New Methods for Determination of Key Mineral Species in Acid Generation Prediction by Acid-Base Accounting

MEND Report 1.16.1c

April 1991

NEW METHODS FOR DETERMINATION OF KEY MINERAL SPECIES IN ACID GENERATION PREDICTION BY ACID-BASE ACCOUNTING

MEND Project 1.16.1c

April 1991

NEW METHODS FOR DETERMINATION OF KEY MINERAL SPECIES IN ACID GENERATION PREDICTION BY ACID-BASE ACCOUNTING

Final Report By:

Norecol Environmental Consultants Ltd.
Suite 700, 1090 West Pender Street
Vancouver, British Columbia
V6E 2N7

Work on this project was conducted under the auspices of the Department of Energy Mines and Resources.

DSS FILE NUMBER: 38SQ.23440-0-9194

DSS CONTRACT NUMBER: 23440-0-9194/01-SQ

EXECUTIVE SUMMARY

A review of chemical literature has been completed to find new methods for determining important mineral phases in the generation of acidic water from waste rock. Methods were ranked and four procedures selected for preliminary testing. Recommendations are made for improvement to the acid-base accounting procedure that may reduce the effects of atypical mineral associations in metal deposits.

A number of different methods are available for estimation of the concentrations of total sulphur and sulphur forms in mineral waste and ore samples. Techniques to discriminate between sulphur as different types of sulphates, and sulphur as pyrrhotite, pyrite and base metal sulphides are available.

A key concern in the measurement of neutralization potential is that the presence of silicates and ferrous iron-bearing minerals may lead to anomalously high results. Methods to directly and quantitatively determine calcium and magnesium carbonates are not commercially available. Modification of the current neutralization potential procedure by adding hydrogen peroxide, and analysis of hydrochloric acid leachate for calcium, magnesium, and iron are recommended to address this problem.

Methods were ranked using weighting schemes which emphasized phase analysis, rapid inexpensive analysis, or suitability for mine site laboratories. Four methods were selected for limited testing using mixtures prepared from samples of known mineralogical composition. These methods were: (a) determination of sulphur as pyrrhotite and pyrite; (b) field determination of sulphur as pyrite; (c) modification of conventional U.S. EPA neutralization potential procedure by filtration of leachate and addition of hydrogen peroxide; and (d) determination of carbonates by metal analysis. Procedure (a) performed well for each mineral matrix tested. Further development of the other procedures is required, particularly those dealing with carbonate analysis. Standard reference materials for this type of project are required to refine the methods.

It is recommended that routine acid-base accounting include a supporting mineralogical description to provide confidence in the chemical results. A number of mineral phase-specific procedures are available for testing and these should be selected on a project-by-project basis, depending on the complexity of the mineralogy and the Phase of the project.

SOMMAIRE EXECUTIVE

Un examen rétrospectif des ouvrages de chimie a été réalisé dans le but de découvrir de nouveaux procédés pour déterminer les phases minérales importantes de la production d'eau acide par les stériles. Les procédés utilisés ont été classés et quatre d'entre eux ont été choisis en vue des essais préliminaires. Des recommandations ont été faites pour améliorer le système de rapport sur le procédé relatif à la base acide qui peut réduire les effets des associations de minéraux atypiques présentes dans les gisements.

Différents procédés pour évaluer les concentrations de soufre total et les composés sulfurés présents dans les déchets de l'industrie minérale et les échantillons de minerais sont disponibles. Des techniques établissant une distinction entre le soufre et les divers types de sulfates, le soufre sous forme de pyrrhotine, de pyrite et de sulfates de métaux de base ont également été mises au point.

La mesure du potentiel de neutralisation constitue une préoccupation des plus importante car la présence de silicates et de minerais de fer peut donner des résultats au-dessus de la normale. Il n'existe actuellement sur le marché aucune méthode de détermination directe et quantitative des carbonates de calcium et de magnésium. Pour résoudre le problème, on recommande de modifier le procédé actuel de mesure du potentiel de neutralisation du magnésium et du fer par l'addition de peroxyde d'hydrogène et l'analyse des produits de lixiviation acides et chlorhydriques.

Les procédés ont été classés au moyen de schémas de pondération qui mettaient l'accent sur l'analyse des phases, l'analyse rapide et peu coûteuse, ou l'applicabilité du procédé dans les laboratoires situés sur le site minier. Quatre procédés ont été sélectionnés pour des essais limités au moyen de mélanges préparés à partir d'échantillons de composés minéralogiques connus. Ces procédés sont les suivants : (a) la détermination du soufre en tant que pyrrhotine et pyrite; (b) la détermination, sur le terrain, du soufre en tant que pyrite; (c) la modification de la procédure classique de neutralisation du potentiel par filtration du produit de lixiviation et l'addition de peroxyde d'hydrogène (EPA -É.-U.) et; (d) la détermination des carbonates par l'analyse du métal. La méthode (a) a donné de bons résultats lors de l'essai de chaque matrice minérale. Le développement des autres méthodes doit se poursuivre, en particulier celles qui portent sur l'analyse du carbonate. Pour perfectionner les méthodes, des matériaux de référence ordinaires tels ceux qui ont été utilisés pour réaliser ce projet sont requis.

On recommande de documenter les essais sur la base acide et de joindre aux rapports courants une description minéralogique confirmant les résultats des analyses chimiques. Un certain nombre de méthodes, applicables en particulier dans la phase minéralogique, sont disponibles à des fins d'essai. Le choix de la méthode appropriée doit être fait en fonction de chaque projet et en tenant compte de la complexité de la minéralogie et de la phase du projet.

TABLE OF CONTENTS

Page

TABLE OF CONTENTS (continued)

Page

TABLE OF CONTENTS (continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

1.0 INTRODUCTION

1.1 Terms of Reference

Norecol Environmental Consultants Ltd. of Vancouver, British Columbia was retained by the Department of Supply and Services Canada (DSS), on behalf of the Department of Energy, Mines and Resources, Canada Centre for Mineral and Energy Technology, Mineral Sciences Laboratories, to evaluate new ways of analytically identifying mineral species important in the generation of acidic waters from rock wastes. This report has been prepared as required in the terms of DSS contract No. 23440-0-9194/01-SQ.

1.2 Background

Exposure of rock or soil containing reactive sulphide minerals to oxidants (typically oxygen) in the presence of water can result in the production of acidic and metal-rich surface and ground waters. This runoff is commonly referred to as acid mine drainage (AMD) or, more recently in British Columbia, as acid rock drainage (ARD) (British Columbia Acid Mine Drainage Task Force 1989). The latter term is preferred because acidic waters can be produced anywhere sulphide-bearing rock is naturally present (for example, in gossans (Day and Cowdery 1990)) or artificially (for example, mines, transportation routes (Byerly 1990), and commercial developments (Guilcher 1987; Lond 1987; Worgan 1987)).

Growing concern regarding the impact of ARD on the environment around mining developments has led regulators to require reliable predictions of the potential for generation of acidic waters from newly excavated rock. Prediction technologies have developed in two directions:

1) **Static geochemical tests**, involving determinations of whole rock geochemistry and attempt to relate this to the eventual potential for development of acidic drainage. These methods include acid-base accounting (ABA), a procedure specifically developed to evaluate the relative quantities of acid-generating and acid-consuming minerals.

2) **Kinetic geochemical tests**, involving determination of actual rates of rock weathering and release of acidity and metals under controlled laboratory or field conditions. These methods include humidity cell tests, column tests and lysimeters, shake flask tests, and the use of small-scale waste rock piles and mine tailings ponds.

Acid-base accounting, the primary focus of this study, is the first type of test used on any project where acidic drainage is a potential concern, and therefore the results of ABA are the first indication of potential problems. In addition, the results may be used to design detailed waste rock management plans, in conjunction with kinetic tests, and to classify waste rock and tailings as they are produced. Consequently, improved static tests should have the following properties:

- results are mineral phase-specific and unambiguous (not matrix dependent);
- results can be produced inexpensively and quickly, preferably in conjunction with other tests; and
- test can be carried out using relatively simple equipment in an on-site laboratory.

Many currently available methods do not meet any of these conditions.

1.3 Project Scope

The objectives of this project were as follows:

1) to find methods in the analytical chemistry literature that may be applicable to acid generation testing and provide a greater degree of confidence in determination of specific mineral phases than is currently possible;

2) to find reliable, inexpensive chemical methods for acid generation testing that take advantage of recent advances in simultaneous multi-element analysis;

3) to initially test the most promising methods; and

4) to make recommendations for future testing and development of methods for acid-base accounting.

The project involved a review of literature to identify suitable methods that may be used for identifying key mineral species in the generation and neutralization of acid. At the same time, the capabilities of simultaneous multi-element methods were reviewed, and laboratory managers consulted to evaluate the commercial viability of new approaches. All methods were then ranked in terms of ability to determine distinctive mineral phases, relative cost and commercial availability, and feasibility for use in small on-site testing laboratories.

A series of mineral mixtures were prepared from known mineral specimens and were analysed using selected promising procedures.

1.4 Acknowledgements

Norecol Environmental Consultants Ltd. acknowledges the following people and organizations for assisting in this project:

- Bacon Donaldson & Associates, Richmond, B.C. prepared the rock mixtures and conducted acid-base accounting and new procedures.
- Brenda Caughlin and Lloyd Twaites of Chemex Laboratories, North Vancouver, B.C. answered questions on ICP-ES, and classical methods of sulphur forms analysis.
- Stanya Horsky of the University of British Columbia Department of Geological Sciences answered questions on x-ray diffraction.
- Carlo Giovanella of the U.B.C. Department of Geological Sciences provided the samples of siderite.

All parts of the project were conducted and coordinated by Norecol employees Stephen Day and Patrice Rother.

2.0 CURRENT STATUS OF ACID-BASE ACCOUNTING

2.1 Classical Theory of Acid-Base Accounting

The objective of acid-base accounting is to analytically estimate the quantities of minerals capable of generating acid, and minerals that may naturally consume acid when weathered. Based on theoretical considerations, these quantities are expressed in the same units so that an "account" showing the relative excess of one component over the other can be prepared.

The potential to generate acid is estimated by measuring the total quantity of sulphur in a sample. This is usually expressed as percent sulphur by weight but must be converted to calcium carbonate units for use in acid-base accounting. This is achieved by writing two ideal reactions for net acid generation:

- oxidation of iron disulphide:

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

- acid consumption by calcium carbonate:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$$

Based on these reactions, 1 mole of sulphur produces 2 moles of H^+, which can be neutralized by 1 mole of $CaCO_3$. Therefore, 1 mole of sulphur is theoretically equivalent to 1 mole of $CaCO_3$. The weight equivalency is 1 g S to 3.125 g $CaCO_3$, therefore sulphur concentration (in percent) is multiplied by 31.25 to yield maximum potential acidity (MPA) in kg $CaCO_3$/t of rock.

Classically, the quantity of acid-consuming minerals is estimated by adding a known excess of mineral acid to the sample and measuring the amount of acid consumed (Sobek *et al.* 1978). The result, neutralization potential (NP), is expressed in equivalent quantities of calcium carbonate on the assumption that calcite is usually the acid-consuming mineral.

The overall potential for acid generation is assessed by calculating the net neutralizing potential (NNP):

$$NNP = NP - MPA$$

If the above reactions are accepted at face value, a negative NNP indicates a potential to generate acid. A positive NNP implies a net excess of acid-consuming minerals. Some of the inherent disadvantages of this approach, as relevant to this study, are presented in Section 2.2, below.

2.2 Assumptions and Problems with the Acid-Base Accounting Method

Several assumptions made in ABA calculations cannot be ignored if results are to be interpreted meaningfully and valid conclusions are to be drawn.

2.2.1 Assumptions in the Calculation of MPA

The following assumptions are made in the calculation of MPA:

- all sulphur is in the form of iron disulphide (typically pyrite) and can be oxidized;
- oxidation of sulphur-bearing minerals is the only source of acidity;
- the oxidant is gaseous oxygen;
- both sulphur and iron are assumed to oxidize;
- the products of the reaction are free sulphate ions, iron (III) hydroxide precipitate, and acidity as free protons (H^+); and
- neutralization of acidity results in the release of gaseous or dissolved carbon dioxide.

Morin (1990) provides several examples of replacing FeS_2 with other minerals and using different types of oxidants. The result is widely different ratios for converting percent sulphur to units of equivalent $CaCO_3$. For example, if the mole ratio of metal to sulphur is 1:1, stochiometrically it is not possible to generate acid. If the reactions are written for pyrrhotite ($Fe_{1-x}S$, or $Fe^{II}_{1-3x}Fe^{III}_{2x}S$ for an electroneutral structure, where $x = 0$ to 0.2), the basic relationship between moles of sulphur and calcium carbonate holds:

$$Fe_{1-x}S + 3(3-x)/4O_2 + (5-3x)/2H_2O \rightarrow (1-x)Fe(OH)_3 + SO_4^{2-} + 2H^+,$$

It is unlikely that the actual reaction products will be the same as for pyrite.

Whole rock analysis for total sulphur assumes that all sulphur is in a reduced form that can be oxidized to generate acidity. However, this assumption is incorrect if the sulphur is in its highest oxidation state as in sulphates such as barite and gypsum.

The focus on sulphur assumes that weathering of sulphur-bearing minerals is the only source of acidity. In the theoretical reaction given in Section 2.1, the hydrolysis of Fe^{3+} is a major source of acidity. Iron (III) may be produced by the weathering of other minerals (for example, iron silicates) and therefore can also produce some acidity. The emphasis on sulphur-bearing minerals is generally justified due to their much greater reactivity.

The assumption that neutralization occurs by release of CO_2 is partly not valid because as pH rises, neutralization of acidity will occur mainly by the reaction:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-.$$

In comparison to the classical neutralization reaction referred to in Section 2.1, one mole of calcium carbonate can only neutralize one mole of H^+. Recent researchers (Brady and Hornberger 1990) have argued, based on this reaction, that percent sulphur should be converted to calcium carbonate equivalents using a factor of 62.5. This is an extreme view because neutralization will occur by a combination of both neutralization reactions.

Primarily, the first assumption can have a major impact on the prediction of potential to generate acid. If forms of non-oxidizable or slowly oxidizable sulphur (such as sulphate, or organic sulphur) are ignored, the potential for acid generation can be grossly overestimated. Furthermore, different forms of sulphide minerals should be identified because some of these will not produce acidity when oxidized, or are known to produce acidity at different rates (for example, pyrrhotite typically oxidizes at a greater rate than pyrite).

2.2.2 Assumptions in the Estimation of NP

The following assumptions are made in the estimation of NP:

- minerals capable of neutralizing hot weak hydrochloric acid will actually consume sulphuric acid produced from rock weathering; and
- the laboratory neutralization reaction is comparable to natural neutralization reactions.

Unfortunately, data comparing laboratory neutralization potential with natural neutralization of acid is very limited. For example, some silicates are likely to be digested by the laboratory test but the actual ability of these minerals to neutralize acidic drainage is unknown.

In some cases, minerals which are not naturally net acid-consuming will consume acid in the NP test. For example, iron carbonate occurring either as the mineral siderite or in solid solution in other carbonates (for example, ankerite) can produce very misleading results. Naturally, iron carbonate may weather in acidic conditions by:

$$FeCO_3 + 3/2H_2O + 1/4O_2 \rightarrow Fe(OH)_3 + CO_2$$

or in pH-neutral conditions by:

$$FeCO_3 + 5/2H_2O + 1/4O_2 \rightarrow Fe(OH)_3 + HCO_3^- + H^+.$$

Therefore, siderite is not naturally likely to consume acid and may actually produce low pH water when weathering in pH-neutral conditions. In the determination of NP, siderite may consume acid by the reaction:

$$FeCO_3 + 2H^+ \rightarrow Fe^{2+} + CO_2 + H_2O$$

because the Fe^{2+} will be slow to oxidize to Fe^{3+} and precipitate as $Fe(OH)_3$. This results in unstable endpoints to the back titration in the Sobek *et al.* (1978) procedure (Morrison *et al.* 1990).

A second mineral that may create anomalous results for NP determined using hydrochloric acid is pyrrhotite. Pyrrhotite ("FeS") will consume acid with the release of H_2S:

$$FeS + 2HCl \rightarrow Fe^{2+} + H_2S + 2Cl^-$$

Every mole of sulphur consumes two moles of acid and the hydrogen is mostly lost as volatile hydrogen sulphide. This reaction could result in high neutralization potentials which should in fact be accounted for in the MPA estimation. However, if the Fe^{2+} produced in the reaction were to be oxidized to Fe^{3+} and subsequently precipitated, the overall reaction could produce as much acid as is consumed:

$$Fe^{2+} + 1/4O_2 + 5/2H_2O \rightarrow Fe(OH)_3 + 2H^+.$$

It appears there are several minerals that can produce false overestimations of neutralization potential. Current methods must be applied with extreme care and interpreted with reference to any mineralogical anomalies. In this regard, neutralization potential tests are much more likely to produce anomalous results than are sulphur determinations.

2.3 Developments in Acid-Base Accounting

Since ABA was endorsed by the U.S. EPA in the report by Sobek *et al.* (1978), there have been several attempts to refine the approach to account for some of the problems described above.

2.3.1 Developments in Sulphur Analyses (MPA)

Total sulphur analysis is a considerable overestimation of oxidizable sulphur, particularly when there is abundant sulphur in organic forms, as in sedimentary rocks associated with coal seams. For this reason, sulphur determined as total sulphide is now used routinely to quantify the readily oxidizable forms of sulphur. The analysis involves a weak hydrochloric acid digestion to determine sulphur as weak acid soluble sulphates, and a separate strong nitric acid/bromine attack to digest sulphide and sulphate minerals. The concentration of sulphur as sulphide minerals is then estimated by difference. The difference between the total sulphur concentration, and sulphur as sulphide and sulphate minerals is determined and should be accounted for mineralogically.

Recent developments in the area of sulphur analyses in acid generation testing have focused on the use of hydrogen peroxide to oxidize pyrite (Lawrence *et al.* 1989; B.C. AMD Task Force 1989). This method is essentially unproven at this time.

2.3.2 Developments in Estimation of NP

Developments in the area of NP estimations, which are readily available at commercial laboratories, have focused on replacing the hydrochloric acid in the test with sulphuric acid (Bruynesteyn and Hackl 1984); running the test for a 24-hour period at room temperature (rather than heated for 1 hour) (Lawrence *et al.* 1989; Bruynesteyn and Hackl 1984); and direct determination of carbonate content (Lawrence *et al.* 1989; B.C. AMD Task Force 1989). All these tests have certain advantages although there are limitations:

- Use of sulphuric acid is thought to better represent actual ARD conditions, although field ARD is usually far more complex than simple sulphuric acid. In addition, $CaSO_4$ is much less soluble than $CaCl_2$, potentially leading to saturation as $CaCO_3$ is dissolved. NP may be underestimated.
- Room temperature tests are thought to be preferable to near-boiling-point digestions because actual leaching conditions in the field are likely to be low temperature. However, in some cases the reaction may not proceed to

completion at room temperature, leading to comparison of a type of kinetic test (NP) with a true static test (MPA).

