MINERALOGICAL CHANGES DURING NP DETERMINATIONS AND THEIR IMPLICATIONS

Y.T. John Kwong, Ph.D.
Senior Environmental Scientist
Klohn-Crippen Consultants Ltd.
Suite 114, 6815-8th Street NE, Calgary, Alberta, Canada T2E 7H7
Telephone: 403-274-3424; Facsimile: 403-274-5349;
e-mail: John.Kwong@cal.klohn.com

and

Keith D. Ferguson, P.Eng.
Manager, Environmental Affairs
Placer Dome Canada Limited
600-1055 Dunsmuir Street, Vancouver, BC, Canada V7X 1L3

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ABSTRACT

To determine the effective acid-neutralizing minerals during acid digestion in neutralization potential (NP) measurements, 26 samples from the Mount Milligan deposit were tested under three chosen conditions: 0.1N HCl for 24 hrs (standard procedure), 0.5N HCl for 48 hrs and 0.5N HCl for one week. The respective NP for each sample was determined by back titration with NaOH. The titration residues were analyzed by x-ray powder diffractometry and compared with the original sample to detect changes in mineralogy.

Calcite followed by dolomite and Fe-dolomite were found to be the most efficient acid-neutralizing minerals occurring in the samples tested. Only about 50% of the available NP in Fe-dolomite was consumed in the standard digestion procedure. Among the silicates, biotite, chlorite and amphibole contributed significant to minor amounts of NP (0.2-1.5 kg CaCO3/tonne per wt% mineral). Prolonged acid treatment did not bring about additional NP due to the release of Fe and Al in the later stages of silicate dissolution which, upon hydrolysis, generated some acid. Quartz, muscovite, plagioclase and K-feldspar did not appear to change much during the acid digestions.

Two conclusions can be drawn from the investigation: (1) Mineralogical information is required for the proper interpretation of acid rock drainage prediction testwork; and, (2) Although feldspars may provide a long-term sink for acidity in a geological time frame, the less abundant mafic silicates may have played a more significant role in short-term acid-neutralization than what has been recognized to date.

Keywords: Neutralization potential (NP), acid digestion, mineralogical changes, carbonate NP, silicate NP, acid rock drainage prediction

INTRODUCTION

Recent research on acid rock drainage (ARD) prediction has shown that mineralogical information is essential in the proper interpretation of both static and kinetic test data (Kwong, 1993; Sherlock et al., 1995). An accurate measurement of the neutralization potential (NP) in a test sample is recognized as the weakest link in the acid-base-accounting (ABA) procedure, the most widely used static test in ARD prediction (Lapakko, 1994). Depending on the mineralogy of a test sample and the acid digestion procedure applied, the NP obtained by the standard back titration methods (Sobek et al., 1978; Lawrence, 1990) may not reflect the true acid-neutralizing capacity of the sample. To shed light on mineralogical changes occurring during acid digestion and to identify common effective acid-neutralizing minerals other than the carbonates, a laboratory investigation has been conducted using a suite of samples from the Mount Milligan deposit. It is the purpose of this paper to document the experimental results and briefly discuss their implications on interpretation of static and kinetic test results for ARD prediction.

SAMPLE DESCRIPTION AND ANALYTICAL METHODS

Mount Milligan is an approximately 300-million-tonne porphyry copper-gold deposit located in the northern end of the Quesnel Belt in central British Columbia (Sketchley et al., 1995). The host rock of the Mount Milligan deposits, varying from monzonite, trachyte, latite to basaltic andesite in composition, contains abundant silicate minerals with a high base-metal(s)/(Si±Al) ratio (e.g., pyroxene, calcic plagioclase) which can potentially provide a significant long-term sink for hydrogen ion upon weathering (Loughnan, 1969; Ollier, 1984; Sverdrup, 1990). Carbonate alteration associated with the mineralization also furnishes some rock with readily available carbonate neutralization potential (carbonate-NP).

