On-site and Laboratory Investigations of Spoil in Opencast Collieries and the Development of Acid-Base Accounting Procedures

Report to the Water Research Commission

by

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The Steering Committee responsible for this project consisted of the following persons:

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Mr. K. Pietersen	Water Research Commission
Mr. P. du Toit	Chamber of Mines of SA
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Executive Summary

1 Introduction

Acid mine drainage is a widespread phenomenon affecting the quality of water at many South African collieries. Techniques to determine the likely leachate quality are numerous and have, thus far, been applied without uniformity. This report outlines the research conducted on acid mine drainage and the standardisation of methodologies to be followed to quantify the potential and magnitude of acid mine drainage under South African opencast mining conditions.

As such, this study was focussed on the following aspects:

- To investigate the applicability of existing global Acid-Base Accounting technologies to South African opencast coal mines.
- To refine Acid-Base Accounting methodologies for local conditions through experimentation.
- To establish a creditable database, detailing results from this investigation for future reference.
- To select and recommend Acid-Base Accounting methodologies to be used in South African opencast coal mines.

Acid mine drainage occurs when sulphide minerals in rock are oxidised, usually because of exposure to moisture and oxygen. This results in the generation of sulphates, metals and acidity that can have manifold environmental consequences. It is therefore of utmost importance to the mining industry to know the characteristics/capacity of waste rock, overburden, pit walls, pit floor and tailings to produce acid mine drainage.

1.1 ABA and ABATE

Acid-Base Accounting (ABA) is a first order classification procedure whereby the acid-neutralising potential and acid-generating potential of rock samples are determined, and the difference (net neutralising potential) is calculated. The net neutralising potential, and/or the ratio of neutralising potential to acid-generation potential, is compared with a predetermined value, or set of values, to divide samples into categories that either require, or do not require further determinative acid potential generation test work.

Although the project has been abbreviated as the Acid-Base Accounting (ABA) project, the project aims are to define a suite of acid-drainage prediction, applicable to South African opencast coal mine conditions. The result is that a new acronym, ABATE (derived from **Acid-Base**: **A**ccounting, **T**echniques and **E**valuation), has been defined to include all these methods. This also prevents any confusion from arising in the use of the term ABA, since most people associate ABA with the static test component of drainage chemistry prediction, rather than the entire suite of tools. Figure i shows the relationship ABA has to the overall ABATE concept and illustrates the different components needed to accurately predict mine drainage quality, depending on the objectives and onsite conditions.

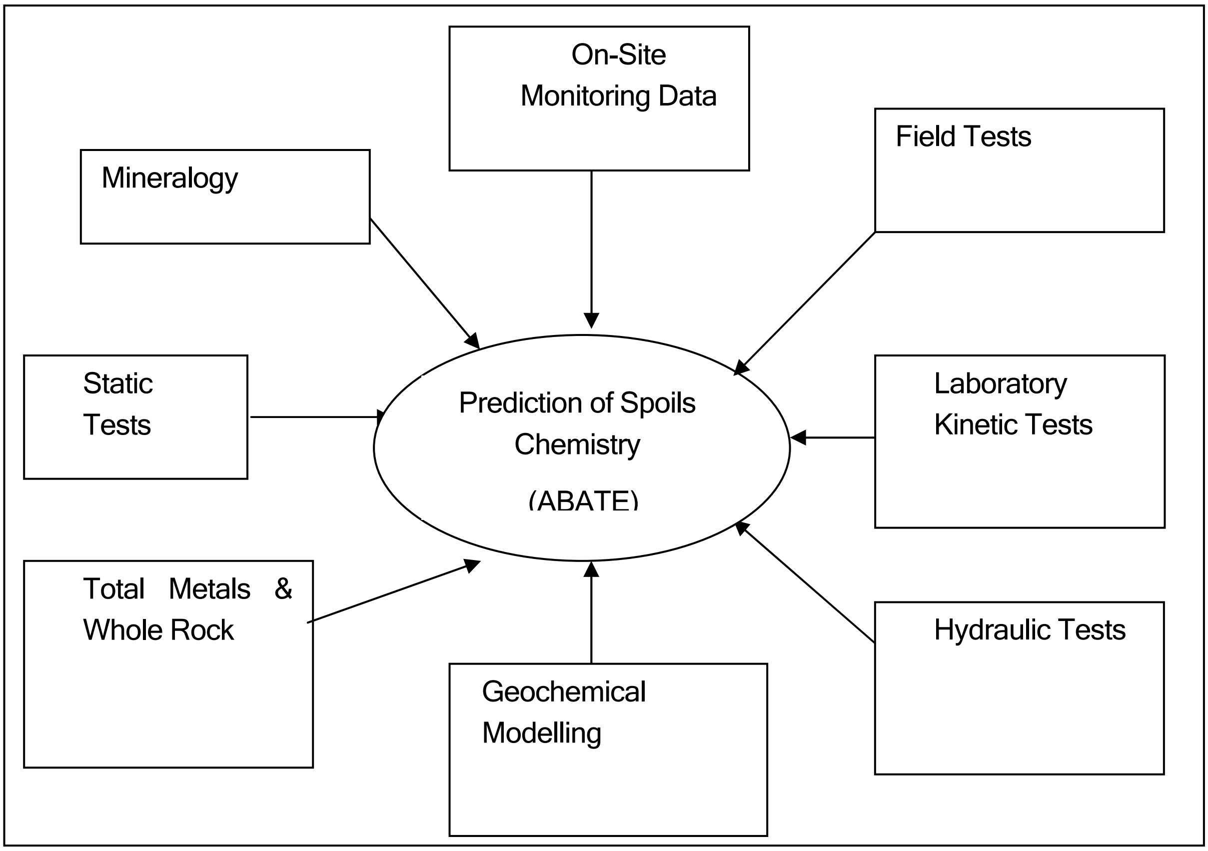

Figure i. The Prediction Wheel for Mine Drainage Chemistry and ABA's part therein (after Morin and Hutt, 1999).

2 Method of investigation

The research for this project was achieved by doing the following:

- Extensive literature review of relevant documents, journals, guidelines, websites and theses.
- Selection of appropriate ABA methods to test.
- Evaluation of different static test methodologies.
- Extensive long-term kinetic testing using several methodologies.
- Discussion with all relevant role players in South Africa in the form of personal meetings and a Specialist Workshop outlining findings and progress.
- Evaluation of modelling methods.

- *In situ* testing of spoil material through test pits.
- Application of ABA to case studies to compare ABA with the field situation.

3 Prediction Methods

Accurate prediction potentially offers the most cost-effective means of reducing the impact of AMD on the environment and the associated costs by allowing advanced planning for prevention and control. The objective of a prediction program is to reduce uncertainty to a level at which potential risk and liability can be identified and effective extraction, waste handling and, where necessary, mitigation and monitoring strategies can be selected (Price, 1998).

The scope of a prediction program will depend on site-specific conditions and factors. Some programs might comprise a few simple tests requiring only a relatively short period and a modest budget. Others can involve extensive testing and analysis lasting several months or even more than 1 - 2 years, with much higher costs. The approach required might include some or all of the following :

- Initial assessment and site reconnaissance.
- Sampling.
- Chemical, mineralogical and physical analyses.
- Short-term leaching tests.
- Geochemical static tests (Acid-Base Accounting).
- Geochemical kinetic tests.
- Mathematical models.

4 Static Methods (Acid-Base Accounting)

Generally when Acid-Base Accounting is referred to it is the so-called static methods, which are involved. These are screening methods to determine the difference between the acid-generating capability and the acid-neutralising potential of a particular sample.

4.1 ABA Terminology

- AP (Acid Potential) = S% x 31.25
- NP (Neutralisation Potential) = the capacity of a sample to consume acid
- NNP (Net Neutralising Potential) = NP - AP
- NPR (Neutralising Potential Ratio) = NP: AP

Units: Usually kg of $CaCO_3$ equivalent of net neutralisation potential per ton of rock

4.2 Types of static test

The following procedures are the most commonly used static test methods:

- Paste pH.
- Peroxide methods.
- Static Net Acid Generation (NAG) procedure.
- BC Research Initial test.
- Sulphur content.
- BC Research Confirmation Test.
- COASTECH modified biological oxidation test.
- Sobek Neutralisation Potential method.
- Carbonate NP determination.
- Modified Acid-Base Accounting procedures for Neutralising Potential.
- Lapakko Neutralisation Potential test procedure.
- Calculated NP.
- Net Carbonate Value (NCV) for Acid-Base Accounting.

4.3 Considerations, Advantages and Limitations of Acid-Base Accounting

Acid-Base Accounting is often a first or second step in determining the mine drainage chemistry. It has been used very widely with success, locally and internationally. It is however important to point out that, although it can be used very fruitfully, particularly in classifying samples into potentials for acid generation, there are several factors to consider.

The principal advantages of ABA are:

- They are relatively cheap
- Interpretation is based on decades of international research/experience
- Methods of interpretation are clear and well established
- Results are obtained quickly
- Correlation to field has been shown by case studies (local and abroad)

The limitations of ABA are thus the following (most of these also apply to several other methods used):

- It only provides a possibility of occurrence.

- Reaction rates are ignored. (ABA generally tests the fast reacting species; slow reacting neutralising species will usually not prevent acidification).
- It assumes instant availability of reactive species. (However, nearly all rock samples lacking carbonates which are fast reacting and thus instantly available, or not of dunite composition (predominantly olivine + serpentine) have insufficient NP to be classifiable as 'not potentially acid-generating' if the minimum limit for this category was to be set at, for example, 20 kg CaCO3 equivalent/tons of material (Errington, 1991)).
- Simple reaction stoichiometry is assumed.
- Size effects are ignored (Limestone particles of greater than 6.4 mm are coated with precipitates and are only 20% utilised when acid conditions are in evidence (Scharer *et al.*, 2000). However from this paper it is clear that if a 4:1 NPR is used then only 10% fines is required for the system to react as expected. From the trenches dug in the spoils, a > 10% fines ratio is a valid assumption in South African conditions, therefore in spoils this limitation is a minor consideration).
- Extrapolation to the field is uncertain when volumetric calculations cannot be made.

4.4 Suggested Methods

Based on the research at the IGS, the following are the suggested methods for Acid-Base Accounting:

1. Paste/Initial pH and solution products.
2. Acid potential using hydrogen peroxide or Leco furnace.
3. Oxidation products analysed (when using H_2O_2).
4. Neutralising potential using sulphuric acid.

From this project the following are considered important:

- Acid-Base Accounting is an excellent first-order tool to determine whether mine waste has the potential to form acidic drainage.
- The methods developed as part of this project are in agreement with methods used internationally.
- Modifications that have been made and suggested are all scientifically justifiable.
- Well-established criteria exist for the classification of individual samples as potentially acid-generating or neutralising.

- When samples are obtained at specific locations with depth, the use of depth normalisation and volumetric calculations provides an established methodology of evaluating ABA results for an entire spoil area.
- Initial pH-methods in the laboratory yield similar results. A standard ratio of 1 g sample:10 g water is suggested since it compares well to traditional paste pH-values, yet provides sufficient supernatant for analysis of naturally available leachable elements.
- Where material is to be used for neutralisation, acid leachable metals should be determined since these levels may be extremely high if acidification was to occur.
- The hydrogen peroxide acid potential method and the Total S, determined using a Leco analyser, should provide similar assessment of acid potential.
- The hydrogen peroxide method, however, provides additional information such as an indication of oxidised pH (which can provide an indication of NNP and therefore acts as a form of quality control) and the levels of different potential contaminants, which can be released. Only reactive sulphur species are determined, thereby removing confusion over total S, sulphate S and organic S contributions.
- The neutralisation method recommended is a modification of the Sobek method that uses sulphuric acid, no fizz test and a twenty-four hour measurement period. Its use is justified since sulphuric acid rather than HCl reacts in the field, the results compare very well, the removal of the fizz test leads to greater consistency and the twenty-four hour period negates the siderite temporary buffering. The recommended methods are discussed fully with supporting evidence in the report.

4.5 Assessment of recommended Static methods

The proposed static test methods compare to those used internationally. The modifications suggested to the methods are all justified and should result in a more consistent application of the methods in South Africa.

These methods can thus be used with great certainty and success for the screening and placing of waste rock in the coal mines of Southern Africa.

4.6 Screening Criteria

One of the major advantages of static tests is that well-defined sets of screening criteria have been developed to interpret these tests. Although these criteria can sometimes provide slightly contradictory interpretations, their combined use can lead to good classification of tested samples into classes of non-acid-generating to acid-generating, with a slight grey area inbetween. It has been suggested that the criteria should be area/site specific. The researchers agree with this sentiment but feel that until there is a large enough, comparable Acid-Base Accounting database in South Africa, international criteria should be used.

The criteria are the following:

4.6.1 Net Acid-Generating Test (NAG) pH

This set of criteria is based on the final pH obtained in the NAG test. These subdivisions are slightly arbitrary and these can serve as a rough guideline but not as stand-alone criteria in categorising the samples.

Final pH in NAG Test	Acid-generating Potential
> 5.5	Non-acid-generating
3.5 to 5.5	Low risk acid-generating
<3.5	High risk acid-generating

The 5.5 upper limit is derived from the carbon dioxide/pure water equilibrium pH of 5.69. Any sample tested with deionised water commonly used in laboratories requires this value to be used as reference rather than a theoretical neutral pH of 7.

4.6.2 Net Neutralising Potential (NNP)

The use of NNP often leads to uncertainties. The reason for this is that research and experience have shown that there is a range from -20 to 20 kg/t $CaCO_3$ where the system or sample can either become acidic or remain neutral. However, when used in conjunction with the other criteria, this uncertainty can be resolved.

Where Net Neutralising Potential (NNP) = Neutralising Potential (kg/ton CaCO3) - Acid-Generating Potential (kg/ton CaCO3)

The criteria are as follows:

If NNP = NP - AP < 0, the sample has the potential to generate acid.

If NNP = NP - AP > 0, the sample has the potential to neutralise acid produced.

More specifically any sample with NNP < 20 is potentially acid-generating and any sample with NNP > -20 might not generate acid.

4.6.2.1 Neutralising Potential Ratio (NPR)

Guidelines for screening criteria based on ABA (from Price *et al.,* 1997b).

POTENTIAL FOR ARD	INITIAL NPR SCREENING CRITERIA	COMMENTS
Likely	<1:1	Likely AMD generating
Possibly	1:1 - 2:1	Possibly AMD generating if NP is insufficiently reactive or is depleted at a faster rate than sulphides
Low	2:1 - 4:1	Not potentially AMD generating unless significant preferential exposure of sulphides along fracture planes, or extremely reactive sulphides in combination with insufficiently reactive NP
None	>4:1	No further AMD testing required unless materials are to be used as a source of alkalinity

The criteria above can also be plotted to give a visual indication of the potential.

4.6.2.2 % S and NPR

A set of rules, which has been derived based on several of the factors calculated in ABA, was reported by Soregaroli and Lawrence (1998). It has been shown that for sustainable long-term acid generation, at least 0.3% Sulphide -S is needed. Values below this can yield acidity but this is likely to be only of short-term significance. Using this fact and the NPR values, another set of rules can be derived:

1. Samples with less than 0.3% Sulphide-S are regarded as having insufficient oxidisable Sulphide-S to sustain acid generation.
2. NPR ratios of >4:1 are considered to have enough neutralising capability.
3. NPR ratios of 3:1 to 1:1 are considered inconclusive.
4. NPR ratios below 1:1 with sulphide-S above 0.3% are potentially acid-generating.

4.7 Reporting

It is recommended that all results be reported in units of kg/ton rock. All the ABA results should be expressed in units of kg/ton $CaCO_3$ for standardisation. It is recommended that one of two formats be used; either the ABACUS tool or the WISH format.

4.8 Integrating the criteria

In order to be consistent with the application of criteria, a simple Excel-based tool called "Acid-Base Accounting Cumulative Screening tool" or ABACUS has been developed. This tool applies all the rules outlined above and incorporates several of the graphical presentations. It is felt that this will assist both the practitioners and regulators in obtaining consistent application and interpretation of the rules associated with ABA. The tool is very simple and is menu/button driven, with macros programmed to guide the user and lead them to the correct interpretation.

5 Field methods

Detailed fieldwork is suggested. This should include the following:

- Water sampling and ongoing monitoring.
- Representative sampling of spoil material, preferably through boreholes so that volumetric and depth determinations can be made.
- *In situ* profiling of water.
- Test pits in established spoils to determine areal and age variation.

Until there is a sufficiently large database for the South African coalfields, it is recommended that statistical methods be used to determine the number of samples required. Methods with illustrations of their application are given in the report.

Their suggested inclusion is due to the fact that these measurements:

- Provide the best kinetic reactor there is (As Morin and Hutt (1997) state “Undoubtedly the most valuable and representative kinetic test that can be operated at a minesite is the full-scale operation of minesite components").
- Give the most reliable measurements.
- Help to determine current situation.
- Provide understanding of controls on chemistry.
- Allow comparison to ABA.
- Act as an early warning system.
- Assist in decision on appropriate control measures.

6 Kinetic Tests

For material where the potential for acid generation is uncertain or rates of reaction are required, kinetic test work is performed to attempt to define acid generation characteristics. The term kinetic is used to describe a group of test work procedures wherein the acid generation (and metal solubilisation and transport) characteristics of a sample are measured with respect to time (Mills, 1998g and Chemex labs, 1997).