- Direct determination of carbonate content has been promoted because it eliminates the possibility of including weakly neutralizing silicates in NP. However, almost all carbonate minerals contain some iron, which is not a useful natural acid neutralizing agent.

The first two variations may result in underestimating NP. Carbonate determination may in some cases severely overestimate NP if iron-bearing carbonates are abundant.

3.0 REVIEW OF CHEMICAL ANALYTICAL METHODS TO DETERMINE ABA PARAMETERS

3.1 Approach to Chemical Analysis

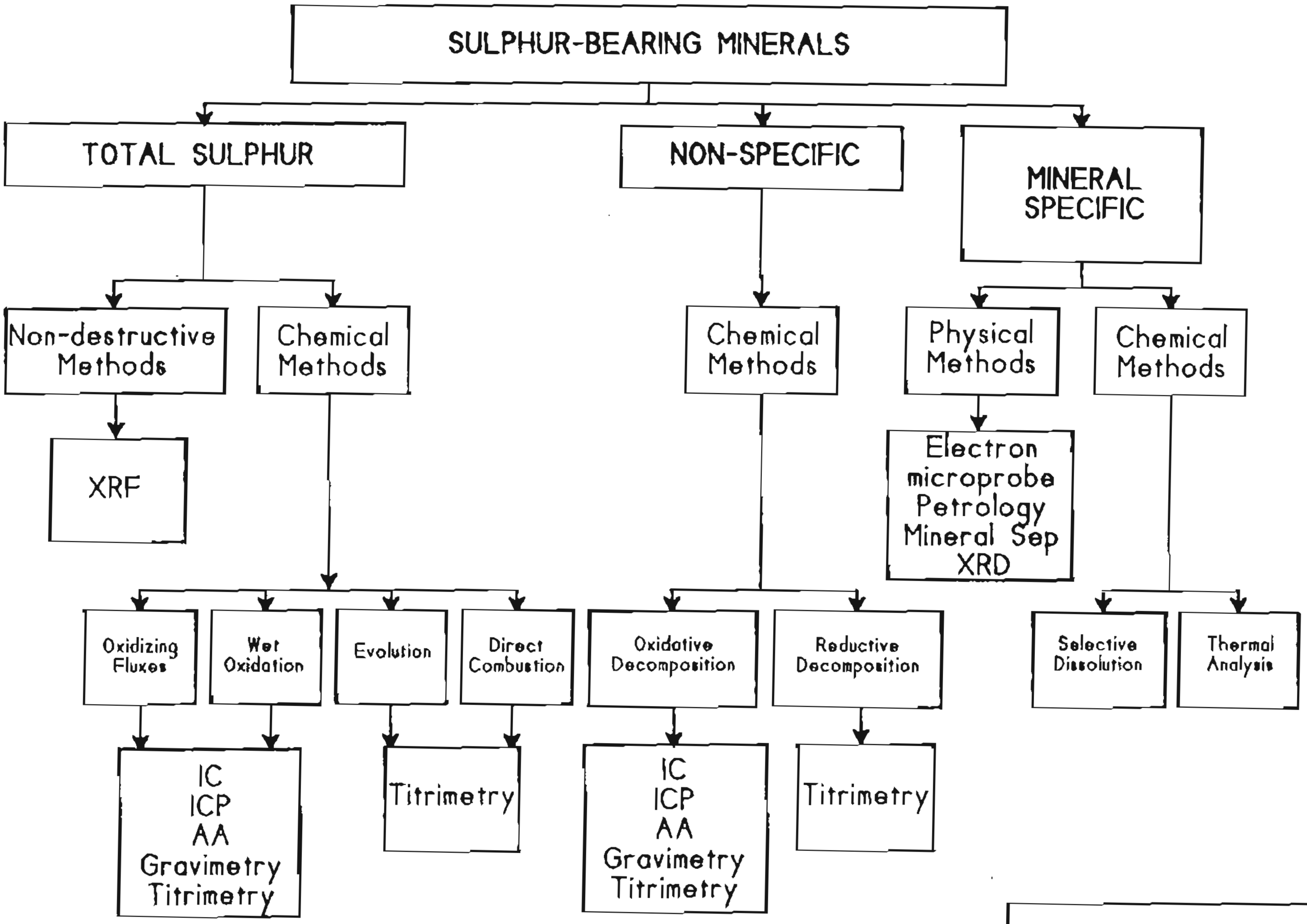
3.1.1 Acid-generating Minerals

As indicated in Section 2.2.1, it is generally assumed in ABA that the oxidation of sulphur and hydrolysis of iron from sulphur- and iron-bearing minerals is the source of acidity. Hydrolysis of iron (III) is the largest source of acidity in the theoretical reactions, and ferric iron is present in minerals that do not contain sulphur. However, the current study focuses on sulphur-bearing minerals because these are the most reactive and the most likely to generate acidity in quantities that would be of concern at mine sites.

Analytical methods for sulphur-containing minerals are generally subdivided into procedures to determine 1) total sulphur and 2) sulphide forms. Given the focus of this study on minerals with acid-generating potential, some mineral-selective procedures that may be used to quantify minerals of particular interest, such as pyrite, pyrrhotite, and barite, were also reviewed.

There is a wide selection of methods for determining total sulphur (Figure 3.1.1-1). Generally, most methods involve a decomposition procedure, followed by analysis for sulphate, H_2S, or the associated metal. X-ray fluorescence (XRF) is a useful nondestructive physical method to determine total sulphur.

Methods for analyzing sulphide minerals were divided into nonspecific (i.e. "total sulphide") and mineral-specific methods (Figure 3.1.1-1). Total sulphide determination involves decomposition of the sample through either oxidation or reduction, followed by an analytical finishing technique. In addition, sulphide-selective leaches could be developed for application to rock samples. Mineral-selective procedures refer to those methods that determine the amount of sulphur present as a certain mineral phase (for example, pyrite). Physical methods considered include electron microprobe and X-ray



ANALYSIS OF SULPHUR-BEARING MINERALS

Figure no. 3.1.1-1

CANMET NEW ABA METHODS

Date Mar. 1991

Drawn by NORECOL

diffraction (XRD). Chemical methods include selective dissolution procedures and thermal analysis.

3.1.2 Acid-neutralizing Minerals

A classification scheme for methods to determine acid-neutralizing minerals is shown in Figure 3.1.2-1. For each mineral group, classifications based on physical and/or chemical properties of minerals are described. Chemical methods for carbonates are further subdivided into neutralization potential-type tests, carbonate determinations, and metal analyses.

3.2 Methods to Determine Sulphur and its Forms

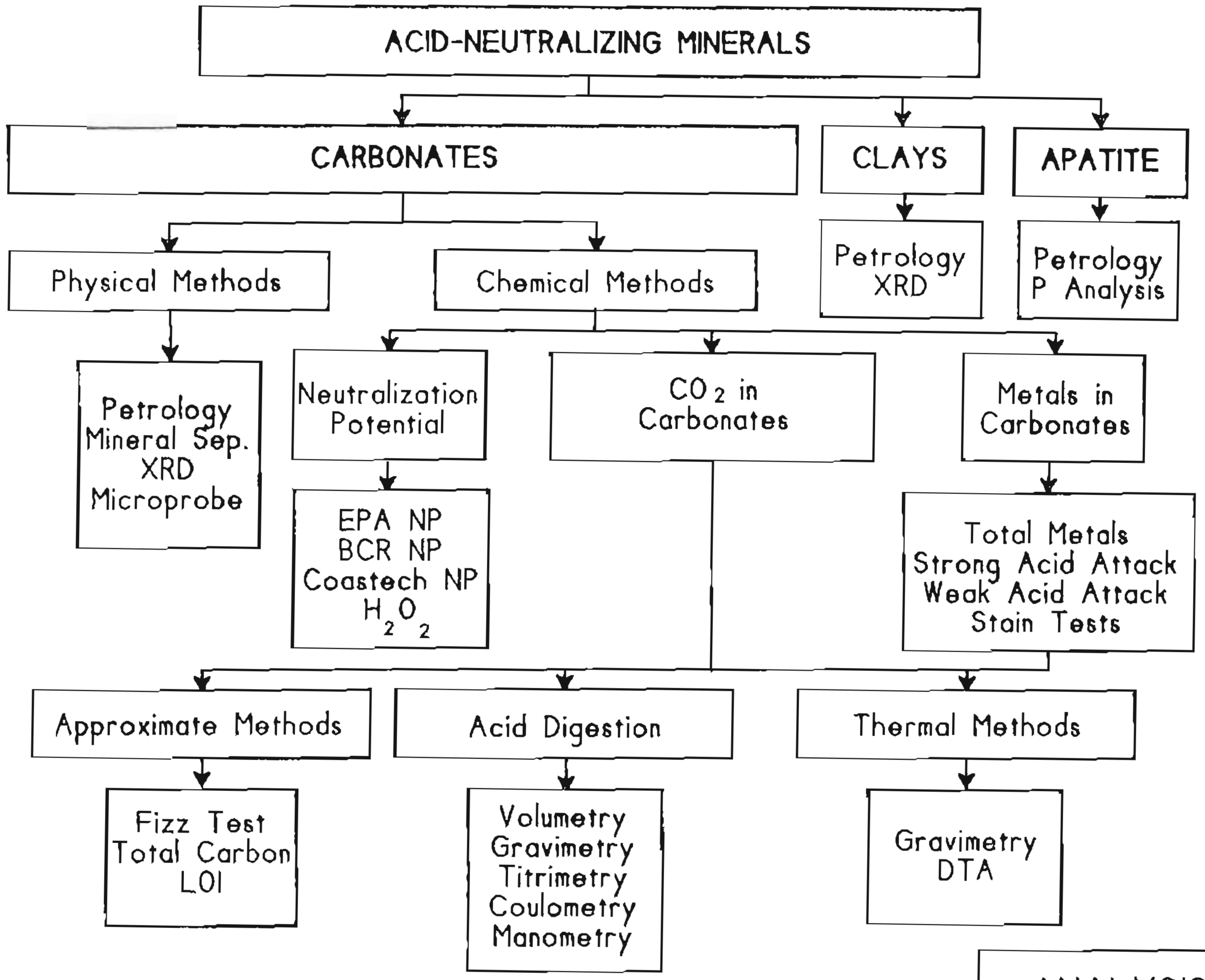
3.2.1 Types of Sulphur-bearing Minerals

Minerals or other substances in rocks containing sulphur can be divided into four main types:

- sulphide minerals which include iron-bearing (for example, pyrite, pyrrhotite, marcasite, chalcopyrite, arsenopyrite) and non-iron-bearing (for example, galena, sphalerite, chalcocite, etc.) forms;
- sulphate-containing minerals which include the barite group (for example, barite, anhydrite and anglesite) and hydrous and basic sulphates (for example, gypsum, alunite, jarosite) (Hurlbut and Klein 1977);
- organically bound sulphur in unmetamorphosed sedimentary rocks; and
- native sulphur.

The first group is regarded as the most important in generation of acidity, although sulphides with a metal to sulphur ratio of exactly 1:1 will theoretically not generate acid.

Sulphates are generally not regarded as acid generators because the sulphur present is already in its highest oxidation state. However, dissolution of limonite containing jarosite ($KFe_3(SO_4)_2(OH)_6$) or other iron sulphates (melanterite) in heavily oxidized rock will generate acidity because some iron (II) will oxidize and precipitate iron (III) hydroxide.



ANALYSIS OF ACID-NEUTRALIZING MINERALS

CANMET NEW ABA METHODS

Figure no. 3.1.2-1

Date Mar. 1991

Drawn by NORECOL

This form of sulphur may be important in gossan-type deposits, although the acidity is stored as reduced iron, rather than reduced sulphur.

Organically-bound sulphur is very common in sedimentary rocks associated with coal deposits and in some low temperature metal deposits. This sulphur is usually in an oxidizable form but is generally regarded as very slowly reactive and not important in the process of acid generation.

Native sulphur is associated with some vein deposits and as an intermediate oxidation product in sulphide deposits. It is oxidized slowly and generally is not sufficiently abundant to be a source of acidity.

3.2.2 Physical and Chemical Properties of Sulphur-bearing Minerals

3.2.2.1 Sulphide Minerals

Physically, the sulphide minerals are readily recognized macroscopically and microscopically due to distinctive colour, lustre, crystal form, hardness and other special properties. For example, pyrite is readily distinguished from pyrrhotite because pyrite is harder, has a brassy colour, and is non-magnetic. However, marcasite is physically indistinguishable from pyrite unless the marcasite forms fibrous masses.

All sulphide minerals are susceptible to attack by strong oxidizing reagents such as concentrated nitric acid. In the presence of oxygen, sulphides break down thermally to produce sulphur dioxide.

3.2.2.2 Sulphate Minerals

Sulphate minerals also have diverse physical characteristics. Gypsum and anhydrite are readily recognized by low hardness and crystal form. Barite is much denser than the other sulphates or other silicates with which it may be confused. There are a large number of different iron-bearing sulphates and as a result, they cannot generally be identified based on their physical features.

Gypsum, anhydrite, and the iron sulphates are all soluble in hot dilute hydrochloric acid (Hurlbut and Klein 1977). However, barite is resistant to attack by some strong acid mixtures such as aqua regia, but is susceptible to decomposition by strong basic solutions.

3.2.2.3 Organically-bound Sulphur

Organically-bound sulphur does not occur in a distinctive mineralogical form. Its presence can be recognized by its association with organic-rich sedimentary rocks.

3.2.2.4 Native Sulphur

Where abundant, native sulphur is easily recognized by its yellow colour. Sulphur is moderately reactive, yielding SO_2 when heated in the presence of oxygen. Sulphur is not attacked by nonoxidizing acids, but dissolves when heated with concentrated sulphuric or nitric acid.

3.2.3 Determination of Total Sulphur

Early methods for determining acid-generating potential were based on the analysis of total sulphur and the ability of the rock to neutralize acid. However, as described in section 2.2.2, there are shortcomings associated with the application of this approach, since the presence of sulphate-containing minerals, such as barite and gypsum, and organic sulphur forms, can result in high total sulphur contents which will not be representative of acid-generating potential.

Nevertheless, methods for measuring total sulphur remain important tools in ARD research, as general indicators of the materials present, and as indicators of acid-generating potential following various pretreatments of the sample to eliminate the above-mentioned interferences (e.g. dilute HCl pretreatment to remove soluble sulphates).

Quantification of sulphur in a rock or ore sample generally requires a pretreatment or digestion procedure to convert the sulphur into a determinable form, followed by a finishing technique to measure the sulphur form. Traditionally, wet chemistry techniques, such as the classic gravimetric analysis involving precipitation of barium sulphate, were used. These time-consuming methods are now being replaced with instrumental methods, such as ion chromatography.

3.2.3.1 Chemical Methods

Sample Preparation Techniques

The following approaches were found in the literature to have been used for the analysis of total sulphur in rocks and/or sulphide minerals:

Strong Alkaline Oxidizing Fluxes

Strong alkaline oxidizing fluxes are capable of strong oxidizing action without the aid of atmospheric oxygen, and are useful for decomposing materials that contain greater amounts of the reduced forms of sulphur (Allbright and Thompson 1970).

Oxidation of sulphur is promoted by fusion with an alkaline compound. Stallings *et al.* (1980) used a Na_2O_2 fusion technique on various geological and soil samples, followed by determination of sulphate-sulphur by ion chromatography. Although they did not specifically use sulphide minerals as the reference materials, they found excellent agreement with literature values for three USGS reference silicate rocks, and had an average recovery of $91 \pm 11\%$ of the sulphur in added zinc sulphide. The fusion technique has the advantages of being rapid and simple.

Sodium carbonate (Na_2CO_3-KNO_3) fusion methods may also be used (Allbright and Thompson 1970).

Wet Oxidation

In these methods, oxidizing acid mixtures typically containing HNO_3 are used to dissolve the samples, and gaseous products such as sulphur dioxide and hydrogen sulphide are retained in solution by strong oxidants, which convert the reduced forms to sulphate (Allbright and Thompson 1970). Bromine is often used to convert sulphides to sulphates (Young 1974).

Evolution Methods

H_2S evolution techniques nearly always involve solution of the sample with HCl, absorption of the evolved H_2S in ammoniacal zinc sulphate or cadmium chloride solution, followed by titration with potassium iodate to a permanent blue colour (Allbright and Thompson 1970). Pyrite, however, is not completely soluble in HCl.

Direct Combustion

Direct sample combustion in a furnace, followed by the absorption and titration of the SO_2 evolved (e.g. Leco analysis) is a rapid, commercially-available technique for measuring total sulphur.

Analytical or Finishing Techniques

As indicated above, instrumental methods are gradually replacing traditional wet chemistry methods such as barium sulphate precipitation and iodometric titrimetry for the quantitative determination of total sulphur. However, these two chemical methods have been included in this report due to their predominance in the classical literature and their use as comparative techniques in the testing of newer instrumental methods.

Gravimetric

The most common procedure for gravimetric determination of total sulphur is precipitation of sulphur as barium sulphate. This technique requires that the sample be pretreated (oxidative decomposition) such that a solution containing sulphate ions results. The general analytical procedure (summarized from Allbright and Thompson 1970) involves the addition of concentrated HCl and an excess of 10% $BaCl_2$ to a hot (near boiling) sample solution. After precipitation, the sample is reheated to near boiling and reduced in volume. The precipitate is filtered (ashless quantitative filter paper), washed free of chlorides, and heated to displace the moisture. The paper is charred and ignited, and the barium sulphate precipitate is cooled in a desiccator and weighed.

Iodometric Titrimetry

This method is useful for determination of sulphur as sulphur dioxide (SO_2) produced in the high-temperature combustion of sulphur-containing materials (ASTM 1966 cited in Allbright and Thompson 1970). KIO_3 is added to a titration vessel containing a weak solution of HCl, KI, and starch to produce I_2 (blue colour), according to the following equation:

$$KIO_3 + 5KI + 6HCl \rightarrow 6\,KCl + 3\,H_2O + 3\,I_2$$

As the SO_2 from the combustion enters the titration vessel, the following reaction takes place:

$$SO_2 + I_2 + 2\,H_2O \rightarrow 2\,HI + H_2SO_4$$

Upon the addition of a small amount of standard KIO_3 solution, free I_2 is released and a blue colour is produced; the SO_2 from the combustion reacts with the free I_2 to produce HI and the blue colour fades.

Iodometric procedures are also widely used to determine H_2S (eg. following reductive decomposition of the sample material). Hydrogen sulphide reacts with iodine according to the following reaction:

$$H_2S + I_2 \rightarrow S + 2H^+ + 2I^-$$

Ion Chromatography

Ion chromatography may be used to quantify sulphur as sulphate, following sample dissolution. Calibration (i.e. peak area vs concentration) is required for the matrix used. The ion chromatograph can be largely automated, which is useful for large numbers of samples and, therefore, in commercial application (Stallings *et al.* 1988).

