.69) by the CaCO₃/C ratio indicates there is 64.08% calcite present which translates to a NP of 640.08 which is in very good agreement with the actual measured NP of 632.38.

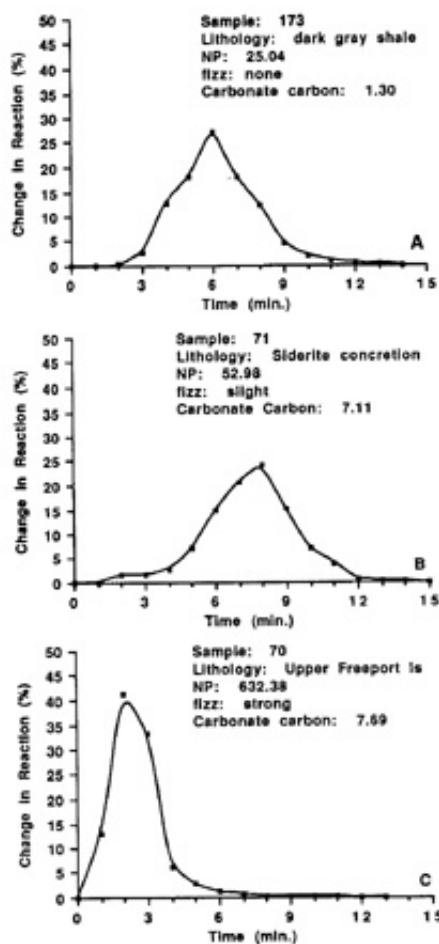


Figure 3: CO₂ coulometry profiles for selected overburden samples.

The primary difficulty in determining the neutralization potential of overburdens is that the presence of siderite affects both the accuracy and the precision of the method. Because siderite is very common in the coal-bearing strata of the eastern United States, NP values are often questioned. This is particularly true if the NP is accompanied by an assigned fizz rating of zero (none). NP's which have fizz ratings of zero are often discounted because they are interpreted as being attributable to the presence of siderite. If the overburden sample exhibits a fizz of one or more (e.g. 71), there is no criterion by which one can interpret the NP as being valid. In the case of overburden sample (71), the dominant carbonate phase is siderite, yet it produced an NP of 52.98. CO₂ coulometry can very accurately differentiate calcite from siderite. This method also can determine if the carbonate is present as a mixture by a bimodal CO₂ coulometry profile; however, the method cannot yet accurately quantify

individual components of a multiple phase system.

Because CO₂ coulometry can accurately differentiate between calcite-bearing and siderite-bearing overburdens, the NP determination methodology has been modified in an attempt to provide siderite-free NP's. The modification is very simple. Because siderite is at least partially digested in the NP digestion step, a large amount of Fe²⁺ can potentially go into solution. During the titration process, the Fe²⁺ is partially oxidized to Fe³⁺; however, this reaction does not necessarily go to completion over the short time span of the determination. Because the precipitation of ferric hydroxide generates H⁺ it is necessary to accelerate the oxidation of Fe²⁺ to Fe³⁺ which will eventually precipitate as a ferric hydroxide (ferrihydrite) during the NaOH titration step. In order to speed up the Fe oxidation, a 30 wt% H₂O₂ solution is added. The overburden sample is digested as in the conventional NP determination; however, after cooling the leachate is filtered, five mL of 30 wt.% H₂O₂ is added and then reboiled for three to five minutes. After cooling, the leachate is titrated using the conventional NP guidelines.

Table 1 summarizes some of the results. The NP's of samples (173) and (171) are slightly different from those reported in Morrison, Atkinson, and Scheetz (1990) because they were redetermined from different splits. In the first set of data (173, 71, and 63) the addition of H₂O₂ had a profound impact on the NP value. In these samples, where siderite is present, the NP's were lowered by 54.07, 38.20, and 13.90%, respectively. In overburden sample (63), the NP value was not as affected as in samples (173) and (71) because calcite was the dominant carbonate phase.

The second set of data in Table 1, sample (171), focuses on the problem of incorrectly assigned fizz ratings. Because determining fizz ratings is very subjective, the addition of H₂O₂ is warranted. Overburden sample (171) is a siderite-bearing black to dark gray shale. Three sets of analyses were run, all in triplicate. In the first sequence, the sample was run according to the correct conventional NP determination. In the second sequence, an incorrect fizz rating was intentionally assigned to determine to what extent a larger volume of HC1 would effect the NP value when using the conventional NP methodology. In the third sequence, an incorrect fizz rating was intentionally assigned; however, this time the modified NP determination was used. All of these determinations were performed manually, as opposed to using an automated titration system. Comparing these runs clearly indicates that an incorrectly assigned fizz rating, and therefore digestion procedure, can have a profound impact on the resulting NP. By adding H₂O₂, the error is lessened and the precision of the method increased.

Table 1. Comparison of conventional and modified NP determinations among selected overburden samples.

Sample	Fizz	Carbonate Mineralogy	NP	NP _{hydrogen peroxide}
173	0	Siderite (12.54%)	25.04	11.50
71	1	Siderite (68.58%) Calcite ?	52.98	32.73
63	1	Calcite, siderite	65.59	56.47
171	0	Siderite (6.63%)	14.41 ± 1.47	-
171	1	Siderite (6.63%)	23.51 ± 1.03	10.25 ± 0.13

Despite the addition of five mL of 30 wt.% H₂O₂, the NP's of overburdens in which siderite was the only identifiable carbonate phase, did not go to zero. The explanation for this may be two-fold.

The first explanation is that not all of the Fe²⁺ has oxidized to Fe³⁺ and has not precipitated as ferric hydroxide. Because this reaction has not gone to completion, erroneously high NP values could be reported.

The second explanation is more complex and requires further research to substantiate. Siderite is rarely phase pure in nature (Mozley 1989). Microprobe analysis presented in Morrison, Atkinson, and Scheetz (1990) has documented the occurrence of Ca and Mg present in siderites as well as Mn. If Ca and/or Mg is present in significant amounts it may explain why certain siderite-bearing overburdens still possess NP despite the addition of H₂O₂. The relationship between the field neutralization of acidic drainages by Ca-bearing siderites has yet to be documented.

Conclusions

The characterization of the carbonates present in the coal-bearing strata of the eastern United States using the conventional NP determination can be inaccurate. This inaccuracy is due to the presence of siderite which affects the stability of the NaOH titration endpoint. Conclusions of the research completed thus far include: 1) siderite is ubiquitous in the coal-bearing strata examined thus far; 2) the presence of siderite can profoundly effect the NP value; 3) incorrectly assigned fizz ratings, and thus digestion procedures, can affect the accuracy of the NP determinations; 4) CO₂ coulometry can be used to very accurately determine the carbonate carbon contents of overburdens; 5) the CO₂ evolution rate during the carbonate carbon determination is a function of which carbonate phases are present, and these rates can be used to determine if the overburden contains calcite, siderite, or a mixture of carbonate phases; 6) the effect of siderite on the determination of NP can be minimized using H₂O₂; 7) because siderite occurs in overburdens which contain reactive carbonate phases (e.g. calcite and/or dolomite), the addition of H₂O₂ is warranted because there is no criterion to judge the validity of an NP whose assigned fizz rating is greater than zero; 8) the observed siderites were not phase pure, an observation in good agreement with the literature; and, 9) despite the addition of H₂O₂ many siderite bearing overburdens still possess NP. This may be attributable to the pH of the NaOH back titration endpoint (pH = 7.0)

and/or the presence of Ca and Mg in the siderite.

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