Applicability of a New and More Efficient Approach to the ABCC Test

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ABSTRACT

Acid Rock drainage (ARD) from mining waste such as tailings, waste rock, leach piles, etc, is currently one of the most important environmental concerns of mining activities. In order to address this problem, different prediction tests exist that allow the characterization of mine wastes and the assessment if these have the potential to generate acid drainage in the future.

One of the existing prediction tests is the ABCC (Acid Buffering Characteristic Curve) test, which allows one to determine the percentage of the neutralization potential (NP) of a sample that effectively reacts to neutralize acid at different pH values (MEND Report 1.20.1 (2009); Warwick A. et al. 2006). This test involves a slow titration with hydrochloric acid (HCl), and the continuous recording of pH values. The shape of the resulting curve indicates the capacity of the sample to neutralize acids.

The procedure of the ABCC test consists of adding water to a sample in a proportion of 2% (w/v), and then titrate every 15 minutes with HCl (under continuous agitation), until the mixture reaches a pH value of 2.8.

This test yields a good estimation of the neutralization capacity of a sample; however, one of its main disadvantages is the long analysis time per sample. Therefore, the objective of this study is the search of an appropriate development time of the test, which would result in fewer analysis times per sample and thus a cost reduction.

The results show that reducing the time of acid addition resulted in curves with no significant statistical variations when compared to the ones obtained with the original protocol. In consequence, it can be established that it is possible to conduct the ABCC test in a significantly shorter time while still obtaining meaningful results.

Keywords: Test ABCC, NP, Acid drainage, static test, massive mine waste

INTRODUCTION

Acid Rock Drainage (ARD) is a phenomenon which is produced through the exposure of sulphide minerals (such as pyrite) to atmospheric oxygen and water. As a product of mining activities, this phenomenon can be accelerated due to the increased exposure of these minerals to the environment, as is the case with massive mine wastes, such as tailings, waste rock and leach piles, among others. Consequently, ARD is one of the most important environmental problems of mining activities today.

To address this problem, a series of procedures were developed that allow for the characterization of the materials which compose mining wastes, in order to assess whether or not these will potentially generate acid drainage in the future. Among the most common methods are static prediction tests, i.e., those which include only one measurement in time. These tests are conducted on a laboratory scale, and include the most well known and performed tests the ABA (Acid Base Accounting) test and the NAG (Net Acid Generation) test.

On the other hand, there are other static prediction tests that are not as common, but similarly produce important information that permits the characterization of these minerals. One of these tests is the ABCC test, which has the objective to determine which percentage of the NP of a sample effectively reacts to neutralize the pH at different pH levels (MEND Report 1.20.1 (2009); Warwick A. *et al.* 2006).

The ABCC test involves a slow titration of a mixture of 100 mL DI water and 2 g sample with HCl, until a pH of 2.8 is reached, which is monitored continuously. Approximately every 15 minutes small volumes of HCl are added, and the pH value is recorded once it is stable. The volume and concentration of the added acid varies according to the range of NP values of the sample. High acid volumes and concentrations are used on samples with high NP values, and vice versa. Finally, the added quantity of HCl is converted into kg CaCO3/tonnes, the latter which is then plotted (x-axis) against measured pH (y-axis) (MEND Report 1.20.1 (2009); Warwick A. *et al.* 2006).

Although this test gives a good estimation of the neutralization capacity of a sample, it has the main disadvantage that the analysis per sample is time consuming. Therefore, the objective of this study is to find an appropriate execution time, which can secure reliable results while reducing associated costs.

METHODOLOGY

The study compromised the application of the original ABCC test as well as a modified protocol, in which the time interval of HCl addition was varied (15, 5 and 3 minutes) by using tailings samples which correspond to samples from the copper flotation process. Afterwards, results were compared to determine whether or not significant differences could be observed. This comparison used statistical tools for each of the analyses conducted. Additionally the NP was determined to characterize the sample and to estimate the capacity of neutralizing acid, which is necessary in order to define the conditions of the ABCC test. The methodology of the conduction of the study is described below.