Inductively Coupled Plasma Spectrometry (ICP)

Sulphur is not currently routinely analyzed using ICP, due to the short wavelength at which S atomic emission occurs (180.735 nm, Pritchard and Lee 1984). In order to detect the sulphur emission lines, the optical path needs to be purged with a gas other than air (air will absorb the emission), or operated in a vacuum. However, newer instruments are now being equipped with vacuum optical systems, suggesting that S may in the future be detected as part of multi-element ICP scans. As is often the case with ICP analyses, it may be difficult to select a digestion procedure suitable for sulphur as well as other elements. This may be a direction of future research in the quantitative analysis of rock and ore samples for sulphur.

A useful application of ICP is in analyzing for metals (Fe, Cu, and others) following digestion of rock samples. The quantities of metals present, determined in a multi-element scan (Floyd *et al.* 1980, Zeng *et al.* 1986), can be used as a measure of the sulphide minerals present. Matrix effects are a likely problem. Foulkes *et al.* (1988) reported a slurry atomization technique for directly introducing finely-ground solid samples into the plasma. This technique may warrant further study, as applied to total elemental analysis of rock and ore samples, since it eliminates the need for time-consuming and often hazardous digestion procedures, and simplifies the matrix matching by offering the potential for calibration using simple aqueous standards. Halicz and Brenner (1987) reported that grinding time and associated particle size appeared to control the reliability of analytical calibration of the ICP when using high-solids nebulizers.

Atomic Absorption Spectrophotometry (AA)

Although atomic absorption (AA) spectrophotometry cannot be used for sulphur analysis, it can be used for the analysis of metals in the solution produced by digestion of rock samples. The metals results can then be used as a measure of sulphide minerals present. Olade and Fletcher (1974, 1976) utilized AA following wet chemical digestion to determine the distribution of sulphide-iron and copper in bedrock associated with porphyry copper deposits in Highland Valley, British Columbia.

3.2.3.2 Non-destructive Methods

X-Ray Fluorescence (XRF)

XRF is a rapid and relatively direct method of analysis for many elements in geologic samples. The elements contained in the sample, when subject to high energy X-ray radiation, absorb some of the radiation, and emit (fluoresce) a portion of the applied radiation. The wavelength (and therefore energy) of the fluoresced X-ray is characteristic of the element in question. Sulphur, because of its atomic number and associated radiation energies, is particularly well suited to determination by XRF (Fabbi and Moore 1970).

3.2.4 Determination of Sulphur Forms

As indicated previously, much of the acid generation from a rock sample arises from the oxidation of sulphide minerals. Therefore, analytical methods which quantify the sulphide-sulphur present may present a useful approach to determining acid-generating potential. However, as sulphur may occur in rocks and minerals as sulphides and sulphates (both soluble and insoluble), determination of the various forms is often necessary.

3.2.4.1 Chemical (Decomposition) Methods

Separation procedures for various phases of sulphur minerals is often based on their differential solubilities. For example, some sulphides of Fe and Mn are soluble in dilute mineral acids. Sulphides of Ag, Hg, Pb, Cu, Bi, Cd, Co, and Ni are decomposed by strong mineral acids (Hanley and Czech 1970). Minerals expected to have a low to moderate sulphide content may be attacked with mild alkaline fluxes (eg. Na_2CO_3,Na_2CO_3-MgO, or Na-K_2CO_3 mixtures), which utilize atmospheric oxygen as the oxidizing agent. Strongly oxidizing fluxes, such as Na_2CO_3-$KClO_4$ (5:1), Na_2CO_3-KNO_3 (2:1) and Na_2O_2, are recommended for materials containing high levels of sulphidic sulphur (Hanley and Czech 1970).

Sulphide-bound metals in silicate rocks may be determined following treatment of the rock (powder) sample with 3-5 mL bromine to attack the sulphides and not the silicate matrix, and stirring gently for 12 hours or more (Czamanske and Ingamells 1970). The bromine oxidation was effective with all sulphides treated, including chalcopyrite, galena, pyrite, pyrrhotite, sphalerite, and cinnabar.

Wet oxidation procedures may also be used, and several schemes have been developed to convert sulphur as sulphide to sulphur as sulphate followed by sulphate analysis (total sulphur). A separate sample is analyzed for sulphate-sulphur, and the sulphide-sulphur is determined by difference.

3.2.5 Mineral-selective Procedures

Procedures have been developed for identifying various sulphur-containing minerals that are associated with acid-generating rock materials. Determining sulphur content as individual minerals in carbonaceous rocks and coals may be useful because of the different rates of dissolution and weathering (and hence generation of acid) among mineral species. For example, pyrite is usually assumed to be the principal mineral involved in acid generation from these types of deposits. Thus, determining that sulphur is present as pyrite may provide a better indication of acid-generating potential than determination of total sulphur, or even total sulphide sulphur.

The following summary outlines some of the more relevant methods.

3.2.5.1 Chemical Methods

Determination of Pyrite

The quantification of pyrite in rock and mineral samples requires separation of the pyritic (iron sulphide) sulphur from sulphate sulphur and organic sulphur. Two separate chemical routes, oxidative and reductive decomposition, are available for separation of pyrite (Hanley and Czech 1970).

Oxidative decomposition methods produce sulphate and ferric ions from pyrite, either of which may be determined. Several oxidative procedures have been outlined (Fieldner and Selvig 1951, Mott 1950, van Hees and Early 1959, cited in Hanley and Czech 1970) for measuring pyritic sulphur in coal samples, which involve the extraction of pyritic and sulphate sulphur (total S) with dilute nitric acid, and the extraction of sulphate sulphur with dilute hydrochloric acid. The procedure developed by Mott (1950, cited in Hanley and Czech 1970), which uses 5 N hydrochloric and 2 N nitric acid for treating simultaneous samples, is recommended when the greatest accuracy is desired.

A reductive method for pyrite determination has been developed for oil shale (Smith *et al.* 1964, cited in Hanley and Czech 1970 and Young 1974), using lithium aluminum hydride as the reducing agent. The liberated H_2S may be titrated directly. Sulphate sulphur can be removed first by digestion with dilute perchloric acid and may be determined by precipitation as barium sulphate.

Another reductive procedure for rock analysis (Young 1974) is based on the fact that sulphide sulphur is evolved as hydrogen sulphide when the sample is heated with phosphoric acid, and can be determined by absorption and iodometric titration. If the sample is heated with a mixture of stannous chloride and phosphoric acid, both sulphide and sulphate sulphur are evolved as hydrogen sulphide (total S) (Nagashima *et al.* 1973 cited in Young 1974).

Semi-quantitative Determination of Pyrite

A semiquantitative method for measuring pyrite-sulphur, which involves oxidation of the rock sample with H_2O_2, was reported by Finkelman and Giffin (1986). In this procedure, a known volume of 15% H_2O_2 is added to rapidly oxidize pyrite in the sample, causing the pH of the solution to drop. As the rate of pH change was considered a function of the pyrite content, the authors used two different methods for quantifying pyrite. One method involved monitoring the rate of change of sample pH over time and comparing this to similar pH curves generated for pyrite standards. The second method involved measuring the sulphate concentration in the reacted peroxide solution. While this method remains semiquantitative, it may be useful as a rapid field test when accuracy is not critical (eg. as a preliminary test).

A leaching procedure using a mixture of H_2O_2 and ascorbic acid at room temperature, followed by a leach with warm ammonium acetate solution, was reported by Peachey and Allen (1977) for the dissolution of sulphide and other mineral phases in geochemical exploration samples. However, the leaching system did not provide quantitative results, and a significant amount of S^{2-}, SO_4^{2-}, CO_3^{2-}, PO_4^{2-}, and MoO_4^{2-} phases were dissolved.

Determination of Pyrrhotite

A method for separation of pyrite and pyrrhotite in ore and mill products has been developed (McLachlan 1934). Pyrrhotite is solubilized by treatment with hot 2:1 (water:acid) HCl; pyrite is decomposed by treating the remaining residue in concentrated nitric acid. The iron concentration is then measured in the solutions, and pyrrhotite and pyrite contents calculated from these data. When magnetite is present, the result for pyrrhotite may be corrected by determining magnetite in a separate sample. A separate sample of the material in question is digested with bromine and HNO_3 until all sulphides have gone into solution. Successive quantities of water are added and decanted until all the iron is removed from the solution. 1:1 HCl is added to the residue, and the sample heated until the magnetite goes into solution. The iron content is determined for this solution and subtracted from the above pyrrhotite-iron value to give the true pyrrhotite-iron value.

Determination of Sphalerite and Galena

Czamanske and Ingamells (1970) reported procedures for the selective dissolution of (a) galena from sulphide mixtures by treatment with $FeCl_3$ at room temperature, and (b) sphalerite from pyrite using a solution of 1% $KMnO_4$ and 15% NaOH.

Determination of Copper Sulphides

A $KClO_4$-HCl leach method was developed by Olade and Fletcher (1974) as a rapid procedure for the estimation of sulphide-copper in granodiorites. The procedure was further utilized (Olade and Fletcher 1976) to determine the distribution of sulphur, sulphide-iron and sulphide-copper in bedrock associated with porphyry copper deposits in Highland Valley, British Columbia. While not specific for iron sulphides, the technique does appear useful for estimating sulphide distribution, and has the advantages of being extremely rapid and simple, and not requiring the use of hot acids.

Other Sulphur-bearing Minerals

Separation of other sulphur-bearing minerals is sometimes useful, especially where these minerals interfere with prediction of acid-generating potential.

Total sulphur as sulphate may be determined by digesting the sample using a saturated Na_2CO_3 solution.

The sulphate-sulphur of anhydrite or gypsum may be separated from barite or from the sulphide-sulphur of ores (Young and Hall 1947, cited in Young 1970) by dissolution with neutral 10% ammonium chloride solution. Barite and the sulphides of cobalt, copper, iron, lead, and zinc remain virtually insoluble.

Baritic sulphur may be determined by digesting with 1:2 HCl and 2 g NaF (Puzankova and Dymov 1968, cited in Young 1974).

3.2.5.2 Differential Thermal Analysis

Differential Thermal Analysis (DTA) has been used, in combination with Evolved Gas Analysis (EGA), to qualitatively and quantitatively describe mineral mixtures (Morgan 1977). Briefly, a mineral or rock sample is heated at a steady rate in a closed system. The temperature of the sample is monitored during the procedure, and the evolved gas passes through to detectors (CO_2, H_2O, SO_2). As the minerals in the mixture decompose, peaks representing temperature changes (exothermic or endothermic reactions as various decompositions take place) assist in the characterization of the minerals, while corresponding concentrations of evolved gas are used to quantify the mineral materials present in the sample. In analyzing sulphide minerals, evolved SO_2 may be measured using a fuel cell-based detector. Calibration is by a standard gas containing a known amount of SO_2 in nitrogen. Care must be taken to minimize self-generated atmosphere effects (SO_2) (Morgan 1977).

3.2.5.3 Physical Methods

The electron microprobe has become a useful tool for quantifying the chemical composition in various mineral samples. The sample is bombarded with electrons, and the back-scattered electron images are compared to standards of similar mineral composition. Kase (1987) used this technique to characterize chalcopyrite samples by measuring total S, Cu, Fe, Zn, and Sn contents.

Sulphide minerals may be identified specifically and directly by X-ray diffraction (XRD) (Hanley and Czech 1970). However, this approach is useful only if the metal sulphide in question is present in moderate ($>2\%$) amounts. XRD is further described in Section 3.3.4.

Petrographic analysis using reflected and transmitted light microscopy will provide a thorough quantification of the abundance of different sulphur-bearing minerals. However, the method is semi-quantitative and labour intensive.

Sulphide minerals may be physically separated using a variety of methods based on magnetic (e.g. pyrrhotite), electromagnetic, and electrostatic properties. Flotation may also be used. None of these methods are suited to routine analysis of small samples.

3.3 Methods to Determine Acid-neutralizing Minerals

3.3.1 Types of Acid-neutralizing Minerals

Minerals potentially capable of neutralizing acid under natural conditions can be divided into four groups:

- calcium and magnesium-bearing carbonates such as calcite, aragonite, magnesite, and ankerite;
- readily soluble non-resistant clay silicate minerals typically formed by hydrothermal alteration or chemical weathering at surface such as kaolinite and chlorite;

- naturally-occurring oxides and hydroxides of calcium, aluminum, and magnesium such as brucite, diaspore, and gibbsite; and
- phosphates of which the only significant example is apatite.

Several minerals capable of neutralizing acid but resulting in release of high concentrations of regulated metals are not referenced. These include several carbonates (smithsonite, witherite, cerussite, malachite, and azurite), several oxides of manganese and iron, a few silicates that contain zinc, copper, and lead as major components, and rare phosphates.

Carbonate minerals (especially calcite) are regarded as the most effective natural acid neutralizing agents. There is very little evidence that silicates and hydroxides in the absence of carbonates can effectively neutralize acidity, although water chemistry clearly indicates that these minerals are being dissolved (Evangelou 1983; Alpers and Nordstrom 1990). Phosphate rock is being investigated as an ameliorant for acid generation (Renton *et al.* 1988) and there is abundant natural evidence that apatite buffers acidity (Scott and Taylor 1987).

The following section of this report focuses on the determination of carbonates.

3.3.2 Physical and Chemical Properties of Carbonates

Physically, the carbonates are not readily distinguished using macroscopic features unless there is sufficient material to measure specific gravity, colour and crystal form. The exceptions are the copper and zinc carbonates. In thin section, carbonates of calcium, magnesium, and iron cannot be distinguished, unless the slide is stained (Deer *et al.* 1966).

All carbonates are soluble in dilute (10%) hydrochloric acid to some degree. However, only calcite readily effervesces in cold acid without powdering the sample. The other carbonates require powdering and the acid must be warmed. As the mineral is dissolved, carbon dioxide is evolved and the cationic specie enters solution.

Carbonates break down thermally to the oxide and carbon dioxide. The temperature at which thermal breakdown occurs is different for each carbonate and is the basis for the analytical technique known as differential thermal analysis (DTA, Section 3.3.5.4 below).

3.3.3 Physical and Chemical Properties of Other Potentially Acid-neutralizing Minerals

Silicate, hydroxide, and oxide minerals have diverse physical properties. The fine grained clay-silicate minerals (such as kaolinite, sericite, and chlorite) can usually only be distinguished by overall rock appearance and colour, the geological environment and other subjective descriptors, or by preparation of thin sections and x-ray diffraction.

Many silicates and most oxides are refractory and therefore resistant to attack by weak acids. The dissolution of clay-silicates is usually complex due to the release of silicon and aluminum, which typically results in the formation of gelatinous silica residues and coatings of aluminum hydroxides.

The physical properties of apatite do not allow it to be readily distinguished from several silicate minerals unless there is sufficient sample to determine crystal form, colour, and hardness. Apatite is soluble in both nitric and hydrochloric acids.

3.3.4 Analytical Methods Using the Physical Properties of Carbonates

3.3.4.1 Petrographic Examination and Grain Counts

Petrographic examination may involve identification of minerals in large samples with limited magnification (hand lens, binocular microscope) or preparation of mounted thin sections for examination using a petrographic microscope. Petrologists usually include the "fizz test" (Section 3.3.5.2) in the visual examination. Carbonates are generally indistinguishable using physical characteristics although iron-bearing carbonates are darker and weather to produce an iron oxide coating. These carbonates are also denser than calcium and magnesium-bearing carbonates.

In thin section, all carbonates have moderate relief and high birefringence (Deer *et al.* 1966), and can be clearly distinguished from silicates. However, individual carbonate species cannot be recognized without staining (Section 3.3.5.3). Grain counts may be used to estimate the modal quantities of different minerals but the procedure is labour intensive and not suited for routine analysis.

Visual estimation of mineral concentrations in hand samples generally requires experience and may not be accurate if there is a significant very fine-grained component of an important mineral species. Nonetheless, a geologist with experience with a particular suite of rocks can provide precise estimations of mineral concentrations that correlate well with values obtained from chemical analysis.

3.3.4.2 Mineral Separation

In some cases, different minerals can be separated using specific density, magnetic, electromagnetic, or electrostatic properties. The weight of a separated mineral component is expressed as a percentage of the rock mass. As a group, carbonates do not have special properties which might allow them to be separated from an alumino-silicate rock matrix.

3.3.4.3 X-Ray Diffraction (XRD)

In X-ray diffraction, a beam of X-rays of known wavelength (l) is directed at powdered rock or mineral specimens. The sample is rotated through a range of incident angles (Θ) and diffraction peaks are produced, which are characteristic of the crystal lattice. This information can be used to identify the mineral from standard tabulations. The method has been used widely to determine carbonate forms both quantitatively and qualitatively (Roselle 1982; Yamamoto 1985; Bristol 1971; Despard 1988).

The primary disadvantage of XRD is the problem of interferences in complex mineral mixtures. Therefore, the mineral tested must be very abundant in the sample. For semi-quantitative XRD, calibration curves must be prepared for each project (S. Horsky, personal communication), the detection limit is unacceptably high (greater than 2%, Morrison *et al.* 1990), and the method is not commercially available.

Qualitative XRD is commercially available, and can provide a rapid indication of the types of carbonates (calcite, dolomite, magnesite, siderite) present provided that the minerals are not present in low ($<10\%$) quantities.

3.3.4.4 Electron Microprobe/Scanning Electron Microscope (SEM)

In the electron microprobe and SEM, a beam of electrons is directed at a mineral grain resulting in a fluorescence spectrum that can be matched to standard spectra. Minerals present can then be identified using the elemental composition of the grain. Some instruments can then be programmed to scan the sample for other grains of the same mineral (Yasuhasa 1976).

This method can be applied to identification of carbonate species and the recognition of impurities (for example, iron in calcite, calcium in siderite). Although the method is capable of providing estimates of relative proportions of different carbonate minerals in a rock sample, it is generally more suited to locating rare grains of unusual precious or indicator minerals.

3.3.5 Analytical Methods Using the Chemical Properties of Carbonates

3.3.5.1 Variations on the NP Determination

EPA Neutralization Potential with Post-Oxidation by Hydrogen Peroxide

As described in Section 2.2.2, the EPA neutralization potential (Sobek *et al.* 1978) can be overestimated due the presence of siderite because Fe^{2+} released is incompletely oxidized to Fe^{3+}. The endpoint of the back-titration is also unstable. A similar problem arises when there is pyrrhotite in the sample.

Morrison *et al.* (1990) developed a procedure to deal with the common presence of siderite in overburden from coal seams. The conventional EPA procedure was followed, but after the hydrochloric acid leach was completed, the leachate was filtered, 5 mL 30 wt. % H_2O_2 was added, and the solution reboiled prior to back-titrating. The procedure resulted in reduction of NP in samples containing some siderite, although NP was not reduced to zero when siderite was the only carbonate. This was attributed to incomplete oxidation and precipitation of iron and the presence of non-sideritic carbonates in the sample.

The authors also noted that the subjective fizz test (Sobek *et al.* 1978) can have a profound effect on the NP if siderite is present. A fizz rating of 1 will yield a much higher NP than a fizz rating of 0. The addition of H_2O_2 will reduce this error.

