A method to calculate the neutralization potential of mining wastes

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Abstract The determination of neutralization potential (NP) of mining wastes is an essential part of waste characterization for acid rock drainage (ARD) prediction. Interpretation of NP values requires consideration of the mineralogical composition of the waste. Different minerals can neutralize acid drainage at different rates and in different pH ranges. The test conditions of widely used laboratory procedures to determine NP do not distinguish between such differences and overestimation of NP can often result. A simple procedure is proposed in which the effective NP is calculated based on mineralogical composition and the relative reactivities of component minerals. Mineralogical composition is calculated from easily determined analytical values using a CIPW normative procedure. Comparison of calculated NP values for 92 samples with experimentally determined values from tests designed to prevent the overestimation of NP indicates that the method is successful in predicting an effective NP value in most cases. The procedure is considered to be a cost-effective means of providing confident routine ARD prediction when used in combination with other tests and analyses.

Key words Acid rock drainage · Mineralogy · Neutralization · Norm calculations

Introduction

Acid rock drainage (ARD) from waste rock, tailings, and other mine components, is the single most important environmental concern in the mining industry. Proponents of new mines and operators of existing mines are required to provide evidence that waste materials to be generated during operation can be stored in a manner that will prevent or mitigate the generation of ARD and the migration of heavy-metal-contaminated runoff and seepage into downstream watercourses both during operation and long after mine closure. To provide confident waste management plans that will allow permitting to proceed and the acceptance of closure measures, proponents and operators must characterize the various wastes and other components from current or proposed mining activities in order to predict future performance of the materials when disposed of under environmental conditions (Price and Errington 1994). Uncontrolled ARD emissions can result in significant ecological disruption in sensitive and productive receiving waters.

Acidic drainage and the associated heavy-metal contamination are due to natural oxidation reactions taking place when wastes containing sulfide minerals are exposed to air and water, with sulfide-oxidizing bacteria contributing a significant role in the process (Kleinmann and others 1981). However, acidic drainage and heavy metals can be attenuated due to reactions with neutralizing minerals contained in the wastes. Almost without exception, wastes are initially characterized using tests known as static prediction tests which attempt to determine the balance between the acid potential (AP) of the material, derived by quantifying the acid-producing components, and the neutralization potential (NP), determined by measuring the quantities of acid-consuming components. Although there are several test methods available, by far the most commonly reported procedure is the acid base accounting test of Sobek and others (1978).

In a typical static test, the acid potential of a sample is determined by calculating the theoretical quantity of acid that could be produced if the total sulfur content of a sample is converted to sulfuric acid. In the standard acid base accounting test of Sobek and others (1978), the neutralization potential is determined by boiling a small quantity of finely ground sample in excess hydrochloric acid to calculate the acid consumption. Clearly, under actual conditions of waste disposal, not all sulfur will oxidize to produce acid. Neither will all the neutralizing capability, as determined under the vigorous conditions of the test, be available for reaction. Despite these shortcomings, the results of static tests are used as an initial screening process to characterize a waste either as “safe

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for disposal" if NP exceeds AP or as "potentially acid generating" if AP exceeds NP. In the latter case, the waste will possibly require a method of disposal designed to either prevent acid generation or to mitigate its impact. Classification of a waste is based on consideration of either the difference between NP and AP, termed the Net Neutralization Potential (Net NP) or, more importantly, the ratio between NP and AP. Errors in measuring either of the two parameters, or a failure to take into consideration the rate or extent to which acid generation and/or neutralization will occur can, therefore, result in a mis-classification of a rock type.