To determine the relative stability of component minerals in various rock types occurring in the Mount Milligan property, a selected suite of 26 pulverized grab rock and tailings samples were digested at room temperature under three chosen conditions: 0.1N HCl for 24 hours (standard procedure); 0.5N HCl for 48 hours; and, 0.5N HCl for 1 week. The corresponding acid neutralization potential of the bulk sample in each case was then determined by back titration with NaOH. The solid residue collected after each acid digestion and subsequent back titration was analyzed by powder x-ray diffractometry (XRD) and compared with the original sample to detect the destruction of any minerals under the three acid-attack conditions.

To aid quantification of mineral abundance, the major and trace element composition of the raw samples was determined by inductively-coupled plasma spectroscopy following digestion in a HF-HNO_3-HCl mixture. Polished thin sections were made from representative sub-samples and the mineralogy ascertained by point-counting (400 points) under a scanning electron microscope (SEM) equipped with an energy dispersive x-ray (EDX) analyzer. In addition, assuming that all the carbon in the samples occurs in an inorganic form as alkali-earth carbonates (i.e., calcite, dolomite and/or magnesite), the theoretical carbonate-NP of each sample was calculated based on the total carbon content. Integrating these data together would allow an allocation of contributions from the component carbonates and silicates towards the titration NP measured in each sample.

RESULTS AND INTERPRETATION

A complete tabulation of all analytical data is furnished in Kwong (1996). In this paper, only the salient features are illustrated and discussed.

Figure 1 is a plot comparing the results of the three modified forms of NP determinations (carbonate-NP, 48-hr NP and 1-wk NP) with that obtained by the modified Sobek method involving 24 hours of acid digestion at room temperature (standard NP). Two observations are immediately evident from the plot:

1. With only two exceptions, the carbonate-NP underestimates the effective neutralization potential of the sample suite relative to the standard NP.
2. Whereas both the longer-term acid digestions generally render a higher NP than the standard NP, the 1-week digestion results are more comparable with the 48-hour digestion results.

These observations can readily be explained in terms of the mineralogical composition of the individual samples and the acid-leaching behavior of the relevant minerals. The first observation indicates that minerals other than the carbonates in the sample suite can furnish significant neutralization capacity. Only when the alkali-earth carbonates are the only source of neutralization potential in a particular sample will the theoretical carbonate-NP be equal to the measured standard NP. The second observation suggests that prolonged acid attack may not necessarily release additional NP resulting from the destruction of the more refractory minerals. This in turn implies that metal release from the component minerals, especially complex silicates, is not as straight-forward as that described by the many overall acid-neutralization reactions frequently quoted in the acid mine drainage literature (e.g., Ritchie, 1994). A couple of examples will suffice to demonstrate the relative stability of various minerals under the different acid-leaching scenarios.

