

Article



The Application of Thermal Decomposition for Determination of Carbonate Acid-Neutralising Capacity for Improved Acid Mine Drainage Prediction

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Abstract: This study developed an industry-applicable, thermal decomposition methodology for quantification of carbonate mineral acid neutralisation capacity (ANCtherm-carb) for waste rock, tailings, and other mined materials. Standard titration-based methods for ANC can be compromised due to contributions from silicate minerals, ion exchange, Fe-rich carbonates, and other transition metal carbonates. C emission (CO₂ and CO) was measured using IR in a N₂ atmosphere. C_{neut} (wt%) was calculated using the C emission at 800 or 1000 °C minus the C emission at 400, 450 or 500 °C and the weight of sample prior to decomposition (Equation (2) of this manuscript). This value was then input into Equation (3) of this manuscript to calculate ANC_{therm-carb}. Good correlation of ANC_{therm-carb} for single-mineral carbonates with ANC_{calc}, calculated from bulk assay concentrations for Mg, K, Na, Ca, and Mn, was achieved. Thereafter, 18 waste rock samples were examined, resulting in the correlation of $ANC_{therm-carb}$ versus non-standard $ANC_{titrate-carb}$ (titration methodology adapted to focus on carbonate neutralisation only) with $R^2 = 0.96$. This correlation is valid for samples containing both non-neutralising carbonates (siderite) and sources of neutralisation arising from non-carbonates (Mg-clay) within this waste rock system. Typically, mining operations use total C measurements for assessment of carbonate neutralisation potential in the block and mining model. This method provides an effective means to cheaply analyse for carbonate neutralisation potential with assignment of potentially acid-forming and non-acid-forming blocks to waste rock cells, etc.

Keywords: acid mine drainage; mine waste rock characterisation; acid neutralisation capacity; mineral carbonates; thermal decomposition

1. Introduction

Acid mine drainage (AMD) is an internationally-recognised environmental issue arising, primarily, from the exposure of pyrite (FeS₂) to weathering, resulting in the formation of acid and simultaneous metalliferous drainage [1]. One of the first steps to determine if AMD is likely is the geochemical characterisation of mine waste materials. For this characterisation process, standardised, internationally-recognised methods are applied [2]. Many of these acid base-accounting (ABA) standardised tests have been reviewed in [3]. Often, the first step in ABA is the definition of both the maximum potential acid (MPA) generation and the acid neutralisation capacity (ANC) for a specific material. The net acid production potential (NAPP) is then defined as MPA minus ANC. If this value is positive, then the waste is likely to be acid generating. This initial assessment is, thereafter, complemented by other analyses such as net acid generation testing, neutralisation potential ratio (NPR) determination and kinetic leach columns [4,5]. A NPR assessment in block/mining models is often used to assign acid-generating material, but during initial or detailed characterisation studies, it is also common to explore more broadly with AMIRA International Ltd classifications, etc. [4,5].

The standard approach for definition of ANC is by titration in the Sobek test [4], the results from which often depend on subjective initial fizz rating tests to determine the amount of acid to be added for full carbonate dissolution, and subjective times for reactions to occur after carbonate dissolution on back-titration to pH 7. Carbonate minerals can be subjectively divided into three categories under Sobek test conditions:

(i) Those that provide acid neutralisation in the ratio of $2H^+$ per carbonate dissolved. These include calcite (CaCO₃), magnesite (MgCO₃) and dolomite (Mg,Ca)₂(CO₃)₂). Copper carbonate minerals, e.g., malachite (Cu₂CO₃(OH)₃), azurite (Cu₃(CO₃)₂(OH)₂), and manganese carbonate minerals, e.g., rhodochrosite (MnCO₃), also fall into this category, as the aqueous Cu and Mn do not hydroxylate at neutral pH (unless present at very high concentrations). Released metals such as Mn and Cu from carbonate minerals are acknowledged as potential contributors to neutral metalliferous drainage (NMD) but this is not discussed further in this work. However, this needs to be considered as part of any AMD risk assessment process.

(ii) Carbonate minerals that produce less neutralisation, for instance, ferroan dolomite $(Ca(Mg_x,Fe_{(1-x)})(CO_3)_2)$ and ankerite $Ca(Mg_x,Mn_y,Fe_{(1-x-y)})(CO_3)_2)$. For these minerals, the degree of neutralisation produced is dependent on the cations present that do not hydroxylate at neutral pH, e.g., Ca^{2+} , Mg^{2+} or Mn^{2+} . In contrast, ferrous iron (Fe²⁺) will oxidise to ferric iron (Fe³⁺) and form a neutral hydroxylation complex releasing acid. Consequently, the maximum amount of neutralisation, $2OH^-$ per carbonate, is decreased by the concentration of the Fe, i.e., 1-x or 1-x-y. The same concept applies to any other cations within these mineral frameworks that hydroxylate at neutral pH.

(ii) Carbonate minerals that do not produce any net neutralisation on dissolution. The most common of these minerals is siderite (FeCO₃). The lack of neutralisation potential for siderite is now well acknowledged in the literature [6].