Testing of this method is extremely limited. However, it offers a solution to the problem of slow oxidation of ferrous iron in the conventional NP test.

3.3.5.2 Determinations of Total Carbonate by Approximate Methods

"Fizz" Test

The dilute (10%) hydrochloric acid fizz test is the basic field test for the presence of carbonates. A drop of acid is added to a surface of the mineral to be tested. A rapid effervescence with cold acid indicates that the carbonate is primarily calcite. If the carbonate mineral must be powdered to achieve a reaction with cold acid, the mineral is likely to be dolomite or magnesite (Deer *et al.* 1966). Siderite and ankerite will only react with heated acid.

The test is useful as an indicator of abundant concentrations of calcite but when concentrations are low and minerals are disseminated the results are inconclusive.

Total Carbon

Total carbon can be determined by igniting the sample in a Leco furnace and measuring the quantity of CO_2 released, or by using a number of very strong oxidants in solution or as fusions (Jeffery 1981).

Although readily determined, total carbon is a very poor indication of total carbonate content because carbon may be present in a number of forms including graphite and organic carbon.

Loss-on-Ignition (LOI)

Loss-on-ignition is determined from weight difference and is used as an indication of total volatile content of the sample. Since water is commonly present, LOI is not acceptable for estimation of total carbonate content (Jeffery 1981; Yamamoto 1985).

3.3.5.3 Determination of Total Carbonate and Carbonate Species Using an Acid Digestion

Acid digestions followed by measurement of evolved CO_2 are very widely available and commonly employed to determine total carbonate content and, in some cases, the form of carbonate. The acid used depends on the particular method. Hydrochloric acid (strength varying from 0.1 N to 5 N (Tiessen *et al.* 1983; Lawrence *et al.* 1989) is typically used, however, for methods where the CO_2 is absorbed in solid sodium hydroxide, Jeffery (1981) prefers dilute phosphoric acid or EDTA. Morrison *et al.* (1990) used 2N perchloric with an apparatus using an automatic coulometric cell. Sviridenko *et al.* (1983) used nitric acid. Sulphuric acid was not used in any of the studies reviewed.

Total Carbonate by Volumetric, Gravimetric, and Titrimetric Methods

The simplest method for determination of total carbonate involves dissolution of the sample in HCl and measurement of the gas produced (Jeffery 1981; Maxwell 1968; Dreimanis 1962). The test is carried out using a test tube with a graduated closed side arm. The solution is heated until no further gas is produced. The volume of gas must be corrected to standard temperature and pressure conditions to measure the molar quantity of CO_2 evolved. The method is not suitable for very low ($<0.2\%$) or very high ($>6\%$) carbonate levels and the evolution of H_2S due to breakdown of pyrrhotite, or H_2 due to metal contamination, would bias results. Mercuric chloride can be added to the solution to prevent the latter problem.

Gravimetric methods involve either digesting the sample using acid and measuring the difference in weight of the sample, or absorption of the CO_2 in a suitable solid, usually sodium or potassium hydroxide. Measuring differences in the weight of the sample is only suited to high carbonate contents ($>6\%$).

Titrimetric methods involve absorption of the evolved CO_2 in a solution of hydroxide (Jeffery (1981), barium hydroxide; Tiessen *et al.* (1983), sodium hydroxide; Johnson and Maxwell (1968), potassium hydroxide). The excess alkali is titrated to determine the amount of CO_2 absorbed.

Total Carbonate and Carbonate Forms by Coulometry

Coulometric methods are an electrical variation on titrimetric methods. In a coulometric cell, CO_2 evolved by acid dissolution is absorbed in a solution. A constant potential difference is maintained across the cell and changes in the current in the system are measured and used to calculate the quantity of CO_2. Coulometry is widely used because it can provide low detection limits (0.01%) using very simple equipment in small laboratories (Morrison *et al.* 1990; Sviridenko *et al.* 1983).

Morrison *et al.* (1990) used curves obtained from a coulometric cell to determine the forms of carbonate. Using standards containing pure minerals, they found that calcite, dolomite and siderite reached peak reaction rates at 2, 5 and 9 minutes respectively, producing a distinct family of curves. The form of carbonate in several rock samples was identified. The method is qualitative but is capable of detecting low levels of carbonate. In this respect, this approach compares very favourably to XRD.

Carbonate Forms by Manometry

Evangelou *et al.* (1985) described a manometric method whereby rock samples are digested using HCl and the evolved gas pressure, measured by a pressure transducer, is used to calculate the rate of evolution of CO_2. The method is not specific for different carbonate minerals but measures the reactivity of carbonate in the rock. For example, calcite encapsulated in oxide or silicate might have a reactivity comparable to dolomite or siderite. The method is also prone to interferences due to evolution of gas by other reactions such as dissolution of pyrrhotite. This problem may explain the inconclusive results described in Lawrence *et al.* 1989.

3.3.5.4 Determination of Carbonate by Thermal Decomposition

When carbonates are heated they break down to form metal oxides and CO_2. The breakdown temperature is different for each carbonate mineral and is the basis for identification using the method known as differential thermal analysis (DTA) or evolved gas analysis (EGA). DTA has been very widely applied (Warne 1977; Ke-long 1979a, 1979b; Warne and Mitchell 1979; Milodowski and Morgan 1980). Carbon dioxide produced from a heated sample is carried to a non-dispersive, infra-red CO_2 detector.

Milodowski and Morgan (1980) indicate that the method has a possible detection limit of 50 ppm carbonate mineral. The first carbonate to break down upon heating is cerussite, followed by smithsonite, siderite, magnesite, calcite and dolomite, strontianite, and finally witherite. Their results indicate that smithsonite, siderite and magnesite are virtually indistinguishable, as are dolomite and calcite. Since magnesite and smithonsite are uncommon in many geological environments, the method may provide a reliable distinction between iron, and calcium and magnesium-bearing carbonates, although it is not clear how ankerite and ferroan dolomite will behave.

3.3.5.5 Determination of Metals in Carbonates

Analysis of metals commonly found in carbonates following a digestion is generally not done, perhaps because CO_2 is easily measured. However, it is apparent that none of the above-referenced methods will provide a quantitative measurement of carbonate forms. Because simultaneous multi-element determinations are now commonly available, determination of all carbonate types may be possible.

Total Metals - Non-destructive and Wet Chemical Methods

Methods for measuring total metal contents in rock samples are not appropriate because the metals in carbonates (Ca, Mg, Fe, Ba, Zn, Sr, Pb, Cu) also occur in other common silicates, oxides and sulphides.

Non-destructive analytical methods capable of determining these metals include X-ray fluorescence and neutron activation analysis. The results from these tests can be interpreted using a normative calculation that would also require CO_2, and H_2O^+ and H_2O^- values.

Partial Extractions Using Strong Acids

Strong acid dissolutions are offered by most commercial laboratories as part of standard multi-element packages. The digestion reagent is usually aqua regia (3:1 $HCl:HNO_3$) which was originally selected because it readily dissolves carbonates, sulphides, and some oxides and hydroxides. Some silicates are also partially attacked.

It is unlikely that this approach can be used routinely to specifically determine carbonates because many other minerals containing the important metals are attacked. For example, Fe in sulphides, Ca in feldspars, and Mg and Fe in ferro-magnesian silicates are likely to interfere with the determination of Ca, Fe, and Mg in carbonates. Nonetheless, it is possible to establish a reliable, predictive correlation between Ca and Mg determined using aqua regia and carbonate content (Geddes Resources 1990).

Partial Extractions Using Weak Hydrochloric Acid

A logical means of estimating concentrations of carbonate forms from metals analysis involves digesting the sample using weak acid and analyzing the leachate (Lim *et al.* 1977; Li *et al.* 1986). The final analysis would currently be determined by AA, although ICP would provide a comprehensive scan (see section 3.3.7).

The main disadvantage of this approach when compared to evolved CO_2 analysis is that minerals other than carbonates may be dissolved (Bock 1979). Many of these minerals, including pyrrhotite, some oxides and hydroxides, and sulphates, contain Fe and Ca. Pre-leaching the sample with water or other water-based solvents may make it possible to remove some of these minerals, as described in sequential extraction procedures (Li *et al.* 1986; Percival *et al.* 1990). At the stage where carbonates are determined, the leachate should be analyzed for Ca, Mg, Fe, Ba, Cu, Zn, Sr and Pb, using ICP, AA or other methods.

Stain Tests

Stain tests are qualitative methods in which individual mineral grains can be stained for modal analysis. Stain tests are available for distinguishing calcite and dolomite (Deer *et al.* 1966).

3.3.6 Chemical Determination of Apatite

Apatite can be determined semi-quantitatively using XRD, or quantitatively by measuring phosphorous. Because apatite is usually the only form of phosphorous in many rock types, and the mineral is soluble in moderately strong acids, any of a number of wet chemical approaches may be used (for example, aqua regia digestion followed by ICP finish). Phosphorous can also be determined non-destructively by XRF.

Highly carbonaceous rocks may contain organically-bound phosphorous which could yield a misleading apatite determination. No examples of apatite-specific digestions in the presence of organic matter were found.

3.3.7 Use of Simultaneous Multi-element Methods

Improvements in inductively coupled plasma (ICP) as a source for emission spectroscopy now allows many elements to be determined simultaneously. Carbon cannot be determined by ICP due to its high first ionization potential which approaches that of argon. In any case, carbon is usually driven off during the acid digestion that precedes the ICP analysis. However, the ICP yields very low detection limits for all metals found in carbonates. The current limitation of the method results from the common use of an aqua regia or a total (nitric-perchloric-hydrofluoric) acid digestion. The machine is calibrated for this particular matrix (B. Caughlin, personal communication) and must be re-calibrated for a different digestion, such as weak hydrochloric acid.

4.0 RANKING OF METHODS

4.1 Description of Ranking Scheme

To facilitate evaluation of the methods reviewed, a ranking scheme that allowed the assignment of a numerical score to each method, based on nine criteria was developed. The criteria in the ranking scheme included both technical and cost efficiency considerations, which would be important in decision-making regarding methods selection for the purposes of determining ARD potential.

A numerical rating was assigned to each criterion (Table 4.1-1 provides a detailed description of the rating system). These nine ratings were added together to give a base score (the "maximum possible" score would be 21). Each criterion was then given a weight factor, such that the methods could be numerically evaluated for effectiveness with respect to the following analytical goals:

Quantitative Phase Analysis

The ranking system to evaluate the procedures for quantitative phase analysis weights "phase analysis" most heavily, followed by "detection limit" and "matrix sensitivity" (Table 4.1-2). It was assumed that, when the primary objective of an analysis was to determine mineral phases, the type of equipment and level of operator skill were not of critical concern, because of the more detailed and accurate information requirement. Analytical costs and completion times were not considered. The maximum possible score with respect to Quantitative Phase Analysis, with the weights applied, is 18.

Rapid, Inexpensive Commercial Lab Methods

This weighting system rated the analytical methods according to "matrix sensitivity", "detection limit," "phase analysis," "method status," "cost," and "time to complete"

TABLE 4.1-1

RANKING SYSTEM FOR EVALUATING ANALYTICAL METHODS

CRITERION	DESCRIPTION OF RATING VALUE
Detection Limit	0 = semi-quantitative 1 = 2 x current < 10 x current[1] 2 = comparable to current 3 = < 0.5 x current
Phase Analysis	0 = total component (eg. total S) 1 = mineral group specific 2 = mineral phase specific
Equipment Required	0 = not commercially available (research) 1 = commercially available (large labs only) 2 = can be operated in small laboratory/field lab 3 = minor, very inexpensive instrumentation
Skill Level of Operator	0 = highly trained research specialist 1 = technical specialist with experience 2 = trained individual without experience
Analytical Steps/Digestion Complexity	0 = complex (> two steps; preconcentration) 1 = requires a separate test for interference 2 = one-step digestion 3 = non-destructive or direct method
Sensitivity to Mineral Matrix	0 = special calibration for each job 1 = interference from some matrices 2 = negligible interferences; easily corrected
Method Status	0 = described by one author 1 = generally accepted; not tested commercially 2 = commercially available
Cost	0 = very expensive; labour intensive 1 = comparable to currently[1] available methods 2 = 50% of current methods 3 = part of a multi-element scan
Time Required for Test	0 = more than two weeks 1 = comparable to current[1] 2 = very rapid (same day)

---

[1] "Current" - method parameters defined as follows:

METHOD	DETECTION LIMIT	COST (1990)	TURNAROUND TIME
Neutralization potential	1 kg $CaCO_3$/t	$40	<2 days
Total Sulphur	0.001% S	$25-$30	<2 days
Sulphide (HNO_3/Br)	0.01% S	$10-$20	1 week
Sulphate (H_2O/HCl)	0.01% S	$10-$20	1 week

TABLE 4.1-2

WEIGHTING SCHEMES BASED ON ANALYTICAL OBJECTIVES

CRITERIA	OBJECTIVE		
	QUANTITATIVE PHASE ANALYSIS	RAPID & INEXPENSIVE METHODS	LOW TECHNOLOGY METHODS
Detection Limit	2	2	1
Phase Analysis	4	1	0
Equipment	0	0	4
Operator Skill	0	0	2
Steps in Analysis	0	0	1
Matrix Sensitivity	2	3	2
Method Status	0	1	1
Estimate of Costs	0	1	2
Time to Complete	0	1	3

(Table 4.1-2). Matrix sensitivity was given the greatest weight because rapid methods must be relatively free of interferences, requiring only routine correction procedures. The maximum possible score in this ranking system is 21.

Low Technology Mine Lab Scale Methods

Low technology methods are those that would be appropriate for small on-site laboratories where conditions are not suitable for sensitive and expensive equipment. It was assumed that the primary objective of the low technology methods would be to rapidly test relatively large numbers of samples (by field personnel) for prescreening purposes. Weighting for these methods considered "equipment," "time to complete," "estimate of costs," "operator skill," "matrix sensitivity," "steps in analysis," "method

status," and "detection limit" (Table 4.1-2). Thus, these tests combine many criteria, and the maximum possible score, with weights applied, is 40.
A summary of the methods considered in the ranking scheme is given in Table 4.1-3.

4.2 Results of Ranking

4.2.1 Sulphur Methods

Sixteen sulphur analysis methods were ranked, including analytical techniques to determine total sulphur, sulphide forms, pyrite (Finkelmann and Giffen 1986), and one pyrite/pyrrhotite mineral-specific method (McLachlin 1934).

Ion Chromatography (i.e. of sulphate) was ranked based on the method used by Stallings *et al.* (1988). Therefore, it was considered in this report as a total sulphur technique. IC could probably be used following selective leaches which oxidize sulphide forms to sulphate. Similarly, the "Digest/ICP Sulphur" method, which involves direct determination of sulphur in an acid or sodium hypobromite digest using ICP (Pritchard and Lee 1984), is currently used for analysis of total sulphur, but may in the future be used for the analysis of sulphur forms, as the applicability of sulphur ICP analysis increases (i.e. matrix effects overcome; suitable selective leaches developed).

ICP is used as the finishing technique for several digestion/leach techniques. AA may be substituted for ICP without changing the ranking, since in most cases (except "Digestion/ICP Sulphur" and "Slurry/ICP Metals") the method of sample dissolution is being considered, not the analytical finishing technique. Generally, AA currently is more commercially available than ICP.

"Leco Total S" was included in the ranking because it is currently commercially available and commonly used for the determination of total sulphur.

TABLE 4.1-3
SUMMARY OF METHODS RANKED

METHOD	ABBREVIATION	REFERENCE
I. Sulphur Methods		
Pyrite/pyrrohite Selective Dissolution	Py/Po Wet Method	McLachlin 1934
HNO_3 Oxidation/Sulphate Analysis	HNO_3/Oxid/Sulphate	n/a
Sulphide - Selective Leach/AA Analysis of Metals	$KClO_3$ - HCl Leach	Olade and Fletcher 1974, 1976
Electron Microprobe	Electron Microprobe	n/a
Differential Thermal Analysis - Evolved Gas Analysis	DTA - EGA	n/a
Quantitative Xray Diffraction	Quant. XRD	n/a
Qualitative Xray Diffraction	Qual. XRD	n/a
H_2O_2 Oxidation of Pyrite	H_2O_2 Oxidation	Finkelmann and Giffen 1986
Slurry Atomisation/ICP Analysis of Metals	Slurry/ICP Metals	Foulkes *et al.* 1988; Halicz and Brenner 1987
Na_2O_2 Fusion/Sulphate Analysis by Ion Chromatography	Ion Chromatography	Stallings *et al.* 1988
Total Sulphur by Combustion in Leco Furnace	Leco Total S	n/a
NaOH Digestion/ICP Anaysis of Metals	NaOH/ICP Metals	Floyd *et al.* 1980
Mineral Separation	Mineral Separation	n/a
HCl/HNO_3 Digestion/ICP Analysis of Metals	HCl-HNO_3/ICP Metals	Zeng *et al.* 1986
X-Ray Fluorescence Spectroscopy	XRF	Fabbi and Moore 1970
Na_2OBr Digestion/ICP Analysis of Sulphur	Digestion/ICP Sulphur	Pritchard and Lee 1984
II. Acid-neutralizing Mineral Methods		
HCl Digestion/AA Analysis of Metals	HCl/AA Metals	n/a
HCl Digestion/ICP Analysis of Metals	HCl/ICP Metals	n/a
Quantitative X-Ray Diffraction	Quant. XRD	n/a
Qualitative X-Ray Diffraction	Qual. XRD	n/a
Classical Methods (Volumetry, Gravimetry, Titrimetry following HCl Digestion)	Classical Methods	Various; Section 3.3.5.3
Carbonate Manometry	Carbonate Manometry	Evangelou *et al.* 1985
Differential Thermal Analysis-Evolved Gas Analysis	DTA - EGA	Various; Section 3.3.5.4
Electron Microprobe	Electron Microprobe	n/a
B.C. Research Acid Consumption Test	BCR Acid Consumption	n/a
Environmental Protection Agency Neutralization Potential	EPA NP	Sobek *et al.* 1978
Carbonate Coulometry	Carbonate Coulometry	Morrison *et al.* 1990; Sviridenko *et al.* 1983
Decomposition with Aqua Regia/ICP Analysis of Metals	Aqua Regia/ICP Metals	Geddes Resources 1990
EPA NP Procedure Modified by Coastech	Modified EPA - Coastech	MEND 1990
EPA NP Procedure Modified by H_2O_2 Addition	Modified EPA - H_2O_2 Addn	Morrison *et al.* 1990
Carbonate Stain Tests	Stain Tests	n/a
Petrology	Petrology	n/a
HCl Acid Fizz Test	Fizz Test	n/a
Total Metal Determination	Total Metals	n/a
Total Carbon by Combustion in Leco Furnace	Leco Total C	n/a
Loss-on-Ignition	Loss-on-Ignition	n/a
Mineral Separation	Mineral Separation	n/a

XRF is a nondestructive method for the determination of total sulphur in rock and mineral samples. It is not currently commercially available. Similarly, the electron microprobe and DTA-EGA are useful for sulphide determination, but are not currently available commercially.