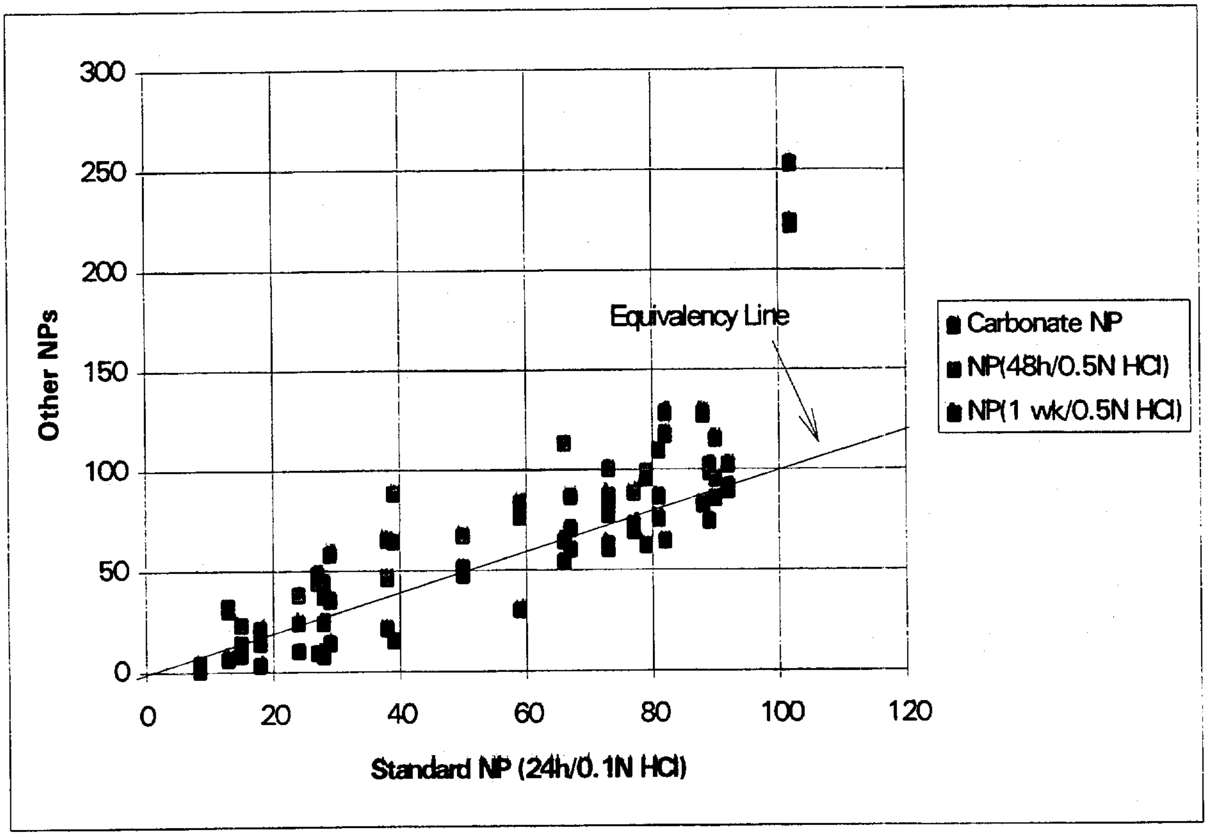

Figure 1. A comparison of assorted NPs versus standard NP for the Mt. Milligan samples.

Figure 2 shows the mineralogical changes associated with acid digestion of a sample composed mainly of quartz and Fe-rich dolomite with subordinate to minor amounts of plagioclase and muscovite. The sample gave a calculated carbonate-NP in excess of 250 kg $CaCO_3$ equivalent /tonne. However, less than half of the Fe-rich dolomite was depleted in a regular 24-hour acid digestion. Thus the standard NP appears to underestimate the actual NP of the sample. All the dolomite was destroyed upon 48 hours of digestion in 0.5N HCl (Figure 2). The associated minerals did not furnish additional NP with prolonged acid digestion and the measured 48-hour NP was essentially the same as the 1-week NP. Since the dolomite is Fe-rich,