The following list shows different categories of tests:

- Humidity cells
- Column tests
- Accelerated biological oxidation tests
- Field tests
- Specialised test apparatus

The most popular kinetic test is the humidity cell test. Therefore, this type of test formed the focus of the kinetic testing research in this project. The test simulates accelerated weathering of the sample. This is done by passing moist air followed by dry air through the sample chamber; moist air for three days, followed by dry air for three days and distilled water on the seventh day. This one-week cycle is typically run for 20 weeks, according to the ASTM standard.

As part of this project, 24 kinetic tests were run on various samples. In addition to the usual reasons for doing these tests, the objectives were to obtain repeatability, determine the influence of different methodologies and compare traditional tests with other methods. From tests done in this project, the following findings are the most important:

- The humidity cell procedure used in this project was repeatable. Cells run with duplicate samples yielded results which were very similar.
- Good correlation was found between standard humidity test methodologies and more simplified methods. Three sets of duplicate tests illustrated that cheaper and less labour intensive test protocols could yield similar results.
- The ABA results and the results from the kinetic tests were in good agreement. This provides verification for both methods.
- Humidity cells can provide reaction rates for different samples. Reaction rates for all the cells tested could be obtained.
- Increasing the humidity causes an increase in the reaction rate, in agreement with international research.
- The rates of flushing were sufficiently high to prevent secondary mineral precipitation.
- Humidity cells may not provide an indication of acidity for samples that are uncertain, according to the static test results.
- Standardised tests should be used, wherever possible, to build up a database of rates for the coalfields.

- Where the influence of any particular aspect, e.g. the effect of a cover, is to be proved using a kinetic test, a standard test should be done as reference, for comparison.
- The degree and rate of NP depletion can be determined from these cells.
- The theoretical depletion of NP correlated very well with the pH-development in the cells that acidified.
- A modified NAG/kinetic test showed that under highly oxidising conditions acidification of large boulders will occur due to reactions at the surface of the boulders. This acidification implies that the neutralising potential of the rock may be overestimated by any static NP determination.
- The Ca+Mg/SO_4 ratio appears to be an excellent early indicator of imminent acidification.
- Humidity cells should be able to provide “threshold” values for acid and neutralising potentials. This will greatly enhance the usefulness and likely success of the prediction of acidity.
- The usefulness of these cells for direct translation to field rates is, as yet, unclear, from this research and that done worldwide.
- The variability observed in most spoils as far a mineral, rock/fine size and distribution and depth of soil cover makes the determination of sufficient kinetic tests for spoils an unfeasible task.
- The suggested ASTM test period of 20 weeks is shown to be insufficient, by the research done in this project. This makes standardisation of the procedure extremely difficult.

Detailed methodologies for the operation of humidity cells and the interpretation thereof are given in the report.

7 Modelling

Computer models are another approach to the prediction of acid generation. As part of the development of the ABATE methods, a short review of geochemical modelling was included. Although this does not pertain directly to ABA, geochemical modelling is increasingly seen by many in South Africa as the method of choice for the prediction of long-term drainage from mines.

This section highlights the advantages, requirements and limitations for geochemical modelling. Each modelling code or method has particular advantages and disadvantages as far as availability, cost, ease of use and inherent assumptions and weaknesses. In each case, the appropriate code or method must be used based on the type of answer required. By highlighting the usefulness of these models and their basic data requirements, along with the uncertainties involved in geochemical models, the user/researcher will, it is hoped, be in a position to select an appropriate model method and geochemical modelling code. This section provides guidance in terms of the uncertainties, requirements and output from geochemical models.

Geochemical models need several input parameters, which have been accurately determined. Without accurate data, the uncertainties increase and the models can then only be used to highlight the most important processes and show what the influence of different variables are.

- Selection of appropriate model tool is vital.
- There are numerous models that can be used for geochemical modelling. The applicability of each model needs to be assessed according to the on-site conditions, availability of data and objectives of the modelling.

The advantages of geochemical models are that they:

- Provide long-term (+100 years) estimates of changes/trends in ARD quality.
- Enable a comparison between different options in terms of:
    - Discard dump design.
    - Operational procedures.
    - Rehabilitation scenarios.
- Provide the basis for comparing the risk and costs associated with each option.
- The models are often associated often associated with large uncertainties.

Illustration using simulations of simplified hydrogeochemical systems, showed how relatively minor variations (relative to the uncertainty of most of the data used in the models) can yield significantly different results. Several different simulations were done to illustrate a particular aspect.

The applicability of modelling was tested by comparison to the humidity cell outflow. Using methodologies discussed in the report and knowledge of the mineralogical make-up, ABA results and outflow volumes, it was possible to simulate the cells satisfactorily. The simulations did, however, show how sensitive the outcome is to slight changes in input parameters.

Geochemical modelling is regarded as an advanced step in the ABATE process.

Despite these limitations, geochemical modelling can be a very useful tool in the prediction of drainage quality, when used in conjunction with data appropriate to the objectives.

8 Case studies

Three case studies showed the application of ABA to a field scale. Fieldwork included test pits dug at the different mines to obtain an *in situ* determination of the acidification and on-site conditions. The most important findings from the case studies are summarised below.

- All of the studies showed a good correlation between static ABA and observations in the field.
- The spoils are extremely heterogeneous. Great variation in particle size, moisture content and type of material was observed in test pits dug in the spoil.
- The depth of soil cover has no apparent impact on the spoil water chemistry. Oxygen and moisture penetrate into the system, regardless of the thickness of soil cover.
- Temperatures in the dug pits can be very low at surface in winter. A rapid increase in the spoil temperature with depth is present in most pits and at 3 m, temperatures around 20°C have been recorded. In several of the dug pits, elevated temperatures ranging from 25 - 50°C have been recorded.
- There are localised areas of acidification; these are due to specific optimal microclimates. It seems that mineralogical composition plays a more important role than age of the spoils.
- Mine A showed how several of the components in the ABATE process could be used to determine the likely quality emanating from the mine.
- Case study 2 illustrated an excellent correlation with ABA from core boreholes, *in situ* determinations, subsequent ABA and kinetic testing.
- Case study 3 used an example of a mine classified previously as an unlikely acid producer. *In situ* determinations in spoils of various ages showed that in the upper two to three metres the spoil was pH neutral to slightly alkaline. Long-term monitoring data from the borehole nearest the test pits, spanning more than a decade, showed that the water quality in the area was currently neutral to slightly alkaline.
- Other reported case studies from South African coal mines illustrated the use and value of ABA as a tool in the assessment of coal mine water chemistry.
- The most significant of these illustrates how ABA from an area where mining has long ceased, which is experiencing vast problems with AMD, consistently predicts that acidification is likely.

9 Further research

From the findings and experiences in this project the following suggested future research is needed:

1. Determination of threshold values for ABA parameters in South African coal mines.
2. Integration of all ABA and drainage (monitoring) in the coalfields to find regional trends and correlation to assist in the early identification and management of AMD in South Africa.
3. Extensive testing and validation of model codes used in AMD prediction.
4. Development of an affordable, user-friendly reactive transport model that can be used in South African coal mines.

10 AIMS AND ACCOMPLISHMENTS

The following is a discussion of the degree to which the aims of the project have been reached.

To investigate the applicability of existing global Acid-Base Accounting technologies to South African opencast coal mines.

An extensive review of available ABA procedures was done. Chapters 1-3 detail the theory of AMD, the use of international ABA methods, their methodologies and advantages/disadvantages of each method. Discussions with prominent practioners in the field of AMD in South Africa through personal meetings and workshops provided background to the currently used methods in South African opencast mines. The results from *in situ* test pits in the spoils at three different collieries were compared to static tests and showed an excellent correlation.

To refine Acid-Base Accounting methodologies for local conditions through experimentation.

Chapter 4 outlines the ABATE strategy for the integrated use of available tools in an approach that allows the tools to fit the objective and on-site situation. Chapter 5 details the results from testing of different static ABA methods and variations in methodologies. Chapter 6 describes the twenty-four kinetic tests done as part of this project. Repeatability and variation in methodology and apparatus were all tested to obtain a clear understanding of the impact of these aspects. From all these tests, recommendations have been made for methods to be used in South Africa.

To establish a creditable database, detailing results from this investigation for future reference.

All the results from this investigation are detailed in the report. The results are also in Excel spreadsheets for easy access and future reference. Where applicable the results are in a format compatible with the WISH software.

To select and recommend Acid-Base Accounting methodologies to be used in South African opencast coal mines.

From the extensive testing of the static methods a standardised method for initial pH, neutralisation potential and acid potential have been recommended. The reasons/advantages of the recommended methods have also been discussed. The recommended methodologies for static tests, kinetic tests, field methods and modelling have been outlined in a summary document of methods. An easy to use spreadsheet tool, ABACUS, has been developed to standardise the interpretation of static ABA data and, where the suggested sampling methodology has been followed, to provide a method for extrapolation to the field through volume-weighted techniques.

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ALSO AVAILABLE ON THE ATTACHED CD ROM

are the

Recommended Methods for Conducting and Interpreting Analytical Geochemical Assessments at Opencasrt Collieries in South Africa

and

ABACUS, a button-driven spreadsheet to assist users in interpretation of Acid-Base Accounting data.

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1 INTRODUCTION

Acid mine drainage is a widespread phenomenon affecting the quality of water at many South African collieries. Techniques to determine the likely leachate quality are numerous and have, thus far, been applied without uniformity. This report outlines the research conducted on acid mine drainage and the standardisation of methodologies to be followed to quantify the potential and magnitude of acid mine drainage under South African opencast mining conditions.

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- Evaluation of modelling methods.
- *In situ* testing of spoil material through test pits.

- Application of ABA to case studies to compare ABA with the field situation.

1.2 ACID MINE DRAINAGE

Acid mine drainage (AMD) occurs when sulphide-bearing minerals in rock are exposed to air and water, oxidising the sulphide sulphur to sulphuric acid (BC Mining Watch (1996), Durkin (1996), Durkin and Herrmann (1996), Evangelou (1995), Evangelou and Zhang, (1997), Hadley and Snow (1974), Moses *et al.* (1987) and Robertson (1996)). AMD and heavy metals pollution can poison groundwater and drinking water and destroy aquatic life and habitat. The acid dissolves heavy metals such as lead, zinc, copper, arsenic, selenium, mercury and cadmium into ground- and surface water (Hadley and Snow, 1974). Heavy metals kill, because they prevent the energy that is essential for life from being produced, by binding with -SH (mercaptan) functional groups in enzymes and other proteins (Stevenson, 1997). Certain bacteria, naturally present, can significantly increase the oxidation rate. The contaminated water is often reddish-brown in colour, indicating high levels of oxidised iron (Hadley and Snow, 1974). Bright orange coloured water and stained rocks are usually telltale signs of acid mine drainage. The orange colour is due to ferric hydroxide ($Fe(OH)_3$) (yellow boy) precipitating from the water. The precipitate forms as acid mine drainage becomes neutralised. At low pH-values the metal ions remain soluble. When the pH rises, the iron oxidises and precipitates out. Depending on the conditions, the orange coloured precipitates may form inside the mine, or several miles downstream. The precipitates can be harmful to aquatic life in several ways. The clumps reduce the amount of light that can penetrate the water, which affects photosynthesis and the vision of animals. When the precipitate settles, it blankets the streambed, smothering the bottom-dwellers and their food resources (Acid Mine Drainage Chemistry, 1997). AMD can develop at several points throughout the mining process in underground workings, open pit mine faces, waste rock dumps, tailings deposits and ore stockpiles. Acid generation can last for decades, centuries, or longer and its impacts can travel many miles downstream. Roman mine sites in Great Britain continue to generate acid drainage, 2000 years after mining ceased (BC Mining Watch, 1996). Acid drainage from mining operations has a long history, dating back thousands of years to Phoenician times when the Iberian Pyritic Belt in Spain, from where the Rio Tinto (Red River) flows, was first exploited (Miller, 1998).

Industry, labour, government and environmentalists agree on one issue: that AMD is the number one environmental problem facing the mining industry (BC Mining Watch (1996), Domvile *et al.* (1994), Lawrence and Wang (1997) and Schafer Laboratory (1997)). Waste rock and tailings are the most important sources of AMD. There is no dispute that AMD:

- devastates fish and aquatic habitat,
- is virtually impossible to reverse with existing technology,

- once started, costs millions annually to treat and can continue for centuries (BC Mining Watch, 1996) and
- is very complex to control and treat (Lawrence and Day (1997), Evangelou (1995)).

AMD is a severe environmental pollution problem associated with coal and other sulphide-containing ore mining operations, and results mainly from the oxidation of pyrite. It is estimated that each year in the US, the wet cleaning of coal alone leaves behind aqueous slurries of refuse containing at least 10 million tons of pyrite (Evangelou and Zhang, 1995).

It is only relatively recently that the full implications of its impact have been acknowledged in mine planning. Nordstom *et al.* (1999) report on the famous Iron Mountain site, at Richmond California. This mine has drainage with a negative pH (as low as -3.6), metals around 200 g/L and sulphate as high as 760 g/L. This contamination is a result of AMD resulting from of pyrite oxidation. The Equity Silver Mine in Northern BC, for example, received permits in 1979 to operate without proper consideration for the potential of AMD. Within months it became an infamous site of contamination due to the generation of metal-contaminated and acidic drainage from waste rock, tailings and many structures around the mine site, which had been constructed from acid-generating rock (Lawrence and Day, 1997). Harries (1998) estimates that in Australia the operational costs of AMD related actions run to approximately $60 million per year. He states that several Australian sites could require over $100 million each if the release of pollutants was to be reduced to a level with minimal ecological impact. Published costs of rehabilitating historic acid drainage sites have been estimated to be between $US 2 and 35 billion for the USA and between $C 3 and 5 billion for Canada.

1.2.1 ARD/AMD

There is some confusion between ARD and AMD. It is important to recognise the difference between naturally occurring Acid Rock Drainage (ARD) and the massive quantities of effluent created through human activities in the mining process. AMD (BC Mining Watch, 1996 and Feasby *et al.,* 1997), highway construction, quarrying, logging activities and civil engineering works (Halifax airport, Nova Scotia) (Downing and Mills, 1998a) all generate significant amounts of harmful effluents. Explorationists use natural ARD products (gossans) as an aid to mineral exploration (Downing and Mills, 1998a). While the oxidation of sulphides may be described as a natural geochemical process, mining increases the exposure of acid-generating surfaces by many orders of magnitude. Natural exposure of sulphide-bearing mineralisation took place in the context of geologic time-scale. What naturally occurred over 10 000 years on a glacier-scoured mountainside, is now compressed into the time frame of a 20-year mine life. In addition, natural weathering patterns could never have created a concentrated 70 million ton fractured rock pile under any circumstances, nor a 40 million ton deposition of crushed and ground tailings sand (BC Mining Watch, 1996). ARD is generally used in Canada for acid drainage due to mining, while in South Africa we use the term Acid Mine Drainage. It is suggested this be adopted as standard to differentiate the natural process from mining induced oxidation. In many instances in South Africa the acid is neutralised by the natural buffering of the surrounding/co-disposed rock. This results in a neutralised solution with an elevated salt content, as is typically found at many South African collieries.

1.3 STAGES IN THE DEVELOPMENT OF AMD

The development of AMD involves a complex combination of organic and inorganic processes and reactions. To produce severe acid drainage, where the pH of the system drops below 3, sulphide minerals must create an optimum micro-environment for rapid oxidation and must continue to oxidise for a sufficiently long time to exhaust all of the neutralisation potential of the rock. The potential of sulphide rock to generate acid is strongly related to the amount of alkaline, often calcareous, material in the rock.

When reactive sulphide rock is initially exposed to flowing water and oxygen, sulphide oxidation and acid generation begins. Any calcium-based carbonate in the rock immediately neutralises this small amount of acidity and maintains neutral to alkaline conditions in water passing over the rock (Broughton *et al.,* 1992). As acid generation continues and the neutralising agent is consumed or is rendered ineffective in further neutralisation, the pH of the water decreases, which in turn enhances the conditions for further acid generation. As the rate of acid generation accelerates, the pH progressively decreases in a step-like manner. Each plateau of relatively steady pH represents the dissolution of a neutralising mineral that becomes soluble at that pH. If the rate of acid generation remains high enough to remove all of the neutralisation potential in the rock, the pH-values will drop below 3 and AMD will become severe (See Figure 1). These various stages can last for weeks, months, or centuries until the sulphide minerals completely oxidise and the rock becomes inert, or until special waste management and AMD control actions are taken (Durkin and Herrmann, 1996). The various stages are mineralogy dependent, and in South Africa often the observed quality is near neutral, high salt content, water due to carbonate buffering. Once this has been depleted, pH-values tend to fall relatively rapidly. Table 1 shows some of the more important buffering phases encountered (See page 23).

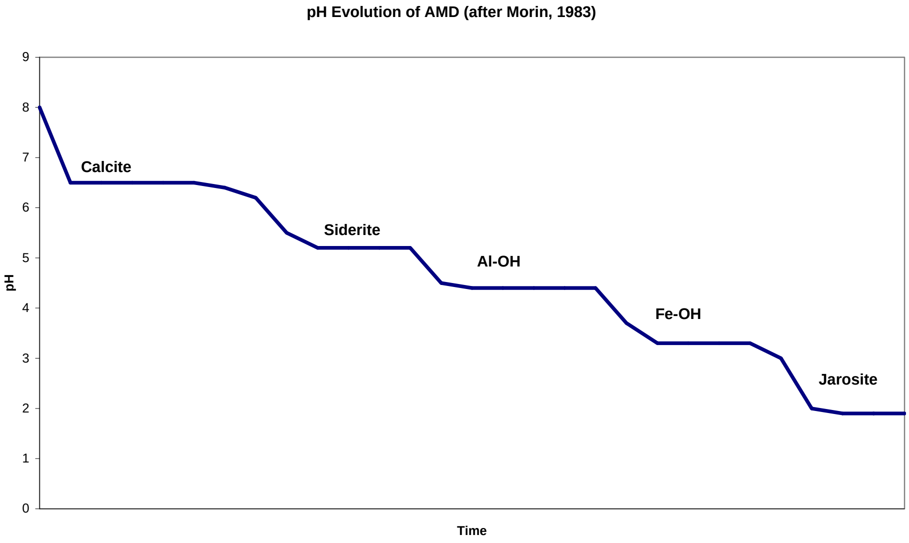


Figure 1. Stages in pH evolution as a result of different buffering minerals (after Morin, 1983).