The presence of Fe-containing carbonate minerals can result in erroneously high ANC values in the standard Sobek ANC test due to the slow hydroxylation and precipitation of Fe^{3+} [6,7]; complete oxidation results in no net acid neutralisation (e.g., Equation (1) for siderite). Consequently, there is potential to inaccurately measure the ANC of iron-rich carbonate waste rocks. This can be rectified by the application of the modified Sobek test [7], wherein peroxide is added to ensure full oxidation and hydroxylation of the dissolved Fe but this can induce unrealistic reactions in some other minerals (e.g., pyrrhotite, chalcopyrite).

$$FeCO_{3(s)} + 3H^{+} + 0.25O_{2} \rightarrow Fe^{3+} + H_{2}CO_{3} + 0.5H_{2}O$$

$$Fe^{3+} + 3H_{2}O \rightarrow Fe(OH)_{2} + 3H^{+}$$
(1)

The ANC titration process is also known to capture a proportion of neutralisation from fast-reacting silicates (e.g., chlorite, Table 18 in [8]). There exists disagreement concerning the usefulness of neutralisation arising from silicate dissolution [9] or ion exchange [10] in terms of extents and rates, e.g., too slow from silicates and too fast from ion exchange. It is also noted that many transition metal cations are present in solution at neutral pH as demonstrated by the issue of NMD and hence any assumption of their complete precipitation at neutral pH following an ANC back-titration is clearly incorrect. It is therefore desirable to develop a robust automated method for identification and quantification of carbonate mineralogies that do, and do not, contribute to ANC.

Considerable analysis has been carried out on thermal decomposition properties of mineral carbonates [11–15] but only a limited number of studies have examined the application of thermal decomposition for determination of carbonate ANC. Hammack [16] used evolved gas analysis in a 10% O₂ and 90% N₂ atmosphere and concluded that bicarbonates gave rise to CO₂ peaks in the range of 100–200 °C, the transition metal carbonates in the range of 220–520 °C, and the alkaline earth carbonates between 220–440 °C and 520–660 °C.

However, the number of carbonate phases examined was limited to sodium bicarbonate, manganous carbonate and calcium carbonate.

A controlled-atmosphere programmed-temperature oxidation (CAPTO) apparatus [17] was used for analysis of emission of CO_2 , H_2O , SO_2 and NO_2 from coals [18] but the focus of this study was the characterisation of the coals and not the determination of ANC. This was also the case for [19] which focused on how magnesite, siderite, calcite, dolomite and ankerite affected the calorific capacity of coal.

More recently, a methodology based on selective thermal decomposition of different carbonates (calcite, dolomite, and siderite) to provide well-resolved carbon dioxide evolutions has been tested [20]. The method used controlled gas flow and temperature ramping in a modified LECO analysis with continuous Fourier-transform infrared (FTIR) CO₂ analysis of gas evolved. This approach successfully determined the concentrations of alkaline earth- and transition metal-carbonates in coal over-burden samples. Thereafter, a methodology was developed using thermogravimetric and differential analysis for the quantification of siderite, calcite and dolomite [21] but this study was not focused on the determination of carbonate ANC. A thermal procedure, therefore, potentially provides an alternative direct method of correctly determining carbonate neutralisation capacity in mine rock and tailings wastes but requires development for application to a greater range of carbonate minerals and non-coal ore bodies.

The potentially important, unique role for the thermal decomposition method may be the analysis of problematic samples shown to contain significant siderite and other nonneutralising carbonates to give correct information on ANC available from carbonates in the waste. In the study described herein, we have sought to adapt the method as given in [20] to develop an industry-applicable approach for carbonate ANC determination, avoiding issues of slow-reacting carbonates and non-neutralising carbonates. Single-mineral samples were used to validate and refine the process, followed by the assessment of waste rock samples from a mine project site.

2. Materials and Methods

2.1. Mineralogy and Bulk Assay

Quantitative X-ray diffraction analysis was carried out on the 'single' mineral carbonate samples. Powder X-ray diffraction data were collected using a Bruker D8 Advance Eco X-ray diffractometer (Bruker, Billerica, MA, USA) with Co K α radiation (λ = 1.7902 Å) at 35 kV and 28 mA, across the 2 θ range 10–90° with a step size of 0.02°. A Fe filter was used to reduce the Co K β X-ray emission intensity. Each sample for XRD analysis was micronized using a micronizing mill (XRD-Mill, McCrone, Westmont, IL, USA). Phase identification was carried out using the Diffrac. EVA software (Bruker, Billerica, MA, USA; Version 3.0) with application of the ICDD PDF-4+ database (International Centre for Diffraction Data, Newtown Square, PA, USA). Corundum (15 wt%) was added to each sample as an internal standard and for quantification of the amorphous/unknown component. Quantitative phase analysis was performed using the computer program TOPAS (Bruker; Version 4.2). Uncertainties of the resulting XRD analysis at the 95% confidence level are estimated to be $\pm \chi^{0.35}$ where χ is the wt% of a given crystalline phase [22]. The amorphous/unknown components were determined to be negligible and have not been included in Table 1 (i.e., the sum of the wt% mineral phase for each sample is 100 wt%).