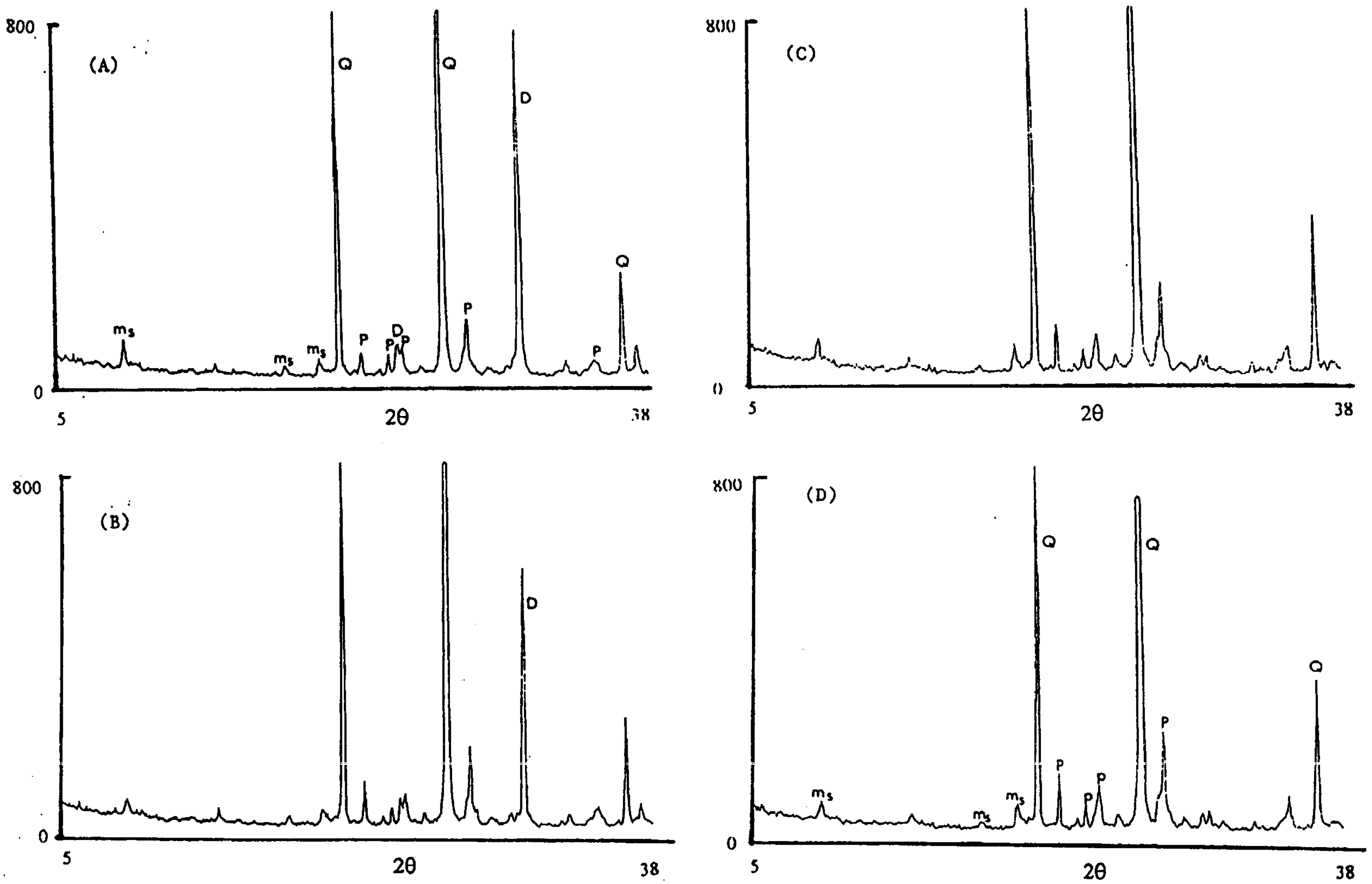

Figure 2. Mineralogical changes resulting from acid digestion of a sample enriched in Fe-dolomite. (A-untreated sample; B-residue after 24 hr in 0.1N HCl; C-residue after 48 hr in 0.5N HCl; D-residue after 1 wk in 0.5N HCl.) The minerals are: D=dolomite; ms=muscovite; P=plagioclase (albite); Q=quartz.

