Estimation of Calcium and Magnesium Carbonate Neutralization Potential for Refined Acid-Base Accounting Using Electron Microprobe and X-Ray Diffraction

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ABSTRACT

Acid-base accounting (ABA) is intended to estimate the quantities of minerals potentially capable of generating and neutralizing acid using chemical procedures. The neutralization potential (NP) component of ABA is more complex than acid potential (AP) because the minerals quantified in the analytical result may or may not contribute significantly to acid neutralization under field conditions. Calcium and magnesium carbonates (e.g. calcite, dolomite) are highly effective acid neutralizing minerals. However, alumino-silicates are digested to varying degrees during the NP determination but have weak actual acid neutralizing effect at near neutral pH due to the release of aluminum and to kinetically-slow reaction rates. NP determinations can therefore over-estimate effective NP and lead to non-conservative acid-base accounts.

This paper presents a method for calibrating routine NP and/or inorganic carbon determinations to calcium and magnesium carbonate content using electron microprobe to estimate the actual compositions of carbonate minerals, and quantitative x-ray diffraction (XRD) to estimate the quantities of the minerals. A small lithologically representative sub-set of samples is used to develop correction factors which are then applied to routine ABA data. Application of the method is illustrated for the Galore Creek Project, a copper-gold porphyry-type deposit in northwestern British Columbia which has the carbonate minerals calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), ankerite ($CaFe(CO_3)_2$), siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$).

Additional Key Words: acid rock drainage, neutralization potential.

INTRODUCTION

Acid-Base Accounting

Acid-base accounting (ABA) was first described in a regulatory context by Sobek et al. (1978) and remains the most commonly applied analytical procedure for evaluation of the potential for significant depression of pH in water contacting mine wastes (MEND, 2000). The actual ABA procedure has undergone several refinements (MEND, 1991) but the overall basis for the method remains the same. ABA is intended to be an analytical surrogate for estimation of mineralogical components that tend to cause pH depression (acid potential) and pH buffering (neutralization potential) when mine wastes are exposed to atmospheric weathering conditions.

The acid potential (AP), or maximum potential acidity (MPA, in Sobek et al., 1978) is determined by analysis of sulphur. This acts as a surrogate for iron disulphide (typically pyrite) which is assumed to oxidize to release protons:

$$FeS_2 + 15/4\,O_2 + 7/2\,H_2O \rightarrow Fe(OH)_3 + 4H^+ + 2SO_4^{2-} \tag{1}$$
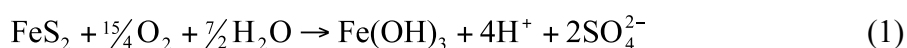
Acid potential is commonly calculated from the sulphur as sulphide content in percent multiplied by 31.25 to express the result in parts per thousand of calcium carbonate equivalents (kg $CaCO_3$/t).

Neutralization potential (NP) is usually determined by an acid digestion and back-calculation titration procedure and is intended to represent the rock components that could consume protons released by iron sulphide oxidation. The neutralization reaction is usually presented as complete reaction of protons with calcium carbonate, and the result is similarly expressed in parts per thousand of calcium carbonate equivalents (kg $CaCO_3$/t):

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3^0 \qquad (2)$$
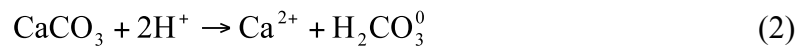
AP Limitations
There are some limitations with conventional AP determinations. For example, not all forms of sulphide generate acid when oxidized (Day et al., 2000), and some sulphates contribute acid when dissolved in water (Lapakko, 1992). Nonetheless, oxidation of iron sulphide releases protons dissolved in water. This can generate very low pH conditions leading to concentrations of potential contaminants in water that commonly exceed regulatory standards by orders-of-magnitude.