Quantitative mineralogical characterisation, of the mine site project samples, was carried out using scanning electron microscopy (SEM) combined with automated mineral liberation analysis (MLA; FEI Quanta 600 Mineral Liberation Analyser, at 15 kHz at 90k counts s⁻¹) at Rio Tinto's Research and Technical Development Centre (Melbourne, Australia). This system utilises two X-ray-collecting silicon drift detectors (Bruker XFlash 6130 detectors) which measure spectra expressed as normalised counts per second per channels along the keV scale. The MLA measurement type utilised during this project was the GXMAP measurement mode. Samples were prepared as 8 individual carbon-coated

polished blocks for each waste rock sample using representative splits (>200 g) of material available from the coarse rejects (-2 mm) from drill core assay sample preparation.

Bulk assays were carried out using mixed acid digestion followed by ICP-OES (inductively coupled plasma—optical emission spectroscopy) detection. Total C was measured by LECO.

Table 1. Quantitative XRD analyses (wt%) of the carbonate mineral samples. Where a specific mineral was not identified as being present the cell has been left empty.

Mineral Phase	Standard Stoichiometry	Magnesi	te Siderite	Rhodochrosite	Dolomite	Calcite	Azurite	Malachite	Ankerite
Quartz	SiO ₂	0.2	2.5	4.3	0.5	0.2	0.8	0.3	44
Calcite	CaCO ₃				1.1	99.8			
Dolomite	$CaMg(CO_3)_2$	17.9			98.5				7.6
Rhodochrosite	MnCO ₃			95.7					
Azurite	$Cu_3(CO_3)_2(OH)_2$						99.2		
Magnesite	MgCO ₃	81.9							
Malachite	Cu ₂ CO ₃ (OH) ₂							99.7	
Siderite	FeCO ₃	0.1	91.5						27.3
Ankerite	$Ca(Fe^{2+},Mg)(CO_3)$	2							7.2
Hematite	Fe ₂ O ₃	-	5.9						
Sphalerite	ZnS								13.8

2.2. Acid Neutralisation Capacity by Titration

2.2.1. ANC Titration Methodology (1)-ANCtitrate-all

The objective of this methodology is to capture all measurable ANC, i.e., carbonate, silicate, and ion exchange, while ensuring non-neutralising carbonates, e.g., siderite, are not included. The methodology (1) titration protocol followed the standard AMIRA Test Handbook [4] methodology with 2 drops of 30% H₂O₂ solution added after back-titration to pH 4.5, prior to further titration to pH 7. In a modification of this methodology (developed by Levay and Co Environmental Services—unpublished), if the pH of the solution had not equilibrated within 1 min a further 2 drops of H₂O₂ solution was added and so forth until the pH was equilibrated. For the siderite 'single-mineral' sample, a total of 6 drops of H₂O₂ was added. For all other minerals only 2 drops H₂O₂ solution were required.

2.2.2. ANC Titration Methodology (2)-ANCtitrate-carb

This methodology was applied only to waste rock samples and is the same as methodology (1) except for a change in the target digestion pH prior to back-titration, from 0.8-1.5 to 1.5-2.0, and back-titration to pH 8.3 rather than pH 7. The change in target digestion pH was made with the purpose of reducing silicate and ion-exchange neutralisation so that mostly only carbonate neutralisation is measured. The increased final pH after back-titration is to ensure the full hydroxylation of metal cations (e.g., Cu²⁺ and Zn²⁺) other than Na⁺, K⁺, Mg²⁺ and Ca²⁺, so that these do not contribute to the measured ANC.

2.3. Thermal Decomposition

A feed single-carbonate mineral sample (100 mg, <75 μ m) was placed in a preheated quartz tube (3 cm diameter) furnace at each of the temperatures of 400, 500, 600, 700, and 800 °C. CO₂ emission was then measured for 30 min using IR detection (TSI 7575 Q-Trak, with 982 IAQ probe). A 30 min decomposition duration was found to be sufficient in all cases for CO₂ formation to have ceased at each temperature. The CO₂ emission (and in a later iteration also the CO emission) from each single-mineral sample was measured at the given temperature before heating the furnace to the next highest temperature and the introduction of a fresh sample. The weight of each sample was measured before and after heating. The carrier gas used was either O₂ or N₂ at the flow rate of 100 mL min⁻¹.

For the mine site project samples, thermal decomposition of each sample was carried out at 450 and 1000 $^{\circ}$ C for 30 min, using different sub-samples, in a N₂ atmosphere at gas

flow rate of 100 mL min⁻¹. Thermal ANC is then calculated from the difference in the total of the CO and CO₂ off-gas, measured using IR, at these two temperatures.

C_{neut} (wt%), the C associated with carbonate neutralisation is calculated using Equation (2).

 $C_{\text{neut}}(\text{wt\%}) = \frac{100 \times ((\text{weight}(C) \text{ emission at 800 or 1000 °C}) - (\text{weight}(C) \text{ emission at 400, 450 or 500 °C}))}{\text{weight of sample prior to decomposition}}$ (2)

 $ANC_{therm-carb}$ is then calculated using Equation (3).

$$ANC_{therm-carb} = 30.6 \times C_{neut}(wt\%) \times 32.065/12$$
(3)

3. Results

3.1. Single Minerals

3.1.1. Mineralogy and Bulk Assay

The quantitative mineralogy for the selected 'single' carbonate minerals is given in Table 1. All these carbonate minerals were present in their respective samples at >90 wt% except for magnesite and ankerite. The bulk assay for the single-carbonate minerals is provided in Supplementary Material (SM) Table S1.