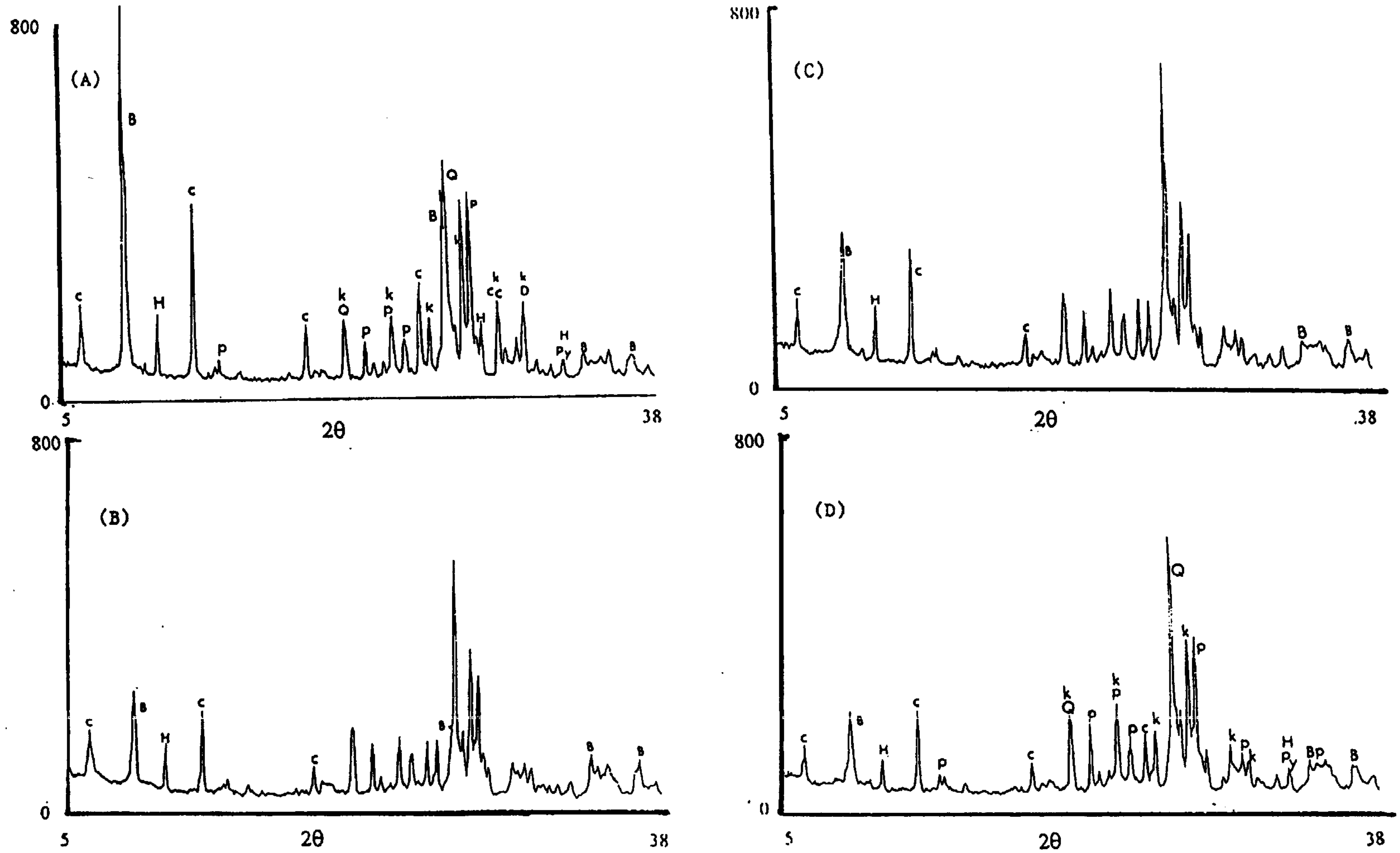

Figure 3. Mineralogical changes in a tailings sample (A) as a result of acid digestion: 24 hr in 0.1N HCl (B); 48 hr in 0.5N HCl (C); and, 1 wk in 0.5N HCl (D). Note that calcite, Cc, and dolomite, D, were depleted in 24 hr. Prominent and moderate destruction respectively of biotite, B, and chlorite, c, were evident after 24 hr followed by a slower rate of depletion of both minerals with prolonged acid digestion. Partial destruction of amphibole, H, was not evident until after 1 wk. Quartz, Q, potassium feldspar, k, plagioclase, p, and pyrite, py, appeared to be largely unaffected.

the ferrous iron released upon acid attack would subsequently undergo oxidation and hydrolysis to generate some acid. The theoretical carbonate-NP (calculated based on calcite stoichiometry) should, as observed, exceed the maximum measured NP rendered by complete destruction of the dolomite with prolonged acid digestion (Figure 1).