NP Limitations
Unlike AP, NP determinations by titration often produce complex results which can in turn lead to uncertainty in the acid-base account. The basis for the titration procedure (equation 2) is that the minerals dissolved during the acid titration will be reactive under natural conditions and will be capable of raising pH to the same level as acid consumption with calcium carbonate, which under most circumstances should be above 7. However, the procedures for determining NP involve addition of 0.1 N (or stronger) hydrochloric acid resulting in strongly acidic conditions (for example, pH 1.5 to 2.0, MEND, 1991) which dissolves many common rock forming minerals in addition to calcium carbonate. In particular, alumino-silicates (e.g. feldspars and micas) consume acid releasing aluminum which in turn releases protons through hydrolysis buffering drainage at pH between 4 and 5:

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \qquad (3)$$

An increase in drainage pH from below 3, as typically produced by iron sulphide oxidation to near 5 (neutralization by alumino-silicates), represents "neutralization of protons". However, this may not result in a pH that significantly affects the solubility of common contaminants with respect to regulatory water quality standards. Commonly, very stringent water quality standards must be met "end-of-pipe" rather than downstream of a dilution zone in the receiving environment. For example, at below pH 5 copper is soluble in the tens of grams per litre, and it is only at pHs above 7 that copper concentrations approach typical acceptable effluent levels (e.g. 0.3 to 0.6 mg/L, Canada, 2002) and surface water quality protection standards (e.g. 2 to 4 µg/L, CCME, 1999). Furthermore, silicate minerals react slowly (Jambor, 2003) and silicate NP is often insufficient to maintain near-neutral pH levels. Therefore, reported NP typically reflects both carbonate and silicate minerals, the latter of which may have limited value in raising pH to levels which control contaminant concentrations.

The mineralogical limitations of NP determinations and the various modifying procedures have been thoroughly evaluated by others (e.g. Lawrence and Wang, 1996; Lapakko 2003) and will not be reviewed in detail here. The MEND (1991) modified NP

method performs the acid digestion at room temperature conditions in an effort to reduce silicate dissolution compared to the boiling conditions in the Sobek et al (1978) method; however, acid addition still occurs to pH 1.5 to 2.0. Direct determination of carbonate has been considered to address the problem of silicate dissolution. However, in this approach iron carbonates (e.g. siderite, iron component of ankerite and dolomite) contribute to the resulting carbonate NP but do not increase the pH to greater than 6 due to the release, oxidation and hydrolysis of ferrous to ferric iron when these carbonates are dissolved. Skousen et al. (1997) considered that iron carbonates could contribute to NP in the Sobek et al. (1978) method due to incomplete iron oxidation and proposed addition of hydrogen peroxide (to complete iron oxidation) after the initial digestion step before back-titration. In contrast, Jambor (2003) concluded that ferrous iron was oxidized during the MEND (1991) procedure without the need for hydrogen peroxide because the end-point pH is 8.3 rather than 7.0 in Sobek et al. (1978). Lapakko (1992) showed that the MEND (1991) procedure came close to approximating the calcium and magnesium carbonate content determined by x-ray diffraction (XRD). In general, none of the standard NP methods consistently quantify the silicate component of NP. There have been other efforts to quantify the mineralogical basis of NP; for example, the acid-base characteristic curve (ABCC) is an attempt to evaluate the contribution of different mineralogical groups by monitoring the pH during acid addition (AMIRA, 2002). The method requires interpretation of the pH trend which can lead to ambiguity.

In summary, the NP methods are particularly susceptible to the effects of dissolution of silicate minerals which may not be reactive under field conditions (with some exceptions, Jambor, 2003). However, the two main NP methods (Sobek et al., 1978 and MEND, 1991) are well-established and have been widely used for over 30 years.

Therefore, this paper presents a method to calibrate conventional NP determinations to the calcium and magnesium carbonate composition of mine waste materials. The method allows an existing ABA database to be re-interpreted in terms of reactive carbonate mineralogy thereby addressing directly the concerns about alumino-silicates and iron carbonates without extensive re-analysis using special methods. The presented method does not require the use of proprietary or costly analytical methods. The method is not intended to evaluate the reactivity of the minerals involved in acid neutralization which must be studied by other means.

METHODS
Sample Selection
A suite of samples representing the mineralogical variability of the waste materials is selected. Important factors in the selection include the range in types of silicates and carbonates that may be a result of differences in rock types and hydrothermal alteration and therefore the response of the NP method.

Chemical Determinations
Each sample is submitted for analysis of the same acid-base accounting procedures as the database to be calibrated. Due to the numerous specific factors that affect individual NP results, the same laboratory (and ideally the same analyst) performs the determinations as produced the database. In addition, the samples are submitted for determination of total inorganic carbon (TIC) to indicate carbonate content. A coulimetric carbon dioxide method is used rather than determination of total carbon to avoid uncertainty due to non-carbonate forms of carbon.

Mineralogical Determinations
Each sample is submitted for three types of mineralogical determinations:

- Optical mineralogy is determined on polished thin sections. Carbonate mineral grains are identified for subsequent microprobe analyses. Approximately 10 to 20 grains are selected in each section.

