

Effect of carbonate mineralogy in the neutralization potential: Why different static tests lead to contradictory classification of ARD?

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Static tests are widely used to predict Acid Rock Drainage (ARD) from tailings containing sulfide minerals. These tests consist in measuring the neutralization and the acid potential of the waste, tailings and ores. The so-called Neutralization Potential (NP) and Acid Potential (AP) are defined differently according to the different static test protocols. These tests are relatively quick and inexpensive and are broadly applied during the first stages of environmental assessment (Plante et al., 2012; Capanema and Ciminelli, 2003; Lawrence and Wang, 1997).

The AP values are calculated by the total sulfur or sulfur-sulfide content (Plante et al., 2012; Lawrence and Wang, 1997; Sobek et al., 1978). The NP values are measured through the addition of fixed amount of acid, that is consumed by the sample and the residual acidity is back titration with sodium hydroxide. Carbonate minerals and some silicates contribute to neutralization potential. However, it is observed that these contributions depend on the carbonate phases, silicate content, aluminium, iron and manganese content (oxidizable/hydrolysable elements) present in the sample. Calcite (CaCO_3) has the highest neutralizing acid capability. Other minerals are dolomite ($\text{CaMg}(\text{CO}_3)_2$), magnesite (MgCO_3), ankerite ($\text{Ca}(\text{Fe}, \text{Mg})(\text{CO}_3)_2$), and siderite (FeCO_3). Among these, the least effective neutralizer is siderite, because the neutralised acid is released again by Fe^{2+} oxidation/ hydrolysis, thus resulting in no net neutralization.

In the present work, waste and tailings samples from gold ore mining were submitted to the following static tests: Modified-Sobek acid base accounting (MABA) (Lawrence and Wang, 1997), standard acid neutralization capacity (ANC), and ANC modified for siderite (ANC-SID) (Stewart et al., 2006). All these tests are based on the Sobek acid-base accounting (ABA) protocol (Sobek et al., 1978). The MABA test replaces acid attack at boiling temperature by acid attack at room temperature for longer times (24 h instead of 1-2h in the original ABA-Sobek). In addition, the final pH digestion should remain between 2 -2.5, and titration end-point pH of 8.3. Beyond that, staged addition of hydrochloric acid and different volumes defined by fizz ratings were proposed. Standard ANC and ANC-SID protocols are similar to original ABA-Sobek. The final pH digestion should be between 0.8-1.5 and the back titration runs up to pH 7; temperature is kept slightly lower (80-90°C); 2 drops of 30% H_2O_2 is added at pH 5 to oxidise and promote hydrolysis of any remaining dissolved Fe^{2+} . The ANC-SID is a modified ANC test designed to account for the effects of siderite. The test involves larger amounts of H_2O_2 than those in the standard ANC method and titration of the filtered solution after digestion over a longer time period.

Tests to determine NP were carried out in triplicate; one sample was submitted to back-titration with NaOH and the others were collected to analyse the solid residues. Total sulfur, sulfur-sulfide, total carbon and carbon-carbonate contents were determined by LECO and selective leaching. Residual total carbon contents were also analyzed.

The results showed S-sulphide content varying from 0.66-3.45% and C-carbonate 0.68-8.1% (Table 1). Siderite and ankerite were the main carbonate phases identified by Raman spectroscopy; calcite appeared as a minor phase. The sulfide phases were mainly pyrite and pyrrhotite (not shown).

Table 1 – Chemical and Raman analyses

Samples	% S total	%S-sulfide	%C Total	% C-carbonate	**NP-CO3 (kgCaCO ₃ /t)	Carbonate phases (relative amount)
AM1	0.94	0.86	0.93	0.68	57	Siderite » Calcite
AM2	1.53	1.53	2.14	0.99	83	Ankerite » Calcite
AM3	4.18	3.34	3.94	3.85	321	Ankerite » Siderite
AM4	3.67	3.45	9.32	8.07	673	Siderite » Ankerite
AM5	0.75	0.66	3.54	3.34	278	Calcite » Siderite » Ankerite

* C-organic matter - identified in all samples, except AM3. Expressive amount in AM2 around 50%

** NP-CO3 calculated based on C-carbonate content.

Two criteria were used to evaluate the acid-generating potential (Table 2): (i) NNP (NP – AP) expressed in kgCaCO₃/t and (ii) NP/AP ratio. Typically interpretation based on NNP parameter are: acid generation is uncertain for NNP values between -20 and 20 kgCaCO₃/t, acid generation is likely for NNP values below -20kgCaCO₃/t, and non acid generation for NNP values above 20kgCaCO₃/t. According to NP/AP criteria, the ARD classification as: acid generating if NP/AP < 1; non acid generating if NP/AP > 1; and uncertain, if 1 < NP/AP < 2 (Plante et al., 2012).