Next to the carbonates, biotite, chlorite and amphibole (in order of decreasing reactivity) are the silicate minerals evidently susceptible to acid attack in the Mount Milligan sample suite. Figure 3 compares the mineralogy of a tailings sample containing all these minerals in addition to quartz, plagioclase and K-feldspar and that of the residues after acid digestion for different duration. All the calcite and most of the dolomite in the sample were depleted after a 24-hour digestion in 0.1N HCl. A prominent reduction in the reflection peaks for biotite and less so for chlorite was observed after the same period of acid attack. Continual reduction in the corresponding peak intensity with prolonged acid digestion was observed for both minerals but at a slower rate. On the other hand, a significant depletion of amphibole became evident only after a week's digestion in 0.5N HCl. Quartz and the two types of feldspars, in contrast, appeared largely unaffected by the acid attack up to a week's duration.

Minor to trace amounts of pyroxene and epidote were also detected in some of the samples in the sample suite. However, their scarcity coupled with overlapping reflection peaks with the major minerals prevent a clear demonstration of their response to the acid digestions.

Assuming that (1) the maximum titration NP was a true measure of the acid neutralization of a sample; and, (2) biotite, chlorite and amphibole were the only silicate minerals susceptible to acid attack in the test samples, it is possible to calculate the equivalent NP of each of these minerals by making appropriate assumptions with regard to their ideal composition and the distribution of elements among various minerals. Thus, selecting a sample in which biotite is the dominant reactive silicate and assuming that the other silicates in the same sample do not furnish any additional NP, it can be calculated that the maximum NP rendered by short-term acid digestion (up to 1 week in 0.5N HCl) of biotite is 1.5 kg $CaCO_3$ equivalent/tonne per wt.% of the mineral occurring in a sample of the suite (Kwong, 1996). Similarly, it can be shown that the maximum NP furnished by each wt.% of chlorite and amphibole are 0.9 and 0.2 kg $CaCO_3$ equivalent/tone, respectively. These values constitute only a fraction of the theoretical maximum NP for the three minerals, which are 5.92, 4.98 and 6.46 kg $CaCO_3$ equivalent/tonne per wt.%, respectively.

The validity of the derived silicate NP values can be tested by back calculating the "effective" NP based on mineral abundance for each sample and comparing it with the corresponding maximum NP obtained in the titration procedures. Figure 4 illustrates such a comparison. Lacking accurate data for pyroxene and epidote, the former is considered to have the same NP as amphibole and the latter that of chlorite in the calculation of "effective" NP. As is evident from Figure 4, the calculated NP generally correlates well with titration NP, lending support to the contention that the carbonates, biotite, chlorite and amphibole are the primary acid-neutralizing minerals occurring in the Mount Milligan rocks. The feldspars, on the other hand, have insignificant acid neutralization capacity.

Minor discrepancies between the calculated NP and titration NP can readily be explained in terms of sample heterogeneity and poor precision of various techniques for measuring mineral abundance. For example, point-counting under a SEM with EDX capability showed that the sample with the largest discrepancy between the theoretical NP and titration NP contains a significant amount of pyroxene which was not detected by XRD because of peak interference.