The largest discrepancies in static tests and their interpretation arise in the assessment of the neutralizing potential (Lawrence and Wang 1996). Many minerals can neutralize acid and, if present in a waste, can either delay the onset of ARD or can prevent its generation if present in sufficient excess. However, different minerals will buffer pH in different ranges so that the presence of certain neutralizing minerals does not necessarily prevent the pH of the drainage from falling below critical values with respect to the requirements of the receiving waters (BC AMD Task Force 1989; Jurjovec and others 1995). Furthermore, different minerals have different reactivities (Sverdrup 1990). For low reactivity minerals, their presence in a waste will not necessarily provide protection against ARD if the rate of neutralization is less than the rate of acid generation. Carbonate minerals such as calcite and dolomite are the most effective neutralizing minerals because they have relatively high reactivity and neutralize acid in the circumneutral pH range. Silicate minerals can also be important neutralizers because of their abundance, but their relative reactivities range from intermediate relative to the carbonates (for example, the Ca-rich feldspars) to extremely slow (for example, the K-feldspars; Goldich 1938). Sherlock and others (1995) have reviewed the role of carbonates and silicates in acid rock drainage neutralization.

Discrepancies in the measurement of NP in static tests can be understood if the mineralogy of a sample is considered. Under the high acidity (0.1 or 0.5 N hydrochloric acid) and high temperature conditions of the Sobek test, a high NP value might result even though the sample under test may have a low carbonate content. This is because many other minerals, including a number of silicate minerals with a range of reactivities, will dissolve under the rigorous test conditions and contribute to the apparent NP value. Under environmental conditions, such high acidities are unlikely to be encountered. Effective, or practical, NP values will be much lower, restricted to the contribution by those minerals which will dissolve or alter under conditions of lower acidities (higher pH). Several studies have shown that the Sobek procedure has a significant tendency to overestimate NP (Lawrence 1990; Lawrence and Wang 1996). Alternative tests have been developed to provide more practical values of AP and NP, such as the Modified ABA procedure of Lawrence (1990), in which NP is determined by performing the acid digestion at ambient temperatures in lower and controlled conditions of acidity to provide a pH at the end of the digestion in the range 2.0–2.5. AP is calculated on the basis of the sulfide content of the sample, instead of the total sulfur content as in the Sobek method. Lapakko (1994) has proposed that the acid digestion should be controlled to an end pH of 6 so that only the contribution of carbonate minerals to the NP is measured. The NP due to carbonate minerals (Carbonate NP; Lawrence and others 1989; BC AMD Task Force 1989; Norecol 1991) can also be determined from analysis of the inorganic carbon content which is usually assigned to calcium carbonate. The Lapakko and the Carbonate NP methods, however, do not take into account the potential neutralizing contribution of the reactive silicate minerals which has been shown in several studies to provide some neutralizing capacity under field conditions (Lapakko 1988; Morin and others 1988; Alpers and Nordstrum 1990; Blowes and others 1992; Kwong 1993; Sherlock and others 1995). The importance of mineralogical factors in ARD prediction has been stressed in a number of studies (Norecol 1991; Kwong 1993; Morin and Hutt 1994; Lawrence and Wang 1996).

Calculation of NP based on mineralogy – theory and methodology

It is evident from the preceding discussion that knowledge of the mineralogy of an individual sample or lithological group would greatly assist in the interpretation of a static test result. This paper proposes a method to calculate the effective NP based on the mineralogical composition of a sample and relative mineral reactivity, to be used in conjunction with static tests and other analyses. At first, it might seem preferable to use direct determination of the mineralogical composition using standard analytical techniques as an alternative to calculating the composition. Indeed, if detailed quantitative mineralogical data are available, these can be used as inputs to the proposed method. However, since a typical waste characterization study can involve the analysis and testing of a large number of samples, sometimes in excess of 1000, the cost of determining mineralogy based on classical techniques such as optical microscopy and X-ray diffraction (XRD) is likely to be prohibitive as a routine procedure. Furthermore, the level of detection of more widely available techniques such as XRD is not sufficiently low to allow fine quantitative distinctions to be made in the calculation of NP. For the purposes of waste management planning, differences in NP values of 10 kg/tonne $CaCO_3$ equivalent can be significant. Routine XRD carried out in commercial laboratories cannot usually provide quantitative identification of minerals if they are present in quantities less than 10% by weight (Norecol 1991), equivalent to 100 kg/tonne.