1.4 ACID-BASE ACCOUNTING (ABA) and ABATE

Acid-Base Accounting (ABA) is a first-order classification procedure whereby the acid-neutralising potential and acid-generating potential of rock samples are determined and the difference (net neutralising potential) is calculated. The net neutralising potential and/or the ratio of neutralising potential to acid-generation potential, is compared with a predetermined value, or set of values, to divide samples into categories that either require, or do not require, further determinative acid potential generation test work. Different methods of conducting ABA test work will generate different sets of sample data for evaluation. Rules and guidelines have been developed by mine regulatory and permitting agencies (e.g. Price and Errington (1995), Steffen, Robertson and Kirsten (1991) and Brady *et al.* (1994)) for ABA procedures (Mills, 1998c). ABA indicates the overall balance of acidification potential (AP) and neutralisation potential (NP) (Schafer Laboratory, 1997).

In its most basic form, ABA is simply a screening process. It provides no information on the speed (or kinetic rate) with which acid generation or neutralisation will proceed and because of this limitation the test work procedures used in ABA are referred to as Static Procedures (Mills (1998c), Ziemkiewicz and Meek (1994)).

The potential for a given rock to generate and neutralise acid is determined by its mineralogical composition. This not only includes the quantitative mineralogical composition, but also individual mineral grain size, shape, texture and the spatial relationship with other mineral grains. The term "potential" is used because even the most detailed mineralogical analysis, when combined with ABA, can give only a "worst case" value for potential acid production and, depending upon the NP procedure used, a "worst case", "most likely case" or "best case" value for potential neutralisation capability. The field generation and neutralisation of AMD represent the degree to which these potential values are realised in practice (Mills, 1998c).

Neutralisation potential measures the sum total of carbonates, alkaline earths and bases available to neutralise acidity and represents the most favourable condition. Calculations of the maximum potential acidity and neutralisation potential are structured to equate the two measurements to a common basis for comparison. The resulting values, expressed as calcium carbonate equivalent, are compared to compute a net acid-producing or neutralising potential. Material exhibiting a net acid production potential of 5 tons/1000 tons of overburden material or more as calcium carbonate equivalent is classed as toxic or potentially toxic (Hunter, 1997b and Sobek *et al.,* 1978).

Proposed new mines in British Columbia are required to evaluate potential AMD generation in considerable detail and to demonstrate comprehensive planning to prevent or suppress AMD generation at all phases of mine operation, from development to closure and post-closure. Such evaluation must include pit walls, overburden, waste rock, tailings and any other material produced by the mining process.

Application of this Acid-Base Accounting method to overburden handling and placement plans throughout the USA and Canada, has generally been effective in eliminating or reducing adverse water quality impacts. It becomes a more powerful tool when used in conjunction with hydrologic data, mining and reclamation plans, mineralogy data, etc. (Perry, 1997).

The primary **advantages** of the Acid-Base Accounting method are:

1. Short turn-around time for sample processing.
2. Low cost.
3. Relatively simple analytical procedures.
4. Relatively simple interpretation of results (Hunter, 1997b; Evangelou and Zhang, 1995).

Depending on the type of information required and the on-site conditions (complexity, disposal methods, available information, etc.), different portions of the methods need to be applied.

1.4.1 ABATE

Although the project has been abbreviated as the Acid-Base Accounting (ABA) project, the project aims are to define a suite of acid-drainage prediction, applicable to South African opencast coal mine conditions. The result is that a new acronym, ABATE (derived from Acid Base: Accounting, Techniques and Evaluation), has been defined to include all these methods. This also prevents confusion arising in the use of the term ABA, since most people associate ABA with the static test component of drainage chemistry prediction, rather than the entire suite of tools.

Figure 2 below shows the relationship ABA has to the overall ABATE concept and illustrates the different components needed to accurately predict mine drainage quality, depending on the objectives and on-site conditions. This figure is referred to as the so-called "prediction wheel" in drainage chemistry determination (Morin and Hutt, 1999).

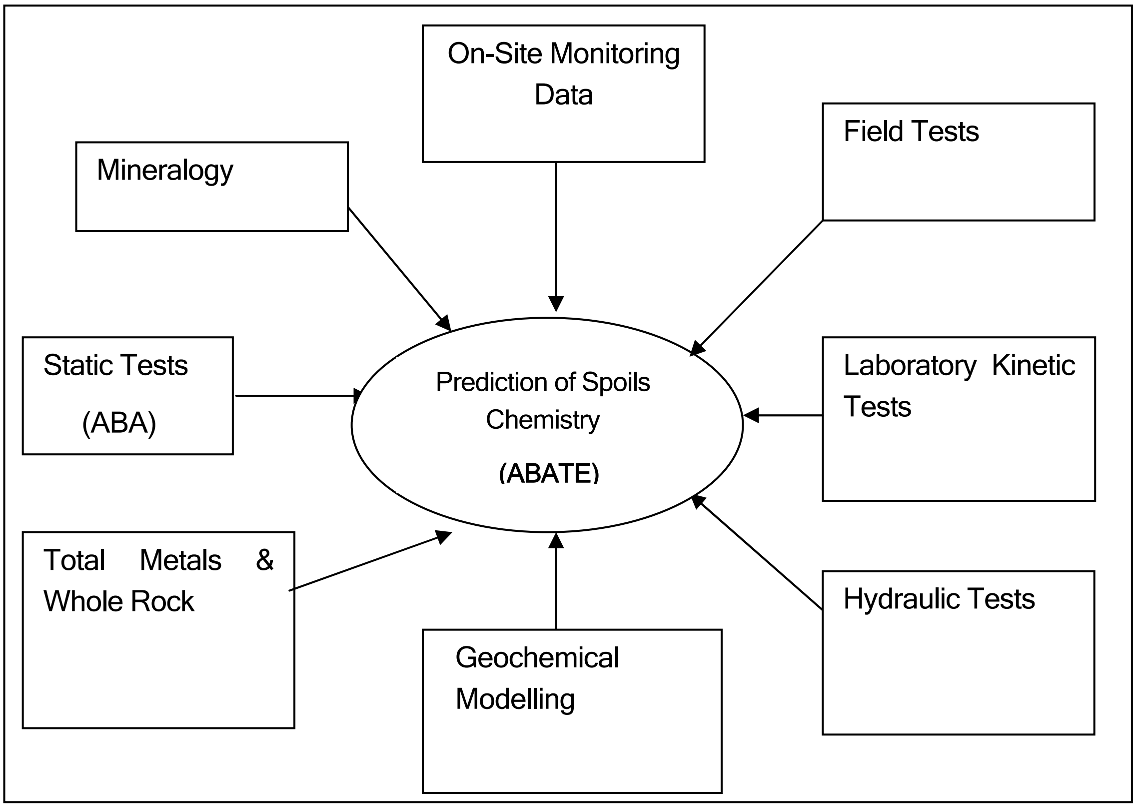


Figure 2. The Prediction Wheel for Mine Drainage Chemistry and ABA's part thereof (after Morin and Hutt, 1999).

2 BASIC CHEMISTRY OF AMD GENERATION

2.1 THE SULPHUR CYCLE

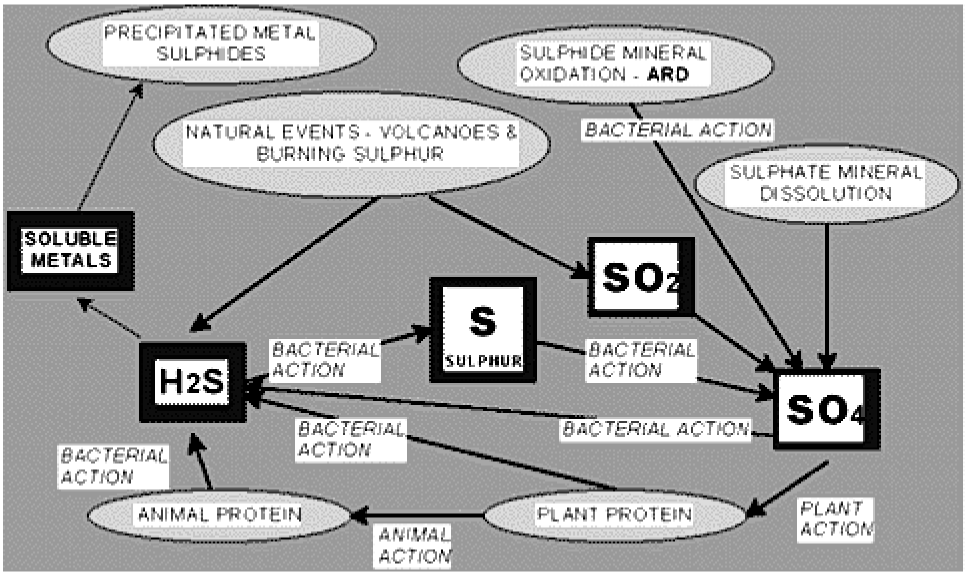


Figure 3. Simplified Sulphur cycle for mineral deposits (from Mills, 1998b).

The environmental sulphur cycle involves many physical, chemical and biological agents. A simplified schematic diagram of the cycle is shown here, which shows the major phases of sulphur cycling in relation to mineral deposits. As such, the figure indicates the relationships between sulphur, S, hydrogen sulphide, H_2S, sulphur dioxide, SO_2 and the sulphate ion, SO_4^{2-}. In mineral form, sulphur may be present as sulphides (e.g. pyrite, FeS_2, chalcopyrite, FeS.CuS and pyrrhotite, FeS) and/or sulphates (e.g. gypsum, $CaSO_4.2H_2O$ and barite, $BaSO_4$). Sulphur in minerals may move through the cycle as a result of the oxidation of sulphides to sulphate and/or the dissolution of sulphates. For example, oxidation of pyrite to sulphuric acid may be immediately followed, *in situ*, by acid neutralisation by calcium carbonate (calcite) to form calcium sulphate (gypsum). The reaction of hydrogen sulphide with dissolved metal ions may precipitate metallic sulphides, which are chemically indistinguishable from naturally occurring sulphide minerals.

At some mines, sulphur is added to the cycle as sulphur dioxide in processes such as the Inco/SO_2 process for cyanide destruction in the treatment of tailings. This added sulphur is oxidised to sulphate ion (Ingles and Scott, 1987), most of which remains free, but some of which combines with lime, CaO, in the tailings to form gypsum (Mills, 1998b).

2.2 ACID GENERATING REACTIONS

Acid mine drainage impacts stream and river ecosystems in several ways through acidity, ferric iron (Fe^{3+}) precipitation, oxygen depletion and release of heavy metals associated with coal and metal mining, such as aluminium, copper, gold, lead, manganese, silver, uranium and zinc (AMD Chemistry, 1997).

Pyrite (FeS_2) an iron disulphide (commonly known as fool's gold), is one of the most important sulphides found in the waste rock of mines. When exposed to water and oxygen, it can react to form sulphuric acid (H_2SO_4). The following oxidation and reduction reactions express the breakdown of pyrite that leads to acid mine drainage.

(1) $FeS_2 + 7/2\ O_2 + H_2O \Rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$

(2) $Fe^{2+} + 1/4O_2 + H+ \Rightarrow Fe^{3+} + 1/2\ H_2O$ (rate limiting step)

(3) $Fe^{3+} + 3H_2O \Rightarrow Fe(OH)_3$ (yellow boy) $+ 3H^+$

(4) $FeS_2 + 14Fe^{3+} + 8H_2O \Rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$ (AMD Chemistry, 1997 and Evangelou, 1995)

Reaction 1 shows oxidation of the disulphide, thus releasing ferrous iron (Fe^{2+}) and two protons. In **Reaction 2,** the ferrous iron is oxidised to ferric (Fe^{3+}) which hydrolyses to form ferric hydroxide (an insoluble compound at pH greater than 3.5) and in the process, as shown in **Reaction 3**, three more protons are released. Thus for every mole of pyrite five protons are released. However, since one proton is consumed for the oxidation of ferrous to ferric, only four protons are actually produced (Evangelou, 1995). Upon initiation of pyrite oxidation, the ferric iron can be reduced by the pyrite itself, as shown in **Reaction 4** (Stumm and Morgan (1970), Singer and Stumm (1970)).

Therefore, pyrite continues to oxidise as long as ferric iron (Fe^{3+}) is generated. The conversion of ferrous to ferric is also the rate-limiting step in the oxidation of pyrite. However, since oxidation of ferrous to ferric in the pH-range of 3 is extremely slow (half-life in the order of 100 days), it appears that pyrite oxidation in this pH-range would be extremely slow, unless oxidation of ferrous at low pH is catalysed by micro-organisms (Singer and Stumm, 1970). In the pH-range of 2.5 - 3.5 (Jaynes *et al.*, 1984), *Thiobacillus ferrooxidans* rapidly oxidise ferrous iron to ferric iron. Iron-oxidising bacteria can accelerate the rate of Fe^{2+} oxidation by a factor of 10^6 (Singer and Stumm (1970), Dugan (1975)). Also, sulphur-oxidising bacteria such as *T. thiooxidans and T. ferrooxidans* can eliminate the need for ferric iron when in the presence of oxygen and some organic substrate (Evangelou, 1995). The reactions shown by 1-4 have also been summarised by Nordstrom (1982) in Figure 4. At low pH (<4.5) pyrite is oxidised by Fe^{3+} much more rapidly (Appelo and Postma, 1993) than by O_2, and more rapidly than dissolved Fe^{2+} is oxidised by O_2 to Fe^{3+} (Evangelou, 1995). This process rapidly consumes all Fe^{3+} and pyrite oxidation would cease unless Fe^{3+} is replenished by the process of oxidation of Fe^{2+} by oxygen (Appelo and Postma, 1993). For this reason,

Reaction 2 is known to be the rate-limiting step in abiotic pyrite oxidation (Singer and Stumm, 1970).

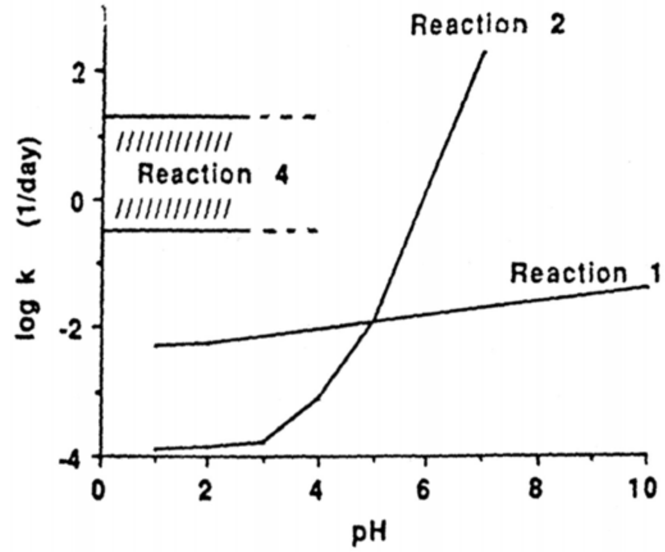


Figure 4. Comparison of rate constants as a function of pH for Reactions 1, 2 and 4 (from Evangelou, 1995).

T. ferrooxidans is an acidophilic chemolithotrophic organism that is ubiquitous in geologic environments containing pyrite (Nordstrom, 1982). Thus, in the presence of *T. ferrooxidans* and under low pH-conditions, pyrite oxidation can be described by **Reactions 2** and **4**. **Reaction 3** taking place at pH-values as low as 3, is a readily reversible dissolution/precipitation reaction that serves as a source as well as a sink of solution Fe^{3+} and is a major step in the release of acid to the environment (Evangelou, 1995). The red colour often seen in streams receiving acid mine drainage is actually a stain on the rocks called "Yellow Boy" or Ferrous Hydroxide ($Fe(OH)_3$) formed during **Reaction 3** (AMD Chemistry, 1997).

Acidity is caused by the liberation of hydrogen ions (H^+) in three of the four reaction steps.

The overall chemical reaction can be simplified to:

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

In the above reaction, every mole of pyrite yields four moles of acidity (Cohen (1996), Durkin and Herrmann (1996), Kempton *et al.* (1997) and Morin and Hutt (1994)). Observe the necessity for air and water (although the process can occur in a dry environment) (Cohen, 1996). **Reactions 1-4** can also be seen in the model (Figure 5) by Stumm and Morgan (1981).

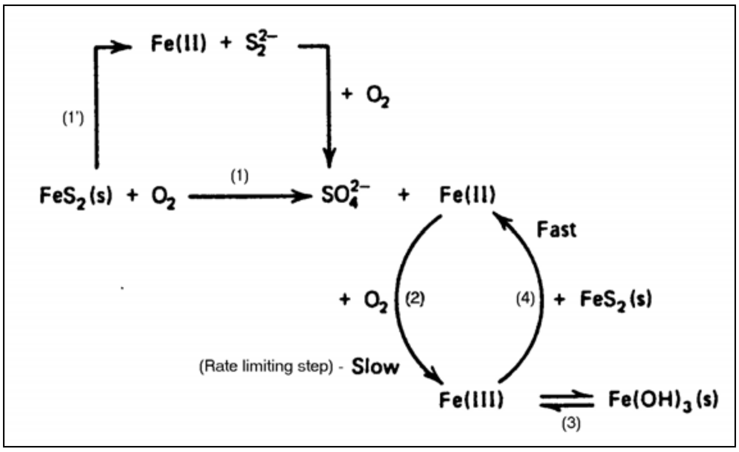


Figure 5. Model for the oxidation of pyrite (from Stumm and Morgan, 1981).