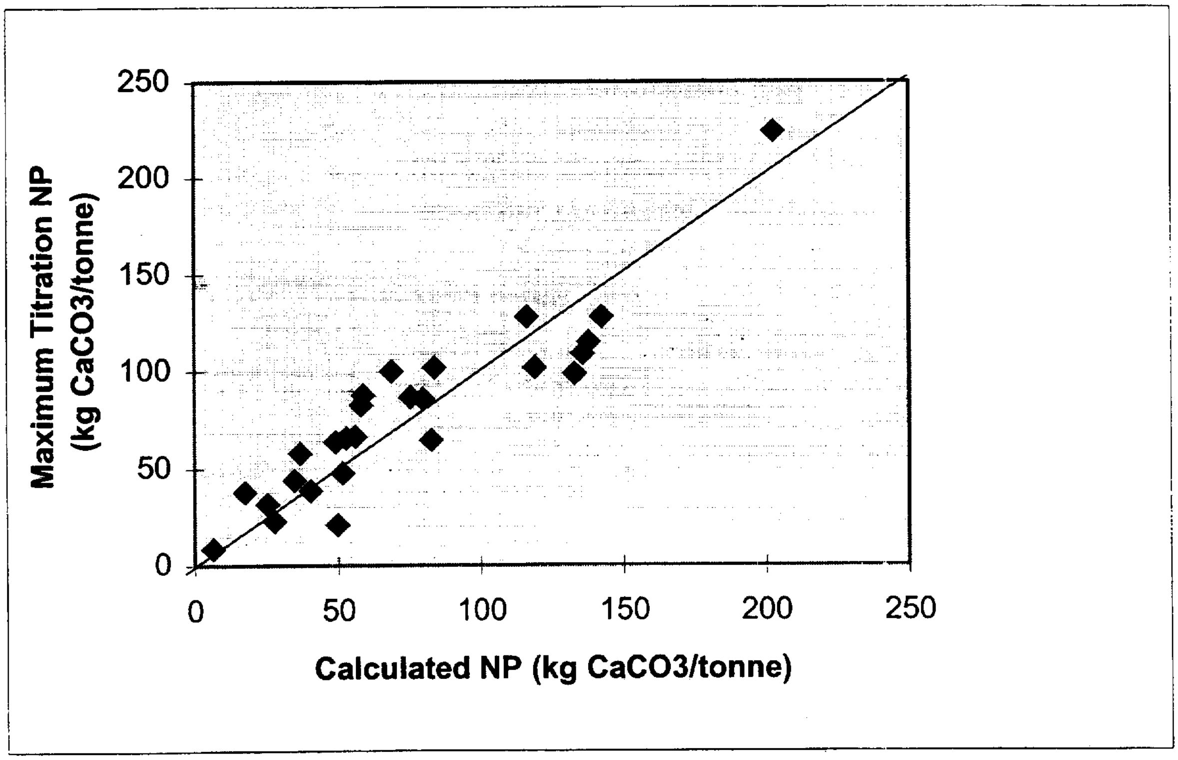

Figure 4. A comparison of maximum titration NP and calculated NP based on mineral abundance.

The lumping of amphibole and pyroxene together has thus led to an underestimate of the silicate NP contribution. A closer examination of samples containing both chlorite and epidote, on the other hand, showed that the grouping of the two minerals together did not lead to significant discrepancies. Thus, it is concluded that epidote has a similar NP as chlorite but pyroxene is apparently characterized by a higher NP than amphibole. However, more work is required to establish an operational NP for pyroxene in the Mount Milligan rocks.

DISCUSSION

Sources of NP in A Geologic Sample

The identification and partial quantification of minerals destroyed during acid digestion in this study clearly demonstrate that silicates in addition to carbonates can furnish significant acid neutralization capacity. Because of their natural abundance, the feldspars have frequently been assumed to play a more significant role than minor mafic silicates in acid neutralization (e.g., Morin and Hutt, 1994). Although the capability of feldspars to attenuate acidity over a long time period has been well-documented (Moss and Edmunds, 1992), the results of this study show that mafic silicates like biotite, chlorite, pyroxene and amphibole are more efficient acidneutralizers in the short term. For example, in the Mount Milligan sample suite, the biotite NP is at least an order of magnitude higher than that of feldspars (<0.1 kg $CaCO_3$ equivalent/tonne). Thus, 5 modal per cent of biotite will provide more NP than 50 modal per cent of feldspars. Moreover, the frequently observed coating of feldspar surfaces by clay minerals (especially kaolinite under mildly acidic conditions) in the field as a result of weathering will further reduce the efficiency of feldspars as acid-neutralizing minerals.