3.1.2. ANC by Titration—Methodology 1

Table 2 provides the ANC values calculated from Ca, Mg alone, and with Na and K, and with Na, K, and Mn, ANC derived from the total carbon assay (ANC_{IC}, it is assumed that no organic C is present) and ANC measured by titration methodology (1) (ANC_{titrate-all}). For these systems, the method of derivation of ANC using Na, K, Ca, Mg and Mn is acceptable due to the lack of minerals, other than carbonates, likely to contain these elements (ANC due to Na and K is minor). It is noted that this method of derivation of ANC would likely not be realistic for more complicated real mineral assemblages where these elements may not be readily soluble. The rationale for the calculation of ANC based on these cations can be found in their Pourbaix diagrams [23]. On dissolution, these cations will remain unhydroxylated until high pH. This ensures the ions provide acid-neutralising capacity irrespective of the ANC test pH regime.

	ANC _{IC} (LECO Total Carbon)	ANC (Ca, Mg Assay)	ANC (Ca, Mg, Na, K Assay)	ANC _{calc} (Ca, Mg, Na, K, Mn Assay)	ANC _{titrate-all}
Dolomite	1070	1027	1045	1047	1027
Magnesite	1168	1125	1127	1127	1140
Calcite	923	993	994	994	989
Siderite	907	144	144	144	175
Malachite	346	1	2	2	212
Azurite	433	3	3	3	207
Rhodochrosite	915	81	81	853	811
Ankerite	382	168	169	184	201

Table 2. Calculated ANC from bulk assay data and measured ANC by titration (ANC_{titrate-all}, fizz rating 4, methodology (1)) for single-mineral carbonate samples. Units for all ANC are kg H_2SO_4 t⁻¹.

 $ANC_{titrate-all}$ was similar to that calculated from total carbon or from the bulk solids assays for Ca, Mg, Na and K for calcite, dolomite and magnesite (Table 2). For siderite, the $ANC_{titrate-all}$ was also similar to that calculated from the bulk assay of Na, K, Mg and Ca suggesting effective oxidation and precipitation of the iron component of the siderite, i.e., the dissolution of siderite did not provide neutralisation.

For malachite and azurite the ANC calculated from the bulk assay of Ca, Mg, Na and K was much less than the ANC_{titrate-all}, which in turn was less than the ANC_{IC} calculated from total carbon. This suggests that some Cu²⁺ remained in solution despite titration to pH 7. The Pourbaix diagram [23] indicates this to be possible as aqueous Cu²⁺ is shown to be present at pH 7 at Eh (SHE) >200 mV, therefore being measured as neutralisation, although also likely to have the potential to generate NMD. The amount of Cu in the

sample required to remain in solution as Cu^{2+} to achieve the measured average ANC for these phases is 13.4 wt% for azurite and 13.7 wt% for malachite, or 24% and 23% of the Cu present in the samples, respectively.

For rhodochrosite, the ANC_{titrate-all} was of similar magnitude to the ANC_{IC} (811 cf. 915 kg H₂SO₄ t⁻¹) but was much greater than the ANC calculated from the bulk assay of Ca, Mg, Na and K. This suggests that much of the Mn has remained in solution and therefore constitutes neutralisation, although also likely to have the potential to generate NMD. Again, the Pourbaix diagram [23] suggests that this is reasonably the case with both high pH and Eh required for precipitation of $MnO_{2(s)}$. The amount of Mn in the sample required to remain in solution to achieve the measured ANC is 43.2 wt% or 93% of the Mn available in the rhodochrosite sample. ANC_{calc} calculated from Ca, Na, K, Mg and Mn (Table 2) is 853 kg H₂SO₄ t⁻¹ as compared to the measured ANC_{titrate-all} value of 811 kg H₂SO₄ t⁻¹. The conclusion that rhodochrosite provides viable neutralisation from Mn agrees with the findings of [6], although the risks of NMD need to be acknowledged.

The ankerite sample was a more complicated system than the other samples as it contained more dolomite than ankerite and almost the same amount of siderite as ankerite (Table 1). Given the presence of siderite, and likely Fe in the ankerite, it is predictable that the ANC_{IC} calculated from the total carbon assay (Table 2) is greater than the titrated ANC_{titrate-all} (382 cf. 201 kg H₂SO₄ t⁻¹). The ANC_{calc} calculated from the bulk assays for Ca, Mg, Na, K and Mn is in good agreement with the titrated ANC at 184 kg H₂SO₄ t⁻¹.

3.1.3. Thermal Decomposition

The decomposition behaviours of these selected carbonate minerals were studied using gravimetric and IR analyses of the emitted gases in O_2 or N_2 environments.

Using O₂ as the Carrier Gas

In Figure 1, the CO₂ emissions across sequential temperature ranges are shown, i.e., <400 °C, 400-500 °C, etc. The data in Figure 1 are presented as Equation (4):

 $100 \times (\Delta CO_2 \text{ emission}) / \text{ (total expected CO}_2 \text{ from the LECO total C measurement)}$ (4)



Figure 1. Percentage (%) of expected CO₂ emission as a function of temperature range using O₂ as the carrier gas.