- Microprobe analysis is performed on each carbonate grain to determine its calcium, magnesium, iron and manganese content.

- Quantitative X-Ray Diffraction (QXRD) is performed on each sample using the Rietveld (1969) method.

Interpretation Method
Step 1 – Evaluate Microprobe Data
Microprobe data for carbonate minerals are plotted on a ternary diagram with the diagram apexes at Ca, Mg and Fe+Mn using the molar proportions determined for each mineral grain. This initial screening step is used to confirm that the microprobe data conform to the expected range of compositions and solid solutions of common carbonate minerals (calcite ($CaCO_3$), magnesite ($MgCO_3$), siderite ($FeCO_3$), rhodochrosite ($MnCO_3$) and dolomite-ankerite $Ca(Mg,Fe)(CO_3)_2$). Any rare grains showing substantial deviation from the expected compositions may be analytically uncertain and should not be included in the next step. If several grains have unusual compositions, these may need to be evaluated further and compared to the QXRD data.

Step 2 – Calculate Carbonate Mineral Formulae
The next step in the interpretation is to estimate the average composition and resulting formula weight of carbonate minerals in the samples according to the types of carbonate minerals that can usually be distinguished by QXRD. The simple carbonates (e.g. calcite and siderite) can be distinguished but generally not ankerite and dolomite. Therefore, the solid solution between ankerite and dolomite is represented by a single composition and formula weight. The interpretation at this step also considers any variation in mineral composition linked to rock type and other factors. For example, a range in the composition of dolomite-ankerite may reflect different types of hydrothermal alteration. The average compositions of each of the individual carbonate minerals are represented in the form:

$$Ca_wMg_xFe_yMn_zCO_3 \tag{4}$$

Where $w+x+y+z = 1$.

The calculated formulae of each of the carbonate minerals are then used to calculate their average formula weights ($FW_{mineral}$) using the respective mole weights (m) of Ca (40.1 g/mole), Mg (24.3 g/mole), Fe (55.8 g/mole), Mn (54.9 g/mole) and carbonate (60.0 g/mole):

$$FW_{mineral} \text{ (g/mole)} = w_{mineral} \cdot m_{Ca} + x_{mineral} \cdot m_{Mg} + y_{mineral} \cdot m_{Fe} + z_{mineral} \cdot m_{Mn} + m_{CO_3} \tag{5}$$

The formula weights for the dolomite-ankerite series are normalized to one mole of carbonate rather than two moles as in the normal formulae for binary carbonates. As a result, the formula weights are all close to 100 g/mole.

Step 3 – Compare Analytical Carbonate Content with Mineralogical Carbonate Content

The third step is to calculate TIC indicated by the QXRD (TIC$_{QXRD}$ in %C) from:

$$TIC_{QXRD} = AW_C \cdot \sum_{mineral} \frac{P_{mineral}}{FW_{mineral}} \tag{6}$$

The P$_{mineral}$'s are the proportions of each mineral indicated by the QXRD report. AW$_C$ is the atomic weight of carbon (12 g/mole). The resulting values are graphically compared to the analytical TIC. Any significant departures from equivalence should be evaluated, but the purpose is to determine if the QXRD is producing an approximation of the analytical carbonate content. Samples containing high levels of amorphous materials will report greater TIC$_{QXRD}$ than indicated by coulimetric analyses because the XRD determination is normalized to 100% crystalline components. This does not represent a limitation of the procedure.

Step 4 – Calculate Fraction of Carbonate Associated with Calcium and Magnesium Carbonate

The total fraction of the carbonate in each sample occurring as calcium (f$_{Ca}$) is calculated using:

$$f_{Ca} = \frac{\sum_{mineral}\left[w_{mineral} \cdot IC_{mineral}\right]}{TIC_{QXRD}} \tag{7}$$

Where, the inorganic carbon content associated with each mineral (IC$_{mineral}$ in %,C) is calculated from:

$$IC_{mineral} = AW_C \cdot \frac{P_{mineral}}{FW_{mineral}} \tag{8}$$

The calculation is then repeated to obtain f$_{Mg}$, f$_{Fe}$ and f$_{Mn}$ using the x$_{mineral}$, y$_{mineral}$ and z$_{mineral}$ indicated for each mineral in equation (4). The fraction associated with both calcium and magnesium carbonate components is:

$$f_{Ca} + f_{Mg} \tag{9}$$

This fraction can then be applied to the analytical TIC to estimate the analytical quantity of calcium and magnesium carbonates for each sample:

$$(f_{Ca} + f_{Mg}) \cdot TIC \tag{10}$$

This can then be compared to the analytical neutralization potential and other surrogates for acid neutralizing minerals to estimate the degree to which they represent the calcium and magnesium carbonate mineral content.