Sulphide and mineral-specific methods ranked included a sulphide-specific $KClO_3$-HCl leach developed by Olade and Fletcher (1974, 1976), a wet method for the determination of pyrite and pyrrhotite (McLachlin 1934), and a peroxide oxidation (Finkelmann and Giffen 1986) for rapid, semi-quantitative determination of pyrite.

4.2.1.1 Quantitative Phase Analysis

When accurate results aimed at quantitative phase analysis were considered (Table 4.2.1-1), the wet method for the determination of pyrite and pyrrhotite (McLachlan 1934, modified as described in Section 5.3.1) had a score of 16 out of a possible 18. This method appeared to be mineral-specific, with a detection limit comparable to currently available methods if iron is determined by AA rather than titrimetrically as described in the original paper. It was anticipated that the matrix sensitivity would be minimal, and that it was worthy of further testing to determine its merits as a potential ARD prediction method.

Two other methods scored highly when this weighting system was used. The $KClO_3$HCl leach followed by AA determination of metals (Olade and Fletcher 1974, 1976) scored 16 for quantitative phase analysis. Sulphide dissolution with HNO_3 followed by oxidation (with bromine) and sulphate analysis ("HNO_3/Oxid/Sulphate") scored 14. This method is more widely utilized than the selective dissolution procedure described above.

The electron microprobe, DTA - EGA, and Quantitative XRD all scored 13 out of 18 in this scheme. These methods are useful in determining mineral phases and are most often used as research tools.

TABLE 4.2.1-1

RANKING OF SULPHUR METHODS
QUANTITATIVE PHASE ANALYSIS

CRITERIA	DETECTION LIMIT	PHASE ANALYSIS	EQUIPMENT	OPERATOR SKILL	STEPS IN ANALYSIS	MATRIX SENSITIVITY	METHOD STATUS	ESTIMATE OF COSTS	TIME TO COMPLETE	SCORE
WEIGHT FACTOR	2	4	0	0	0	2	0	0	0	
MAXIMUM POSSIBLE	3	2	3	2	3	2	2	3	2	18
Py/Po WET METHOD	2	2	1	1	0	2	1	2	0	16
KClO$_3$-HCl LEACH	2	2	1	1	2	2	0	0	1	16
HNO$_3$/OXID/SULPHATE	2	2	1	1	0	1	2	1	1	14
ELECTRON MICROPROBE	0	2	0	0	2	2	1	0	0	12
DTA-EGA	1	2	0	0	3	1	1	0	0	12
QUANT. XRD	2	2	0	0	3	0	1	0	0	12
H$_2$O$_2$ OXIDATION	0	2	3	2	2	2	0	2	2	12
QUAL. XRD	0	2	1	1	3	1	2	0	0	10
SLURRY/ICP METALS	2	0	1	1	2	2	1	1	1	8
ION CHROMATOGRAPHY	2	0	1	1	2	2	0	1	1	8
NaOH/ICP METALS	2	0	1	1	2	2	0	3	1	8
MINERAL SEPARATION	0	2	1	0	0	0	0	0	0	8
LECO TOTAL S	2	0	1	2	3	1	2	1	1	6
HCl-HNO$_3$/ICP METALS	2	0	1	1	0	1	0	3	1	6
XRF	2	0	1	1	3	0	1	1	0	4
DIGESTION/ICP SULPHUR	2	0	1	1	1	0	0	2	1	4

4.2.1.2 Rapid, Inexpensive Commercial Lab Methods

The wet method for pyrite and pyrrhotite ("Py/Po Wet Method") had the highest score (15 out of a possible 21) as a rapid, inexpensive method, primarily due to its high rankings for matrix sensitivity and detection limit (Table 4.2.1-2).

The $KClO_3$-HCl leach also had a relatively high score when criteria describing rapid, inexpensive methods were weighted. The qualities of this method that contributed to this score were phase analysis (sulphides), detection limit, and matrix sensitivity. Its applicability to an AA finish (for metals) suggests this method could possibly be adapted commercially.

NaOH used as an alkaline oxidant followed by metal analysis using ICP also scored highly (14 out of 21) as a rapid, inexpensive method. Although this is a total sulphur method, it is part of a multi-element scan and could also yield information about the metal concentrations in samples.

The $KClO_3$-HCl leach (followed by AA determination of metals) had the next highest score (13 out of 21). This method is particularly useful for determining sulphide copper (Olade and Fletcher 1974; 1976).

4.2.1.3 Low Technology/Mine Lab Scale Methods

As a low technology method appropriate for a field lab, the H_2O_2 oxidation method for measuring pyrite content (Finkelmann and Giffen 1986) had the highest score by a wide margin (32 out of a maximum possible of 40 points) (Table 4.2.1-3). The merits of this method which contributed to its high score, included very inexpensive equipment requirement, a low level of operator skill, one-step digestion, low matrix sensitivity, inexpensive costs, and short completion time.

TABLE 4.2.1-2

RANKING OF SULPHUR METHODS
RAPID, INEXPENSIVE COMMERCIAL LAB METHODS

CRITERIA	DETECTION LIMIT	PHASE ANALYSIS	EQUIPMENT	OPERATOR SKILL	STEPS IN ANALYSIS	MATRIX SENSITIVITY	METHOD STATUS	ESTIMATE OF COSTS	TIME TO COMPLETE	SCORE
WEIGHT FACTOR	2	1	0	0	0	3	1	1	1	
MAXIMUM POSSIBLE	3	2	3	2	3	2	2	3	2	21
Py/Po WET METHOD	2	2	1	1	0	2	1	2	0	15
NaOH/ICP METALS	2	0	1	1	2	2	0	3	1	14
$KClO_3$-HCl LEACH	2	2	1	1	2	2	0	0	1	13
SLURRY/ ICP METALS	2	0	1	1	2	2	1	1	1	13
HNO_3/OXID/SULPHATE	2	2	1	1	0	1	2	1	1	13
ION CHROMATOGRAPHY	2	0	1	1	2	2	0	1	1	12
H_2O_2 OXIDATION	0	2	3	2	2	2	0	2	2	12
HCl-HNO_3/ICP	2	0	1	1	0	1	0	3	1	11
LECO TOTAL S	2	0	1	2	3	1	2	1	1	11
ELECTRON MICROPROBE	0	2	0	0	2	2	1	0	0	9
DTA-EGA	1	2	0	0	3	1	1	0	0	8
LEACH/ICP SULPHUR	2	0	1	1	1	0	0	2	1	7
QUANT. XRD	2	2	0	0	3	0	1	0	0	7
QUAL. XRD	0	2	1	1	3	1	2	0	0	7
XRF	2	0	1	1	3	0	1	1	0	6
MINERAL SEPARATION	0	2	1	0	0	0	0	0	0	2

TABLE 4.2.1-3

RANKING OF SULPHUR METHODS
LOW TECHNOLOGY/MINE LAB SCALE TESTS

CRITERIA	DETECTION LIMIT	PHASE ANALYSIS	EQUIPMENT	OPERATOR SKILL	STEPS IN ANALYSIS	MATRIX SENSITIVITY	METHOD STATUS	ESTIMATE OF COSTS	TIME TO COMPLETE	SCORE
WEIGHT FACTOR	1	0	4	2	1	2	1	2	3	
MAXIMUM POSSIBLE	3	2	3	2	3	2	2	3	2	40
H_2O_2 OXIDATION	0	2	3	2	2	2	0	2	2	32
NaOH/ICP METALS	2	0	1	1	2	2	0	3	1	23
LECO TOTAL S	2	0	1	2	3	1	2	1	1	22
ION CHROMATOGRAPHY	2	0	1	1	2	2	0	1	1	19
SLURRY/ICP METALS	2	0	1	1	2	2	1	1	1	19
HCl-HNO_3/ICP	2	0	1	1	0	1	0	3	1	19
$KClO_3$-HCl LEACH	2	2	1	1	2	2	0	0	1	17
LEACH/ICP SULPHUR	2	0	1	1	1	0	0	2	1	16
Py/Po WET METHOD	2	2	1	1	0	2	1	2	0	16
HNO_3/OXID/SULPHATE	2	2	1	1	0	1	2	1	1	15
XRF	2	0	1	1	3	0	1	1	0	13
QUAL. XRD	0	2	1	1	3	1	2	0	0	11
ELECTRON MICROPROBE	0	2	0	0	2	2	1	0	0	6
DTA-EGA	1	2	0	0	3	1	1	0	0	6
QUANT. XRD	2	2	0	0	3	0	1	0	0	5
MINERAL SEPARATION	0	2	1	0	0	0	0	0	0	4

Other than the peroxide oxidation method, none of the methods ranked appeared suitable for use in the field, due to the requirement of some type of laboratory instrument. For example, "NaOH/ICP Metals" (score 23) and "Slurry/ICP metals" (score 19) require an ICP spectrometer; "Ion Chromatography" (score 22) requires an ion chromatograph; and "Leco Total S" (score 20) requires a Leco apparatus.

4.2.2 Acid-neutralizing Mineral Methods

Twenty-one different types of methods have been assigned scores according to the ranking scheme (Section 4.1, Table 4.1-3). These include conventional methods (such as Sobek *et al.* (1978) "EPA NP," "BCR Acid Consumption" test), and modifications of the conventional method ("Modified EPA-Coastech" (Lawrence *et al.* 1989); "Modified EPA-H_2O_2 Addn" (Morrison *et al.* 1990)). Volumetry, gravimetry, and titrimetry are placed together as "Classical Methods." Metal determination following weak HCl digestion is included in two items, viz., ICP and atomic absorption (AA) because the latter is commercially available but the former is preferred.

4.2.2.1 Quantitative Phase Analysis

Identification of carbonate forms by a weak HCl digestion followed by metal analysis by either ICP or AA had the highest scores (16 out of possible 18, Table 4.2.2-1). Both approaches have lower detection limits than are currently available, and are potentially capable of distinguishing all forms of carbonate in rock. However, the methods are sensitive to matrix interferences caused by digestion of non-carbonate minerals.

In this respect, analysis of the leachate for sulphate would be required to determine whether any sulphur-bearing minerals were solubilized. This analysis would be quantitative for gypsum. Iron interference could be caused by dissolution of pyrrhotite and iron sulphates. Nonetheless, magnesium and calcium in the leachate should provide a good indication of their respective carbonates when combined with mineralogical reports.

TABLE 4.2.2-1

RANKING OF CARBONATE METHODS QUANTITATIVE PHASE ANALYSIS

CRITERIA	DETECTION LIMIT	PHASE ANALYSIS	EQUIPMENT	OPERATOR SKILL	STEPS IN ANALYSIS	MATRIX SENSITIVITY	METHOD STATUS	ESTIMATE OF COSTS	TIME TO COMPLETE	SCORE
WEIGHT FACTOR	2	4	0	0	0	2	0	0	0	
MAXIMUM POSSIBLE	3	2	3	2	3	2	2	3	2	18
HCl/AA-METALS	3	2	2	1	1	1	0	2	1	16
HCl/ICP-METALS	3	2	1	1	1	1	0	3	1	16
QUANT. XRD	2	2	0	0	3	0	1	0	0	12
CLASSICAL METHODS	2	1	2	1	2	2	1	0	1	12
CARBONATE MANOMETRY	1	2	2	0	2	1	1	0	0	12
DTA-EGA	1	2	0	0	3	1	1	0	0	12
ELECTRON MICROPROBE	0	2	0	0	3	2	0	0	0	12
BCR ACID CONSUMPTION	2	1	3	1	2	1	2	1	1	10
EPA NP	2	1	3	1	2	1	2	1	1	10
QUAL. XRD	0	2	1	1	3	1	2	0	0	10
CARBONATE COULOMETRY	0	2	2	0	2	1	1	0	0	10
AQUA REGIA/ICP METALS	3	1	1	1	1	0	0	3	1	10
MODIFIED EPA - COASTECH	2	1	3	1	1	1	0	1	1	10
MODIFIED EPA - H_2O_2 ADDN	2	1	3	1	2	1	0	1	1	10
STAIN TESTS	0	1	3	1	2	2	1	0	1	8
PETROLOGY	0	1	2	0	3	1	2	0	1	6
FIZZ TEST	0	1	3	2	2	0	2	2	2	4
TOTAL METALS	3	0	1	1	3	0	0	2	0	6
LECO TOTAL C	2	0	1	2	3	0	0	0	0	4
LOSS-ON-IGNITION	0	0	2	2	2	0	0	1	1	0
MINERAL SEPARATION	0	0	2	1	0	0	0	0	0	0

Quantitative XRD and differential thermal analysis ("DTA-EGA") are promising methods for distinguishing different carbonate phases (score 12 out of 18). Both methods are highly sensitive to different mineral matrices and matrix complexity, and it is questionable whether they can yield the reported detection limits. As indicated by Despard (1988), qualitative XRD (score of 10 out of 18) is an excellent initial method to assist in the interpretation of other less specific tests such as neutralization potential.

4.2.2.2 Rapid, Inexpensive Commercial Lab Methods

Determination of metals by ICP following HCl digestion is the most promising method in this category (score 15 out of a possible 21) (Table 4.2.2-2). This combination of digestion and final analysis is not yet commercially available. Use of AA to determine metals had the next best score of 14 out of 21. Classical methods of CO_2 determination (score 13 out of 21) are still used by most laboratories to determine carbonate and can be made specific for calcium carbonates. Determination of metals following an aqua regia digestion has an anomalously high score at 11 out of 21 despite the lowest possible score (0) for "matrix sensitivity". This method can be calibrated to carbonate content for specific projects (Geddes Resources 1990).

The neutralization potential-type methods had scores of 12 ("EPA NP," "BCR Acid Consumption") and 10 ("Modified EPA - Coastech," "Modified EPA - H_2O_2 Addn"). Their scores are lower than the three highest scoring methods (which use metal determinations) due to higher costs and higher detection limits.

4.2.2.3 Low Technology/Mine Lab Scale Methods

Surprisingly, the classical fizz test yields the highest score (30 out of a possible 40) (Table 4.2.2-3). This test is extremely simple to perform and can provide semi-quantitative results. The following information may be obtained:

- types of carbonate phases present (by use of cold or warm acid);
- relative quantity of carbonate; and

TABLE 4.2.2-2

RANKING OF CARBONATE METHODS
RAPID, INEXPENSIVE COMMERCIAL LAB METHODS

CRITERIA	DETECTION LIMIT	PHASE ANALYSIS	EQUIPMENT	OPERATOR SKILL	STEPS IN ANALYSIS	MATRIX SENSITIVITY	METHOD STATUS	ESTIMATE OF COSTS	TIME TO COMPLETE	SCORE
WEIGHT FACTOR	2	1	0	0	0	3	1	1	1	
MAXIMUM POSSIBLE	3	2	3	2	3	2	2	3	2	21
HCl/ICP-METALS	3	2	1	1	1	1	0	3	1	15
HCl/AA-METALS	3	2	2	1	1	1	0	2	1	14
CLASSICAL METHODS	2	1	2	1	2	2	1	0	1	13
EPA NP	2	1	3	1	2	1	2	1	1	12
BCR ACID CONSUMPTION	2	1	3	1	2	1	2	1	1	12
AQUA REGIA-ICP METALS	3	1	1	1	1	0	0	3	1	11
MODIFIED EPA - H_2O_2 ADDN	2	1	3	1	2	1	0	1	1	10
MODIFIED EPA - COASTECH	2	1	3	1	1	1	0	1	1	10
STAIN TESTS	0	1	3	1	2	2	1	0	1	9
ELECTRON MICROPROBE	0	2	0	0	3	2	0	0	0	8
TOTAL METALS	3	0	1	1	3	0	0	2	0	8
DTA-EGA	1	2	0	0	3	1	1	0	0	8
CARBONATE MANOMETRY	1	2	2	0	2	1	1	0	0	8
QUANT. XRD	2	2	0	0	3	0	1	0	0	7
QUAL. XRD	0	2	1	1	3	1	2	0	0	7
FIZZ TEST	0	1	3	2	2	0	2	2	2	7
PETROLOGY	0	1	2	0	3	1	2	0	1	7
CARBONATE COULOMETRY	0	2	2	0	2	1	1	0	0	6
LECO TOTAL C	2	0	1	2	3	0	0	0	0	4
LOSS-ON-IGNITION	0	0	2	2	2	0	0	1	1	2
MINERAL SEPARATION	0	0	2	1	0	0	0	0	0	0

TABLE 4.2.2-3

RANKING OF CARBONATE METHODS
LOW TECHNOLOGY/MINE LAB SCALE TESTS

CRITERIA	DETECTION LIMIT	PHASE ANALYSIS	EQUIPMENT	OPERATOR SKILL	STEPS IN ANALYSIS	MATRIX SENSITIVITY	METHOD STATUS	ESTIMATE OF COSTS	TIME TO COMPLETE	SCORE
WEIGHT FACTOR	1	0	4	2	1	2	1	2	3	
MAXIMUM POSSIBLE	3	2	3	2	3	2	2	3	2	40
FIZZ TEST	0	1	3	2	2	0	2	2	2	30
EPA NP	2	1	3	1	2	1	2	1	1	27
BCR ACID CONSUMPTION	2	1	3	1	2	1	2	1	1	27
CLASSICAL METHODS	2	1	3	1	2	2	1	0	1	26
MODIFIED EPA - H_20_2 ADDN	2	1	3	1	2	1	0	1	1	25
MODIFIED EPA - COASTECH	2	1	3	1	1	1	0	1	1	24
STAIN TESTS	0	1	3	1	2	2	1	0	1	24
HCl/AA-METALS	3	2	2	1	1	1	0	2	1	23
HCl/ICP-METALS	3	2	1	1	1	1	0	3	1	21
AQUA REGIA/ICP METALS	3	1	1	1	1	0	0	3	1	19
LOSS-ON-IGNITION	0	0	2	2	2	0	0	1	1	19
PETROLOGY	0	1	2	0	3	1	2	0	1	18
TOTAL METALS	3	0	1	1	3	0	0	2	0	16
CARBONATE MANOMETRY	1	2	2	0	2	1	1	0	0	14
LECO TOTAL C	2	0	1	2	3	0	0	0	0	13
CARBONATE COULOMETRY	0	2	2	0	2	1	1	0	0	13
QUAL. XRD	0	2	1	1	3	1	2	0	0	13
MINERAL SEPARATION	0	0	2	1	0	0	0	0	0	10
ELECTRON MICROPROBE	0	2	0	0	3	2	0	0	0	7
DTA-EGA	1	2	0	0	3	1	1	0	0	7
QUANT. XRD	2	2	0	0	3	0	1	0	0	6

- approximate reactive form of carbonate (by duration and intensity of effervescence).

In some cases, the fizz test may be all that is required in the field if previous work has demonstrated the correlation between these results and other ABA parameters.

The "EPA NP" and "BCR acid consumption" methods scored 27 out of a possible 40 points. "Classical methods" were ranked the next highest with a score of 26. The NP-type tests may be carried out using very simple, inexpensive equipment and reagents, although the addition of an automatic titrator would increase production. Classical methods may require specialist glassware and an accurate top-loading pan-type balance.