 ΔCO_2 emission is, for instance, the CO_2 emission measured at 500 °C minus that measured at 400 °C. The data are normalised by the LECO total carbon measurement to assess whether the decomposition is complete.

Calcite and dolomite decomposed at >600 °C to also give approximately 100% CO₂ emission (Figure 1). Malachite and azurite also decomposed to give 100% CO₂ emission, at <400 °C. Magnesite progressively decomposes between 400 and 700 °C to give approximately 100% total CO₂ emission.

Siderite and rhodochrosite were found to decompose at >400 °C but with only approximately 80% CO₂ emission up to 800 °C. Ankerite progressively decomposed from 500 °C upwards and even at 1000 °C (note data between 800 and 1000 °C are not shown in Figure 1) only gave rise to approximately 80% CO₂ emission (Figure 1). Remnant C in the residues were all found to be less <1 wt% and measurement of CO emission (also using IR) for siderite at 700 °C was found to equate to 0.68 wt% C. This, therefore, does not explain the 'missing' CO₂ emission for siderite of approximately 20%. As the 'missing C' is neither in the emitted gases as CO or in the solids the most likely explanation is that the initial measurement of LECO total C was too high. The total CO₂ emissions would suggest carbon concentrations of 3.8, 8.6 and 8.3 wt% C for ankerite, siderite and rhodochrosite as compared to the assay values of 4.7, 11.1 and 11.2 wt% C, respectively.

Magnesite, dolomite and calcite show approximately 100% total weight loss as compared to the expected weight loss based on the CO_2 emission (Table 3) assuming decomposition to CaO and/or MgO and emission of CO_2 . The weight losses for siderite, ankerite and rhodochrosite are also close to 100% of those calculated based on the total CO_2 emission (Table 3) assuming decomposition to FeO and MnO for siderite and rhodochrosite, respectively, and based on stoichiometric Equation (5) for ankerite.

$$Ca(Mg, Fe, Mn)(CO_3)_{2(s)} \to CaO_{(s)} + \frac{1}{3}MgO_{(s)} + \frac{1}{3}FeO_{(s)} + \frac{1}{3}MnO_{(s)} + 2CO_{2(g)}$$
(5)

Temperature	Magr	nesite	Dolo	Dolomite		Calcite Siderite		
(°C)	Meas	Calc	Meas	Calc	Meas	Calc	Meas	Calc
400	1	1	0	0	1	1	3	3
500	14	14	2	2	1	1	21	21
600	44	44	4	4	2	2	32	32
700	51	51	23	23	27	27	33	33
800	51	51	47	47	44	44	33	33
Temperature	Ankerite		Rhodochrosite		Azurite		Malachite	
(°C)	Meas	Calc	Meas	Calc	Meas	Calc	Meas	Calc
400	1	1	4	4	31	23	28	22
500	6	6	12	12	30	23	28	22
600								
000	7	7	20	20	31	23	28	22
700	7 7	7 7	20 30	20 30	31 30	23 23	28 28	22 22

Table 3. Measured weight loss and weight loss calculated from the CO₂ emissions (wt%) for singlemineral carbonates. Meas—measured; Calc—calculated.

However, it can be seen from Table 3 that malachite and azurite give rise to greater than expected weight loss based on measured CO_2 , assuming H_2O and CO_2 emissions and decomposition to CuO. However, the total carbon values of 5.3 wt% for azurite and 4.2 wt% for malachite are less than suggested by quantitative XRD (6.9 wt% and 5.4 wt%, respectively) or by the Cu assay (7.0 wt% and 5.6 wt%). If the expected weight loss, assuming 100% CO_2 emission, is calculated using the quantitative XRD derived carbon concentrations, then the calculated weight loss would be 30.5 wt% for azurite and 28.0 wt% for malachite, both very close to the measured weight loss.

It is clear from Figure 1 that there exists good separation of malachite, azurite (<400 °C) and siderite (400-600 °C) from calcite and dolomite. However, there is not good separation of siderite from either rhodochrosite or magnesite. 'Ankerite' is not directly interpretable

due to it being mixed phase. Although these Cu-containing carbonate minerals (azurite and malachite) have been shown to contribute to ANC_{titrate-all} by back-titration to pH 7 (Section 3.1.2) it was considered desirable to discriminate against these minerals during thermal decomposition determination of ANC_{therm-carb}.

To attempt to deconvolute the decomposition temperatures of siderite and magnesite, further measurements using the same conditions were undertaken at 450 and 550 °C. Nevertheless, there was still no clear temperature demarcation of the decomposition of siderite and magnesite using O_2 as the carrier gas. The best temperature, as for the measurements shown in Figure 1, remained 500 °C with 26.8% and 64.9% of the CO₂ emission from magnesite and siderite occurring below this temperature. This would not provide adequate deconvolution of these carbonate minerals.

Using N₂ as the Carrier Gas

Comparison of thermal measurements of carbonate minerals undertaken in air [11] and in N_2 [19] have indicated that the temperature of decomposition of siderite is significantly decreased in N_2 , as compared to air, whereas the temperature of decomposition of magnesite is much less affected. The decomposition temperatures of calcite and dolomite, while significantly decreased, remain above that for magnesite.