The NP results may vary significantly for a given sample, depending on the method employed in the NNP or NP/AP evaluation. Consequently, a high discrepancy in the parameters used to classify ARD potential can be observed. Except for AM2, classified as uncertain by NP/AP, NP-CO₃ (calculated) criteria classified the samples as no acid generating (NPAG)(Table 2). The calculate neutralization potential (NP-CO3) was estimated from C-Carbonate content, assuming that all C-carbonate content present in the sample is calcite (Table 1). The ARD classification assessed by MABA tests is more conservative. AM1 is classified as acid generating (PAG), AM2, AM3 and AM4 as uncertain and AM5 as no acid generating (NPAG). The question is: which method is more reliable?

Comparison of the different NP values for each samples are presented in Fig. 1a. Except for AM2, for all the remaining samples, NP-CO3 values are higher than the other NP's values. For AM2 all NP's values are closer, which can be related to the absence of siderite. The difference between NP-CO3 and the other NP's increases with increasing siderite content.

The discrepancy of NP-ANC and NP-ANC-SID with NP-MABA is also attributed to the content of siderite. Stewart et al (2006) showed that for siderite content higher than 15%, the NP-ANC-SID values are lower than NP-ANC. The samples AM3 and AM4 presented NP-ANC-SID lower than NP-ANC whereas the samples AM1 and AM5 showed similar NP-ANC and NP-ANC-SID values.

Table 2 – Static test results from different methods on the samples.

PARAMETERS	SAMPLES				
	AM1	AM2	AM3	AM4	AM5
AP	27	48	104	108	21
NP-MABA	12	63	187	116	119
NP-ANC-SID	37	79	195	173	194
NP-ANC	26	77	290	446	212
NP-CO3	57	83	321	673	278
NP-MABA AP					
NNP	-15	15	83	8	99
NP/AP	0.4	1.3	1.8	1.1	5.8
NP-ANC-SID AP					
NNP	10	31	90	65	174
NP/AP	1.4	1.6	1.9	1.6	9.4
NP-ANC AP					
NNP	-1	29	186	338	191
NP/AP	1.0	1.6	2.8	4.1	10.3
NP-CO3 AP					
NNP	30	35	216	565	258
NP/AP	2.1	1.7	3.1	6.2	13.5

All units expressed as kgCaCO₃/t, except NP/AP, unit-less.

	NPAG - no potential acid generation
	UNC - uncertainty potential zone
	PAG - potential acid generation

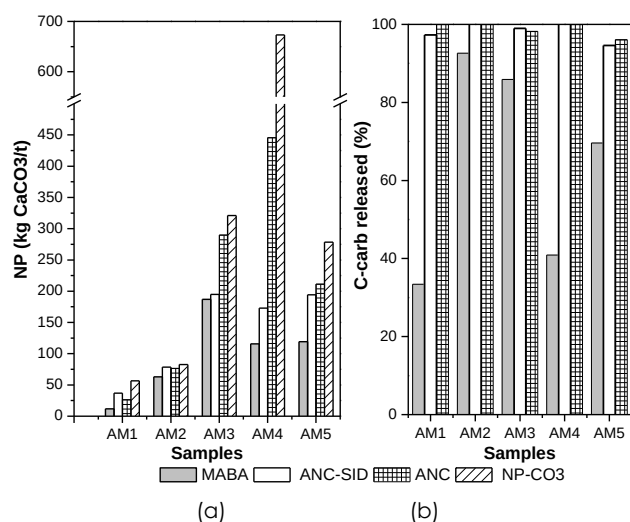


Figure 1: (a) neutralization potential (NP) values. (b) C-carbonate release (%) different static tests on the samples.

Ankerite, despite the presence of iron in its structure, exhibits a good neutralizing performance in the MABA tests, similarly to calcite. Samples containing predominantly ankerite (AM2 and AM3) showed an expressive C-carbonate dissolution during MABA tests (>90%) (Figure 1b) whereas partial C-carbonate dissolution (35-70%) was observed for the samples with siderite. Raman spectroscopy analyses confirmed reminiscent siderite in all MABA residues (not shown). Nearly total carbonate dissolution was achieved during ANC and ANC-SID tests - % C-released of 90-100%. This is expected considering the more aggressive conditions of ANC's tests.

In conclusion, a misclassification of ARD generation potential can occur when the NP value is evaluated without mineralogy understanding. Higher discrepancies were observed when NP was based on C content (%). The NP-ANC-SID method accounts for the presence of siderite only for content higher than 15%. NP-MABA presented the lowest values for all samples due to incomplete siderite dissolution, as shown by Raman and residual C-carbonate content. Hence, the siderite effect is low. The NP-MABA protocol was shown to be simpler and more realistic to predict ARD from a broader sample composition.

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