During the initial stage, pyrite oxidation is a relatively slow process (Ivanov, 1962). Most iron released during the initial stages of pyrite oxidation ends up as iron hydroxide, due to the relatively high pH on pyrite surfaces (Fornasiero *et al.,* 1992 and Ivanov, 1962). However, as acid production continues and the pH in the vicinity of the pyrite surface drops below 3.5, formation of ferric hydroxide is hindered and activity of Fe^{3+} in solution increases. Under these conditions, oxidation of pyrite by Fe^{3+} becomes the main mechanism for acid production in mining waste (Singer and Stumm, 1970 and Moses *et al.,* 1987). Singer and Stumm (1970) reported that Fe^{3+} can oxidise pyrite at a much higher rate than O_2. This can be seen in Figure 5 for the oxidation of pyrite (Stumm and Morgan, 1981) and in the following reaction (Evangelou and Zhang, 1995):

$$FeS_2 + 14Fe^{3+} + 8H_2O \Leftrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

-------O_2---------------

Iron-oxidising bacteria

It has been reported that pyrite in mining waste or coal overburden is initially oxidised by the atmospheric O_2, producing H^+, SO_4^{2-} and Fe^{2+}. The Fe^{2+} can be further oxidised by O_2 into Fe^{3+} that in turn hydrolyses and precipitates as amorphous iron hydroxide releasing additional amounts of acid (Nordstrom, 1982).

In addition to pyrite, the presence of both oxygen and water is required for process progression (Evangelou, 1995 and Mills, 1998a). The process is complex because it involves chemical, biological and electrochemical reactions and varies with environmental conditions. Factors such as pH, pO_2, specific surface and morphology of pyrite, presence or absence of bacteria and/or clay minerals, as well as hydrological factors, determine the rate of oxidation. There is, therefore, no single rate law available to describe the overall kinetics of pyrite oxidation for all cases (Evangelou, 1995). This has important ramifications in that removal of the oxygen source (e.g. by total submersion under water) or the water source (e.g. conditions of aridity) will halt AMD production. AMD production would also be considerably slowed or halted by the termination of *T. ferrooxidans* reproduction by a bactericidal agent. The end products are sulphuric acid and ferric sulphate. Sulphuric acid is also an important intermediate product. From the onset of pyrite oxidation, pH falls (acidity increases) quickly and then stabilises, typically at values around pH 2.5 to 3.0. The pH of stabilisation is normally determined by the optimal habitat requirement of the site-specific strain of bacteria (Mills, 1998a).

If pyrite and/or pyrrhotite are the only sulphide minerals open to atmospheric oxidation, the products of the oxidation process are those described above. Depending upon the availability of water and oxygen, reactions may not always approach completion and in such cases intermediate phases of chemical compounds or minerals may remain at the oxidation site.

The reaction of sulphuric acid with pyrite is described by Levinson (1974):

$$FeS_2 + H_2SO_4 \Leftrightarrow FeSO_4 + H_2S + S$$

This accounts for the presence of small amounts of native sulphur at outcrops. This could also explain why H_2S is a common gas around coal mines and mine dumps, other than the H_2S which is ascribed to bacterial sulphate reduction.

If metallic minerals (such as galena (lead sulphide, PbS), chalcopyrite (iron-copper sulphide, FeS.CuS), sphalerite (zinc sulphide, ZnS)) in addition to pyrite and pyrrhotite are present, there may be a secondary effect of the oxidation of the iron-sulphur minerals to sulphuric acid and ferric iron (Mills, 1998a).

The stable pH developed (2.5-3.0) and the products of sulphuric acid and ferric sulphate create conditions where the ferric iron ion itself can act as an oxidant. In the absence of ferric iron at pH 2.5-3.0, sulphuric acid will dissolve some heavy metal carbonate and oxide minerals, but has little reactive effect on heavy metal sulphides. However, ferric iron ion is capable of dissolving many heavy metal sulphide minerals, including those of lead, copper, zinc and cadmium, by the general reaction:

$$MS + nFe^{3+} \Leftrightarrow Mn^{+} + S + nFe^{2+} \quad (7)$$

Where: MS = solid heavy metal sulphide; Fe^{3+} = aqueous ferric iron ion; Mn^{+} = aqueous heavy metal ion; S = sulphur; Fe^{2+} = aqueous ferrous iron ion.

This process, together with the acidic environment, allows significant amounts of heavy metals to be solubilised by AMD. In addition, many metallic elements are often present at trace levels within the minerals pyrite and pyrrhotite. Oxidation of these minerals can therefore release and mobilise these trace elements.

Untreated (not neutralised) AMD creates two quite distinct environmental problems - the acidity from sulphuric acid (which is invariably a product by definition) and the heavy metal solubilisation caused by ferric iron (which may occur under the conditions described above). It is important that these two effects be recognised as separate, since their consequences to ecosystems are distinct, and because AMD generation and heavy metal transport are separate processes (Mills, 1998a).

2.2.1 REACTION MECHANISMS

Fe^{3+} is the major pyrite oxidant in the acidic pH region, while O_2 is expected to be the direct pyrite oxidant at neutral to alkaline pH (Stumm and Singer, 1970). Moses *et al.* (1987) demonstrated that Fe^{3+} might be a very effective oxidant at circum neutral pH. Pyrite oxidation over the pH-range of 2 - 9 was favoured in the presence of Fe^{3+}, as opposed to dissolved O_2 and a low concentration of Fe^{3+} was very effective in oxidising pyrite. Luther (1987) explained that the faster rate of pyrite oxidation by Fe^{3+} was due to the fact that Fe^{3+} can bind chemically to the pyrite surface whereas O_2 cannot.

2.2.2 THE ROLE OF MICRO-ORGANISMS IN THE SULPHUR CYCLE

Micro-organisms (most frequently bacteria) are often integrally involved in the chemical alteration of minerals. Minerals, or intermediate products of their decomposition, may be directly or indirectly necessary to their metabolism. The dissolution of sulphide minerals under acidic conditions (AMD), the precipitation of minerals under anaerobic conditions, the adsorption of metals by bacteria or algae and the formation and destruction of organometallic complexes are all examples of indirect micro-organism participation. Where minerals are available as soluble trace elements, they serve as specific oxidising substrates, or are electron donors/acceptors in oxidation-reduction reactions, they may be directly involved in cell metabolic activity (Mills, 1998b).

2.2.2.1 OXIDATION PROCESSES

Oxidation of sulphur or sulphides for energy production is restricted to the bacterial genus *Thiobacillus*, *Thiomicrospira* and *Sulfolobus*. These bacteria all produce sulphuric acid as a metabolic product. These bacteria are known to accelerate the generation of AMD from pyritic and pyrrhotitic rocks under suitable conditions. Domenico and Schwarz (1990) and Singer and Stumm (1970) report that sulphide oxidation catalysed by bacteria may have reaction rates six orders of magnitude (i.e. 1,000,000 times) greater than the same reactions in the absence of bacteria.

AMD is the product formed by the atmospheric (i.e. by water, oxygen and carbon dioxide) oxidation of the relatively common iron-sulphur minerals pyrite and pyrrhotite in the presence of bacteria (*Thiobacillus ferrooxidans*) and any other products generated as a consequence of these oxidation reactions.

An important reaction involving *T. ferrooxidans* is the oxidation of ferrous to ferric iron (Fe^{2+} to Fe^{3+}).

$4Fe^{2+} + O_2 + 4H^+ = Fe^{3+} + 2H_2O$ (rate limiting step)(Singer and Stumm, 1970)

Ferric iron is a powerful oxidising agent. Even at a Fe^{3+}/Fe^{2+} ratio of 1:1,000,000, a Redox potential of greater than +0.4 V is generated, which is sufficient for the attack of most base metal sulphides (Dutrizac and MacDonald, 1974). Consequently *T. ferrooxidans*, in generating Fe^{3+}, is indirectly responsible for the dissolution of base metal sulphide minerals and the mobilisation of metallic cations such as Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+}. Base metal sulphides react only very slowly with sulphuric acid in the absence of ferric iron (Roman and Benner, 1973). The importance of Redox potential in determining metal solubility and transport can be clearly seen for copper in the Eh-pH diagram for the $Cu-H_2O-O_2-S-CO_2$ system (from Garrels and Christ, 1965).

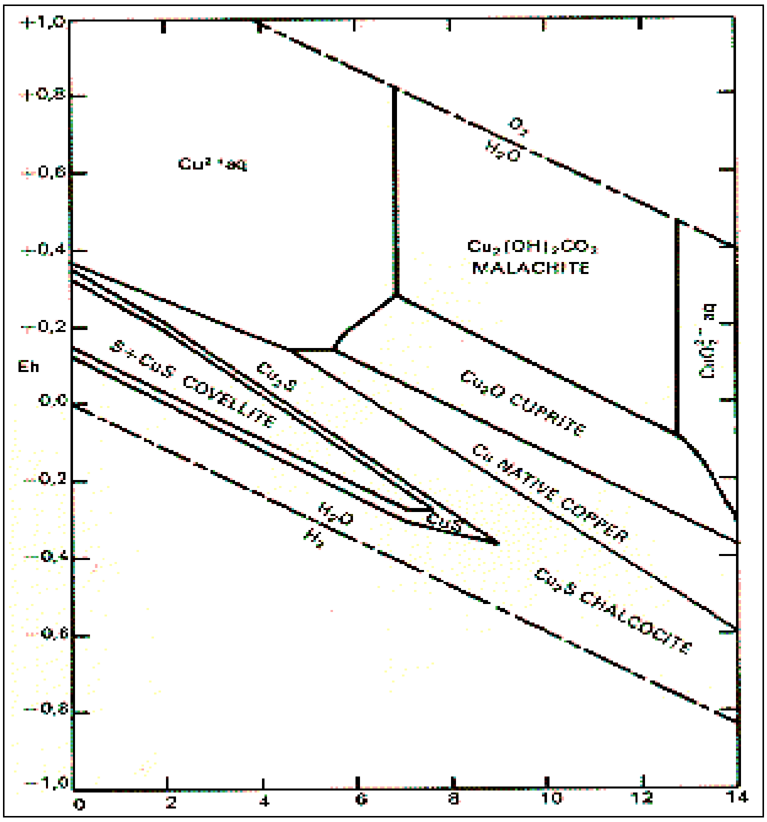


Figure 6. Eh-pH diagram for $Cu-H_2O-O_2-S-CO_2$ system (from Garrels and Christ, 1965).

The effects of bacteria upon the rate of dissolution of sulphate from pyrite are highly pronounced, as demonstrated by Scharer *et al.* (1991).

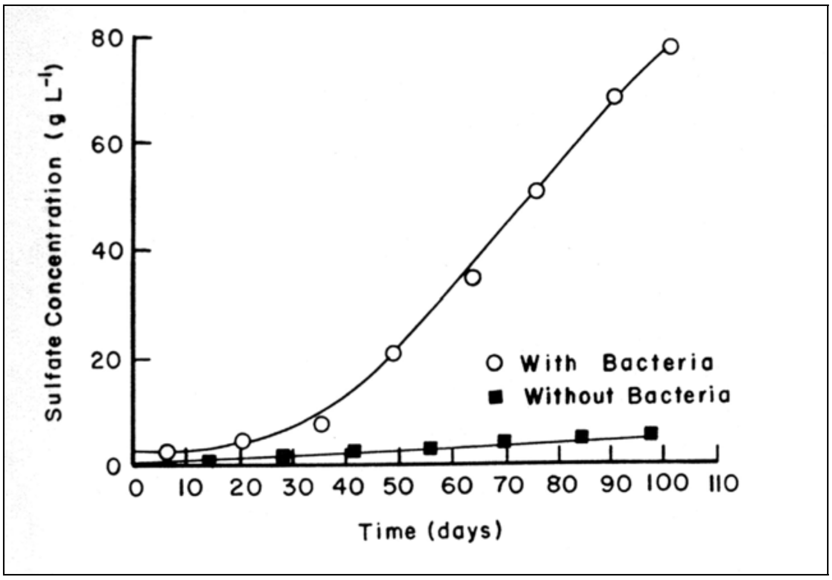


Figure 7. Pyrite oxidation kinetics in mine waste at 21°C and pH 3 in the presence and absence of bacteria (from Scharer et al., 1991).

The typical pH habitat of *T. ferrooxidans* of 1.5 to 3.5 does not develop spontaneously. It is currently believed (Mills, 1998b) that these conditions are produced by a consortium of bacteria acting in succession. Such a succession may include *T. thioparus* at neutral pH, giving way to dominance by metallogenium bacteria under mildly acid conditions (pH 3.5 to 4.5) (Walsh and Mitchell, 1972) and finally *T. ferrooxidans* dominance at low pH. Maximum activity is reached around pH 3.2 (Figure 8), whereas minimum activity is reached at approximately pH 1.5 and pH 5 (Jaynes *et al.,* 1984).

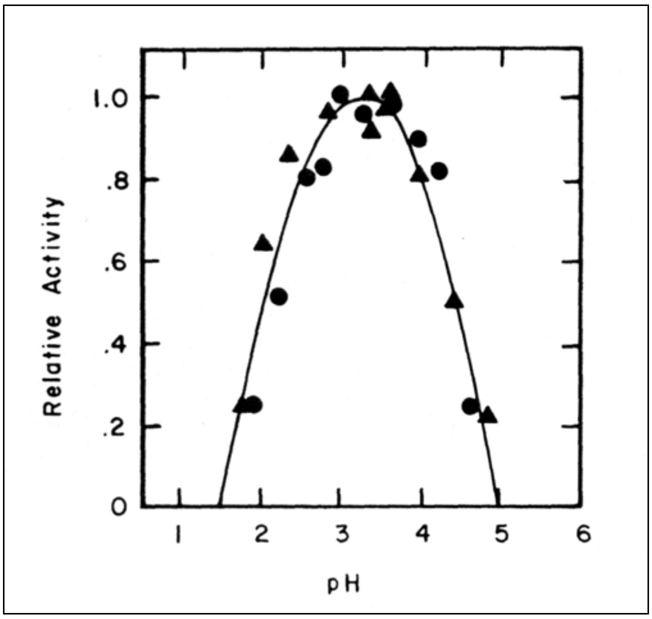


Figure 8. Influence of pH on relative activity of ***T. Ferrooxidans*** *(from Jaynes et al., 1984).*

The metabolic activity of *T. ferrooxidans* is temperature dependent, with an optimum at 30-35°C and falling with both increasing and decreasing temperature, reaching a minimum at approximately 5°C and 55°C (Roman and Benner (1973), Jaynes *et al.* (1984)).

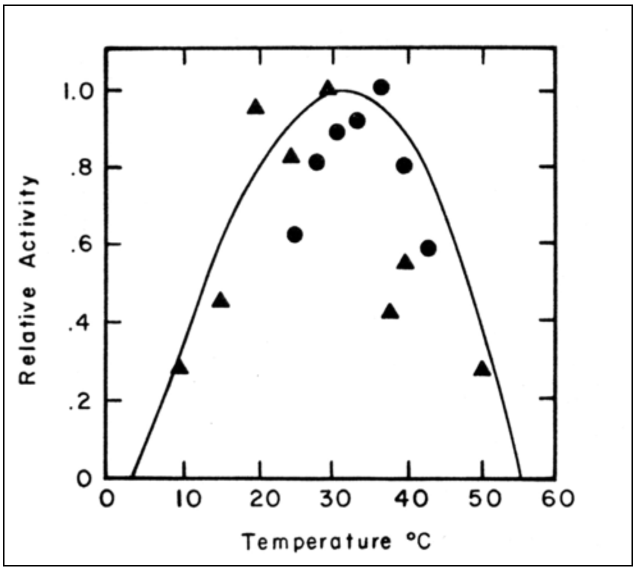


Figure 9. Influence of temperature on relative activity of ***T. ferrooxidans*** *(from Jaynes et al., 1984).*

The data in Figure 10 show that *T. ferrooxidans* (obligate aerobes) activity ceases when O_2 is depleted. However, bacterial activity resumes even under extremely small increases in O_2 content and reaches a maximum at approximately 0.01 mole fraction of O_2 or 1% (Jaynes *et al.,* 1984).

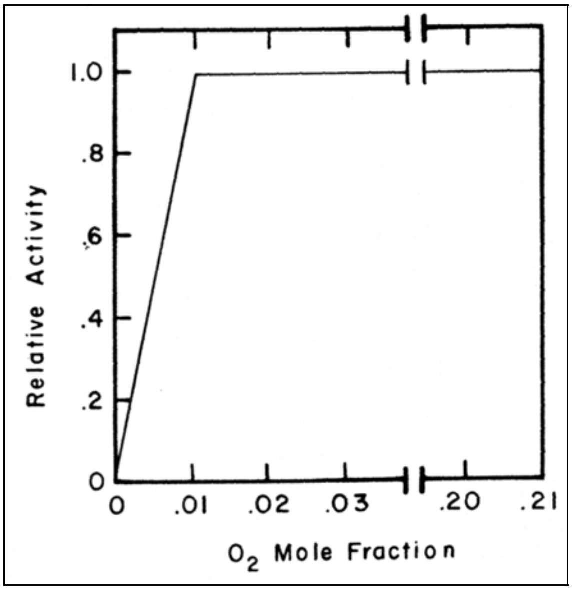


Figure 10. The influence of O_2 concentration on relative activity of ***T. ferrooxidans*** *(from Jaynes et al., 1984).*

The kinetics of acid generation can be seen in Figure 11 below. In the absence of biologically catalysed oxidation, oxidation rates are relatively slow for all pH-conditions (Robertson, 1996).