Following from these observations the CO₂ (and CO) emissions from rhodochrosite, magnesite and siderite were analysed at 400, 450, 500, 550, 600, 700 and 800 °C using N₂ as the carrier gas (decomposition duration 30 min, 100 mL min⁻¹ gas flow rate; Figure 2). Magnesite shows little change. The decomposition of rhodochrosite at 600–700 °C is smaller in N₂ carrier gas as compared to O₂ carrier gas. The decomposition temperature of siderite is significantly reduced in N₂ carrier gas, as compared to O₂ carrier gas, with negligible decomposition at >500 °C.



Figure 2. Decomposition behaviours of magnesite, rhodochrosite and siderite using N₂ and O₂ carrier gases. To show rhodochrosite on this graph, the data for <400 °C are shown as <450 °C, and the data for 500–600 °C are shown as 550–600 °C. The sum of the values for each mineral across the temperature ranges has been normalised to 100%. The total %C emission, as a % of the total C present, is also provided.

The emissions of C, as a percentage of total LECO carbon, in N₂ carrier gas as compared to O₂ carrier gas increased for rhodochrosite and siderite (77 to 84%; 81 to 85%) but remained unchanged for magnesite (97 to 96%). The agreement (Table 4) between measured weight loss and calculated weight loss using Equations (6)–(8) is good. (Note: the full

weight loss and % CO and CO₂ emission values for the single-carbonate mineral samples with both O_2 and N_2 carrier gas are provided in SM Tables S2–S4.)

Table 4. Measured weight loss and weight loss calculated from the total of CO_2 and CO emissions (wt%) for rhodochrosite, magnesite and siderite in N_2 carrier gas. Meas—measured; Calc—calculated.

Tommorphumo (°C)	Rhodochrosite		Magr	nesite	Siderite	
Temperature (°C) –	Meas	Calc	Meas	Calc	Meas	Calc
450	8	7	3.3	3	24	23
500	17	18	12	12	34	32
550	27	28	43	40	35	32
600	34	34	44	43	35	32
700	35	34	50	50	36	34

Rhodochrosite

$$MnCO_{3(s)} \to MnO_{(s)} + CO_{2(g)}
 MnCO_{3(s)} \to MnO_{(s)} + CO_{(g)} + \frac{1}{2}O_{2(g)}
 \tag{6}$$

Magnesite

$MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)}$	(7)
$MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{(g)} + \frac{1}{2}O_{2(g)}$	(7)

Siderite

$\begin{aligned} & \operatorname{FeCO}_{3(s)} \to \operatorname{FeO}_{(s)} + \operatorname{CO}_{2(g)} \\ & \operatorname{FeCO}_{3(s)} \to \operatorname{Feg} + \operatorname{CO}_{(g)} + \frac{1}{2}\operatorname{O}_{2(g)} \end{aligned} \tag{8}$

3.1.4. Thermal Decomposition ANC of Single-Carbonate Minerals

Figure 3 shows a comparison of the single-mineral carbonate ANC_{therm-carb} values derived from thermal decomposition as compared to the titrated ANC_{titrate-all} (ANC methodology (1), Section 3.1.2). It is clear from this graph that the best correlation to titrated ANC_{titrate-all} is when the decomposition behaviour in N₂ at 450 °C is used for magnesite, siderite and rhodochrosite. The decomposition behaviour of dolomite, calcite, azurite, and malachite were not examined in N₂. However, it is unlikely that the behaviours of these phases would change sufficiently significantly in N₂ carrier gas, as opposed to O₂, to make the application of 450 °C invalid. Were this to be the case an increase from <400 °C decomposition temperature for azurite and malachite and decreases in decomposition temperatures for calcite and dolomite from >600 °C would have to occur on change from the carrier gas from O₂ to N₂. Ankerite was not examined in N₂ carrier gas due to the mixed-phase nature of this sample.

The correlation of ANC_{therm-carb} (using the decomposition at 450 °C where available, otherwise 400 °C) to the ANC_{titrate-all} is shown in Figure 4a. The slope of the line of best fit is close to 1 with correlation coefficient of 0.94. The line of best fit results in smaller values than those measured (i.e., *y*-axis intercept of -108) due primarily to the very low ANC_{therm-carb} values for rhodochrosite, malachite and azurite. Figure 4b shows the correlation of the ANC_{calc} calculated using the bulk assay concentrations of Mg, Na, K, Ca, and Mn (Table 2) with ANC_{therm-carb}. The correlation coefficient is 0.96 with slope of 0.89 and intercept near zero providing confidence in the method of distinguishing neutralising (ANC) from non-neutralising carbonates.



Figure 3. Comparison of ANC derived from thermal decomposition data (ANC_{thermal-carb}) and titration (ANC_{titrate-all}). The numbers in the legend refer to the temperature below which the CO₂ emission was considered to be associated with non-neutralising carbonate phases. Note: The '<450, O₂' data are derived from the 400 °C, O₂ carrier gas values for dolomite, ankerite, calcite, azurite and malachite.