Preparation and ID of the sample

The preparation of the sample consisted of: (1) drying the sample (not exceeding 40°C), and (2) the mechanical preparation of the sample, to obtain a sample of a grain size of 75 μm (for the conduction of ABCC test and determination of NP).

"ABCC-X" corresponds to the sample ID, where "-X" changes according to the analysis or test (Table 1).

Table 1 ID of the sample according to the analysis or test.

ID of the sample	Analysis or Test
ABCC-NP	NP determination
ABCC-(15)	ABCC test every 15 minutes
ABCC-(5)	ABCC test every 5 minutes
ABCC-(3)	ABCC test every 3 minutes

Mineralogical characterization

The mineralogical characterization of the sample was conducted by X- Ray Diffraction using TOPAS software. As observed in Table 2, the XRD analysis showed a sample characterized by the presence of quartz and aluminosilicates, and no presence of neither pyrite nor sulphide ore was detected.

Tabla 2 XRD characterization of the tailing sample tested

Mineral	Chemical Formula	Percentage (%)
SiO_2	Quartz	23.3
$Si_{2.83}Al_{1.17}Na_{0.84}Ca_{0.16}O_8$	Oligoclase An16	22.0
$Si_{2.72}Al_{1.28}Na_{0.75}Ca_{0.25}O_8$	Oligoclase An25	10.7
$Si_{1.5}Al_{0.5}Na_{0.07}K_{0.93}O_8$	Sanidine Na0.07	13.7
$Si_{1.5}Al_{0.5}Na_{0.1}K_{0.9}O_8$	Sanidine Na0.1	11.9
$K_{0.9}FeAl_{0.5}Si_{1.5}O_5(OH)$	Muscovite 2M1	11.0
$K_{1.4}Al_{2.3}Si_{1.7}O_8(OH)_2$	Muscovite 1M	3.1
$H_8Al_{1.75}Fe_{0.25}Mg_5O_{18}Si_3$	Chlorite IIb	0.6
$Al_2H_8Mg_5O_{18}Si_3$	Clinochlore 2M	1.9
$Al_2Si_2O_5(OH)_4$	Dickite (BAILEY)	1.8
$Na_3Mn_5Si_8O_{24}$	Ungarettiite	0.0
FeS_2	Pyrite	0.0

Determination of Neutralization Potential (NP)

The determination of the neutralization potential of the sample was conducted using the Bulk Acid Neutralization method according to Modified Acid Base Accounting (1989). The procedure starts with the “fizz rating” test, which consists of adding 3-4 drops of a 25% HCl solution to a sample mass of 0.5 g, placed in a glass flask or a piece of aluminum foil, in order to observe any “fizz” and its magnitude, which is classified as “none, slight, moderate, or strong fizz”. Afterwards, approximately 2 g of the sample are placed into a 250 mL Erlenmeyer flask, to which HCl is added. The volume and normality (N) of the acid depend on the “fizz rating” (Table 3). In this study, 20 mL of 0.1N HCl were used.

Table 3 Volume and Normality of HCl for NP determination, based in the Fizz Rating (After MEND Project 1.16.1b (2008).

Fizz Rating	Volume (mL)	Normality
None	20	0,1
Slight	40	0,1
Moderate	40	0,5
Strong	80	0,5

The HCl-sample mixture was left to react for 24 hours, placing the Erlenmeyer flask on a shaking apparatus. Finally, the sample is titrated with 0.1N NaOH (corresponding to the normality of HCl used), until a pH of 8.3 was reached. With the data obtained from the titration, the NP was determined in units of kg $CaCO_3$per tons of material, through the following equation:

$$NP = \frac{50a\left[x-\left(\frac{b}{a}\right)y\right]}{c} \quad (1)$$

Where:

NP: neutralization potential in kg $CaCO_3$/tonnes; a= normality of HCl; c= sample weight in grams; x= volume of HCl added in mL; y= volume of NaOH added to reach pH 8.3 in mL; b= normality of NaOH

Test ABCC (Acid Buffering Characteristic Curve)

The ABCC test is an analysis that allows the determination of the percentage that effectively reacts with and neutralizes acid (at different pH values) as it is directly related to the determination of NP described above. For this study, the ABCC test was conducted according to the protocol, as well as with modifications conducted by Fundación Chile.