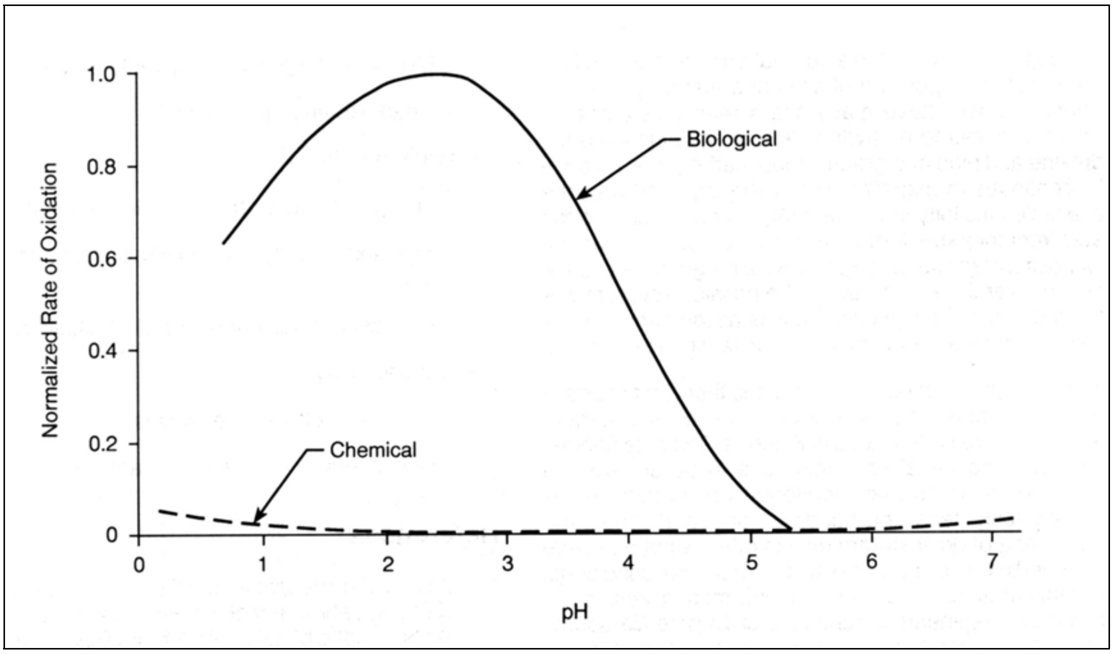


Figure 11. Kinetics of acid generation (from Robertson, 1996).

Leduc and Ferroni (1994) have demonstrated that *T. ferrooxidans* strains are site-specific. They are also capable of adaptation by mutation if their habitat is markedly changed (Mills, 1998a).

The importance of the iron-oxidising species *Leptospirillum ferrooxidans* is now widely accepted and this species can out complete *T. ferrooxidans* under certain conditions. Studies by Schrenk *et al.* (1998) showed that at a mining site at Iron Mountain, California, where the conditions associated with the ore body are below the normal pH and above the normal temperature for *T. ferrooxidans* (pH over 1.3 and temperatures around 30°C), *L. ferrooxidans* is extant over most of the range of conditions sampled. Conditions were generally >40°C and the pH 0.7- 1.0. *L. ferrooxidans* occurs in important subsurface acid-forming environments at temperatures of 30 - 50°C and pH 0.3 - 0.7 (American Geological Institute, 1998). Sulphuric acid-forming reactions are quite exothermic (Nordstrom and Munoz, 1987) and pH's in proximity to pyrite surfaces are likely to be much lower than those measured in bulk solution (Nordstrom and Southam, 1997). *L. ferrooxidans* had a much more controlling effect on AMD than *T. ferrooxidans* at Iron Mountain - the latter was essentially undetectable inside the mine where most acid drainage is found. The role of *L. ferrooxidans* is more significant in contact with the acid-generating ore body (American Geological Institute, 1998).

From the above discussion it is clear that consideration of bacterial behaviour is most important in understanding the process of AMD generation. This is particularly so when "kinetic" tests are used to predict the rate of generation of AMD in the field. Only if the bacterial conditions of test work are identical to those in the field, can rates of AMD generation and/or metal solubilisation be taken from laboratory kinetic test work and used to predict field behaviour with any degree of confidence (Mills, 1998b).

2.2.3 NATURAL REDUCTION IN THE SULPHUR CYCLE

This is the major natural process for the conversion (destruction) of sulphate ions (Warkentin and Rowley, 1994). The direct reduction of sulphate ions to hydrogen sulphide is effected in nature by specialised, strictly anaerobic bacteria of the genera *Desulfovibrio* and *Desulfotomaculum*. These sulphate-reducing bacteria (SRB) are organisms that utilise sulphate, thiosulphate, $S_2O_3^{2-}$, sulphite, SO_3^{2-}, or other reducible sulphur-containing ions as terminal electron acceptors in their respiratory metabolism. In the process, these sulphur-containing ions are reduced to hydrogen sulphide.

The bacteria require an organic substrate. In nature such substrates are generated by the fermentation activities of other anaerobic bacteria on more complex organic substrates. Lactate is used by the SRB during anaerobic respiration to produce acetate and hydrogen sulphide according to the reaction (Cork and Cusanovich, 1979):

$$2CH_3CHOHCOO^- + SO_4^{2-} = 2CH_3COO^- + 2HCO_3^- + H_2S$$

The process may be adapted to a controlled engineering process by the use of anaerobic reaction vessels, carbon monoxide, CO and hydrogen, H_2, or partially oxidised propane or natural gas, as the energy source for the bacteria. This process of sulphate ion to hydrogen sulphide conversion is the first stage of a pilot plant that operated in 1996 at the former Britannia mine site in British Columbia, where the second stage utilised the hydrogen sulphide generated to precipitate copper (Cu^{2+}), zinc (Zn^{2+}) and cadmium (Cd^{2+}) ions from AMD as metallic sulphides (Warkentin and Rowley, 1994). Steffen, Robertson and Kirsten (1991) proposed the use of the underground mine at Faro, YT, as a giant underground SRB reactor to convert AMD sulphate ion to hydrogen sulphide and precipitate zinc contained in the AMD as zinc sulphide. SRB activity in natural wetlands is capable of metal sulphide precipitation from AMD as a result of sulphate to hydrogen sulphide reduction. This concept may be extended to constructed wetlands (Mills, 1998b).

2.2.4 OTHER MICRO-ORGANISM REACTIONS IN THE SULHUR CYCLE

The sulphate ion is taken up from the soil by plants, which incorporate it into protein. Plant protein is consumed by animals and converted to animal protein. Death of plants and animals allows bacterial decomposition of protein in remains to produce hydrogen sulphide and other products in processes involving many fungi, actinomycetes and bacteria such as the heterotroph, *Proteus vulgaris*.

Some bacteria can function in the transition zone between aerobic and anaerobic environments. Hydrogen sulphide may be oxidised to sulphur by bacteria that deposit elemental sulphur in their cells while using oxygen as the terminal electron acceptor.

Hydrogen sulphide may also be oxidised to sulphate photosynthetically by the bacteria *Chromtiacceae* and *Chlorobiaceae* (Mills, 1998b).

2.3 BASIC CHEMISTRY OF AMD NEUTRALISATION

Acid mine drainage depletes the buffering ability of water by neutralising carbonate and bicarbonate ions to form carbonic acid (H_2CO_3) (AMD Chemistry, 1997).

$H^+ + CO_3^{2-} \Leftrightarrow HCO_3^-$

$H^+ + HCO_3^- \Leftrightarrow H_2CO_3$

Once exposed to acid mine drainage, the affected carbonate buffering system is not able to control changes in pH as effectively. The buffering system is completely destroyed below a pH of 4.2 where all carbonate and bicarbonate ions have been converted to carbonic acid. The carbonic acid readily breaks down into water and carbon dioxide (AMD Chemistry, 1997).

$H_2CO_3 \Rightarrow H_2O + CO_2$ (AMD Chemistry (1997), Todd and Reddick (1997))

If the pH of AMD is increased, as would happen with contact with basic minerals such as calcite ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$) or entry into a water system of higher pH, then metallic ions such as Fe^{3+} and Cu^{2+}, Zn^{2+}, Pb^{2+} and As^{3+} will react to eventually form hydroxides as precipitates by the general reaction:

$Mn^+ + nOH- \Leftrightarrow M(OH)_n$

where: OH^- = hydroxyl ion; $M(OH)_n$ = metal hydroxide.

This over-simplification represents chemical neutralisation as it occurs by human intervention, rather than an accurate portrayal of natural occurrence, where the precipitation products are usually carbonates and sulphates and their hydrated and/or hydroxy-complex forms. In nature, acid-generating minerals such as pyrite often occur in close association with acid-neutralising minerals such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) and acid produced from pyrite is neutralised *in situ* by these minerals. The sulphate most commonly formed is gypsum ($CaSO_4.2H_2O$), which is sparingly soluble in water and which therefore contributes to elevated sulphate levels in ground and surface waters (Shaw and Mills, 1998). Small amounts of minerals, naturally present in the waste, can buffer the acid produced in the unsaturated zone, (Morin *et al.*, 1998).

Factors that determine the neutralisation rate by carbonate and silicate minerals include: pH, pCO_2, equilibrium conditions, temperature and the presence of “foreign” ions. Comparison of rates shows that sulphides react fastest, followed by carbonates and silicates (Sherlock *et al.,* 1995).

2.3.1 CARBONATE SYSTEMS

The carbonate system is predominant in controlling the buffering intensity and neutralising capacity of natural waters and represents a complex system involving the transfer of carbon among three phases: solid, liquid and gas. When $CO_{2(g)}$ is brought into contact with water, it will dissolve, forming carbonic acid (H_2CO_3) until an equilibrium state is reached. Depending on the pH of the solution, the carbonic acid will tend to dissociate to hydrogen, bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. The dominant species in solution being H_2CO_3pH<6,3; HCO_3^- 6,3<pH<10,3; and CO_3^{2-} pH>10,3 (Sherlock *et al.,* 1995). The presence or absence of a gas phase is probably the most important factor in controlling the final carbonate equilibrium in water. If the water is pore water or surface water in contact with a gas phase, then carbon dioxide is able to enter the solution and when calcite dissolution occurs, it is referred to as "open system dissolution". In "closed system dissolution" conditions, such as groundwater below water table or tailings ponds below the surface, no gas phase is present to furnish carbon dioxide to solution when calcite dissolves. The solubility of calcite will be different for open and closed systems. Most notable is the increased solubility of calcite within the CO_2-H_2O-$CaCO_3$ (open) system relative to the H_2O-$CaCO_3$ (closed) system at 25°C (Stumm and Morgan, 1981).

Calcite is assumed to consume 2 moles H^+ per mole C, according to the following reaction:

$CaCO_3 + 2H^+ \Leftrightarrow Ca^{2+} + H_2O + CO_{2(g)}$ (Kempton *et al.*, 1997)

The S:C ratio for complete neutralisation of acid from sulphide S by carbonate C (AP:NP) can range between 1:1 and 1:2 (Kempton *et al.,* 1997).

Open System

$FeS_2 + 2CaCO_3 + 3{,}75O_2 + 1{,}5H_2O \Leftrightarrow Fe(OH)_3 + 2SO_4^{2-} + 2Ca^{2+} + 2CO_2$ (carbon dioxide exsolves into the atmosphere)

Acidity produced from 1 mole of FeS_2 (64 g sulphur) is neutralised by 2 moles of $CaCO_3$ (200 g) or 1 g sulphur: 3.125 g $CaCO_3$ (Brady *et al.,* 1994).

Closed System

$FeS_2 + 2CaCO_3 + 3{,}75O_2 + 3{,}5H_2O \Leftrightarrow Fe(OH)_3 + 2SO_4^{2-} + 2Ca^{2+} + 2H_2CO_3$ (carbon dioxide dissolve in water)

H_2CO3 reacts with carbonate in the following reaction:

$H_2CO_3 + CaCO_3 \Leftrightarrow Ca2+ + 2HCO_3^-$

A second reaction depicting the maximum calcium carbonate requirements for acid neutralisation in a closed system may therefore be written as:

$FeS_2 + 4CaCO_3 + 3{,}75O_2 + 3{,}5H_2O \Leftrightarrow Fe(OH)_3 + 2SO_4^{2-} + 4Ca^{2+} + 4HCO_3^-$ (Lloyd and Heathcote (1985), Cravotta *et al.* (1990)).

In this reaction 1 mole of FeS_2 is neutralised by 4 moles of $CaCO_3$, which results in a mass ratio of 1 g pyrite: 6.25 g calcite. MPA (units of mt$CaCO_3$/ 1000mt) is therefore calculated as percent sulphur times 62.5 (Brady *et al.,* 1994). To neutralise the pyrite-derived acidity to neutral levels (pH 7), twice as much calcite is needed to neutralise to slightly acidic levels (pH 4) (Morin and Hutt, 1994). Realistic conditions for the coal mines lie somewhere between the open and closed system, with a tendency towards the closed system (Krantz, 1993). According to Li (Personal Communication, 2000) waste rock piles up to tens of metres react like open systems while tailings usually approximate closed systems below the surface level. He stresses the importance of verifying an open/closed system assumption with the measurement of pore gasses, particularly in critical or borderline cases. Thus, when working in a closed system, the ratio of S:C (AP:NP) will be 1:4.

Calcite neutralisation reaction (calcite dissolution by sulphuric acid):

$H_2SO_4 + CaCO3 = CaSO_4 + H_2O + CO_2$

Dolomite neutralisation reaction (dolomite dissolution by sulphuric acid):

$2H_2SO_4 + CaMg(CO_3)_2 = CaSO_4 + MgSO_4 + 2H_2O + 2CO_2$ (Evangelou, 1995 and Shaw and Mills, 1998).

Calcite treated “waste” is expected to produce better quality leachate than dolomite treated “waste” in terms of SO_4 concentration (Evangelou, 1995).

2.3.2 DISSOLUTION RATE

Temperature is an important factor that controls the dissolution rate of carbonates and silicates as well as the oxidation of sulphides. In general, the change of mineral solubility is proportional to the change in temperature, i.e. an increase in temperature increases the mineral solubility. (Rate constants can change by several orders of magnitude as the temperature is varied by 100°C). The reason for this lies in the exponential dependence on the temperature of the reaction rate constant, which can follow the Arrehenius equation:

$$K = A\, e^{-(Ea/RT)}$$

where A is the pre-exponential factor and Ea the activation energy (Lasaga, 1984)

Exceptions to this, however, include calcite and gypsum, where an increase in temperature results in a decrease in solubility (Morel and Hering, 1993), due to a change in thermodynamic properties. In mining wastes containing carbonates and sulphides, increased temperatures due to exothermic oxidation reactions will increase the oxidation rate but could decrease carbonate solubility, resulting in reduced neutralisation capacity (Sherlock *et al.,* 1995). Sherlock *et al.* (1995) also state that in AMD solutions the presence of significant cation and sulphate concentrations could lead to a decrease in carbonate solubility.

2.3.3 OTHER MINERALS

Other minerals, including some silicates such as plagioclase feldspar, may also neutralise acid produced by sulphide mineral oxidation. Under certain conditions the outflow quality is controlled by depletion of sequential buffering phases - carbonates, hydroxides (gibbsite etc.) followed by aluminosilicates (Ptacek and Blowes, 2000). Usually rates can be orders of magnitude slower than acid-production rates and the oxidation reactions will dominate (Shaw and Mills (1998), Sherlock *et al.* (1995)). Reactions of other gangue minerals may also contribute to the neutralisation potential of the 'system' under specific pH conditions (Ritchie, 1994) for example:

Muscovite dissolution:

$KAl_2[AlSi_3O_{10}](OH)_{2(s)} + H+ + 3/2H_2O => K^+ + 3/2Al_2Si_2O_5 (OH)_{4(s)}$

Biotite dissolution:

$KMg1.5Fe1.5AlSi_3O_{10}(OH)_{2(s)} + 7H+ + 1/2H_2O => K^+ + 1.5 Mg^{2+} + 1.5 Fe^{2+} + H_4SiO_4 + 1/2Al_2Si2O_5 (OH)_{4(s)}$

Albite dissolution:

$NaAlSi_3O_{8(s)} + H^+ + 9/2H_2O => Na^+ + 2H4SiO_4 + 1/2Al_2Si_2O5(OH)_{4(s)}$

Anorthite dissolution:

$CaAl_2Si_2O_{8(s)} + 2H^+ + H_2O => Ca^{2+} + Al_2Si_2O_5(OH)_{4(s)}$

K-feldspar dissolution:

$KAlSi_3O_{8(s)} + H^+ + 9/2H_2O => K^+ + 2H_4SiO04 + 1/2Al_2Si_2O_5 (OH)_{4(s)}$

Iron oxy-hydroxide dissolution:

$Fe(OH)_{3(s)} + 3H^+ => Fe^{3++}$

The dissolution rate of these elements is slow in the neutral pH-range; they dissolve more rapidly as pH decreases (Lapakko, 1994) and therefore provide more acid neutralisation under acidic conditions. The rate of dissolution is too slow to maintain the pH of drainage above 6.0. Where the rate of acid production is high, these minerals therefore usually serve to return the system to more neutral pH-values after the acid production has ceased.