Figure 4. (a) Correlation of ANC_{therm-carb} and ANC_{titrate-all} (ANC methodology (1)). (b) Correlation of ANC_{therm-carb} and ANC_{calc} calculated from bulk assay concentrations for Mg, K, Na, Ca, and Mn. The dark dotted line indicates the ratio of 1:1.

3.2. Mine Site Project Waste Rock Samples

Twenty samples were chosen for analysis based on:

- (1) Samples with the greatest difference between ANC_{titrate-carb} and ANC_{IC} were chosen as these were likely to provide the most information on what is contributing to the ANC values. When ANC_{titrate-carb} minus ANC_{IC} is positive it may be due to noncarbonate neutralisation and when this value is negative it may be due to the presence of siderite.
- (2) Samples that were categorised as uncertain where chosen, i.e., either NAG pH <4.5 and NAPP <0, or NAG pH >4.5 and NAPP >0 (for a description of the net acid generation, NAG, test refer to [4]).
- (3) Samples with either low or high NAG pH with little difference between ANC_{titrate-carb} and ANC_{IC} were not chosen.

The MLA-derived carbonate mineralogy relevant to ANC determination for the 20 mine site samples examined is given in Table 5. In Table 5 the ANC values calculated from total carbon (ANC_{IC}—it is assumed that no organic carbon is present; C is present at <1.5 wt% except for three samples) and measured using ANC titration by methodology (2) (ANC_{titrate-carb}) are compared. For the samples containing elevated siderite and no other detected carbonate minerals (samples 12–20) the ANC_{titrate-carb} is very small indicating that siderite is effectively excluded. The ratio of ANC_{titrate-carb} to ANC_{IC} for the other samples is close to 1 (0.8–1.2) except for sample 3. This sample was found to contain 30.7 wt% Mg-clay by MLA. It is likely that a portion of the Mg-based neutralisation from this clay contributed to the ANC_{titrate-carb} of 118 kg H₂SO₄ t⁻¹ (*cf.* 85 kg H₂SO₄ t⁻¹ ANC_{IC}).

Table 5. Quantitative MLA mineral composition analysis (wt%) of the 20 mine site samples. Total carbon assays have been used to calculate ANC_{IC} (note: it is assumed that there is no organic C). $ANC_{titrate-carb}$ (titration methodology (2)) values are also provided. All ANC values are in units of kg H₂SO₄ t⁻¹. NA—not available. Where a specific mineral (ankerite, calcite or dolomite) was not identified as being present the cell has been left empty.

Sample #	Ankerite (wt%)	Calcite (wt%)	Dolomite (wt%)	Siderite (wt%)	Total C (wt%)	ANC _{IC}	ANC _{titrate-carb}	ANC _{titrate-carb} /ANC _{IC}
1	0.1	0.2	0.1		0.08	7	8	1.2
2				1.3	0.24	20	16	0.8
3		5.8		1.4	1.04	85	118	1.4
4	4.5	0.9	4.6		1.26	103	100	1.0
5	2.2		1.7		0.64	52	60	1.1
6	2.7		8.5		1.62	132	138	1.0
7	1.3	1.2	2.6	0.1	0.70	57	NA	NA
8	1.6		2.9	0.1	0.78	64	NA	NA
9	3.1		12.7		2.36	193	170	0.9
10	5.9		3.4		1.28	105	99	0.9
11	6.3	1.5	7.2		2.14	175	148	0.8
12				1.5	0.24	20	12	0.6
13				2.1	0.28	23	12	0.5
14				4.0	0.44	36	11	0.3
15				8.6	1.06	87	16	0.2
16				4.6	0.60	49	8	0.2
17				2.8	0.48	39	9	0.2
18				2.1	0.34	28	8	0.3
19				1.6	0.26	21	3	0.1
20				2.3	0.34	28	11	0.4

The thermal decomposition data for the mine project samples are provided in Table 6. The % recovery of CO + CO₂ for sample 15 at 450 °C was smaller than expected, being only 46%, given that this sample contained the greatest concentration of siderite at 8.6 wt%. For this reason, the decomposition was repeated at 500 °C, returning 83% emission of the expected CO + CO₂. It is these data that are included in the correlation given in Figure 5.

Comparison of the ANC_{therm-carb} and ANC_{titrate-carb} (methodology (2) ANC) values is given in Figure 5 for the 18 samples for which ANC_{titrate-carb} values are available. The correlation is excellent given the uncertainties involved in both approaches to carbonate ANC measurement. Moreover, the *x*-intercept is small (-3.5) suggesting the absence of systematic (i.e., constant) errors.