4.3 Selection of Methods for Testing

Based on the results of the ranking scheme described above, four high scoring methods were selected for preliminary testing. Two sulphide-specific methods were selected for testing:

- METHOD 1: Determination of pyrite and pyrrhotite forms of sulphur.

- METHOD 2: Determination of pyrite content by hydrogen peroxide oxidation.

Two approaches to carbonate form determination were selected:

- METHOD 3: Modification of conventional EPA neutralization potential determination by addition of hydrogen peroxide.

- METHOD 4: Determination of carbonate forms by HCl digestion and atomic absorption.

The procedures followed by the laboratory are detailed in Appendix 4.3-1.

5.0 TESTING OF SELECTED METHODS

5.1 Test Materials

In the absence of mineralogical standard materials for acid-base accounting it was necessary to prepare mixtures of materials of known mineralogy. Samples of calcite marble, dolostone (nearly pure dolomite), and siderite were used as sources of carbonates. Sulphides were represented by two samples consisting of relatively pure pyrite and pyrrhotite. Both sulphide samples unavoidably contained minor silicate and carbonate impurities. To provide a silicate matrix for mixing, a sample of granodiorite dimension stone was thoroughly crushed.

Prior to preparation of test mixtures, each component rock was analyzed for total metals, CO_2, and sulphur. Based on the simple mineralogies, the mineralogical composition of each sample was estimated. Four mixtures were then prepared (Table 5.1-1) to represent: (1) relatively low levels of calcite, dolomite, and iron sulphides; (2) high levels of the same minerals; (3) low levels of sulphides and carbonates, including siderite; and (4) high levels of carbonates and sulphides.

Each mixture was analyzed three times using each method (section 4.3, Appendix 4.3-1). Each mixture was also analyzed once using current commercially-available ABA methods (total sulphur, EPA neutralization potential, sulphur as HCl-soluble sulphate, sulphur as sulphide using concentrated nitric acid and bromine, and total inorganic CO_2).

5.2 Details of Methods

As described in Section 4.3, four methods were chosen for further testing, two sulphide-specific methods and two methods for determining carbonate forms.

TABLE 5.1-1

MINERAL MIXTURES PREPARED FOR TESTING

MINERAL	MIXTURE			
	1	2	3	4
	Weight %	Weight %	Weight %	Weight %
CALCITE	2	30	1	10
DOLOMITE	1.5	11	1.5	12
GRANODIORITE	92.5	9	92	1
PYRITE	2	30	2	30
PYRRHOTITE	2	20	2	20
SIDERITE	0	0	1.5	27
CALCULATED ASSAY[a]				
Fe	4.57	22.9	5.12	32.9
Ca	3.60	14.4	3.28	8.26
Mg	0.93	2.88	0.93	2.77
S(tot)	1.37	17.0	1.41	17.7
CO_2	1.85	22.1	1.93	23.1
NP, kg $CaCO_3$/t[b]	42.0	502	43.9	526

[a] Bacon Donaldson
[b] Based on CO_2 assay

5.2.1 Method 1

Method 1 is a selective dissolution procedure based on a chemical method developed by Noranda Mines for determining the percentages of pyrite, pyrrhotite and magnetite in massive sulphide ore and mill products (McLachlin 1934). The procedure relies on the relative solubilities of pyrite and pyrrhotite in a hot 2:1 (water:acid) solution of hydrochloric acid. Pyrrhotite was found to be readily soluble in this solution; pyrite practically insoluble.

Briefly, 2:1 HCl is added to finely ground sample (Appendix 4.3-1) and heated to dissolve pyrrhotite. This mixture is then vacuum filtered. In the original method (McLachlin 1934), pyrrhotite was quantified by reducing the filtrate with stannous chloride and determining the Fe content titrimetrically. The filtered residue was further decomposed oxidatively using HNO_3 to release Fe contained in pyrite. The Fe content (pyrite) was then determined titrimetrically. Sulphur contents in the two minerals could then be calculated based on the analyzed Fe content.

For the purpose of this project, the method was simplified to make it more suitable for use in a commercial laboratory. Total sulphur was determined for each mixture. The Fe content (pyrite) was determined using atomic absorption spectrophotometry. Sulphur contained in pyrite (S_{py}) was then calculated and sulphur contained in pyrrhotite (S_{po}) was determined by difference.

5.2.2 Method 2

Method 2 is an oxidative decomposition method for determining pyrite content using H_2O_2 as the oxidizing agent. The method was selected because of its relatively high score as a low technology/mine lab scale method (Section 4.2.1.3) and based on the need for a useful method for rapidly assessing acid-generating potential of sediments and sedimentary rocks (i.e. a preliminary field test). The test can be completed in less than 10 minutes, and is suitable for use under field conditions.

In this method, a pulverized sample is treated with a solution of 15% H_2O_2. The original method suggested two alternatives for determining pyrite content:

- monitoring the rate of pH change as the sample is oxidized (semi-quantitative, <10 minutes per sample); and
- determining the sulphate content of the reacted peroxide solution (to quantify pyrite in about 15 minutes using a portable sulphate test kit).

It was initially felt that this approach might be too simplistic, and that the potential interferences and/or sources of error would be high. Some of the apparent problems included:

- interference from other sulphide minerals (i.e. the method would not be specific for pyrite);
- incomplete oxidation, especially with respect to grain size and the potential difficulty of fine-grinding in the field;
- potential interference from organic sulphur forms, especially in coal-bearing samples, which would be concurrently oxidized by the peroxide; and
- sulphates initially present in the sample would lead to an overestimation of pyrite content.

Each of these issues was discussed in the original paper (Finkelmann and Giffen 1986) and this method was considered worthy of testing as a potential field screening technique for acid generation potential.

It was decided that determination of sulphate in the reacted solution would be preferable to monitoring the rate of pH change. Therefore, the method involved pre-treatment of the sample with 3:1 (water:acid) HCl solution to remove all sulphates, followed by the addition of 15% hydrogen peroxide solution. After allowing the sample to cool, sulphate concentration was determined gravimetrically.

5.2.3 Method 3

Method 3 is a modification of the conventional EPA neutralization potential (NP) determination (EPA 600/2-78-054, Sobek *et al.* 1978) that includes steps to filter the leachate (containing unreacted, excess HCl), adding 5 mL of 30% H_2O_2 and reboiling for 3 to 5 minutes (Appendix 4.3-1). The addition of 30% H_2O_2 was proposed by Morrison *et al.* (1990).

The rationale for this modification is to attempt to eliminate the effects carbonate minerals containing Fe^{II} (i.e. siderite) have on overestimating neutralization potential (as described in Section 2.2.2). Mixtures 3 and 4 contain siderite ($FeCO_3$), which initially consumes H^+, as carbonate and ferrous iron are liberated. Then, ferrous iron is slowly oxidized to ferric iron and hydrolysed, releasing H^+. Theoretically, hydrogen peroxide hastens the second stage and eliminates unstable endpoints in the back titration. Mixture

4 also contains pyrrhotite, which can interfere with achieving a stable end point during the back titration as discussed below.

Ferrous iron is present in all mixtures as pyrrhotite, which will decompose, consuming HCl but releasing most of it as H_2S. The addition of H_2O_2 encourages oxidation of Fe^{2+} to Fe^{3+} thereby releasing as much acid as is consumed.

Results from this method should reflect the presence of calcium and magnesium carbonates.

5.2.4 Method 4

Method 4 involves the determination of carbonate forms using an HCl digestion followed by analysis for Mg, Ca, and Fe by atomic absorption. This digestion method, followed by either ICP or AA, scored highly in the ranking system (Section 4.2.2) for both quantitative phase analysis and rapid inexpensive methods. Atomic absorption spectroscopy was selected for the finishing technique for this study because it is currently more widely available commercially.

5.3 Results of Testing

5.3.1 Expected and Standard Results

The component minerals used for the preparation of sample mixtures were analyzed for total metals (following fusion with $LiBO_2$ and dissolution in 5% HCl), total sulphur and CO_2. The results are shown in Table 5.3-1. Based on these values and the percentage of the minerals present in each sample mixture, the expected results for the methods tested were estimated. The expected results based on the known mineral make up of the mixtures appear in the data tables presented for each individual method (Sections to follow).

The results of the Standard EPA procedure to determine Net Neutralization Potential (NNP) are shown in Table 5.3-2.

TABLE 5.3-1

WHOLE ROCK ANALYSIS[1] OF COMPONENT MINERALS USED IN SAMPLE[2] MIXTURE PREPARATION

	CALCITE	DOLOMITE	GRANODIORITE	PYRITE	PYRRHOTITE	SIDERITE
SiO_2 (%)	5.10	3.13	67.70	0.73	5.29	1.95
Al_2O_3 (%)	1.02	0.22	16.18	0.14	0.21	0.04
Fe_2O_3 (%)	0.79	0.50	4.17	56.75	75.48	54.26
MgO (%)	7.11	20.80	1.16	0.40	0.68	4.18
CaO (%)	43.41	31.09	3.76	18.83	0.36	0.51
Na_2O (%)	0.22	0.05	3.18	0.13	0.06	0.05
K_2O (%)	0.44	0.05	2.73	0.22	0.17	0.05
TiO_2 (%)	0.01	0.02	0.52	0.01	0.01	0.01
P_2O_5 (%)	0.03	0.13	0.12	0.07	0.07	0.10
MnO (%)	0.10	0.02	0.07	0.91	0.25	3.50
Cr_2O_3 (%)	0.012	0.002	0.028	0.009	0.006	0.009
Ba (ppm)	1357	41	1012	46	5	21
Sr (ppm)	1344	65	225	265	17	10
La (ppm)	2	6	47	22	2	2
Zr (ppm)	5	5	87	5	5	7
Y (ppm)	7	5	18	5	5	10
S (%)[3]	0.07	0.03	0.03	35.2	32.0	2.69
LOI (%)	41.2	44.0	0.4	27.2	17.2	30.8
CO_2 (%)[4]	44.15	44.41	0.01	10.57	3.74	34.94
Sum (%)	99.83	100.00	100.24	97.44	99.78	95.40

[1] 200 gram samples are fused with 1.2 g $LiBO_2$ and are dissolved in 100 mL 5% HNO_3

[2] Sample type: pulp

[3] Total S determined by Leco.

[4] CO_2 determined by HCl digestion.

5.3.2 Results of Tested Methods

Copies of the original analytical data received from the laboratory are presented in Appendix 5.3-1. These results show that the reproduceability of the data (triplicate samples were analyzed) was high for all four methods.

TABLE 5.3-2

STANDARD EPA PROCEDURE[1] - SAMPLE MINERAL MIXTURES

	MIXTURE 1	MIXTURE 2	MIXTURE 3	MIXTURE 4
S(tot) (%)	1.41 1.38	17.5 17.5	1.41 1.38	18.3 18.3
S^{2-} (%)	1.22 1.23	16.1 16.4	1.22 1.19	17.7 17.6
$S(SO_4)$ (%) HCl-sol	0.03 0.02	0.26 0.24	<0.01 <0.01	0.29 0.29
CO_2 (%)	2.49 2.42	25.6 26.0	2.23 2.38	27.3 27.2
Paste pH	8.9	7.3	9.0	7.2
NP[2]	52.7 54.4	47 474	41.7 41.7	322 320
MPA[3]	44.1 43.1	547 547	44.1 43.1	572 572
Net NP[4]	8.6 11.3	-70.9 -72.9	-2.4 -1.4	-250 -252

[1] Standard EPA procedure (EPA 600/2-78-054) performed in duplicate
[2] NP = Neutralization Potential
[3] MPA = Maximum Potential Acidity
[4] Net NP = Net Neutralization Potential

Method 1

The results of the selective dissolution procedure are shown in Table 5.3-3, along with the calculated expected results. The results are correlated reasonably well with the calculated values for all four mixtures.

The method produced excellent results for Mixtures 1 and 3 (containing low levels of reactive sulphides). The analytical results for Mixture 3 (0.63% $S_{(py)}$, 0.76% $S_{(po)}$, mean of 3 replicates) compared extremely well to the concentrations of 0.64% $S_{(py)}$, 0.78% $S_{(po)}$ estimated from whole rock analysis, despite the presence of 1.5% by weight siderite

TABLE 5.3-3

ANALYTICAL RESULTS: METHOD 1 - SELECTIVE DISSOLUTION TO DETERMINE PYRITE AND PYRRHOTITE SULPHUR

SAMPLE ID	S(total)[1] (%)	Fe(pyrite)[2] (%)	S(pyrite)[3] (%)	Calculated[4] S (pyrite) (%)	S (pyrrhotite)[5] (%)	Calculated[4] S (pyrrhotite) (%)
Mixture 1	1.39	0.55	0.63	0.57	0.76	0.80
Mixture 2	17.5	8.73	10.02	8.17	7.49	8.82
Mixture 3	1.35	0.55	0.63	0.64	0.72	0.78
Mixture 4	18.3	8.73	10.2	8.90	8.28	8.82

[1] Total sulphur for Mixtures 1 and 3 by Leco method; total sulphur for Mixtures 2 and 4 by a wet method. Results reported are the means of duplicates.

[2] Fe(pyrite) was determined using atomic absorption spectroscopy. Results reported are the means of triplicate samples.

[3] S(pyrite) was calculated from Fe(pyrite)

[4] Estimated from whole rock analysis

[5] S(pyrrhotite) was determined by difference (Total Sulphur - S (pyrite))

present in the sample mixture. Since siderite contains iron, and the method results are based on the determination of Fe in the end digestion, the accurate results indicate that siderite was removed by the HCl pretreatment.

For Mixtures 2 and 4 (containing high levels of sulphide minerals), $S_{(py)}$ was overestimated in both cases. This may be because the filtered residue was incompletely washed in step 6 of the method (Appendix 4.3-1). A further source of error may arise from the determination of $S_{(po)}$ by difference.

The only problem encountered with this laboratory method arose in the filtration step (Step 5, Appendix 4.3-1). Treatment of the mixtures with 2:1 HCl resulted in a gelatinous, sticky material that was difficult to filter. This is likely due to the partial dissolution of silicate materials (granodiorite, for example) contained in the samples. Liquid/solid separation was only achieved by decanting and washing several times.

Method 2

The results for Method 2 were unsatisfactory (Table 5.3-4). For mixtures containing low quantities of sulphide minerals (Mixtures 1 and 3), the $S_{(py)}$ determined was overestimated by 66% and 58%, respectively. This suggests that the method was not specific for pyrite, and that some pyrrhotite was concurrently being oxidized. However, the values obtained for $S_{(py)}$ for Mixtures 1 and 3 using Method 2 were not in good agreement with the calculated $S_{(py+po)}$ numbers either (Table 5.3-4). Therefore this method does not appear to completely oxidize total sulphides present.

TABLE 5.3-4

ANALYTICAL RESULTS: METHOD 2 - DETERMINATION OF PYRITE CONTENT BY H_2O_2 OXIDATION

SAMPLE ID	S(pyrite)[1] (%)	Calculated[2] S (pyrite) (%)	Calculated[2] S(pyrite) + S(pyrrhotite) (%)
Mixture 1	0.95	0.57	1.37
Mixture 2	3.05	8.17	16.99
Mixture 3	1.01	0.64	1.42
Mixture 4	3.68	8.90	17.72

[1] Results reported are the means of triplicate samples
[2] Calculated from whole rock analyses

For Mixtures 2 and 4, containing high sulphide levels, the opposite problem was encountered. $S_{(py)}$ was substantially underestimated, suggesting incomplete oxidation of pyrite. Visually, the residues remaining following H_2O_2 treatment of Mixtures 2 and 4 appeared to contain pyrite (R. Hackl, personal communication).

Method 2 was difficult to carry out, even under laboratory conditions. As the H_2O_2 was added to the sample, excessive frothing occurred, as the reaction rate increased rapidly and the reaction vessel heated. Sample loss was difficult to control. This suggests that the method would need to be modified further for field conditions.

Method 3

Method 3 was a modification of the Standard EPA procedure for determining NP by the addition of hydrogen peroxide. The results (Table 5.3-5) show that the method produced slightly lower NP values (mean of 3 replicates) for Mixtures 2 and 4, but that the average NP value obtained for Mixtures 1 and 3 were 6.3% and 9.8% higher, respectively, than indicated by the standard NP procedure.

TABLE 5.3-5

ANALYTICAL RESULTS: METHOD 3 - MODIFICATION OF EPA NEUTRALIZATION POTENTIAL DETERMINATION BY ADDITION OF H_2O_2

SAMPLE ID	NP (Modified EPA)[1] (kg $CaCO_3$/t)	NP (Standard EPA) (kg $CaCO_3$/t)	NP (Calculated)[2] (kg $CaCO_3$/t)
Mixture 1	57.0	53.6	52.3
Mixture 2	465	475	529
Mixture 3	45.8	41.7	23
Mixture 4	296	321	219

[1] Results reported are the means of triplicate samples

[2] Calculated NP based on known content of Ca and Mg carbonates

Mixture 1 contained low levels of calcite, dolomite and iron sulphides. Results from the conventional and modified procedures, and calculations based on whole rock geochemistry produced results within the limit of experimental errors.

Mixture 2 contained high concentrations of calcite, dolomite, and iron sulphides. It was expected that the NP by the conventional procedure would be greater than the calculated NP due to the presence of pyrrhotite. However, it appears that pyrrhotite did not affect the results. The modified and conventional methods did not produce significantly different results.

Mixture 3 contained a small amount of siderite. As a result, the conventional NP produced a higher NP than would be expected from calcium and magnesium carbonate content. Addition of hydrogen peroxide did not produce a lower NP.

Mixture 4 contained 27% siderite by weight and therefore NP was much greater than expected from calcium and magnesium carbonates. Again, the addition of hydrogen peroxide produced a marginal change in NP.

The results do not confirm the conclusions of Morrison *et al.* (1990). The addition of H_2O_2 did not result in NP values close to that expected from calcium and magnesium carbonates, although filtration of the leachate did help to stabilize the endpoint of the back titration (R. Hackl, personal communication). Results did confirm that the conventional NP determination produces anomalously high results when the sample contains siderite or other iron-bearing carbonates.

Method 4

Method 4 was a determination of carbonate minerals by analyzing for metals released following digestion of the sample with 0.1 N HCl. The results for Ca, Mg, and Fe (%) are presented in Table 5.3-6, along with the calculated, expected values. Dissolution of minerals other than carbonates appears to have occurred.