One mole of calcium feldspar (anorthite) around neutral pH neutralises two moles of acidity and thus this mineral can be twice as effective per mole as calcite at neutral pH (Morin and Hutt, 1994).

The following table (Table 1) has appeared in several publications regarding AMD (SRK (1989), Hodgson and Krantz (1995), James (1997) and van Niekerk (1997)):

Table 1. Buffering pH of some common minerals as reported in several publications.

Mineral	Composition	Buffer pH
Calcite	CaCO3	5.5 - 6.9
Dolomite	CaMg(CO3)2	5.3 - 6.8
Siderite	FeCO3	5.1 - 6.0
Kaolinite	Al2Si2O5(OH)4	3.7 - 4.3
Gibbsite	Al(OH)3	3.7 - 4.3
Ferric hydroxide	Fe(OH)3	3.3 - 3.7
Goethite	FeO(OH)	2.1 - 2.2

This table is somewhat misleading, as it suggests that minerals such as kaolinite and siderite are effective buffers in the overall process. A further factor that needs to be considered when regarding buffering pH-levels of minerals is the partial pressure of carbon dioxide and the rate at which acid generation takes place. Li (Personal Communication, 2000) suggests that reporting buffering levels of carbonates without giving the partial P_{CO2} is misleading as this has a major influence on the pH at which buffering occurs. This will be expanded upon in Section 5.4.

The science and understanding of AMD generation is still developing and there are some mining operations in BC that were developed and operated without the benefit of current knowledge. As a consequence, these mines do generate AMD, which has to be treated by neutralisation. In the metal mines, particularly in British Columbia, AMD is neutralised with lime (CaO) to reduce acidity and to precipitate metals - an expensive and long-term necessity (Mills, 1998a). Although silicate alteration has been shown to contribute to AMD neutralisation and heavy metal attenuation under field conditions (Lapakko, 1994 and Sherlock *et al.,* 1995), reactions are relatively slow and their short- and long-term contribution to the behaviour of wastes needs further understanding (Lawrence and Wang, 1997).

Table 2. Relative Mineral Reactivity at pH5 (from Sverdrup, 1990 and Kwong, 1993).

MINERAL GROUP	TYPICAL MINERALS	RELATIVE REACTIVITY AT pH 5
Dissolving	Calcite, aragonite, dolomite magnesite, brucite	1.0
Fast weathering	Anorthite, nepheline, olivine. garnet, jadeite, leucite, spodumene, diopside, wollastonite	0.6
Intermediate weathering	Epidote, zoisite, enstatite, hypersthene, augite, hedenbergite, hornblende, glaucophane, tremolite,actinolite, gnthophyllite, serpentine, chrysotile, talc, chlorite, biotite	0.4
Slow weathering	Albite, oligoclase, labradorite, montmorillonite, vermiculite, gibbsite, kaolinite	0.02
Very slow weathering	K-feldspars, muscovite	0.01
Inert	Quartz, rutile, zircon	0.004

Kwong (1993) suggested that all of the minerals in the Dissolving, Fast and Intermediate weathering groups (Table 2) be considered as having a practical neutralising capability in the field. In nature, the neutralisation of AMD, either *in situ* or at some distance from the source of generation, results in a difference in rock appearance (oxidised and different in texture and colour from the host rock) and/or additions to bottom sediments or sediment particle surfaces (including rocks and boulders in watercourse beds). Here again, geologists use natural effects as aids in mineral exploration, since the oxidised rock (called gossans) and sediment chemistry are indicative of potential mineral deposits. Gossans, in particular, have been a target of mineral prospectors (as they generally have a reddish-brown to yellow-ochre colour) throughout human history and there are many examples of gossan discovery leading to important economic mining operations.

Minerals are also formed as a result of AMD processes, some of which are rare and highly prized by mineral collectors (e.g. boleite), some are used for jewellery (e.g. malachite) and some form mineral deposits (e.g. chalcocite).

It must be understood that the above is a highly simplified description of the basic chemistry of AMD. For example, the precipitation of hydroxides or related chemicals is dependent upon the aqueous concentration of a metal, the pH and the reduction/oxidation (Redox) potential of the solution as well as the concentrations of other ions. The chemistry of real AMD systems is extremely complex (Mills, 1998a).

2.4 OCCURRENCE OF AMD IN SOUTH AFRICA

AMD in South Africa is associated with the coal and mineral (mainly gold) mining fields. Pyrite is an ubiquitous gangue mineral occurring with metal deposits and occurs associated with the shale and coal seams in the South African coal deposits.

2.4.1 COAL and AMD IN SOUTH AFRICA

Coal occurs in thick seams and is fairly shallow (De Jager, 1992). 40 % of South Africa's coal is produced from opencast mining (Krantz, 1993). Coal occurs in die Karoo System (De Jager, 1992) and no coal will be found underneath the Dwyka series (Plumstead, 1957). A variety of minerals can be found in South African coalfields: silica, feldspar, clay and pyrite. The first three are in a non-reactive state due to their bonding with silica. Through weathering some of the elements can be released. Pyrite and the carbonates, however, are the most reactive (Hodgson, 1992).

As an illustration, in the Witbank Dam Catchment, a total sulphate production of 45 - 90 t/d (average 70 t/d) is produced by opencast mines, largely due to AMD (Hodgson and Krantz, 1995). Extrapolation of this to include future opencasting at existing mines, the sulphate contribution can escalate to an anticipated value of 120 t/d. The latter translates into a sulphate concentration in the Witbank Dam of 450 mg/L. The cumulative consequence of AMD processes on a catchment scale is therefore significant enough to warrant detailed investigation into predictive and management tools.

3 PREDICTION METHODS

Accurate prediction potentially offers the most cost-effective means of reducing the impact of AMD on the environment and the associated costs by allowing advanced planning for prevention and control. The objective of a prediction program is to reduce uncertainty to a level at which potential risk and liability can be identified and effective extraction, waste handling and, where necessary, mitigation and monitoring strategies can be selected (Price, 1998).

A predictive program for AMD involves carrying out a number of integrated and iterative tests, analyses and procedures to assess the future behaviour of mine wastes and other components. Predictive tests vary in complexity of procedure and data interpretation, the time required to achieve a predictive result and cost. It is highly unlikely that any one test can produce all the information necessary to evaluate all mine wastes. Combinations of tests are required to provide a reliable assessment. The scope of a prediction program will depend on site-specific conditions and factors. Some programs might comprise a few simple tests requiring only a relatively short time period and a modest budget. Others can involve extensive testing and analysis lasting several months or even more than 1-2 years, with much higher costs. The approach required might include some or all of the following (Price,1998):

- Initial assessment and site reconnaissance.
- Sampling.
- Chemical, mineralogical and physical analyses.
- Short-term leaching tests.
- Geochemical static tests.
- Geochemical kinetic tests.
- Mathematical models.

These steps in the prediction are currently applied inconsistently in South Africa. The result is that results from AMD prediction programs vary greatly and no uniformity is applied in the interpretation of results. It is this issue that this report intends addressing.

Prediction programs are most commonly associated with new mine projects to assist in the development of plans to store waste and the final close-out of open pit and underground workings in a manner that AMD generation can be prevented or minimised. However, environmental and economic liabilities need to be assessed for existing operations to assess the possible extent of AMD at the site, to implement appropriate control methods into the waste management plan where no or inadequate measures were previously practised and to plan for eventual closure. Similarly, prediction can be used at abandoned mines to allow development of plans for control, remediation and final closure.

The key questions in most prediction programs are:

- Is there a potential for AMD generation?
- Will the potential for acid generation be realised?
- When will the AMD be generated?
- How much AMD will be generated?
- For how long will AMD be generated?
- What will the water quality be?
- Will control measures work?
- Will the mine remain in compliance?

Every prediction program must include the following three steps (Price, 1998):

- Identify and describe all geological materials excavated, exposed or otherwise disturbed by mining.
- Predict the Metal Loading/AMD potential and, where applicable, the timing for each geological material in the forms and environmental conditions in which it will be exposed.
- Develop a mitigation and monitoring program based on the predicted AMD potential and environmental protection needs.

Mechanisms of acid generation and the controls that affect ultimate water quality can vary significantly. Thus AMD generation and transport in a waste rock pile is different from that in a tailings impoundment. In waste rock, air infiltration can occur at the dump at any point and is relatively rapid due to convection and barometric pumping. In tailings, however, air infiltration occurs only at the surface and is limited by the rate of diffusion. Diffusion rates in tailings are, in turn, dependent on the moisture content, with rates extremely slow in areas with high moisture content or saturation (Lawrence, 1997a). All test results have to be extrapolated into the future. **Predictive capability is best achieved by using a combination of data sets and methods, rather than by reliance on any single procedure** (Cravotta, 1997).

3.1 Static Methods

Generally when Acid-Base Accounting is referred to,it is the so-called static methods, which are involved. These are screening methods to determine the difference between the acid-generating capability and the acid-neutralising potential of a particular sample.

Acid-Base Accounting (ABA) is a screening procedure whereby the acid-neutralising potential (assets) and acid-generating potential (liabilities) of rock samples are determined and the difference (net neutralising potential (equity)) is calculated. The net neutralising potential and/or the ratio of neutralising potential to acid-generation potential, are compared with a predetermined value, or set of values, to divide samples into categories that either require, or do not require, further determinative acid potential test work. Just as different methods of accounting present different sets of books to an auditor, so different methods of conducting ABA test work will generate different sets of sample data for evaluation. Rules and guidelines have been developed by mine regulatory and permitting agencies (e.g. Price and Errington (1995), Steffen, Robertson and Kirsten (1992), Miller (1995) and Brady *et al.* (1994)) for ABA procedures that may be likened to the rules and guidelines of financial accounting (Mills, 1998c). ABA indicates the overall balance of acidification potential (AP) and neutralisation potential (NP) (Schafer Laboratory, 1997).

In its most basic form, ABA is simply a screening process. It provides no information on the speed (or kinetic rate) with which acid-generation or -neutralisation will proceed and because of this limitation the test work procedures used in ABA are referred to as Static Procedures (Mills, 1998c and Ziemkiewicz, 1994).

The potential for a given rock to generate and neutralise acid is determined by its mineralogical composition. This includes the quantitative mineralogical composition and also individual mineral grain size, shape, texture and spatial relationship with other mineral grains. The term "potential" is used because even the most detailed mineralogical analysis, when combined with ABA, can give only a "worst case" value for potential acid production and, depending upon the NP procedure used, a "worst case", "most likely case" or "best case" value for potential neutralisation capability (Mills, 1998c).

Neutralisation potential measures the sum total of carbonates, alkaline earths and bases available to neutralise acidity and represents the most favourable condition. Calculations of maximum potential acidity and neutralisation potential are structured to equate the two measurements to a common basis for comparison. The resulting values, expressed as calcium carbonate equivalent, are compared to compute a net acid-producing or acid-neutralising potential. Material exhibiting a net acid production potential of 5 tons/1000 tons of overburden material or more as calcium carbonate equivalent are classed as toxic or potentially toxic (Hunter (1997b), Smith and Sencindiver (1982) and Sobek *et al.*(1978)).

This method of evaluating AMD generation potential (in addition to other methods) is a requirement of regulatory guidelines in British Columbia and other regions, particularly in North America. Proposed new mines are required to evaluate potential AMD generation in considerable detail and to demonstrate comprehensive planning to prevent or suppress AMD generation at all phases of mine operation, from development to closure and post-closure. Such evaluation must include pit walls, overburden, waste rock, tailings and any other material produced by the mining process.

The primary **advantages** of the Acid-Base Accounting method are:

1. Short turn-around time for sample processing.
2. Low cost.
3. Relatively simple analytical procedures.
4. Relatively simple interpretation of results (Hunter (1997b), Evangelou and Zhang (1995)).

The principal **disadvantages** of Acid-Base Accounting are:

1. The method predicts maximum potential acidity and maximum neutralisation capability and implies a 1:1 acid to base reaction. Actual acid production and neutralisation release rates (Mills, 1998c) cannot be predicted with this technique nor can the completeness of the reaction be assessed.
2. Acid-Base Accounting assumes that all acid production is attributable to iron disulphide minerals (chiefly pyrite) and that no acid is produced by sulphate or organic sulphur forms.
3. Measurement of neutralisation potential utilises a hot acid extract to measure carbonates and bases (this is not an issue in the suggested method-see section 5.2.2). Recent work in Texas suggests that this extraction procedure may overestimate neutralisation potential and that a modified method may be needed (Hunter, 1997b).

Application of this Acid-Base Accounting method to overburden handling and placement plans throughout the USA and Canada, has generally been effective in eliminating or reducing adverse water quality impacts. ABA is a legitimate tool for mine drainage quality prediction of coal-bearing rocks of the northern Appalachians and probably other coal-bearing rocks in a temperate climate (Cravotta, 1997). It is the most commonly used procedure for identifying potentially acid-forming materials at mine sites in Australia and South-East Asia (Miller *et al.,* 1994), is typically considered state-of-the-art for overburden analysis (Hunter, 1997b) and is used in overburden in Canada, Australia and Russia (Evangelou and Zhang, 1995). It has a long and successful tradition in eastern USA coal mining (Ziemkiewicz, 1997) and has been applied with some success to mine planning in the East, Midwest and Western coalfields of the USA (Perry, 1997).

It becomes a very powerful tool when used in conjunction with other data such as hydrologic data, mining and reclamation plans and mineralogy data as proposed for ABATE (Perry, 1997).

3.1.1 STATIC GEOCHEMICAL METHODOLOGIES

Static tests are typically simple and inexpensive procedures to prove a preliminary assessment of the potential of a waste or other mine component to generate AMD. They are primarily intended to examine the balance between the acid-producing and acid-consuming components of a sample. Static tests do not provide definitive answers to all questions regarding the future behaviour of wastes and should not be used as such. They do however provide a means to classify wastes according to their potential to produce AMD and indicate the extent and type of further testing and evaluations that should be carried out (Cravotta (1997), Morin and Hutt (1994)).

The following procedures are the most commonly used static test methods:

- Paste pH.
- Peroxide methods.
- Static Net Acid Generation (NAG) Procedure.
- BC Research Initial Test.
- Sulphur content.
- BC Research Confirmation Test.
- COASTECH modified biological oxidation test.
- Sobek Neutralisation Potential Method.
- Carbonate NP determination.
- Modified Acid-Base Accounting procedures for Neutralising Potential.
- Lapakko Neutralisation Potential Test Procedure.
- Calculated NP.
- Net Carbonate Value (NCV) for Acid-Base Accounting.

Static tests for coal mine overburden can be used for more than “screening”. Currently researchers such as Cravotta (1997) have far more faith in ABA than in leaching tests for prediction of mine drainage quality in the northern Appalachians.

3.1.1.1 STATIC PREDICTION METHODOLOGIES

The value of a test method is reflected by its ability to make valid and useful predictions. ABA, with all of its "warts and imperfections” provides a means to make meaningful mine drainage assessments. There is no universal set of magic numbers defining cut-off points on ABA (Perry, 1997). Static test procedures, with or without other analyses and tests, must, however, be used as a preliminary method of classification (MEND Project, 1996). In practice, kinetic testing is often inconclusive and a considerable weight is placed on the results of the static tests (Lawrence and Wang, 1997). This is evident by the fact that most jurisdictions responsible for the issuing of permits to develop and operate mines use the results of static testing as criteria in the classification of wastes for planning purposes (Lawrence and Wang, 1997).

3.1.2 PASTE pH

Paste pH is a measure of the sample's immediate acidity or alkalinity and reflects current geochemical conditions. Samples with a paste pH of 4.0 or less, are classed as acid/toxic regardless of the pyrite and neutraliser balance (Hunter (1997b), Smith and Sencendiver (1982) and Sobek *et al.* (1978)). Solubility and mobility of many trace elements and metals in water are strongly dependent on pH. For example, at pH 4.0 or lower, elements such as aluminium, copper, zinc, lead and chromium can be released into ground- or surface waters (Hunter, 1997b).

The procedure for Paste pH is that currently recommended by the British Columbia Ministry of Employment and Investment, (Energy and Minerals Division) (Price, 1997). It is based on the method of Sobek *et al.* (1978), with modifications by Page *et al.* (1982). In this procedure the solid:solution ration is 1:1. 20 g of air-dry test material and 20 mL of distilled water is mixed thoroughly for 5 seconds. This mixture is allowed to stand for 10 minutes and the pH is measured. According to Price and Kwong (1997), Canadian practitioners make measurements of mixtures of 1 rock : 1 water or 1 rock : 2 water. The pH of crushed rock and overburden is well-documented as an indicator of mineralogy and previous weathering (Ferrari and Magaldi, 1983).

3.1.3 ACID POTENTIAL

3.1.3.1 PEROXIDE METHODS

Several tests using hydrogen peroxide as an oxidant for sulphide minerals have been proposed. The Net Acid Production (NAP) or Net Acid Generation (NAG) test has been developed to provide an alternative procedure to Acid-Base Accounting for acid rock drainage prediction. The NAP test has the advantage of not requiring a sulphur analysis and therefore has the potential of being used as a quick method for use in the field. The NAP test can also provide an accurate quantitative assessment of acid-generation potential when run under controlled laboratory conditions. Work carried out to date indicates that results of the NAP test correlate well with Acid-Base Accounting results, particularly when net neutralisation potential values are relatively low and negative, which is in the range where greater certainty is required. When Net NP values are more negative, NAP values tend to underestimate the acid-generating potential, but this should not seriously affect waste management decisions.