ABCC TEST (Original Protocol) (MEND Report 1.20.1 (2009); Warwick A. et al. 2006)

This test consists of weighing approximately 2 g of sample into a 250 mL Erlenmeyer flask, and adding 100 mL of DI water. Afterwards, the mixture is slowly titrated until a pH of 2.8 is reached, the latter which is continuously monitored. This is carried out by adding 0.1 mL of 0.1 M (molar) HCl every 15 minutes, recording the pH value during this time. The volume and concentration of HCl used in the ABCC test depend on the NP value of the sample (Table 4).

Table 4 Suggested incremental additions and concentration of HCl (After MEND Report 1.20.1 (2009).

NP of sample (kg CaCO3 /tonnes of material)	Concentration of HCl (Molar)	Increments of HCl (mL)
10	0,1	0,1
20	0,1	0,2
50	0,1	0,5
100	0,5	0,2
200	0,5	0,4
500	0,5	1,0
1000	0,5	2,0

Finally, the quantity of HCL added in this test is converted into values of kg $CaCO_3$/tonnes of material (Equation 2), which are plotted against the pH (Y axis) measured every 15 minutes, obtaining the buffering curve.

$$\text{kg CaCO3} = \frac{[(\text{volume HCl (mL)addedx molar concentrationx100})/2]}{\text{sample weight (g)}} \quad (2)$$

ABCC TEST (FCh Protocol)

The procedure of the ABCC test developed by Fundación Chile is similar to the one described above. The difference is that the time interval of acid addition to the sample was modified, with the objective to reduce the time to conduct the test. In this procedure, the same sample and water quantities were used, as well as the concentration and volume of added HCl, as in the original protocol, while adding HCl and recording the pH value every 3 or 5 minutes. As in the original ABCC protocol, results in kg CaCO3/tonnes of material (x-axis) were plotted against the measured pH values (y-axis) to obtain the buffering curve.

Effective neutralization percentage (%RN)

Because the ABCC test allows determining what percentage of the NP actually reacts with and neutralizes acid, this percentage was determined for each of the three curves in this study; afterwards, the obtained results were compared with each other.To determine the percentage of neutralization (%RN) that effectively reacts, it is considered that neutralization reactions only occur until a pH value of 4.0, and the total neutralization capacity of a sample is determined through the Bulk Acid Neutralization Method. In consequence, the amount of NP that reacts is determined from the ABCC curve, with the value of kg CaCO3/tons of material that corresponds to a pH of 4 (Equation 3):

$$\%RN = \frac{(kgCaCO3/tonnesapH\ 4)}{(kgCaCO3/tonsofbulkacidneutralization)} x100 \quad (3)$$

Statistic Analysis

Statistical analysis was applied in order to assess if obtained results are acceptable. To achieve this goal, each ABCC test was conducted in triplicate, and the NP determination in duplicate.

To compare the results obtained from curves ABCC-(5) and ABCC-(3) with the reference curve ABCC-(15), t-student tests were performed for each point (average) of the curves, to determine if significant statistical differences exist. The t-test consists of determining the t value of student calculated from analytical experience, and compare this value with the so-called critical value, which is obtained from the t-student table for a given percentage of reliability. If no significant differences exist between 2 groups, the calculated "t" has to be smaller than the "t" value from the table (ISP (2010)). For all of the statistical measures, a 95% confidence interval was used.