		450 °C			1000 °C		
Sample #	Generated CO (% of Possible Total)	Generated CO ₂ (% of Possible Total)	CO + CO ₂ (% as CO ₂ Combined, of Possible Total)	Generated CO (% of Possible Total)	Generated CO ₂ (% of Possible Total)	CO + CO ₂ (% as CO ₂ Combined, of Possible Total)	ANC _{therm-carb} (kg H ₂ SO ₄ t ⁻¹)
1	5.6	61	70	0.0	93	93	2
2	2.2	69	72	0.0	96	96	5
3	0.3	17	17	0.1	97	97	68
4	0.4	8.5	9.2	0.0	91	91	84
5	0.7	11	12	0.1	102	102	47
6	0.5	14	15	0.6	90	91	101
7	0.8	13	14	0.0	95	95	46
8	0.5	14	15	0.0	96	96	52
9	0.4	9.2	10	1.5	83	86	147
10	0.2	10	10	0.5	97	98	92
11	0.1	6.5	6.7	0.00	89	89	144
12	1.2	75	77	0.5	99	100	5
13	0.6	60	61	0.5	98	98	8
14	1.4	89	92	0.0	97	97	2
15	0.7	45	46	0.5	97	98	45
15 *	0.4	82	83	0.5	97	98	13
16	2.7	82	87	0.0	101	101	7
17	1.9	88	91	0.0	97	97	2
18	2.0	90	94	0.2	108	108	4
19	3.5	75	81	1.5	98	100	4
20	1.9	63	66	1.4	98	100	9

Table 6. Thermal decomposition CO and CO₂ data for the mine project samples and ANC_{therm-carb}.

* Sample 15, decomposition measured at 500 °C.



Figure 5. Correlation of ANC_{therm-carb} (using decomposition data at 450 °C except for sample 15 for which decomposition data at 500 °C was used) with the ANC_{titrate-carb} values. The dark dotted line indicates the ratio of 1:1 (note that R^2 for this line = 0.86). For sample 3 the greater ANC_{titrate-carb} than ANC_{therm-carb} value is likely due to the partial inclusion of neutralisation from Mg-clay in the ANC_{titrate-carb} value.

4. Conclusions

The purpose of this study was to develop an industry-applicable operational methodology for identification and quantification of different carbonate minerals for improved carbonate acid neutralisation capacity (ANC) determination for waste rock, tailings, and other mined materials. In this study, we have sought to adapt the method given in [20] to develop a method for carbonate ANC determination avoiding the issues of slow-reacting carbonates and non-neutralising carbonates.

The conclusions from measurement of the thermal decomposition behaviour of singlemineral carbonate samples are:

- Thermal decomposition of single-mineral carbonates in O₂ carrier gas was found to give good separation of the decomposition of malachite and azurite (<400 °C, considered to be non-neutralising for the purposes of these analyses) and siderite (<600 °C) from calcite and dolomite (>600 °C).
- It was not possible to separate the decomposition events of siderite from rhodochrosite and magnesite in O₂ carrier gas (400–600 °C).
- Thermal decomposition of single-mineral carbonates in N₂ carrier gas depressed the thermal decomposition temperature of siderite (70% decomposition at <450 °C) enabling improved differentiation of siderite from rhodochrosite and magnesite.
- C emission due to 'neutralising' carbonates was calculated by subtracting carbon emission at 450 °C where available, otherwise 400 °C, from the carbon emission at the greatest temperature applied (800 or 1000 °C). Data collected using N₂ as the carrier gas were used if available. Thermal ANC (ANC_{therm-carb}) was thereafter calculated as 30.6 × C wt% × 32.065/12.
- Correlation of ANC_{carb} to calculated ANC (using Mg, K, Na, Ca and Mn) gave rise to the line of best fit of:

$$ANC_{therm-carb} = (0.8992 \times ANC_{calc}) + 17.735$$

with R² of 0.96.

Based on this outcome the conditions of thermal decompositions for each sample at 450 and 1000 °C for 30 min in N₂ carrier gas at flow rate of 100 mL min⁻¹ were defined for examination of mine project waste rock samples.

The conclusions from analysis of 20 real mine samples are:

ANC_{therm-carb} determination using decomposition measurements at 450 °C (and 500 °C for one high siderite sample) and 1000 °C in N₂ carrier gas (flow rate 100 mL min⁻¹) gave excellent correlation to the titration ANC_{titrate-carb} (available for 18 samples, methodology (2)) values (that focused on carbonate ANC):

$$ANC_{therm-carb} = (0.85 \times ANC_{titrate-carb}) - 3.4691 (R^2 = 0.96)$$

• This correlation is valid for samples containing both non-neutralising carbonates and sources of neutralisation arising from silicates and ion exchange.

For the project waste rock samples studied, this methodology for determination of acid neutralisation capacity from carbonate minerals has the potential, with laboratory development, to be reliable and cost-effective. Moreover, using this methodology there should be no need for the feed inorganic carbon concentration to be known for determination of carbonate acid neutralisation capacity as the neutralising carbon component is determined from the difference in $CO_2 + CO$ emission at 1000 and 450 or 500 °C. Further development of this methodology for this system will focus on measurement of the $CO_2 + CO$ emission at 500 °C in N₂ carrier gas with a view to make the determination of ANC_{therm-carb} independent of siderite concentration. It is noted that validation and optimisation would be required for other mineral systems and the effects of and corrections for organic carbon remain to be developed.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/min11111181/s1, Table S1: Bulk assay concentrations for the single carbonate minerals samples (ppm unless stated otherwise), Table S2: Single carbonate CO₂ and weight loss data for thermal decomposition in O₂ carrier, Table S3: CO and CO₂ emissions and weight loss for siderite thermal decomposition in O₂ carrier gas, Table S4: CO and CO₂ emissions and weight loss for siderite thermal decomposition in N₂ carrier gas.

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