The proposed method utilizes the analysis of the major rock-forming elements of a sample, usually referred to as whole rock analysis, in combination with the analysis of inorganic carbon (carbonate), as inputs to the calculations. A major advantage of this approach is that whole rock analyses are often already available, having been determined as part of the exploration and ore-mapping process. The analyses are inputted to a CIPW normative composition calculation, principally developed to determine the mineralogical composition of igneous rocks (Cross and others 1903; Cox and others 1979). In this study, the program NewPet, a menu driven geochemical data handling and plotting package developed at Memorial University, Newfoundland, Canada (Clarke 1993), was used to calculate the CIPW norm.

Following the use of NewPet to determine a mineralogical composition, NP can be calculated by summing the calculated NP values of each component mineral using the relative reactivities of each mineral provided by Sverdrup (1990) and Kwong (1993). Sverdrup suggested that minerals can be divided into different groups (carbonate, silicates and others) in order of relative reactivity in acidic solution. Table 1 shows the groups suggested by Sverdrup, with the reaction rates at pH 5.0 relative to a calcite relative reactivity of 1.00 as calculated by Kwong from the Sverdrup data.

In the more highly acidic and boiling conditions of the acid base accounting test of Sobek and others (1978), rates of reaction will be higher than those presented in Table 1. In such conditions, the rate of reaction of minerals such as the more reactive non-carbonate minerals (fast and intermediate weathering) are apparently significantly high to account for the NP in addition to the dissolving minerals. In some Sobek tests, the acidity of the digestion is probably high enough to allow the dissolution of silicates of lower reactivity (Lawrence and Wang 1996). As previously discussed, such extreme conditions do not normally occur in the conditions found in waste dumps and tailings impoundments. Although the dissolution of some silicates might occur under the lower pH conditions which can develop in wastes, the rate and degree of dissolution and/or alteration will be lower, perhaps by two or more orders of magnitude, than in the Sobek test. The Sobek test clearly, therefore, can overestimate NP availability under actual field conditions for many samples.

The CIPW normative calculation module in NewPet was used to calculate the weight percent of component minerals for 92 samples from 13 different operating or proposed mines using whole rock chemistry and inorganic carbon analyses as inputs. Inorganic carbon was determined using a Coulimetrics Carbonate Carbon apparatus. Whole rock analyses were carried out by Chemex Labs, North Vancouver, using X-ray fluorescence following a lithium metaborate fusion. Ferrous iron was also determined to enable a calculation of both Fe_2O_3 and FeO components. In addition to metals analysis, the analytical suite also includes the loss-on-ignition which is also used as an input parameter to NewPet. The mineralogical compositions of each sample were normalized to a total of 100% if the composition provided by NewPet was less than or greater than 100%.

Table 1

Relative reactivities of minerals at pH 5 [after Sverdrup (1990) and Kwong (1993)]

Mineral group	Typical minerals	Relative reactivity at pH 5
Dissolving	Calcite, aragonite, dolomite, magnesite, brucite	1.00
Fast weathering	Anorthite, nepheline, forsterite, olivine, garnet, jadeite, leucite, spodumene, diopside, wollastonite	0.40
Intermediate weathering	Sorosilicates (epidote, zoisite), pyroxenes (enstatite, hypersthene, augite, hedenbergite), amphiboles (hornblende, glaucophane, tremolite, actinolite, antophyllite), phyllosicates (serpentine, chrysotile, talc, chlorite, biotite)	0.02
Slow weathering	Plagioclase feldspars (albite, oligoclase, labradorite), clays (vermiculite, montmorillonite)	0.01
Very slow weathering	K-feldspars, muscovite	0.01
Inert	Quartz, rutile, zircon	0.004