RESULTS AND DISCUSSION

Determination of Neutralization Potential (NP)

The results of the determination of the NP of the samples present an average NP of 3.257 ±0.085 kg $CaCO_3$/tonnes (Table 5). As this is a positive value, it can be concluded that the sample does not have a high neutralization capacity.

Table 5 Results from the determination of NP.

ID sample	Fizz Test	NP (kg $CaCO_3$/tonnes)	Average NP (kg $CaCO_3$/tonnes)
ABCC-NP (A)	None	3,316	**3,257 ± 0,085**
ABCC-NP (B)	None	3,197	

ABCCTest (Acid Buffering Characteristic Curve)

The results presented below correspond to the analysis of one sample of tailings material, through the ABCC test, conducted in two forms, the original protocol and the modified one (FCh). To obtain reliable results, the sample was analyzed in triplicate for each of the protocols, so that results presented correspond to average values. The first results correspond to the curves obtained from adding HCl at three different time intervals. This volume of HCl was chosen, as all of the tests conducted, especially the original protocol, reached a pH of 3 with this volume. The results of the original protocol were used as a reference of comparison for the results of the modified test.

Comparing the results from the modified tests to the results of the original protocol, it can be seen that no significant differences exist for each of the points of the curve, neither in pH nor kg CaCO3/tonnes values.

Moreover, it can be observed that pH values of the ABCC-(15) curve are slightly greater than for the other two curves, with exception of the first points of the curves (before acid addition). It can be seen that the kg CaCO3/ton values are practically the same in all three curves (see Figure 1).

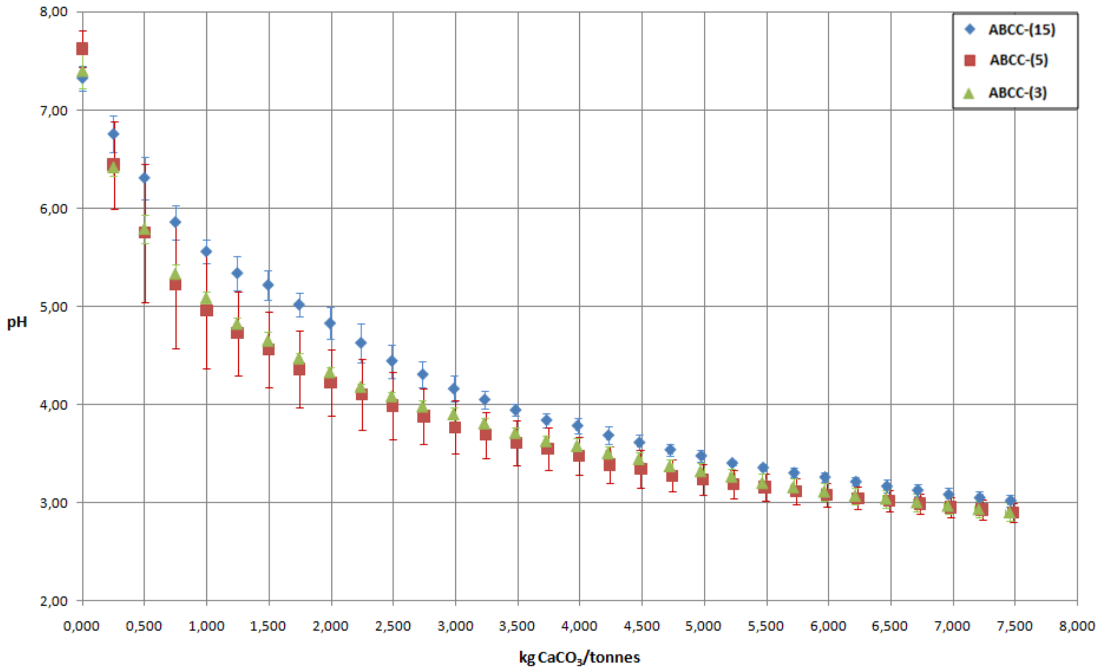

Figure 1 Acid Buffering Characteristics Curves of ABCC-(15) of reference, ABCC-(5) and ABCC-(3) protocols

It can be seen in Figure 1 that the three obtained curves show a similar behavior, and the major difference occurs in the first part of the curve. If the standard deviation is considered, the curves could be even more similar.