EXAMPLE APPLICATION TO THE GALORE CREEK PROJECT
Background
Galore Creek is an alkali porphyry deposit containing economic copper and gold mineralization located in the Coast Mountains of northwestern British Columbia, Canada. The deposit is hosted by late Triassic to early Jurassic syenitic bodies intruded into upper

Triassic volcanic rocks and sediments. The mineralization is associated with potassic alteration and breccia bodies and pyrite accompanies chalcopyrite and bornite. A variety of silicate minerals are present in potassic, propylitic and calc-silicate alteration zones and include orthoclase, chlorite, garnet, epidote, diopside and albite (Enns et al. 1995). Except for diopside, these silicates all contain aluminum. Carbonate alteration is also ubiquitous throughout the deposit and occurs as finely disseminated grains, patches of grains and veinlets.

Acid-base accounting data obtained, as part of feasibility studies and environmental assessment, indicated that acid rock drainage (ARD) potential varied from negligible to potentially acid generating (PAG) due to sulphide sulphur concentrations varying from undetectable (<0.01%) to a few percent (SRK Consulting, 2006). The majority of the rock was classified as non-PAG with average sulphide concentrations below 1% but based on observations of the natural gossan, the PAG component was expected to generate ARD if not managed appropriately. The mine plan was therefore designed to allow operational segregation of the PAG waste rock component and subsequent subaqueous disposal in a constructed impoundment. Based on these requirements, a reliable acid-base accounting method was needed to classify the wastes both during planning and mine operation. Development of this method included evaluation of the performance of the MEND (1991) NP method.

Neutralization Potential Data
The routine acid-base accounting method for the project was the "modified" or "MEND" method (MEND, 1991). For comparison, the Sobek et al. (1978) was also performed on 55 samples. The Sobek method resulted in consistently greater NP than the MEND method (Figure 1), and furthermore, the change in acid strength required by a fizz rating of "moderate" compared to "slight" increased the difference between the two methods (Figure 1). These results implied that at least the Sobek method was dissolving alumino-silicates in the procedure.
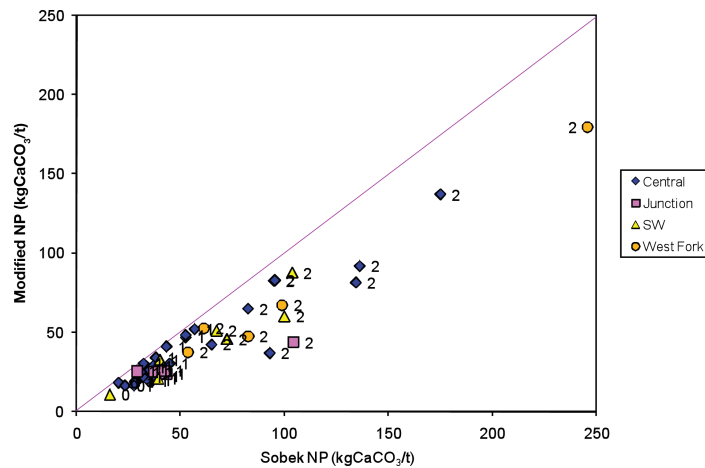

Figure 1. Comparison of Sobek and Modified NP for the four mineralized zones at Galore Creek. The diagonal line indicates parity. The number annotation on each point is the fizz rating in the neutralization potential (0=none, 1=slight, 2= moderate). Diagonal line indicates equivalence.