Using the calculated mineralogy, a NP value was calculated for each sample by adding together the weighted NP values for each component mineral. Weighted NP values for each component mineral were calculated using the relative reactivity values provided in Table 1. Since the units of NP are almost universally expressed in units of kg $CaCO_3$-equivalent per tonne, calculated NP values were converted to these units by using the ratio of the molecular weight of $CaCO_3$ to the mineral. For example, in a sample containing 17.1% anorthite [$(Ca,Na)AlSi_2O_8$], the contribution of anorthite to NP can be calculated as follows, using the relative reactivity value of 0.40 for anorthite relative to calcite ($CaCO_3$):

$$\text{NP contribution} = \frac{17.1}{100} \times \frac{1000\text{ kg}}{1\text{ tonne}} \times \frac{\text{mol. wt. calcite}}{\text{mol. wt. anorthite}} \times 0.40 = 27.2\text{ kg } CaCO_3\text{-equivalent/tonne}$$

An example of whole rock analysis, inorganic carbon analysis, calculated mineralogy, and calculation of NP for each component mineral and the total NP for a sample of waste rock are shown in Tables 2, 3, and 4. In this manner, the NP values for 92 samples were calculated and the results compared with NP values determined experimentally using the method of Sobek and others (1978), using a variation of the Modified ABA method of Lawrence

Table 2
Whole rock chemistry and inorganic carbon analysis (%) for a sample of waste rock

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O_3	K_2O	P_2O_5	C_{inorg}
57.42	0.27	6.34	3.57	14.90	0.28	3.00	7.06	1.54	0.63	0.25	0.88

Table 3
Calculated mineralogical composition (%) of the waste rock sample using NewPet

Quartz	Orthoclase	Albite	Anorthite	Diopside	Hypersthene	Magnetite
25.79	3.72	13.03	8.53	3.80	30.01	5.17
Ilmenite	Olivine	Apatite	Calcite			
0.51	0.00	0.57	7.38			

Table 4
Calculated NP values (kg/t) for component minerals and the total sample of waste rock

Quartz	Orthoclase	Albite	Anorthite	Diopside	Hypersthene	Magnetite
1.7	0.1	0.3	12.5	6.7	5.3	0.0
Ilmenite	Olivine	Apatite	Calcite			TOTAL NP
0.0	0.0	0.7	73.8			101.0

(1990) described in Lawrence and Wang (1996), and based on the analysis of the inorganic carbon content (Carbonate NP). The majority of these values were obtained in a previous study (Lawrence and Wang 1996).

Results and discussion

Figures 1, 2 and 3 show the relationship between calculated NP values and the NP values determined by the Sobek, Modified and Carbonate NP methods for the 92 samples. Linear regression equations and correlation coefficients are indicated on the plots. The results show that the proposed Calculated NP method provides more conservative NP values than the Sobek method. The relationship between Calculated NP values and the values from the Modified and Carbonate NP methods is much more similar, with the Calculated method giving higher values as shown by the regression equations in both cases. This is consistent with the theoretical considerations previously discussed and with the comparison of Sobek values with the other experimentally determined NP values in the Modified and Carbonate NP methods (Lawrence and Wang 1996). This confirms that minerals classified as intermediate, slow, or even very slow weathering in Table 1, react in the digestion conditions of the Sobek method and contribute to the apparent NP of a sample.