Nature of Silicate NP

As most silicate minerals occur in nature as solid solutions with a wide variation in composition, the derived NP for biotite, chlorite and amphibole cannot be applied universally to other mineral deposits. If the composition of these minerals also varies significantly within a deposit, the NP values may only be valid for samples containing mafic minerals of the same composition as that assumed in the calculation. For example, the amphibole-NP derived in this study is unexpectedly low considering the mineral's relative high position in the weathering series (Loughnan, 1969; Ollier, 1984). The explanation lies in its iron-rich composition and well-crystalline morphology. The majority of the amphibole grains occurring in the analyzed samples were fine-grained euhedral actinolite which replaced primary augite and hornblende during hydrothermal alteration or regional metamorphism. In the first place, the paucity of crystal defects helped the mineral to better withstand acid attack. In the second place, the acid generated during subsequent oxidation and hydrolysis of the released iron countered-balanced some of the acid consumed in the dissolution of the amphibole.

The complex nature of the silicate dissolution process also affects the manner silicate NP is rendered. Thus, the slight decrease in measured NP resulted from the 1-week acid digestion of some samples in the Mount Milligan suite relative to that of the 48-hour digestion is largely a consequence of the stepwise mechanisms involved in the dissolution of the relevant silicate minerals. In the dissolution of biotite, for example, the interlayer K^+ ions are readily leached; the release of Mg^{2+} and Fe^{2+} in the octahedral sites then follows but the rate of Mg release is faster than that of Fe; eventually, only upon the destruction of the tetrahedral sheets that Al and Si are released (Acker and Bricker, 1992). The release of Fe and Al in a later stage of the biotite dissolution process will subsequently produce some acid as a result of precipitation of the corresponding hydroxides, thus leading to the apparent decrease in NP. Similarly, Sverdrup (1990) has proposed a mechanism for the dissolution of chlorite whereby all of the Mg but only a portion of the Fe are released in the initial protonation stage. Thus, it is not surprising to find a sample dominated by chlorite render a lower 1-week than a 48-hour digestion NP.

Relevance of Mineralogical Information to Interpreting Static and Kinetic Data

The elucidation of behavior of various minerals during acid digestion in this study demonstrates the importance of incorporating mineralogical data in the interpretation of static and kinetic results for ARD prediction. It has been pointed out above that Fe-rich dolomite is unlikely to totally dissolve given a 24-hour digestion in 0.1N HCl at room temperature. Thus, the modified Sobek NP (Lawrence, 1990) may underestimate the effective sample NP. On the other hand, with acid digestion being conducted at an elevated temperature, the Sobek NP (Sobek et al., 1978) may overestimate the sample NP by enhancing the dissolution of the more refractory silicate minerals like the feldspars. Thus in a sample where the NP is not dominated by an alkali-earth carbonate (like calcite, dolomite, magnesite), the sample mineralogy must be considered to determine whether or not the measured NP is truly representative of the effective sample NP. Additional tests (e.g., 48-hour acid digestion) may be required to render accurate predictive data.

For kinetic data interpretation, a knowledge of sample mineralogy is essentially to determine whether or not the predicted acid-generation and base-depletion rates derived from leachate chemistry will change with time. If a sample is dominated by fast-dissolving minerals like calcite, its NP-depletion rate can be accurately determined with ease. If a sample is dominated by very-slowly reacting minerals like the alkali feldspars, the cation leachate chemistry will be largely controlled by cation-exchange reactions (Kwong, 1996); the NP release rate is unlikely to keep up with the sulfide oxidation rate and both may change with the evolution of the weathering process. A good understanding of the behavior of the component minerals under various pH regimes is then required to accurately predict the final outcome of the long-term water-rock/mineral interactions.

CONCLUSIONS

Based on the results of a detailed mineralogical analysis of a suite of samples from Mount Milligan both prior to and after acid digestion for different lengths of time, the following conclusions can readily be drawn:

1. Besides carbonates, silicate minerals can furnish significant acid neutralization potential in a geologic sample.
2. Mafic silicates like biotite, pyroxene, chlorite, epidote and amphibole are more efficient acid-neutralizing minerals than the more common feldspars.
3. Mineralogical information is indispensable in the proper interpretation of both static and kinetic testwork for acid rock drainage prediction.

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