Carbonate determinations on the same set of samples showed that in general modified NP and total inorganic carbon (TIC) were correlated (Figure 2). Some samples contained more TIC than NP indicating that in these cases carbonate minerals were not contributing to reported

NP, while others had more NP than TIC indicating that minerals other than carbonates were contributing to reported NP. Based on these results it was concluded that NP determinations were not conclusively reflecting the buffering capacity of the calcium and magnesium carbonate component of the rocks.
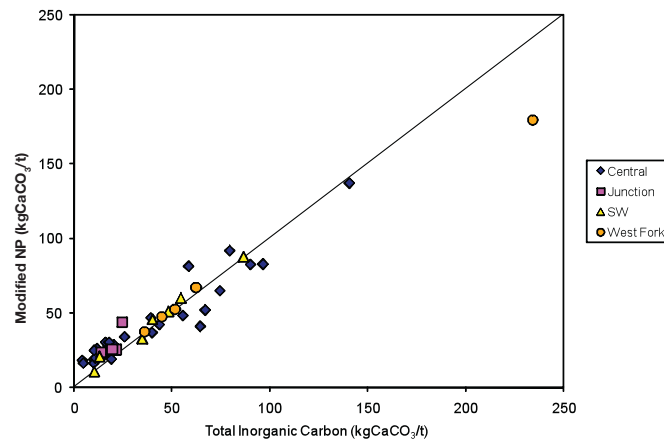

Figure 2. Comparison of Modified NP and Total Inorganic Carbon. Diagonal line indicates equivalence.

Calibration of NP

Methods

A suite of 20 samples was selected to represent different mineralized zones at Galore Creek and a range of rock types and sulphide content. Optical mineralogy was described by Petrascience Consultants Inc. Carbonate grains for microprobe analyses were selected following description of the mineralogy.

QXRD determinations were performed under the direction of Mati Raudsepp at the University of British Columbia (UBC) Department of Earth and Ocean Sciences. Step-scan X-ray powder-diffraction data were collected over a range 3-80°2θ with CoKα radiation on a standard Siemens (Bruker) D5000 Bragg-Brentano diffractometer. Results for carbonate minerals are provided in Table 1.

Electron-probe microanalyses of carbonate were done on a fully automated CAMECA SX-50 instrument at UBC, operating in the wavelength-dispersion mode with the following operating conditions: excitation voltage, 15 kV; beam current, 10 nA; peak count time, 20 s; background count-time, 10 s; spot diameter, 10 μm. The spot diameter did not limit the number of grains that could be probed. Data reduction was done using the 'PAP' $\phi(\rho Z)$ method (Pouchou and Pichoir, 1985). For the elements considered, the following standards X-ray lines and crystals were used: dolomite, Mg$K\alpha$, TAP; calcite, Ca$K\alpha$, PET; rhodocrosite, Mn$K\alpha$, LIF; siderite, Fe$K\alpha$, LIF.

Results and Interpretation

Microprobe results are shown in Figure 3. The majority of mineral grains were either calcite (grey squares) or dolomite-ankerite (mainly dolomite) all of which contained varying amounts of iron. One sample contained several grains of rhodochrosite (magenta squares) and two grains of siderite containing 44% magnesium were found in one sample.
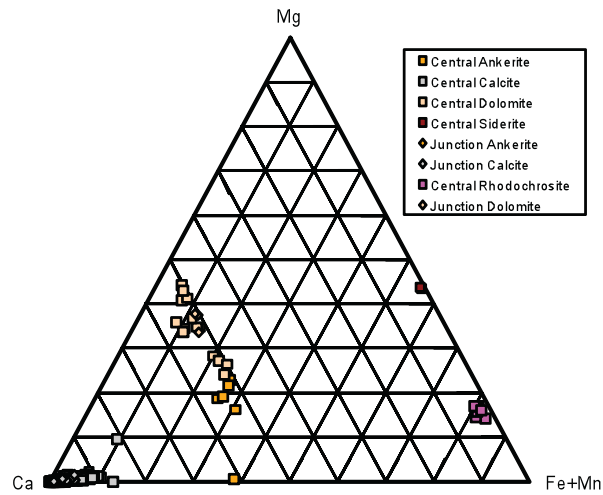
Figure 3. Ternary diagram showing microprobe results.

Using these data, the average composition of mineral grains was calculated (Table 2). TIC_{QXRD} was calculated using equation 6 and compared to analytical TIC (Table 1). With a few exceptions, QXRD reliably quantified the analytical carbonate content in terms of carbonate minerals. Carbonate content determined from QXRD exceeded the analytical total of inorganic carbon content for all but three samples. This may have been due to the presence of non-crystalline phases (e.g. oxides) which were not quantified by QXRD.

Table 1 shows the calculated fraction of the carbonate content estimated to be as calcium and magnesium components of the carbonate minerals ($f_{Ca}+f_{Mg}$). The fraction varied from 22% (rhodochrosite-bearing sample) to near 100% (calcite-containing samples). The average was 80% primarily reflecting the presence of iron carbonate associated with ankerite.