In comparing Figs. 2 and 3, a close correlation between the experimentally determined Modified NP and Carbonate NP values is evident. Differences in the relationship between Calculated NP and Modified and Carbonate NP appear to be small for the whole sample population. However, inspection of the differences between Modified and Carbonate NP values would show significant differences between the majority of correlations for samples from individual mines, with Modified NP values higher in these cases. This difference can also be verified by comparing the regression equations for Figs. 2 and 3. The calculated mineralogical composition has two components: a direct measurement of the carbonate content

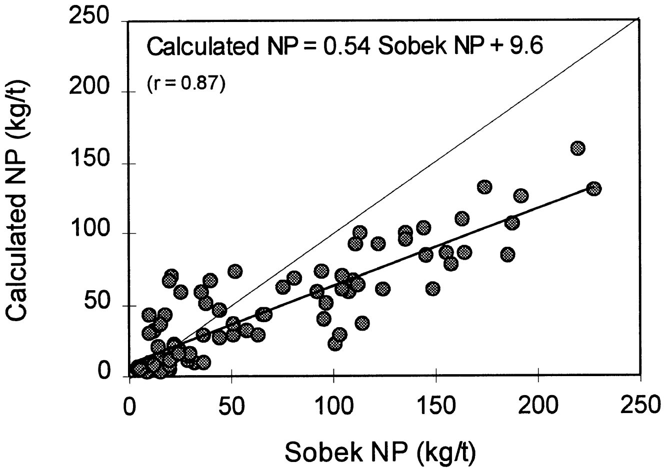

Fig. 1
Comparison of Calculated NP and Sobek NP

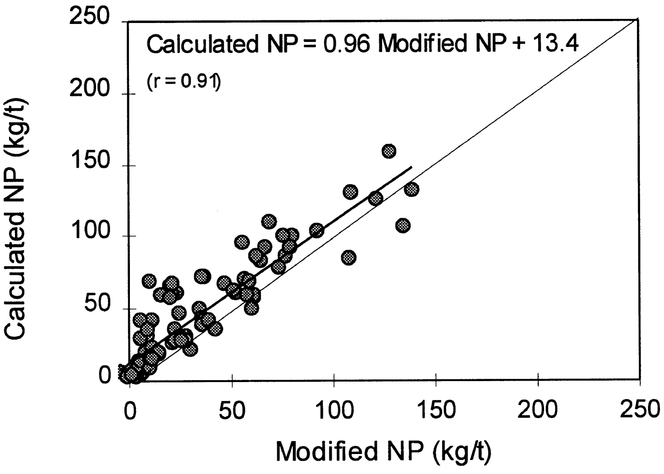

Fig. 2
Comparison of Calculated NP and Modified NP

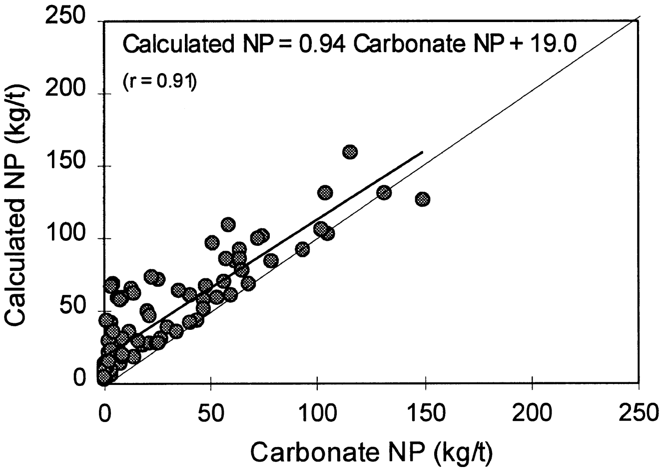

Fig. 3
Comparison of Calculated NP and Carbonate NP

from the inorganic carbon analysis, and an indirect approximation of the silicate mineral content from the whole rock chemistry. NP values calculated from the calculated mineralogical compositions are, in the main, dominated by the carbonate NP, due to the relative reactivity of 1.00 used for calcite. In some cases, however, the contribution of the more reactive silicate minerals to NP can be significant under enviromnental conditions. This is reflected in the higher NP values obtained by the Modified method relative to the Carbonate NP values. A shortcoming with the use of the CIPW norm for this application is that the list of normative minerals calculated follows a prescribed set of anhydrous end-member formulas of the rock forming and common accessory minerals that would form upon the crystallization of a magma. The procedure, therefore, ignores the effects of geological processes which subsequently might take place. Alteration minerals are not predicted. Instead, the chemical compositions of the alteration minerals, if present, are interpreted as primary minerals which are, in many cases, likely to be more reactive than their alteration products in acidic drainage conditions. In such cases, the proposed procedure might predict a higher NP than would actually be available. This could account for the higher Calculated NPs relative to Modified NPs found in this study. It is known, for example, that a high number of the samples tested contain varying quantities of chlorite, a low reactivity alteration mineral, which is not accounted for in the proposed procedure (Lawrence and Wang 1996). A more conservative estimation of NP is to be preferred since values of the ratio of NP to AP, used in the initial classification of wastes, will be correspondingly lower and the receiving environment will be more protected. Users of the procedure must, therefore, be sure to become familiar with mineralogical assessments for the lithological groups under test to determine if an overestimation of NP is being calculated.

Improvements to the proposed procedure could improve the reliability of the technique and confidence in its use. For application at a particular mining project, customized modifications of the CIPW procedure to match actual rock chemistry with identified mineral components in defined lithological groups or waste management units, would provide mining operators with a rapid tool for classifying wastes to match disposal options. Norm calculations to predict the mineralogy of metasomatic rocks and assemblages of other altered rocks has been proposed by Cheng and Sinclair (1994, 1995). Further refinement of the values used