The test relies upon the ability of hydrogen peroxide to oxidise sulphides such as pyrite present in a sample of mining waste to produce sulphuric acid. Acid that is produced is simultaneously neutralised by carbonates and/or other acid-consuming minerals present in the sample. At the end of the reaction, the final pH of slurry provides a qualitative indication of the acid-generating potential. Titration of the slurry to determine the acid content allows calculation of the net acid produced by the peroxide digestion and a quantitative assessment of the acid-generating potential.

The pH recorded at the end of the H_2O_2 digestion step, prior to titration, can provide a qualitative indication of the potential for acid generation for a sample. For example, an interpretation could be as follows (Lapakko and Lawrence, 1993):

Table 3. Final pH and Acid-Generating Potential.

Final pH in NAG Test	Acid-Generating Potential
> 5.5	Non-acid-generating
3.5 to 5.5	Low risk acid-generating
<3.5	High risk acid-generating

Caution should be exercised in interpreting NAP data in this way, since the pH-values obtained are dependent on the specific site lithology and mineralogy. Calibration with other tests and analyses is therefore recommended if the test is to be used in this way (Lapakko and Lawrence, 1993).

The laboratory procedure is given in Appendix 1.

Caution should be exercised in the interpretation of NAG test results for coal reject samples and other materials which may contain a high content of organic material (such as potential acid sulphate soils, dredge sediments and other lake or marine sediments). All organic material must be completely oxidised, otherwise acid NAG results can occur which are unrelated to sulphides. Several aliquots of H_2O_2 reagent may be added to the sample to break down any organic acidity.

Samples with a positive NAP value, high sulphur content and high ANC must be carefully evaluated (Miller *et al.*, 1997).

3.1.3.2 BC RESEARCH INITIAL TEST PROCEDURE FOR EVALUATING ACID PRODUCTION POTENTIAL OF ORE AND WASTE ROCK

This test has been widely used for the determination of AMD potential although it has largely been superseded in many studies by the use of the Sobek and Modified ABA procedures. This has largely been due to the greater inconvenience of carrying out the test in many commercial laboratories, especially when large numbers of samples are submitted for analysis (Lawrence and Day, 1997).

3.1.3.2.1 Assay

The pulverised sample is assayed in duplicate for sulphur total (it is current practice to use sulphide sulphur, not total sulphur (Mills, 1998d)) in a Leco furnace or by wet chemical methods. The acid production potential of the sample, expressed as kg of sulphuric acid per ton of sample (it is current practice to express acid as neutralising potential in kg/ton $CaCO_3$, not H_2SO_4 (Mills, 1998d)), is calculated on the basis of the total sulphur assay (Mills, 1998d).

3.1.3.3 BC RESEARCH CONFIRMATION TEST

3.1.3.3.1 Objectives

- To confirm the results of static prediction testing.
- To determine if sulphide oxidising bacteria can generate more acid from a sample than can be consumed.

3.1.3.3.2 Principles of Test

The acid potential derived by assuming total oxidation of sulphur (sulphides) in static prediction testing may not, under field conditions, be realised. To determine the degree to which the sulphur content of a sample might be oxidised and to assess if this amount of acid is sufficient to overcome the neutralising capacity of the sample, a biological oxidation test can be carried out. The test is usually only carried out if the sample is shown to be potentially acid-producing in static testing.

A pre-acidified pulp containing the finely ground test sample is inoculated with an active culture of sulphide-oxidising bacteria such as *T. ferrooxidans* and agitated under ideal conditions for bacterial oxidation. The pulp pH is monitored until stable, indicating the end of oxidation. An equivalent weight to the original sample is then added in two increments after 24 and 48 hours. The pH is measured 24 hours after each addition. If the pH is above 3.5 at these intervals, the sample is classified as a non-acid producer, since the pH is out of the range considered essential for the growth and oxidative activity of the bacteria. If the pH remains below 3.5, a potential for acid generation is indicated.

3.1.3.3.3 Interpretation of Results

A decreasing pH, following inoculation of the test pulp with bacteria, indicates the biochemical oxidation of sulphides contained in the sample.

Once a stable pH or soluble metal concentration has been achieved, it is assumed that all sulphide available for oxidation has reacted and the maximum of acidity has been generated. By adding more sample equal to the original weight after reaction and observing the pH-change, the ability of the sample to generate acid in excess of its neutralising capacity can be assessed. Specifically, the sample is confirmed to be an acid producer if the pH remains below 3.5. Above this pH, biochemical oxidation is considered to be unlikely and the sample is classified as a non-acid producer.

3.1.3.3.4 Reporting of Results

The results of the test should be tabulated to provide the following information:

Sample description, test duration (days after inoculation), initial pH, pH after biological oxidation, pH after 1st increment of sample addition, pH after 2nd increment of sample addition (final pH) and confirmation of acid production potential (yes/no).

3.1.3.3.5 Advantages of Test

- Relatively low cost and rapid kinetic test.
- Has been widely used in Canada.
- Provides an assessment for the potential of biochemical oxidation.

3.1.3.3.6 Disadvantages of Test

- Although the procedure is apparently simple, tests involving the use of bacteria require experience and can involve the problems of (1) non-optimal use of cultures, (2) use of non-adapted cultures and (3) difficulties of comparing results between different laboratories.
- The acidification procedure creates an unrealistic condition in that the inhibitory effects of the alkaline components of the waste on oxidation reactions are not evaluated and the method does not allow evaluation or modelling of the initial AMD production stages in the upper pH-ranges.
- The amount of acid generated in the test is not corrected for the initial acid added to bring the pH into the range suitable for inoculation. This can bias the result towards an acid classification.
- For samples with high sulphur contents, the amount of sample required by the test procedure might be too large, leading to incomplete oxidation of the available sulphur due to inhibition of reaction by reaction products and low pH (Bruynesteyn and Hackl, 1984).

3.1.3.4 COASTECH MODIFIED BIOLOGICAL OXIDATION TEST

Adopting several modifications to the standard procedure can reduce some of the disadvantages of the BC Research Confirmation Test. The modified test has been used routinely for a number of years (Mills, 1998d).

The initial sample weight is selected on the basis of the sulphur content.

At the end of the test, following the full addition of the extra sample, if the pH is still below 3.5, sodium hydroxide solution (3 to 6 N) is added to the pulp, stoichiometrically equivalent to the acid added initially to bring the pH into the biochemical oxidation range. The final pH is recorded after 1 hour. This procedure removes the bias towards an acid classification (Lawrence and Sadeghnobari, 1986).

3.1.3.5 SULPHUR CONTENT

Acid potential is calculated from a total sulphur analysis:

AP = S% x 31.25 kg $CaCO_3$ equivalent per ton (Sobek *et al.*, 1978)

The use of total-S as a sulphide-S measure may result in a large overestimation of AP (Mills, 1998d and Price, 1997b), where other sulphur species are significant.

The acid potential, AP, is calculated from the sulphide-sulphur content as follows:

AP = Sulphide-sulphur% x 31.25 kg $CaCO_3$ equivalent per ton (Lawrence and Wang, 1997).

Where the sulphate mineral content is very much less than the sulphide mineral content (and in the absence of organic sulphur), sulphide sulphur may be approximated to total sulphur. Whether acid-generation potential may be satisfactorily calculated from total sulphur instead of sulphide sulphur will, therefore, depend upon sample sulphate mineral content and will be site-specific. Unless total sulphur analysis is used, it is necessary to conduct additional analytical procedures in order to determine sulphide sulphur (Mills, 1998c). Acid leachable sulphate sulphur includes gypsum and anhydrite and acid insoluble sulphate sulphur includes barite. The necessity of determining all of these sulphur components or any given suite of samples is rare. For example, for western Canadian metalliferous mines, it is common practice to determine sulphide sulphur as the difference between total sulphur by Leco furnace and acid-soluble sulphate sulphur. The occasional necessity to correct for barite can be determined from barium assays obtained from whole-rock analyses. Acid-generation potential is calculated from the sulphide sulphur content. It is infrequently acknowledged that each analytical stage added to the sulphide determination introduces an additional analytical error and that these errors are cumulative. The recommended procedure for determining the maximum potential for future mineral acid generation is to calculate it using the sulphide -S content measured, using an expanded sulphur speciation analysis. Complete sulphur speciation may not be required if there are no organic -S or sulphate -S components present; however, these assumptions should be verified. (Mills (1998c) Price and Errington (1995), Price *et al.* (1997a & 1997b)). The recommended method, discussed in section 5, eliminates several of these problems.

3.1.4 BASE POTENTIAL

3.1.4.1 THE SOBEK NEUTRALISATION POTENTIAL METHOD

This method involves the determination of NP by digesting a small (2.0 g) sample in excess hydrochloric acid at near-boiling temperatures. A fizz test is used to determine the volume and normality of acid added (Lawrence, 1997b) and is subjective in that it requires a judgement by the test operator (Mills (1998c), Lawrence and Wang, (1997)). In addition, some test laboratories, for convenience, do not carry out a fizz test in strict accordance with the Sobek procedure. Instead, acid additions are made according to a strong fizz rating (Mills, 1998c). The unreacted acid remaining at the end of the digestion is then titrated with NaOH to an end point of 7.0 so that the acid consumed can be calculated.

NP is calculated as follows:

$$NP = \frac{50a\,[x-9b/a)y]}{c}$$

NP = neutralisation potential kg $CaCO_3$ equivalent per ton, a = normality of HCl added in digestion, b = normality of NaOH used in titration, c = mass of sample in grams, x = volume of HCl added in mL, y = volume of NaOH added in titration.

Advantage:

- This test is widely used and is accepted by many regulatory authorities.
- It is a quick and easy, low-cost, test and is ideal for the screening of a large number of samples (Sobek *et al.,* 1978).

Limitations:

- NP overestimated - digestion conditions are more severe than in the field and minerals that will not contribute to NP in the field, react. Like all static tests, however, the test provides no information on the rate and extent of both sulphide oxidation and neutralisation that will occur in the field (Lawrence and Wang, 1997).

3.1.4.2 THE MODIFIED ACID-BASE ACCOUNTING PROCEDURE FOR NP

Modified ABA procedures have been developed primarily to reduce the potential for overestimation of NP values obtained in the Sobek procedure.

The full procedure is given in Appendix 1 but broadly entails the following:

A few drops of 25% HCl are added to 1 - 2 g of pulverised sample and the degree of fizz is observed. A fizz rating is assigned as "none", "slight", "moderate", or "strong fizz".

Based on this differing volumes of HCl are added to a sample of similar weight at times of 0 and 2 hours. After 22 hours the pH is measured and brought into range of 2 - 2.5. After 24 hours the test is terminated and distilled water added to bring the volume to 125 mL. This mixture is then titrated to a pH of 8.3 and the neutralising potential determined.

Calculate the NP of the sample as follows:

$$\frac{\text{Modified NP (kg } CaCO_3\text{/t)} = [(\text{N x vol(mL) of HCl}) - (\text{N x vol(mL) NaOH}) \text{ x } 50]}{[\text{Weight of sample (g)}]}$$

Carbonate NP values must be reduced to account for Fe and Mn carbonates, since they hydrolyse to generate hydrogen ions and therefore have no net neutralising potential (Skousen *et al.,* 1997).

The acid-generating potential of the sample should be calculated on the basis of the sulphide-sulphur content (AP = S= x 31.25). Sulphide-sulphur is typically determined as the difference between total sulphur and sulphate-sulphur, although analysis of other sulphur species such as elemental sulphur and barite-sulphur is sometimes justified. Caution should be exercised for certain samples in interpreting sulphate-sulphur analyses as this form can be either inert (e.g. gypsum) or essentially stored products of acid drainage that could become mobilised if conditions within a waste change (Lawrence and Wang, 1997).

Discrepancies: Results obtained by Kwong and Ferguson (1997) show that the carbonate-NP and modified Sobek underestimate the effective NP of a sample. The standard NP (24 hours) acid digestion appears to underestimate the actual NP and a digestion period of at least 48 hours with 0.5 N HCl digestion is suggested. Mafic silicates like biotite, pyroxene, chlorite, epidote and amphibole are more efficient acid-neutralising minerals than the more common feldspars.

3.1.4.3 CARBONATE NP DETERMINATION

Determination of carbonate NP is a very useful stand-alone measurement to be used in conjunction with the NP value obtained in another static test. Carbonate minerals are a rapidly available source of neutralising components. Analysis of a sample for its inorganic-carbon content allows calculation of carbonate NP, assuming that all inorganic carbon is present as carbonate minerals capable of neutralising acid (Lawrence and Day, 1997). Corrections should be made if mineralogical examination reveals the presence of carbonate minerals such as siderite ($FeCO_3$) and $MnCO_3$, which do not provide net neutralisation due to the acid released when the iron hydrolyses (Lawrence and Day (1997), Skousen *et al.* (1997) and Ziemkiewicz (1997)).

Carbonate NP (kg $CaCO_3$/ton) (Lawrence and Day, 1997)

$$= \frac{\text{mg C in sample x 8.34}}{\text{Weight of sample (g)}}$$

3.1.4.4 COMPARISON OF SOBEK, MODIFIED AND CARBONATE NP

A recent study by Lawrence and Wang (1996) compared NP values obtained by the Sobek, Modified and Carbonate NP procedures for 120 samples from 12 different mines. The study confirmed the tendency for overestimation of NP by the Sobek test. Modified NP and Carbonate NP values were more closely correlated, with Modified values marginally higher in many cases due to the accounting of the more reactive silicate minerals which react under the conditions of the test. Table 4 provides a simple, non-quantitative scheme that illustrates differences in NP values by showing some typical rock forming minerals in order of reactivity and an indication of the approximate extent of reaction achieved in each of the three test methods.

Table 4. Relationship between mineral reactivity and method of NP determination.

Relative Mineral Reactivity	Neutralising Mineral	Extent of reaction by NP Method
More Reactive	Carbonates	Carbonate
	Ca-feldspar, Olivine	Modified
	Pyroxenes, Amphiboles	
	Sorosilicates, Phyllosilicates	
	Plagioclase feldspar	
	K-feldspar	Sobek
Less Reactive	Quartz	

It is clear from the above table that no single NP determination method will give the true, or field, NP for any given sample. As a very broad generalisation, it may be said that for a sample containing carbonates and reactive silicates:

- The Lapakko and Inorganic Carbon-Carbonate methods will tend to give a 'worst case' neutralisation potential, since the carbonates are credited, but other minerals are not.
- The Sobek method will tend to give a 'best case' neutralising potential since all carbonates and other minerals soluble at the lowest pH of the test will be credited.
- The BCRI Initial and Modified Sobek methods will tend to give a 'most likely case' neutralisation potential, since the carbonates and only the most reactive silicates are credited (Mills, 1998c).

Several authors, however, suggest that the ABA methods provide a realistic assessment of the NP since the reactive species are the ones which react. Jambor *et al*. (2000), from their work on the contribution of different minerals to the final NP determined by static tests, suggest that the carbonate NP provides the most realistic assessment of whether a rock or suite of rocks will be acid-generating. They go on to say that most non-carbonate minerals can participate in the attenuation of acidity, but only to a modest degree and only in the longer term, after an AMD scenario has already developed. This finding mitigates some of the criticism of ABA, which points out that the NP methods are only geared towards the faster-reacting minerals. These are therefore the only ones, generally, capable of *preventing* AMD.

In British Columbia, the existing Guidelines (Price and Errington, 1995) state:

"The screening criteria used to evaluate a need for further test work based on Acid-Base Accounting tests are:

Materials with sulphide minerals whose net neutralising potential (NNP = NP - AP) is negative, are likely to be an acid drainage source. Exceptions are possible if the sulphide content is very low and/or there are significant slow release, non-carbonate sources of alkalinity. The acid drainage potential will be considered uncertain if materials have a ratio of neutralisation potential to potential acidity (NP:AP) of less than 4:1."

Basically, **these Guidelines define a "grey zone" for Neutralising Potential Ratio greater than zero and less than 4.** However, based on Price *et al.* (1997b), it is expected that the new Guidelines will define two NPR "grey zones" (Sobek NP/sulphide sulphur AP) as shown in the table below (from Price *et al.,* 1997b):

Table 5. Guidelines for screening criteria based on ABA (from Price et al., 1997b).

POTENTIAL FOR AMD	INITIAL NPR SCREENING CRITERIA	COMMENTS
Likely	<1:1	Likely AMD generating
Possibly	1:1 - 2:1	Possibly AMD generating if NP is insufficiently reactive or is depleted at a faster rate than sulphides
Low	2:1 - 4:1	Not potentially AMD generating unless significant preferential exposure of sulphides along fracture planes, or extremely reactive sulphides, in combination with insufficiently reactive NP
None	>4:1	No further AMD testing required unless materials are to be used as a source of alkalinity

3.1.4.5 BC RESEARCH INITIAL TEST

This test has been widely used for the determination of AMD potential but has largely been superseded in many studies by the use of the Sobek and Modified ABA procedures. This is largely due to the greater inconvenience of carrying out the test in many commercial laboratories, especially when large numbers of samples are submitted for analysis (Lawrence and Day, 1997).

In this method, the NP is determined by titrating a slurrry of the sample with sulphuric acid to an end point of pH 3.5. This end point represents the limit above which bacterial activity is greatly reduced. This acid consumption, in units of kg H_2SO_4 per ton of material, is calculated as follows:

$$\text{Acid Consumption} = \frac{\text{mL } 1.0 \text{ N } H_2SO_4 \times 0.049 \times 1000}{\text{Sample mass (gram)}}$$

This value can be converted to units of kg $CaCO_3$/ton for comparison with the results of Acid-Base Accounting tests. Typically, the test takes at least 24 hours to complete. Although the test is more time-consuming than Acid-Base Accounting, the test is considered to provide a good estimation of the practical NP, since excess acid is not employed as in the Acid-Base Accounting methods. In addition, the use of sulphuric acid provides a better simulation of field conditions than hydrochloric acid. An AP value based on sulphide-sulphur analysis is advisable (Bruynesteyn (1984), Cuncan and Bruynesteyn (1979) and Lawrence and Day (1997)).