TABLE 5.3-6

ANALYTICAL RESULTS - METHOD 4 - DETERMINATION OF CARBONATE MINERALS BY METALS RELEASED FOLLOWING DILUTE HCl DIGESTION

SAMPLE ID	ANALYTICAL RESULTS[1]			CALCULATED RESULTS[2]		
	Ca (%)	Mg (%)	Fe (%)	Ca (%)	Mg (%)	Fe (%)
Mixture 1	1.51	0.64	3.45	1.16	0.27	0.07
Mixture 2	13.8	2.38	14.1	14.74	2.75	0.95
Mixture 3	1.04	0.53	3.92	0.51	0.24	0.70
Mixture 4	7.28	2.24	24.0	8.78	5.40	12.40

[1] Analytical results presented are the means of three replicates

[2] Calculated based on estimated content of carbonate minerals

For Mixture 1, which contains relatively low proportions of carbonates and sulphides, the data for Ca, Mg, and Fe are all higher than the calculated values. The errors are 30% and 137% in the case of Ca and Mg, suggesting that dissolution of the silicate matrix (granodiorite) may be contributing to the analytical results, although silicates are not highly soluble in HCl. Some of the error may be due to incorrect estimation of the mineralogical composition of the samples. The excessively high Fe value (average of 3.45% compared to 0.07% calculated) is likely due to the dissolution of pyrrhotite present in the mixture.

In Mixture 2, the proportions of calcite, dolomite and both sulphides are relatively high. In this high-carbonate mixture, the analytical results for Ca and Mg are relatively similar to the calculated values, differing by 6.3% and 13.5%, respectively. Once again the method resulted in a poor approximation of the Fe content, probably due to dissolution of pyrrhotite.

For Mixture 3, which was low in carbonates and sulphides but contained siderite, the concentrations of Ca, Mg, and Fe were higher than expected (Table 5.3-6). As for Mixture 1, the high values obtained were likely due to dissolution of the silicate matrix and, for the high Fe values, pyrrhotite and siderite.

Mixture 4 contained relatively high levels of carbonates, sulphides, and siderite. As shown in Table 5.3-6, the metals analysis yielded a relatively good estimate of Ca content (average 7.28% compared to 8.78% calculated). However, the Mg content in the HCl solution was approximately 58% lower than the expected 5.40%, and the Fe content was overestimated as with the other three mixtures. As discussed above, the sources of Fe released into solution include pyrrhotite and siderite. The effectiveness of the HCl in dissolving Mg carbonates may have been lowered by the presence of high levels of Fe carbonate as siderite, which may have consumed acid, leaving less available to dissolve the $MgCO_3$.

5.4 Conclusions

5.4.1 Pyrite-specific Methods

Of the two pyrite-specific methods tested, one (selective dissolution of pyrite and pyrrhotite) was selected on the basis of being a quantitative, phase-selective procedure that also rated highly as an inexpensive, fairly rapid method. The other procedure (pyrite determination by H_2O_2 oxidation) was selected due to its high ranking as, and the need for, an inexpensive field method for semi-quantitative determination of pyrite.

The selective dissolution method shows promise as a chemical method for quantifying pyrite and pyrrhotite in waste rock samples. Further testing would be required to determine its suitability for a wide range of rock types consisting of varying mineralogical composition. We found that the method worked very well for samples low in sulphides, and that it slightly underestimated the pyrite content in samples containing large amounts of sulphides.

The hydrogen peroxide oxidation method to determine pyrite content was less satisfactory. This method was also tested by Lawrence *et al.* 1989, although in that study, the rates of pH and temperature change were monitored. The results were found to be "too inaccurate and too erratic to be of real use." In this study measurement of sulphate in the reacted peroxide solution was also found to yield unsatisfactory results.

5.4.2 Determination of Carbonate Form

Two methods for determination of carbonate forms were tested. Addition of H_2O_2 to the leachate from the conventional EPA procedure was evaluated for its effectiveness in removing the effect of siderite. A second method involved analysis of HCl leachate for metals (Ca, Mg, Fe).

Modification of the Standard EPA neutralization technique by the addition of hydrogen peroxide was not sufficient to oxidize Fe^{II} released during the test. Neutralization potentials were comparable to those obtained from the conventional procedure.

The erratic results obtained for the analysis of carbonate content by released metals analysis suggest that digestion of the rock samples with 0.1 N hydrochloric acids for 1 hour was not selective for Ca and Mg carbonates in the sample mixtures used.

6.0 RECOMMENDATIONS

6.1 Refined Approach to Acid-Base Accounting

The current approach to acid-base accounting is limited in that it may produce anomalous results for unusual sample mineralogies. These specifically relate to the dissolution of ferrous iron-bearing minerals in the conventional neutralization potential test, and the presence of different forms of sulphur.

Acid-base accounting may be carried out at three phases in a mining project. First, a few typical samples are analyzed to provide an initial indication of the potential for acid generation in several rock units and tailings. Later in the development, a large scale ABA program may be used to quantify waste rock tonnages. Finally, ABA may be conducted during mining to monitor or classify waste rock for disposal at different locations.

Suggested approaches to ABA at each phase are described below.

6.1.1 Phase 1: Detailed Characterization

The objective of this Phase of analysis should be a detailed characterization of sample mineralogy using mineral phase analyses. Acid-base accounting at this stage could include:

- traditional acid-base accounting (total sulphur, neutralization potential, NP acid strength, paste pH, fizz test);
- calculation of modified neutralization potentials to account for unstable endpoints caused by oxidation of ferrous to ferric iron (pending development of reliable procedures);
- determination of iron sulphide forms (pyrrhotite, pyrite);
- determination of sulphate forms (saturated Na_2CO_3 soluble, and HCl soluble);
- determination of total carbonate content, although not to replace neutralization potential; and

- determination of carbonate forms by metal analysis, possibly using a weak HCl leach.

Acid-base accounting should routinely include analysis of standard materials to compare the reproducibility of the different methods. As a matter of course, laboratories should report their fizz test results, and the strength of acid used in the NP determination.

Regardless of the extent of phase analysis, any acid-base accounting report must be supported by a mineralogical description or XRD analysis of the samples tested. In many cases, this information is essential for reliable interpretation of ABA and recognition of anomalies. Petrographic descriptions are generally comparable in cost to ABA analysis.

6.1.2 Phase 2: Large Scale ABA Programs

For large scale ABA programs it is generally impractical and unnecessary to characterize each sample in detail. Instead, results from Phase 1 may suggest useful correlations between key parameters and eliminate the need for detailed mineral phase analysis. For example, analysis of HCl leachate for Ca may be adequate for carbonate forms, and total sulphur may be correlated with iron sulphide content.

6.1.3 Phase 3: ABA During Mining

During mining, results of ABA can be used to identify different kinds of rock wastes or during waste management planning. Simple robust tests are preferred because laboratory conditions may not be ideal and very rapid turnaround will be required. Generally, sufficient data may be gathered during previous studies to justify use of simple analyses such as the fizz test or volumetric carbonate analysis. The hydrogen peroxide leach procedure (Finkelman and Giffen 1986) for determination of sulphide and acid-generating potential is not recommended at this time.

6.2 Recommendations for Further Investigations

The following additional studies are recommended.

- Standard materials should be developed for acid generation testing to provide a better basis for testing new techniques. These materials should reflect the full range of acid-consuming and acid-generating combinations. Complex mineral mixtures are also required to assess the reliability of new methods for minerals other than pyrite and calcite.
- The method of estimating sulphur as pyrite and pyrrhotite by selective dissolution should be refined. Testing in this study indicated that this simple test may have general application in estimating pyrite and pyrrhotite contents in waste rock and tailings.
- The commonly used neutralization potential-type tests (EPA, BC Research, Coastech methods) should be evaluated for their responses to mineral matrices that include HCl-soluble ferrous iron-bearing minerals.
- In combination with the study of neutralization potential, leachates should be analyzed for metals to evaluate whether analysis for calcium and magnesium would be preferable to the conventional procedures.
- Further testing of the Morrison *et al.* (1990) modification to the EPA procedure is recommended. Results from these authors' paper and this study do not agree. Nonetheless, addition of hydrogen peroxide is a logical solution to the ferrous iron problem. Failure of the method in this study may reflect the high sulphide concentrations in the samples. Filtration of leachate is also recommended to reduce the problem of unstable back titration end points.
- DTA and EGA methods should be investigated since these methods may allow quantification of both sulphide and carbonate forms.

REFERENCES

Allbright, C.S. and C.J. Thompson. 1970. Total Sulfur. Ch. 2 in J.H. Karchmer (ed). The Analytical Chemistry of Sulfur and its Compounds. Part I. Wiley Interscience. New York.

Alpers, C.N. and D.K. Nordstrom. 1990. Stoichiometry of mineral reactions from mass balance computations for acid mine waters. In Gadsby, J.W., J.G. Malick, and S.J. Day (eds). Acid Mine Drainage - Designing for Closure, Bitech Publishers, Vancouver, B.C. 109-130.

Bock, R. 1979. A Handbook of Decomposition Methods in Analytical Chemistry. International Textbook Company 444 pp.

Brady, K.B.C and R.J. Hornberger. 1990. A Manual for Premining Prediction of Coal Mine Drainage Quality - Draft. Unpub. report for the Pennsylvania Department of Environmental Resources Bureau of Mining and Reclamation.

Bristol, C.C. 1971. Quantitative determination of some carbonate minerals in greenschist facies metavolcanic rocks. Can. J. Earth Sci. 9:36-42.

British Columbia Acid Mine Drainage Task Force. 1989. Draft Acid Rock Drainage Technical Guide. Volume I - Technical Guide. B.C. Ministry of Energy Mines and Petroleum Resources, Victoria B.C.

Bruynesteyn, A. and Hackl, R.P. 1984. Evaluation of acid producing potential of mining waste materials. Minerals and the Environment 4:5-8.

Byerly, D.W. 1990. Guidelines for handling excavated acid-producing material. In Gadsby, J.W., J.G. Malick, and S.J. Day (eds). Acid Mine Drainage - Designing for Closure, Bitech Publishers, Vancouver, B.C. 109-130.

Czamanske, G.K. and C.O. Ingamells. 1970. Selective chemical dissolution of sulfide minerals: a method of mineral separation. Am. Min. 55:2131-2134.

Day, S.J. and P. Cowdery. 1990. Prediction of oxidizable sulphide content and neutralization potential in acid generation studies at metal mines. In Gadsby, J.W., J.G. Malick, and S.J. Day (eds). Acid Mine Drainage - Designing for Closure, Bitech Publishers, Vancouver, B.C. 141-152.

Deer, W.A., R.A. Howie, and J. Zussman. 1966. An Introduction to Rock-Forming Minerals. Longman Group. 528 pp.

Despard, T.L. 1988. X-ray diffraction evaluation of coal overburden neutralization potential (abstract). In U.S. Bureau of Mines Information Circular 9183, United States Dartment of the Interior. 413 pp.

Dreimanis, A. 1962. Quantitative gasometric determination of calcite and dolomite by using Chiitick apparatus. J. Sedim. Petrol. 32:520-529.

Evangelou, V.P., K. Roberts, and G.W. Szekeres. 1985. The use of an automated apparatus for determining coal spoil carbonate types content and reactivity. Proceedings of the Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation. December 1985; Lexington, KY; 163-166.

Evangelou, V.P. 1983. Pyritic coal spoils: their chemistry and water interactions. In Augustithis, S.S. (ed) Leaching and Diffusion in Rocks and their Weathering Products, Theophrastus Publishers, SA, Athens. 75-227.

Fabbi, B.P. and W.J. Moore. 1970. Rapid X-ray fluorescence determination of sulfur in mineralized rocks from the Bingham Mining District, Utah. Appl. Spect. 24:426-428.

Finkelman, R.B. and D.E. Giffin. 1986. Hydrogen peroxide oxidation: an improved method for rapidly assessing acid-generating potential of sediments and sedimentary rocks. Rec. Reveg. Res. 5:521-534.

Floyd, M.A., V.A. Fassel, and A.P. D'Silva. 1980. Computer-controlled scanning monochromator for the determination of 50 elements in geochemical and environmental samples by inductively coupled plasma-atomic emission spectrometry. Anal. Chem. 52:2168-2173.

Foulkes, M.E., L. Ebdon, and S. Hill. 1988. Ore and mineral analysis by slurry atomisation-plasma emission spectrometry. Anal. Proc. 25:92-94.

Geddes Resources Ltd. 1990. Stage I Environmental and Socio-economic Impact Assessment. Volume II Environmental Baseline Studies. Submitted for the British Columbia Mine Development Review Process. January 1990.

Guilcher, H. 1987. Acid mine drainage in reactive slates, "The Halifax Airport Case". Proceedings of the Acid Mine Drainage Seminar/Workshop. March 1987; Halifax; 117-126.

Halicz, L. and I.B. Brenner. 1987. Nebulization of slurries and suspensions of geological materials for inductively coupled plasma-atomic emission spectrometry. Spectrochimica Acta, Part B 42B:207-217.

Hanley, A.V. and F.W. Czech. 1970. Nonoxygen-containing inorganic sulfur compounds. Ch. 5 in J.H. Karchmer (ed). The Analytical Chemistry of Sulfur and its Compounds. Part I. Wiley Interscience. New York.

Hurlbut, C.S. and C. Klein. 1977. Manual of Mineralogy (after James D. Dana). John Wiley and Sons, New York. 532 pp.

Jeffery, P.G. 1981. Chemical Methods of Rock Analysis. Pergamon Press.

Johnson, W.M. and J.A. Maxwell. 1968. Rock and Mineral Analysis. John Wiley & Sons. New York.

Kase, K. 1987. Tin-bearing chalcopyrite from the Izumo vein, Toyoha mine, Hokkaido, Japan. Can. Min. 25:9-13.

Ke-long, H. 1979a. Application of DTA-EGA in the quantitative analysis of carbonate minerals (abstract). Ch'ang-ch'un Ti Chih Houeh Yuan Hisueh Pao 87-92.

Ke-long, H. 1979b. Application of thermal analysis to the qualitative and quantitative determination of carbonate minerals (abstract). Ti Ch'iu Hua Hsueh 331-339.

Lawrence, R.W., G.P. Poling, and P.B. Marchant. 1989. Investigation of predictive techniques for acid mine drainage. Report on DSS Contract No. 23340-7-9178/01/SQ. Energy, Mines and Resources, Canada, MEND Report 1.16.1(a).

Li, S., X. Li, Y. Chen, and X. Lu. 1986. Determination of occurrence of modes of elements in sediments - an introduction to slective chemical leaching techniques (abstract). Zhongguo Dizhi Kexuyuan Kuangchan Dizhi Yanjiuso Sokan 18:232-239.

Lim, R., L.J. Gregory, K.L. Leach, and S. Deutscher. 1977. Determination of carbonate minerals in oil shales (abstract). NTIS Report 1977 UCID-17616. 14 pp.

Lond, O.P. 1987. Acid mine drainage from mineralized slate at Halifax Airport. Proceedings of the Acid Mine Drainage Seminar/Workshop. March 1987; Halifax; 137-164.

Maxwell, J.A. 1968. Rock and Mineral Analysis. Interscience Publishers, New York.

McLachlin, C.G. 1934. Increasing gold recovery from Noranda's milling ore. Appendix 2 - Quantitative determination of pyrite and pyrrhotite in Noranda ore and mill products. Am. Inst. Min. Met. Eng. Trans 112:593-596.

Milodowski, A.E. and D.J. Morgan. 1980. Identification and estimation of carbonate minerals at low levels by evolved CO_2 analysis. Nature 286:248-249.

Morin, K.A. 1990. Problems and proposed solutions in predicting acid drainage with acid-base accounting. In Gadsby, J.W., J.G. Malick, and S.J. Day (eds). Acid Mine Drainage - Designing for Closure, Bitech Publishers, Vancouver, B.C. 93-108.

Morgan, D.J. 1977. Simultaneous DTA-EGA of minerals and natural mineral mixtures. J. Thermal Analysis 12:245-263.

Morrison, J.L., S.D. Atkinson, A. Davis, and B.E. Sceetz. 1990. The use of CO_2 coulometry in differentiating and quantifying the carbonate phases in the coal-bearing strata of western Pennsylvania: Its applicability in interpreting and modifying neutralization potential (NP) measurements. Paper presented at the 1990 Mining and Reclamation Conference and Exhibition, Charleston, West Virginia, April 23-26, 1990.

Olade, M. and K. Fletcher. 1974. Potassium chlorate-hydrochloric acid: a sulphide selective leach for bedrock geochemistry. J. Geochem. Explor. 3:337-344.

Olade, M. and K. Fletcher. 1976. Distribution of sulphur, and sulphide-iron and copper in bedrock associated with porphyry copper deposits, Highland Valley, British Columbia. J. Geochem. Explor. 5:21-30.

Peachey, D. and B.P. Allen. 1977. An investigation into the selective dissolution of sulphide phases from stream sediments and soils. J. Geochem. Explor. 8:571-577.

Percival, J.B., Torrace, J.K. and Bell, K. 1990. On the development of a sequential extraction procedure with application to leachability problems. In Gadsby, J.W., J.G. Malick, and S.J. Day (eds). Acid Mine Drainage - Designing for Closure, Bitech Publishers, Vancouver, B.C. 51-62.

Pritchard, M.W. and J. Lee. 1984. Simultaneous determination of boron, phosphorus and sulphur in some biological and soil materials by inductively-coupled plasma emission spectrometry. Anal. Chim. Acta 157:313-326.

Renton, J.J., A.H. Stiller, and T.E. Rymer. 1988. The use of phosphate materials as ameliorants for acid mine drainage. U.S. Bureau of Mines Information Circular 9183:67-75.

Roselle, P. 1982. Quantitative mineralogical analysis of carbonate sediments by x-ray diffraction: a new, automatic method for sediments with low carbonate content. Sedimentology, 29:595-600.

Scott, K.M. and G.F. Taylor. 1987. The oxidized profile of BIF-associated Pb-Zn mineralization: Pegmont, Northwest Queensland, Australia, J. Geochem. Explor. 27:103-124.

Sobek, A.A., W.A. Schuller, J.R. Freeman, and R.M. Smith. 1978. Field and laboratory methods applicable to overburden and minesoils. Report EPA-600/Z-78-0554 Cincinnati, Ohio: U.S. Environmental Protection Agency.

Stallings, E.A., L.M. Candelaria, and E.S. Gladney. 1988. Investigation of a fusion technique for the determination of total sulfur in geological samples by ion chromatography. Anal. Chem. 60:1246-1248.

Sviridenko, Zh.V., A.I. Orzhekhovskaya, E.A. Sidenko, V.B. Shegeda, and L.A. Kharchenko. 1983. Rapid determination of CO_2 in carbonate rocks and minerals by a coulometric method (abstract). Zavod. Lab. 49:16-17.

Tiessen, H., T.L. Roberts, and J.W.B. Stewart. 1983. Carbonate analysis in soils and minerals by acid digestion and two end-point titration. Commun. Soil. Sci. Plant Anal. 14:161-166.

Warne, S.St.J. and B.D. Mitchell. 1979. Variable atmosphere DTA in identification of anyhdrous carbonate minerals in soils. J. Soil Sci. 30:111-116.

Warne, S.St.J. 1977. The detection and elucidation of the iron components present as carbonates, in coal, by variable atmosphere differential thermal analysis. Therm. Anal. Proc. 5th Intl. Conf. 466-3.

Worgan, J. 1987. Acid mine drainage in reactive slates, "the Halifax Airport Case". Proceedings of the Acid Mine Drainage Seminar/Workshop. March 1987; Halifax; 127-136.