Another parameter to compare is the behavior of pH values concerning the amount of HCl added, as shown in Figures 2 and 3. It can be observed that pH values show greater differences among the different tests.

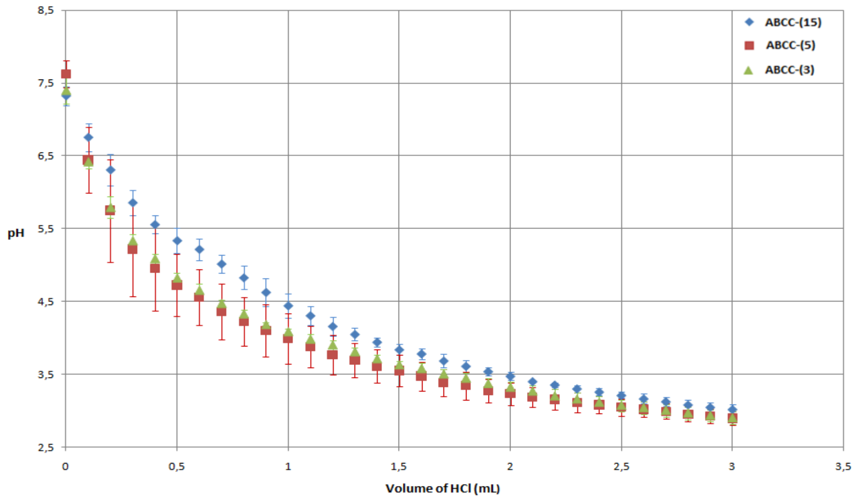

Figure 2 pH vs HCl added for reference ABCC-(15), ABCC-(5) and ABCC-(3) protocols

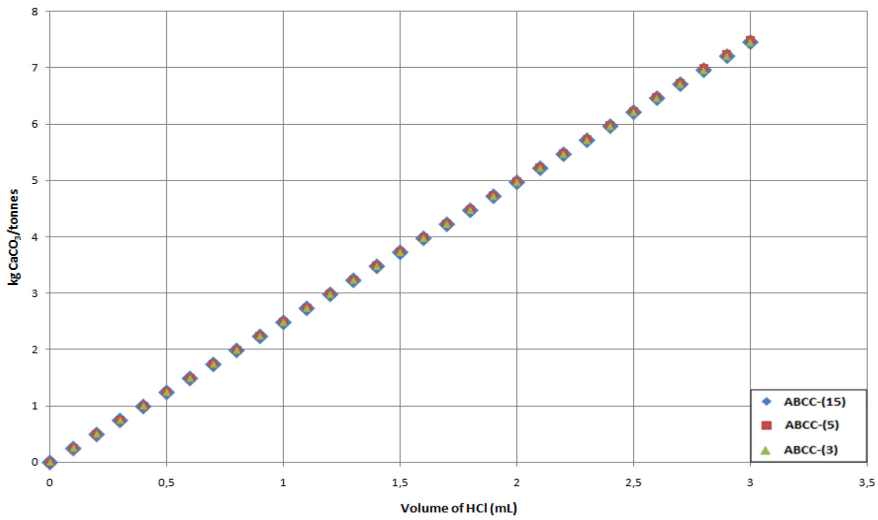

Figure 3 kg $CaCO_3$/tonnes vs HCl added for reference ABCC-(15), ABCC-(5) and ABCC-(3) protocols

All the values obtained and presented in each of the curves can be considered acceptable, as they show standard low deviation values and variation coefficients (%CV), the latter which are < 10% for all points, except 3 pH values in the ABCC-(5) curve (namely, 5.75±0.65; 5.22±0.65 and 4.96±0.59).