for the relative reactivities of minerals is also recommended to improve calculation of a NP value from the predicted mineralogical composition. Use of the procedure described herein is not recommended as the primary method of NP determination for mine wastes. Although a very close correlation between Calculated NP values and practical NP values determined experimentally using methods such as the Modified ABA procedure has been demonstrated for many samples from specific mine locations, not all samples will necessarily provide such good correlation. Application of the procedure might, however, be very useful as a routine and lower cost method for determining NP once the correlation between calculated values and experimental values has been established. As previously discussed, for many exploration projects, whole rock analyses of large number of samples will have already been obtained and could form the basis of a sampling and analytical program to calculate NP values. Since determination of NP by routine laboratory analysis can be uncertain given the range of values that can be obtained depending on sample mineralogy and the conditions of the method used, the more inherently precise whole rock analysis can be used confidently to calculate a practical NP value. The procedure to calculate NP should, therefore, be used in combination with other tests and analyses in the development of overall waste management plan for a specific mining operation. The successful application of the procedure demonstrated here highlights the importance of the mineralogical composition of mine wastes in understanding and determining the potential for acid rock drainage at mine sites.

Summary and conclusions

The NP of a mine waste sample is primarily a function of its mineralogy. Determination of the NP which will be available under environmental conditions is important in the development of confident waste management plans to prevent or control the generation of acidic rock drainage from waste dumps, tailings impoundments and other mine components during mining operations and after mine closure. A method to calculate the NP of mine wastes using whole rock chemistry, a CIPW normative procedure to calculate a mineralogical composition, and a system of classifying neutralizing minerals according to their relative reactivity, has been used for 92 mine waste samples from 12 mine projects. The method of calculating NP has been shown to provide a good correlation with the Modified ABA method (Lawrence 1990; Lawrence and Wang 1996) which was developed to give practical NP values. The method provides a NP value based on the contribution of carbonate minerals and the more reactive silicate minerals which can react with acidic drainage under conditions found in mine wastes. Routine reliance on chemical analysis with its inherent precision might be preferred as the basis for NP determination than the often uncertain determination of NP values by static test procedures. The method can be used as a routine procedure once the correlation with experimental values has been determined and can eliminate the overestimation of NP frequently obtained through the use of the widely used Sobek procedure. Further development of norm calculations to match lithology and mineralogy for specific orebodies could provide additional certainty in predictions. Use of the procedure is recommended as one of several tests that should be used in a waste characterization program for the determination of NP, including elemental analyses, mineralogical assessment and static test procedures.

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