Yamamoto, S. 1985. A comparison of analytical methods of carbonate minerals in dolomitic limestone: examples on the devonian limestone beds, New York (abstract). Bull. Coll. Sci. Univ. Yyukyus, 40:145-156.

Yasuhasa, Y. 1976. A rapid quantitative analysis of carbonate minerals (abstract). In: Ganseki Kobutsu Kosho Gakkaushi 71:120-124.

Young, R.S. 1974. Chemical Phase Analysis. Latimer Trendf and Co. Ltd. Plymouth.

Zeng, H., C. Ji and X. Yuan. 1986. Analysis of sulfides with lead, copper, iron, and zinc matrix by ICP-direct reading spectrometry (abstract). Yankuang Ceshi 5:269-274.

APPENDIX 4.3-1

DETAILS OF SELECTED METHOD PROCEDURES

METHOD 1: DETERMINATION OF PYRITE AND PYRRHOTITE FORMS OF SULPHUR

1. Determine total sulphur of sample using appropriate method[1].

2. Weigh into a 300 cm^3 beaker: 1 g of ground sample if pyrite content is in excess of 10%; or 3 g sample if pyrite content is less than 10%.

3. Add 50 cm^3 of 2:1 HCl (2 parts water to 1 part HCl by volume).

4. Heat on hot plate for about 10 minutes until evolution of H_2S fumes is finished as denoted by testing with lead acetate paper.

5 Vacuum filter through a Gooch crucible lined with an asbestos pad.

6. Wash residue thoroughly with hot water.

7. Transfer crucible with contents to 500 cm^3 beaker, add a pinch of potassium chlorate to residue in crucible, then add sufficient concentrated nitric acid to decompose sulphides.

8. Evaporate to dryness on hot plate, and bake for 25 minutes.

9. Add 50 cm^3 dilute (5 to 10%) hydrochloric acid and wash down with water.

10. Dilute to 300 cm^3.

11. Determine Fe-content of solution using atomic absorption.

12. Report results as sulphur content as pyrite in sample.

13. Determine sulphur as pyrrhotite by difference.

---

[1] In this study, Total S was determined by Leco for samples containing <5% S (samples 1 and 3) and by a wet digestion (HNO_3/Br) method for samples containing >5% S (Samples 2 and 4).

METHOD 2: DETERMINATION OF PYRITE CONTENT BY HYDROGEN PEROXIDE OXIDATION

1. Pulverize 10 g of sample.

2. To remove soluble sulphates, rinse sample with 1:3 (acid:water) HCl as per the standard neutralization potential fizz test (Sobek *et al.* 1976). Allow sample to air-dry.

3. Accurately weigh a 5.00 g sample and place in a 600 mL Pyrex beaker. Add 100 mL of a solution containing 30% reagent-grade hydrogen peroxide solution which has been diluted to 15% with deionized water.

4. Boil solution. Remove from heat and wait about 30 minutes for the reaction to proceed. Allow the solution to cool to room temperature.

5. Determine sulphate concentration in solution by desired procedure. This study used a standard gravimetric method ($BaSO_4$ precipitation).

6. Report results as sulphur in pyrite.

METHOD 3: MODIFICATION OF CONVENTIONAL EPA NEUTRALIZATION POTENTIAL DETERMINATION BY ADDITION OF HYDROGEN PEROXIDE.

1. Digest the sample as described in the conventional NP procedure (Sobek *et al.* 1978):

    - Place approximately 0.5 g of pulverized sample on a piece of aluminum foil.

    - Add one or two drops of 1:3 (v/v) HCl to the sample. The presence of $CaCO_3$ is indicated by bubbling or audible "fizz".

    - Rate the bubbling or "fizz" as none, slight, moderate, or strong and determine the amount and strength (normality) of HCl to use in the digestion procedure according to Table 1 in Sobek *et al.* (1978).

    - Weigh 200 g of pulverized sample into a 250 mL Erlenmeyer flask.

    - Carefully add the appropriate amount of HCl into the flask containing sample.

    - Heat nearly to boiling, swirling the flask every 5 minutes, until reaction is complete. NOTE: Reaction is complete when no gas evolution is visible and particles settle evenly over the bottom of the flask.

    - Add distilled water to make a total volume of 125 mL.

    - Boil contents of flask for one minute and cool to slightly above room temperature. Cover tightly and cool to room temperature. CAUTION: Do not place rubber stopper in hot flask as it may implode upon cooling.

2. After cooling the leachate, filter, add 5 mL of 30 wt % hydrogen peroxide and re-boil for 3 to 5 minutes.

3. Allow to cool and titrate as in the conventional procedure:

    - Titrate contents of flask using 0.1 N NaOH or 0.5 N NaOH (concentration exactly known), to pH 7.0 using an electrometric pH meter and buret. The concentration of NaOH used in the titration should correspond to the concentration of HCl used in the digestion. NOTE: titrate with NaOH until a constant reading of pH 7.0 remains for at least 30 seconds.

4. Report results in kg $CaCO_3$/t

METHOD 4: DETERMINATION OF CARBONATE MINERALS FROM RELEASED METALS

1. Rinse the sample with hot deionized water and allow to dry.
2. Weigh 0.5 g of pulverized sample into a beaker.
3. Add 200 mL of 0.1 N hydrochloric acid.
4. Heat solution for 1 hour, or until effervescence ceases.
5. Allow solution to cool, and filter.
6. Determine calcium, magnesium and iron in filtrate by atomic absorption spectroscopy.
7. Report results as percent Ca, Mg, and Fe in rock.

APPENDIX 5.3-1

LABORATORY DATA

BACON, DONALDSON
& ASSOCIATES LTD.

12271 HORSESHOE WAY
RICHMOND, B.C. CANADA V7A 4Z1
TELEPHONE (604) 277-2322
FACSIMILE (604) 274-7235

CERTIFICATE OF ASSAY

Client:
NORECOL ENVIRONMENTAL CONSULTANTS LTD.
Suite 700 - 1090 West Pender Street
Vancouver, B.C. V6E 2N7

Attention: Stephen Day

File No.: M90-335
Date: December 17, 1990
P.O. No.:

e hereby certify that the following are the results of assays on: 6 Samples

SAMPLE IDENTIFICATION		Sulphur TOT Leco %		Sulphur TOT Wet %				
Pyrite		-		35.2				
Pyrrhotite		-		32.0				
Dolomite		.03		-				
Calcite		.07		-				
Siderite		2.76		2.69				
Granodiorite		.03		-				

PROVINCIAL ASSAYER

BACON DONALDSON & ASSOCIATES LTD.
Ron Williams, Chief Assayer

ACME ANALYTICAL LABORATORIES LTD.
852 E. HASTINGS ST. VANCOUVER B.C. V6A 1R6
PHONE(604)253-3158 FAX(604)253-1716

DATE RECEIVED: JAN 3 1991
DATE REPORT MAILED: Jan 17/91

ASSAY CERTIFICATE

Bacon, Donaldson & Assoc. FILE # 91-0034
12271 Horseshoe Way, Richmond BC V7A 4Z1

SAMPLE#	TOT/C %	TOC %	CO2 %
M90-335 1	.69	.01	2.49
M90-335 2	7.03	.05	25.61
M90-335 3	.63	.02	2.23
M90-335 4	7.56	.13	27.26
RE M90-335 1	.67	.01	2.42
RE M90-335 2	7.12	.04	25.98
RE M90-335 3	.66	.01	2.38
RE M90-335 4	7.51	.11	27.15

- SAMPLE TYPE: PULP

SIGNED BY.......... D.TOYE, C.LEONG, J.WANG; CERTIFIED B.C. ASSAYERS

ACME ANALYTICAL LABORATORIES LTD. 852 E. HASTINGS ST. VANCOUVER B.C. V6A 1R6 PHONE(604)253-3158 FAX(604)253-1716

WHOLE ROCK ICP ANALYSIS

Bacon, Donaldson & Assoc. PROJECT M90-335 File # 90-6278

12271 Horseshoe Way, Richmond BC V7A 4Z1

SAMPLE#	SiO2 %	Al2O3 %	Fe2O3 %	MgO %	CaO %	Na2O %	K2O %	TiO2 %	P2O5 %	MnO %	Cr2O3 %	Ba ppm	Sr ppm	La ppm	Zr ppm	Y ppm	Nb ppm	LOI %	CO2 %	SUM %
CALCITE	5.10	1.02	.79	7.11	43.41	.22	.44	.01	.03	.10	.012	1357	1344	2	5	7	20	41.2	44.15	99.83
DOLOMITE	3.13	.22	.50	20.80	31.09	.05	.05	.02	.13	.02	.002	41	65	6	5	5	20	44.0	44.41	100.00
GRANODIORITE	67.70	16.18	4.17	1.16	3.76	3.18	2.73	.52	.12	.07	.028	1012	225	47	87	18	20	.4	.01	100.24
PYRITE	.73	.14	56.75	.40	10.83	.13	.22	.01	.07	.91	.009	46	265	22	5	5	36	27.2	10.57	97.44
PYRRHOTITE	5.29	.21	75.48	.68	.36	.06	.17	.01	.07	.25	.006	5	17	2	5	5	20	17.2	3.74	99.78
SIDERITE	1.95	.04	54.26	4.18	.51	.05	.05	.01	.10	3.50	.009	21	10	2	7	10	20	30.8	34.94	95.40
STANDARD SO-4	68.83	10.50	3.14	.94	1.47	1.22	1.67	.58	.21	.08	.007	770	179	26	115	18	20	11.4	-	100.22

.200 GRAM SAMPLES ARE FUSED WITH 1.2 GRAM OF LIBO2 AND ARE DISSOLVED IN 100 MLS 5% HNO3.
- SAMPLE TYPE: PULP

DATE RECEIVED: DEC 10 1990 **DATE REPORT MAILED:** Dec 17/90. **SIGNED BY**..........D.TOYE, C.LEONG, J.WANG; CERTIFIED B.C. ASSAYERS

BACON,
DONALDSON
& ASSOCIATES LTD.

12271 HORSESHOE WAY
RICHMOND B.C. CANADA V7A 4Z1
TELEPHONE (604) 277-2322
FACSIMILE (604) 274-7235

TABLE 1
SUMMARY OF CHEMICAL ANALYSIS OF MINERAL SAMPLES

MINERAL	Fe %	Ca %	Mg %	S (tot) %	CO2 %
Calcite	0.55	31.0	4.29	0.07	44.2
Dolomite	0.35	22.2	12.5	0.03	44.4
Granodiorite	2.92	2.69	0.70	0.03	0.01
Pyrite	39.7	7.74	0.24	35.2	10.6
Pyrrhotite	52.8	0.26	0.41	32.0	3.74
Siderite	38.0	0.36	2.52	2.76	35.0

TABLE 2
MINERAL MIXTURES AND CALCULATED HEAD ASSAYS

	Mixture 1	Mixture 2	Mixture 3	Mixture 4
COMPOSITION				
Calcite, g	2	30	1	10
Dolomite, g	1.5	11	1.5	12
Granodiorite, g	92.5	9	92	1
Pyrite, g	2	30	2	30
Pyrrhotite, g	2	20	2	20
Siderite,g	0	0	1.5	27
Total Wt., g	100	100	100	100
CALC. ASSAY				
Fe, %	4.57	22.9	5.12	32.9
Ca, %	3.60	14.4	3.28	8.26
Mg, %	0.93	2.88	0.93	2.77
S (tot), %	1.37	17.0	1.41	17.7
CO2, %	1.85	22.1	1.93	23.1
NP, kg CaCO3/t *	42.0	502	43.9	526

*Based on CO2 assay

**BACON,
DONALDSON
& ASSOCIATES LTD.**

12271 HORSESHOE WAY
RICHMOND B.C CANADA V7A 4Z1
TELEPHONE (604) 277-2322
FACSIMILE (604) 274-7235

ACID BASE ACCOUNTING TEST REPORT

Norecol Environmental Consultants Ltd.
700-1090 W. Pender Street
Vancouver, B.C.
V6E 2N7

Attention : Stephen Day

File No. : M90-335

Report No. : 1

Date Reported : Jan. 15/91

Page: 1
of: 1

Project : Acid Base Accounting Research Project
Standard EPA procedure performed in duplicate

Sample I.D.	S (tot) %	S (2-) %	S (SO4) % HCl-sol	CO2 %	Paste pH	NP	MPA	Net NP
Mixture #1	1.41	1.22	0.03	2.49	8.9	52.7	44.1	8.6
Mixture #1	1.38	1.23	0.02	2.42		54.4	43.1	11.3
Mixture #2	17.5	16.1	0.26	25.6	7.3	476.	547.	-70.9
Mixture #2	17.5	16.4	0.24	26.0		474.	547.	-72.9
Mixture #3	1.41	1.22	<0.01	2.23	9.0	41.7	44.1	-2.4
Mixture #3	1.38	1.19	<0.01	2.38		41.7	43.1	-1.4
Mixture #4	18.3	17.7	0.29	27.3	7.2	322.	572.	-250.
Mixture #4	18.3	17.6	0.29	27.2		320.	572.	-252.

Government Certified Assayer
Ron Williams, Chief Assayer

Notes :

1. Analytical methods employed according to procedures described in "Field and Laboratory Methods Applicable to Overburden and Minesoils", EPA 600/2-78-054, pp. 45-55, 1978
2. NP = Neutralization Potential as determined by acid consumption test
   MPA = Maximum Potential Acidity (%S (tot) x 31.25)
   Net NP = NP - MPA
3. NP, MPA and Net NP are expressed in tonnes CaCO3 equiv. per 1000 tonnes sample
4. Samples with negative Net NP are potential acid producers
5. Total sulphur for Mixtures 1 and 3 were done by LECO method. Total sulphur for Mixtures 2 and 4 were done by a wet method.

BACON,
DONALDSON
& ASSOCIATES LTD.

12271 HORSESHOE WAY
RICHMOND, B.C. CANADA V7A 4Z1
TELEPHONE (604) 277-2322
FACSIMILE (604) 274-7235

ACID BASE ACCOUNTING TEST REPORT

Norecol Environmental Consultants Ltd.
700-1090 W. Pender Street
Vancouver, B.C.
V6E 2N7

File No. : M90-335

Report No. : 2

Date Reported : Jan. 15/91

Attention : Stephen Day

Page: 1
of: 1

Project : Acid Base Accounting Research Project
"Method 1" performed in triplicate
Determination of pyrite and pyrrhotite forms of sulphur

Sample I.D.	S (tot) % wet	Fe (pyrite) %	S (pyrite) %	S (pyrrhotite) %
Mixture #1	1.39	0.57	0.65	0.74
Mixture #1	1.39	0.50	0.57	0.82
Mixture #1	1.39	0.58	0.67	0.72
Mixture #2	17.5	8.60	9.87	7.65
Mixture #2	17.5	8.80	10.1	7.42
Mixture #2	17.5	8.80	10.1	7.42
Mixture #3	1.35	0.54	0.62	0.73
Mixture #3	1.35	0.55	0.63	0.72
Mixture #3	1.35	0.56	0.64	0.71
Mixture #4	18.3	8.60	9.87	8.43
Mixture #4	18.3	8.80	10.1	8.20
Mixture #4	18.3	8.80	10.1	8.20

Government Certified Assayer
Ron Williams, Chief Assayer

Notes :

1. Samples were very difficult to filter after treatment with 2:1 HCl. Liquid solid separation achieved by decanting and washing several times.

BACON,
DONALDSON
& ASSOCIATES LTD.

12271 HORSESHOE WAY
RICHMOND B.C. CANADA V7A 4Z1
TELEPHONE (604) 277-2322
FACSIMILE (604) 274-7235

ACID BASE ACCOUNTING TEST REPORT

Norecol Environmental Consultants Ltd.
700-1090 W. Pender Street
Vancouver, B.C.
V6E 2N7

File No. : M90-335

Report No. : 3

Date Reported : Jan. 15/91

Attention : Stephen Day

Page: 1
of: 1

Project : Acid Base Accounting Research Project
"Method 2" performed in triplicate.
Determination of pyrite content by H2O2 oxidation.

Sample I.D.	S (pyrite) %
Mixture #1	0.95
Mixture #1	0.95
Mixture #1	0.94
Mixture #2	3.05
Mixture #2	3.08
Mixture #2	3.02
Mixture #3	1.04
Mixture #3	1.02
Mixture #3	0.97
Mixture #4	3.65
Mixture #4	3.82
Mixture #4	3.57

Government Certified Assayer
Ron Williams, Chief Assayer

Notes :

1. Samples were treated with dilute HCl according to the EPA NP procedure, rather than "rinsing" as specified in part 2.
2. H2O2 digestion causes rapid extreme frothing, making it difficult to prevent sample loss.

BACON, DONALDSON
& ASSOCIATES LTD.

12271 HORSESHOE WAY
RICHMOND, B.C. CANADA V7A 4Z1
TELEPHONE (604) 277-2322
FACSIMILE (604) 274-7235

ACID BASE ACCOUNTING TEST REPORT

Norecol Environmental Consultants Ltd.
700-1090 W. Pender Street
Vancouver, B.C.
V6E 2N7

File No. : M90-335

Report No. : 4

Date Reported : Jan. 15/91

Attention : Stephen Day

Page: 1
of: 1

Project : Acid Base Accounting Research Project
"Method 3" performed in triplicate.
Modification of conventional EPA NP determination
by addition of hydrogen peroxide

Sample I.D.	NP
Mixture #1	56.7
Mixture #1	57.3
Mixture #1	57.0
Mixture #2	464.
Mixture #2	465.
Mixture #2	465.
Mixture #3	45.7
Mixture #3	45.7
Mixture #3	46.0
Mixture #4	294.
Mixture #4	299.
Mixture #4	295.

Government Certified Assayer
Ron Williams, Chief Assayer

BACON,
DONALDSON
& ASSOCIATES LTD.

12271 HORSESHOE WAY
RICHMOND B.C. CANADA V7A 4Z1
TELEPHONE (604) 277-2322
FACSIMILE (604) 274-7235

ACID BASE ACCOUNTING TEST REPORT

Norecol Environmental Consultants Ltd.
700-1090 W. Pender Street
Vancouver, B.C.
V6E 2N7

File No. : M90-335

Report No. : 5

Date Reported : Jan. 15/91

Attention : Stephen Day

Page: 1
of: 1

Project : Acid Base Accounting Research Project
"Method 4" performed in triplicate.
Determination of carbonate minerals from released metals.

Sample I.D.	Ca %	Mg %	Fe %
	(carbonate minerals)		
Mixture #1	1.48	0.64	3.44
Mixture #1	1.52	0.64	3.48
Mixture #1	1.52	0.65	3.44
Mixture #2	13.8	2.39	14.0
Mixture #2	13.9	2.37	14.0
Mixture #2	13.8	2.38	14.4
Mixture #3	1.04	0.52	3.92
Mixture #3	1.08	0.54	3.88
Mixture #3	1.00	0.52	3.96
Mixture #4	7.36	2.23	24.0
Mixture #4	7.28	2.22	23.6
Mixture #4	7.20	2.28	24.4

Government Certified Assayer
Ron Williams, Chief Assayer