To analyze the differences between values of curves ABCC-(5) and ABCC-(3) related to the reference ABCC-(15), it can be concluded that these are quite low, as the first two curves show percent recovery (%R) between 80% and 110%, low systematic bias values, and complies with the rule that all tcal are smaller than tcrit for the t-student test. Thus, all values are acceptable and no significant differences exist between the reference curve and curves ABCC-(5) and ABCC-(3).

Effective percentage of neutralization (%EN)

This value was determined using the NP value obtained through the Bulk Acid Neutralization Method and of each of the ABCC curves. As in the reference curve (ABCC-(15)), a pH of 4 (4.05) was reached with a volume of 1.3 mL of HCl added, this value was used to determine the kg $CaCO_3$/tonnes values of the ABCC-(5) and ABCC-(3) curves for the determination of the %RN of both curves. The results are presented in Table 6 and 7.

Table 6 Neutralization Potential (NP) through the Bulk method and the capacity neutralization observed in ABCC curves at pH 4.

NP Bulk method (kg CaCO3/tonnes)	NP ABCC-(15) at pH 4(kg CaCO3/tonnes)	NP ABCC-(5) at pH 4(kg CaCO3/tonnes)	NP ABCC-(3) at pH 4(kg CaCO3/tonnes)
3,257	3,232	3,242	3,230

Table 7 Percentage of real neutralization (%RN) calculated of the 3 ABCC curves.

%RN ABCC-(15)	%RN ABCC-(5)	%RN ABCC-(3)
99,22	99,53	99,17

The results indicate that the three calculated %EN values from the ABCC curves are closely related. It can be observed that between curves ABCC-(15) and ABCC-(5), there is a difference of 0.0313 units in %EN; between ABCC-(15) and ABCC-(3), this difference is 0.049. It can be concluded that the difference between the three obtained %RN values is small, and is smaller between ABCC-(15) and ABCC-(3).

CONCLUSION

From the obtained results, it can be concluded that it is feasible to reduce the conduction time of the ABCC test in the manner proposed in this study, as the results indicate that no significant statistical differences exist in the data (curves) when comparing results from the original ABCC test and the test ABCC test modified by Fundación Chile. As shown in this study, the ABCC test with smaller time intervals for the addition of HCl, reliable data are obtained, which are very similar to those obtained by adding acid every 15 minutes.

Thus it was determined that the ABCC test can be conducted in a significantly shorter time, which permits developing studies and projects with reduced response times and costs, while working with reliable data.

Concerning the parameters assessed in the ABCC test, it can be concluded that the pH is the parameter that varies most, i.e. is the most sensitive, and could present an error, as it depends on the conditions under which the test is conducted, as it is an experimental parameter. Changes in kg

CaCO3/ton are minor, as this parameter is determined through a mathematical equation, which always should show a minor error.

It is important to note that all ABCC tests were conducted until a pH of 2.8 was reached as shown in protocols; however, only data until a pH of 3 were used as it was considered appropriate to work until this pH was reached. The results below a pH of 3 showed a very small variation by adding acid. The system is stable below a pH of 3, not producing any significant changes in pH values.

The protocols of the conducted ABCC tests in this study should use standard curves to compare results of a sample; as this was not possible in this study, the ABCC-(15) curve was used as a reference for all comparisons instead.

Finally, to mention that the ABCC tests conducted in this study were based on the description of two standard protocols: (1) MEND ("Prediction Manual for Drainage Chemistry from Sulphidic Geologic Materials (2009) and (2) Warwick A. et. al. (2006). Both protocols indicate that between each addition of acid solution 15 minutes must be waited and no additional information is provided about the reason of this determined time.

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NOMENCLATURE

NP Neutralization Potential

ABCC Acid Buffering Characteristic Curve

%RN Real Percentage of Neutralization

kg $CaCO_3$/tonnes kilograms of calcium carbonate per tonnes of material

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