Finally, the calculated calcium and magnesium carbonate content was compared to modified neutralization potential determinations (Figure 4). Above NP of about 40 kg $CaCO_3$/t, neutralization potential was nearly equivalent to the calcium and magnesium carbonate content. Below this level, NP exceeded calcium and magnesium carbonate content for all but two samples. As this is a consistent bias, it is probably due to the dissolution of alumino-silicate minerals during the NP determinations rather than analytical variability at lower concentrations.

Table 1. X-Ray Diffraction Results.

Sample Number	NP	TIC	Calcite	Mg Calcite	Dolomite-Ankerite	Siderite	Rhodo-chrosite	TIC_{QXRD}	$f_{Ca}+f_{Mg}$
	kg $CaCO_3$/t	%C	%	%	%	%	%	%C	%
599	62	0.94	5.4	0	0.4	0	0	0.70	98
241	26.5	0.16	0	1.8	0.3	0	0	0.25	97
688	27.1	0.26	2.2	0	6.4	0	0	1.07	82
571	29.8	1.07	0.9	0	1.2	0	7.4	1.02	22
418	24.3	0.37	3.5	0	0	0	0	0.42	100
276	22.3	0.07	4.6	0	0	0	0	0.55	100
1134	9.5	0.05	1.2	0	0	0.2	0	0.16	87
1085	19.6	0.15	1.4	0	0	0.6	0	0.23	73
1278	37.4	0.51	1.3	0	2.4	0	0	0.46	85

1032	28	0.19	2.1	0	0	0.4	0	0.29	86
1040	25.9	0.23	1.5	0	0.6	0.5	0	0.31	77
991	38.8	0.31	0	2.6	0.3	0.5	0	0.40	85
832	83.8	1.09	0	5	5.7	0	0	1.31	87
881	39.5	0.46	0	3.6	2.4	0	0	0.73	90
845	45.3	0.50	0	3.5	1.5	0	0	0.61	93
908	65.6	0.95	0	2.7	5.9	1	0	1.17	76
900	57.6	1.15	0	0.6	7.2	2.9	0	1.27	60
785	27.7	0.42	0	2.9	0.6	0	0	0.42	96
818	165.9	2.39	0	10.1	11.2	0	0	2.61	87
835	59.1	0.76	0	3.5	3.9	0	0	0.91	87

Table 2. Average Carbonate Mineral Compositions from Microprobe Data

Mineral	Average Formula	Formula Weight (g/mole)
Calcite	$Ca_{0.97}Mg_{0.01}Fe_{0.01}Mn_{0.02}CO_3$	100.3
Ankerite-Dolomite	$Ca_{0.53}Mg_{0.31}Fe_{0.13}Mn_{0.03}CO_3$	98.0
Siderite	$Ca_{0.01}Mg_{0.44}Fe_{0.54}Mn_{0.02}CO_3$	101.9
Rhodochrosite	$Ca_{0.03}Mg_{0.16}Fe_{0.38}Mn_{0.43}CO_3$	110.0

These findings were used to select an average NP adjustment factor of 10 kg $CaCO_3$/t for the Galore Creek ABA database that accounts for the dissolution of alumino-silicates at low neutralization potentials.
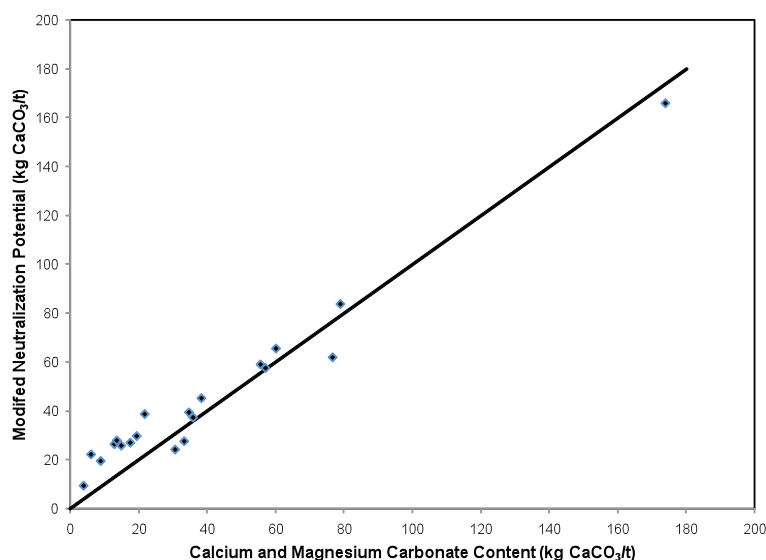

Figure 4. Neutralization Potential Compared to Calcium and Magnesium Carbonate Content. The diagonal line indicates parity.

CONCLUSIONS

Advancements in x-ray diffraction intepretation have resulted in a method which reliably quantifies carbonate content at percent levels and, in conjunction with microprobe data allows carbonate mineral occurrence to be evaluated with respect to neutralization potential. The method can be used to callibrate existing conventional carbonate and neutralization potential data to the calcium and magnesium carbonate content without extensive re-analysis.

REFERENCES

AMIRA International. 2002. ARD Test Handbook. Prediction & Kinetic Control of Acid Mine Drainage. Project P387A. May 2002. 42 pages with appendices.

Canada. 2002. Fisheries Act. Metal Mining Effluent Regulations. Canada Gazette Part II, vol 136. No. 13.

Canadian Council of Ministers of the Environment. 1999. Canadian Environmental Quality Guidelines. http://ceqg-rcqe.ccme.ca/.

Day, S., Coulter, G. and Falutsu, M. 2000. Red Dog Pb-Zn Mine Closure Planning: Phase 1 Geochemical Studies – Characterization of Complex Sulfur Mineralogy. Proceedings from the Fifth International Conference on Acid Rock Drainage Volume I. Denver, CO, May 2000.

Enns, S.G., Thompson, J.F.H., Stanley, C.R. and Yarrow, E.W. 1995. The Galore Creek porphyry copper-gold deposits, Northwestern British Columbia. In ed. Schroeter T.G. Porphyry Deposits of the Northwestern Cordillera of the North America. Canadian Institute of Mining and Metallurgy, Special Volume 46. pp. 630-644.

Jambor, J. 2003. Chapter 6 - Mine-waste mineralogy and mineralogical perspectives of acid-base accounting. In Jambor, J.L., Blowes, D.W. and Ritchie, A.I.M. (editors), Environmental Aspects of Mine Wastes. Mineralogical Association of Canada, Short Course Series Volume 31. Vancouver, British Columbia, 2003. pp 117-145.

Lapakko, K.A. 1992. Characterization and static testing of ten gold mine tailings. In Achieving Land Use Potential Through Reclamation. Proc. 9th National Meeting ASSMR, Duluth, MN, June 14-18, 1992. p. 370-384.

Lapakko, K.A. 2003. Solid Phase Characterization for Metal Mine Waste Drainage Quality Prediction. Preprint 03-93 In Proc. 2003 SME Annual Meeting, February 24-27, Cincinnati, OH (CD-ROM). Soc. For Mining, Metallurgy, and Exploration, Inc. Littleton, CO.

Lawrence, R.W. and Wang, Y. 1996. Determination of neutralization potential for acid rock drainage prediction. Mine Environment Neutral Drainage Program Report 1.16.3. July 1996. 186 pages with appendices.

MEND. 1991. Acid Rock Drainage Prediction Manual. Mine Environment Neutral Drainage Program Report 1.16.1b. March 1991. 71 pages.

Mine Environment Neutral Drainage Program. 2000. MEND Manual – Volume 3 Prediction. Report 5.4.2. December 2000. 108 pages with appendices.

Pouchou, J.L. and Pichoir, F. 1985. PAP φ(ρZ) procedure for improved quantitative microanalysis. Microbeam Analysis, 1985, pp.104-106.

Rietveld, H. M. 1969. A profile refinement method for nuclear and magnetic structures. Journal of Applied Crystallography 2, pp.65-71.

Skousen, J., Renton, H., Brown, H., Evans, P., Leavitt, B., Brady, K., Cohen, L. and Ziemkiewicz, P. 1997. Neutralization potential of overburden samples containing siderite. J. Environ. Qual. 26, pp.673-681.

Sobek, A.A., Schuller, W.A., Freeman, J.R., and Smith. R.M. 1978. Field and laboratory methods applicable to overburden and minesoils. USEPA Report No. 600/2-78-054, 203 pp.

SRK Consulting. 2006. Galore Creek Project ML/ARD Characterization Report. Prepared for Novagold Resources Inc. May 2006. 128pp plus appendices.