3.1.4.5.1 Interpretation

If the acid consumption value (in kg of acid/ton of sample) exceeds the acid-producing potential (kg per ton), the sample will not be a source of acid mine drainage and no additional work is necessary. If acid consumption is less than the acid production potential or the difference is marginal, the possibility of acid mine water production exists and the confirmation test is conducted.

3.1.4.6 LAPAKKO PROCEDURE FOR THE DETERMINATION OF METAL MINE WASTE

This method is a modification of the BC Research Initial Test. The major difference between the two methods is the use of a pH 6.0 end point instead of pH 3.5. This is to accommodate water quality standards and the neutralising potential is given as the amount of acid that could be neutralised to keep the mine with compliance.

In this method, an automatic titrator is used with additions made very slowly. The method is intended to give NP present rather total NP available in reality and consequently the value often exceeds that practically available in the field. If particles sizes were closer to those present in the field, results would approximate the true values more closely.

The method is time-consuming and not generally used for routine assessments.

3.1.4.7 CALCULATED NP

Different minerals can neutralise acid drainage at different rates and in different pH-ranges. The test conditions of widely used and laboratory procedures to determine NP do not distinguish such differences, and overestimation of NP can often result. A simple procedure has been proposed in which the effective NP is calculated based on mineralogical composition and the relative reactivities of component minerals. Mineralogical composition can be calculated from easily determined analytical values (whole rock chemistry and inorganic carbon) using a CIPW normative procedure. Comparison of calculated NP values for 92 samples with experimentally determined values from tests designed to prevent the overestimation of NP, indicates that the method is successful in predicting an effective NP value in most cases. The procedure is considered to be a cost-effective means of providing confident routine AMD prediction when used in combination with other tests and analyses. For application at a particular mining project, customised modifications of the CIPW procedure that match actual rock chemistry with identified mineral components in defined lithological groups or waste management units, would provide mining operators with a rapid tool for classifying wastes to match disposal options (Lawrence and Scheske, 1997).

3.1.4.8 PEROXIDE SIDERITE CORRECTION FOR SOBEK METHOD

Meek (1981) suggested that the NP of certain rock units is overestimated when siderite ($FeCO_3$) is present. Siderite, along with calcite and dolomite, is a common carbonate mineral in the overburden associated with Appalachian coal beds (Cecil *et al.,* 1985). Even though natural weathering of siderite is a slow process, siderite will react if exposed to aqueous and acidic conditions used in the laboratory to determine NP (Doolittle *et al.,* 1992). When present in an overburden sample, siderite's reaction with acid contributes to the apparent alkaline-producing potential of the rock (Meek, 1981 and Wiram, 1992). Continued weathering of siderite, however, produces a neutral to slightly acid solution (Meek, 1981 and Shelton *et al.*, 1984) as indicated in the following reaction (Cravotta (1991), Doolittle *et al.* (1992), Frisbee and Hossner (1995) and Postma (1983)):

$FeCO_3 + 0.25\ O_2 + 2.5\ H_2O = Fe(OH)_3 + H_2CO_3$ [1]

Where $H_2CO_3 = H_2O + CO_2$ (aq)

In the determination of NP, many reaction steps during the titration can affect the pH. The first step in the reaction of siderite with excess hydrochloric acid (HCl) is:

$FeCO_3 + 2HCl = Fe^{2+} + 2Cl^- + H_2O + CO_{2(g)}$ [2]

Because the solution is acidic, the CO_2 is exsolved as a gas. The ferrous iron (Fe^{2+}) produced by Reaction 2 is also unstable and will slowly oxidise to ferric iron (Fe^{3+}) and consume additional HCl:

$Fe^{2+} + 0.25O_2 + HCl = Fe^{3+} + Cl^- + 0.5H_2O$ [3]

The ferric iron ($Fe^{3+)}$ produced will consume base ions upon titration with sodium hydroxide (NaOH) and precipitate as ferric hydroxide:

$Fe^{3+} + 3NaOH = Fe(OH)_3 + 3Na^+$ [4]

The overall reaction is essentially Reaction 1 with the addition of sodium (Na^+) and chloride (Cl^-):

$FeCO_3 + 0.25O_2 + 3HCl + 3NaOH = Fe(OH)_3 + 3Na^+ + 3Cl^- + 1.5H_2O + CO_{2(g)}$ [5]

Reaction 5, which represents the major reactants and products for the NP digestion and titration, shows that 3 mole of acidity (HCl) and 3 mole of base (NaOH) are consumed and that CO_2 is exsolved. As a result, the overall reaction yields a zero NP for siderite (no net acidity or alkalinity). Because the standard NP procedure as outlined by Sobek *et al.* (1978) does not allow sufficient time for ferrous iron oxidation and subsequent precipitation of ferric hydroxide, the procedure accounts for only the initial reaction, resulting in 3 mole of alkalinity (Reaction 2 & 3). Therefore, erroneously high NP values can be generated with samples containing high amounts of siderite. Such an analytical oversight can lead to incorrect post-mining water quality predictions, resulting in premature mine closure and produce costly, long-term reclamation liabilities for mining companies (Wiram, 1992).

Meek (1981) was the first to suggest adding a small quantity of 30% hydrogen peroxide (H_2O_2) to the filtrate of an HCl-digested siderite overburden sample to oxidise ferrous iron to ferric iron before back-titration. Because the resulting ferric iron is precipitated as $Fe(OH)_3$ upon titration, the solution yields a more accurate NP value. The addition of H_2O_2 after the initial titration results in the formation of additional $Fe(OH)_3$ due to enhanced oxidation at higher pH-values.

The method, as developed by a Pennsylvania-West Virginia Overburden Task Force (Leavitt *et al.,* 1995), is given in Appendix 1.

3.1.5 NET CARBONATE VALUE (NCV) FOR ACID-BASE ACCOUNTING

The development of the NCV method for Acid-Base Accounting was brought about by new mining regulations in Nevada State, 1990. A lot of semi-quantitative mineralogic information (XRD-XRF) was available on the Carlin trend gold deposits, including percentages of carbonate and sulphide minerals, which were used to initiate the studies. Percent carbon dioxide (%CO_2) was selected as the common unit for balancing the acid-neutralisation potential (ANP) of the limestone hosted deposits, against the acid-generation potential (AGP) due to the sulphides present.

ANP was calculated based on 44% CO_2 in calcite, 48% in dolomite, 44% in ankerite and 38% in siderite. AGP was calculated based on stoichiometric equivalents of one sulphide being oxidised to sulphuric acid, consuming one carbon dioxide, with a factor of -1.37 times the percentage of sulphide. Sulphide minerals present in the samples included 53% sulphide in pyrite and 20% sulphide in arsenopyrite. The overall stoichiometric equation is as follows:

$$\text{NCV} = 0.44 \times \text{calcite} + 0.48 \times \text{dolomite} + 0.44 \times \text{ankerite} + 0.38 \times \text{siderite} - 1.37 \times 0.53 \times \text{pyrite} - 1.37 \times 0.20\ \text{arsenopyrite},\ \%CO2$$

Drill hole composites were classified into ranges of NCV and plotted on cross sections through the deposits, with negative NCV zones (representing acid-generation potential) being contoured in red. Composites representing waste in 20' mine benches were prepared and submitted for carbonate and sulphide by combustion-infrared absorption spectrophotometry analyses, using industry standard metallurgical assay methods for Carlin ores:

- Total carbon (CT) and sulphur (ST).
- Residual carbon after hydrochloric acid digestion (CR).
- Residual sulphur after pyrolysis at 550°C for one hour (SR).

ANP is calculated by the difference between total carbon and residual carbon after hydrochloric acid digestion and the result is converted to %CO_2 units, using the factor of 3.67. AGP is calculated by the difference between total sulphur, a residual sulphur after pyrolysis and the result is converted to %CO_2 units using the factor of -1.37. NCV is calculated by adding ANP and AGP. The overall equations are as follows:

ANP = 3.67 x (CT-CR) 2.AGP = -1.37 x (ST-SR) 3.NCV = ANP + AGP

After the initial characterisation of the historical deposits, the use of combustion-infrared analyses became the routine method for waste characterisation during active mining and for the evaluation of new projects. The use of XRD-XRF analyses continues to play an important role in the interpretation of the NCV results, even though it is less sensitive than the combustion-infrared methods. Mineralogical ANP and AGP estimates are compared with combustion-infrared NCV results for quality assurance during characterisation of new deposits, to check for method bias.

ANP results are also plotted against AGP results in a scatter plot and a histogram of NCV values is made for each geological waste type in each deposit. Results are interpreted using the following general classification scheme:

1.Inert = 0.1 > NCV > -0.1 and ANP < 0.1 and AGP > -0.1

2.Neutral = 0.1 > NCV > -0.1 and (ANP > 0.1 or AGP < -0.1)

3.Slightly Acidic = -0.1 => NCV > -1

4.Moderately Acidic = -1 => NCV > -5

5.Highly Acidic = -5 => NCV

6.Slightly Basic = 0.1 <= NCV < 1

7.Moderately Basic = 1 <= NCV < 5

8.Highly Basic = 5 <= NCV

Representative samples of core are selected for each of the major geological waste-NCV classifications (> 5%) for further testing, called confirmation tests. Typically, at least 100 bench waste composites are tested for NCV during the initial characterisation program and 10 - 12 select core samples are used for the follow-up confirmation testing.

Testing of these type of samples usually includes NCV analyses, XRD-XRF, other Acid-Base Accounting tests, such as ANP titrations, etc., BC confirmation tests or biological acid production potential (BAPP), meteoric water mobility procedure testing (MWMP,) or synthetic precipitation leaching procedure (SPLP) testing and possibly humidity cell testing, if necessary. Results are used to recommend a routine testing method to be used during the operation of the mine.

Conversion from CO_2 to $CaCO_3$ may be accomplished by dividing by the 0.44 factor.

Run of mine site column testing is probably the best alternative for kinetic testing studies during the life of the mine. Test materials from the geological waste-NCV type confirmation tests may be selected to cover the range of materials to be encountered during waste disposal operations. Several tons of each test material are sampled and one representative half placed in an open tank for exposure to rainfall and the effluent collected and periodically analysed. The other half of the sample needs to be thoroughly characterised, since these are long-term tests. Mine operators may infer from the test results, the worst case of what may be happening inside the waste dumps with similar materials (Bucknam, 1997).

3.1.6 PUTTING THE METHODS TOGETHER

The net acid-generation (NAG) test has proved to be a rapid and cost-effective analytical method of predicting AMD risk for several Schafer projects. NAG or net acid generation pH is an accelerated weathering test using peroxide as an oxidant. A rock sample is crushed and oxidised for 24 hours in a 30% hydrogen peroxide solution. The net effect of acid produced by oxidation of pyrite in the sample and acid neutralisation by dissolution of minerals such as limestone is determined with a simple pH measurement. The NAG pH-values are calibrated to ABA and humidity cell data, to establish site-specific threshold NAG pH-levels. A recent review of NAG pH, NNP and humidity cell data for 40 samples indicates that NAG testing is often superior to traditional Acid-Base Accounting as a predictor of acid-generation potential (Scafer Laboratory, 1997). Graphical presentation of data aids the interpretation and include:

- NP versus AP.
- Paste pH versus NP and/or NPR.
- NPR versus S or S^{2-}
- Surrogate elements (e.g. Ca, Mg, etc.) versus NP.
- Back-titration curves.

All calculated values for AP and NP should be kg CaCO3/ton to compare the two directly.

The developers recognised, as should anyone who uses the test, that the chemistry of pyrite oxidation and carbonate dissolution are not parallel in rate or process. Thus some interpretation must be applied.

3.1.7 FACTORS AFFECTING ACID-BASE ACCOUNTING

3.1.7.1 PARTICLE SIZE

Particle size has a major impact on surface area and mineral exposure. Given the same rock mass, the surface area increases exponentially as the particle size decreases. Consequently, most of the surface area and mineral exposure in a rock dump will typically occur in the finer size fractions (Price and Kwong, 1997). Coarse particles account for most of the mass in a typical waste rock dump. According to McLaren (1986) less than 3% of the mass at the Kitsault mine was estimated to occur in the less than 2 mm particle size fraction. The fines-containing waste rock from Canadian precious and base metal mines had a < 2 mm content of 0 - 35%, with an average of 15 - 25% (Murray, 1977).

3.1.7.2 METHODS

From the discussions above, it is clear that different values for the same sample can be obtained when using different methods. An incorrect understanding of what each method yields and thus not making the necessary corrections can lead to this discrepancy.

3.1.8 SCREENING ASSESSMENT CRITERIA

After the Neutralising Potential (NP) and Acid-Generation Potential (AP or MPA) have been determined for a sample it is necessary to combine these two values in a manner that allows comparison with set criteria based on experience or regulation. The two methods of combination commonly used are:

- The difference in value between NP and AP, or Net Neutralisation Potential (NNP = NP - AP).
- The ratio of NP value to AP value, or Neutralisation Potential Ratio (NPR = NP/AP) .

The former is the preference for Appalachian coal mines and the latter for Western Canadian metalliferous mines (Mills, 1998c).

Methods used to obtain NP and AP values will reflect a NNP or NPR value for a sample but will be particularly affected by the method used for NP determination. Since potentially large ranges of values for NP can, depending upon the procedures used, be obtained for a single sample. It follows that both NNP and NPR are also sensitive to procedures. This has, in the past, resulted in the reporting of a myriad of subclasses of NP, AP, NNP and NPR that are all procedure-specific and has resulted in considerable confusion among practitioners of AMD prediction. These reporting problems have occurred less in Appalachian coal mining, where the Sobek NP and total sulphur MPA have been used fairly consistently, than in North American metalliferous mining. It is partly to ensure consistency of reporting that the British Columbia Guidelines recommend Sobek NP and sulphide sulphur AP (Mills, 1998c).

For 39 Pennsylvania coal mine sites where historical data have been maintained, it has been reported that material with an NNP (Sobek NP - MPA) greater than 15 ton CaCO3/1000 ton had alkaline drainage. For 78% of the same sites, material with an NNP less than or equal to zero had acidic drainage (Brady *et al.,* 1994). For these sites the "grey zone", or range of NNP for which prediction is difficult, is represented by material with NNP of greater than zero, but less than 15 ton CaCO3/1000 ton. Brady (1997) has commented that the siderite modification to the Sobek method (Skousen *et al.,* 1997) may reduce the range of the "grey zone" (Mills, 1998c).

Traditionally in British Columbia, where sample NPR values have fallen in the "grey zone", kinetic test work (humidity cells or columns) have been conducted to clarify sample status with regard to acid-generation potential. However, it should be possible to characterise material in the 4<NPR>2 zone adequately by mineralogical and petrographic test work. Since the Guidelines have not yet been published, there have been no mines permitted under them and the manner in which samples within the 4<NPR>2 will be required to be tested, is unknown.

It should be clear from the above discussion that no single NP determination method will give the true, or field, NP for any given sample. As a very broad generalisation, it may be said that for a sample containing carbonates and reactive silicates:

- The Lapakko and Inorganic Carbon-Carbonate methods will tend to give a 'worst case' neutralisation potential, since the carbonates are credited, but other minerals are not.
- The Sobek method will tend to give a 'best case' neutralising potential, since all carbonates and other minerals soluble at the lowest pH of the test will be credited.
- The BCRI Initial and Modified Sobek methods will tend to give a 'most likely case' neutralisation potential, since the carbonates and only the most reactive silicates are credited (Mills, 1998c and Hyman *et al.,* 1996).

3.2 KINETIC TESTS

3.2.1 LABORATORY KINETIC TESTS

Acid-Base Accounting procedures are used as a screening process to categorise materials into potentially acid-generating, potentially non-acid-generating and uncertain groups. For material where the potential for acid generation is uncertain, kinetic test work is performed to attempt to define acid generation characteristics. The term kinetic is used to describe a group of test work procedures wherein the acid generation (and metal solubilisation and transport) characteristics of a sample are measured with respect to time (Mills, 1998g and Chemex Labs, 1997). ABA methods are referred to as static, because measurements are made over a short and fixed period of time. Procedures are described below for humidity cells, columns and lysimeters, which are the three most commonly used methods of determining kinetic AMD characteristics of drill core, waste and other rock samples and tailings (Mills, 1998g). A procedure for determining the kinetic AMD characteristics of *in situ* rock such as pit walls and the rock surfaces of adits, stopes and other underground workings has been developed through the MEND program and the British Columbia ARD Task Force. This procedure is called "Mine Wall" (MEND, 1995).

Humidity cells are typically laboratory units using a sample size of about 1 - 15kg. Columns may be of laboratory-, pilot plant- or site scale with the sample size ranging from a few kg to hundreds of kg. Lysimeters are site scale units with the sample size typically in the ton range. The Mine Wall Procedure has been used on exposed rock surfaces no greater than 1 m by 1 m (Price, 1997).

The main **advantages** of kinetic tests:

- Tests methods are designed to simulate field conditions. (If pyrite oxidation rates and mechanisms can be better understood, it is possible that AMD can be stopped at the source so that complications downstream from minesites will be eliminated (Jerz and Rimstidt, 2000)).
- Reaction rates (kinetics) can be evaluated. Researchers such as Stromberg and Banwart (1999) have shown a good correlation between oxygen consumption and sulphate production in laboratory columns.
- Well-characterised test materials can be utilised.
- Leaching of overburden constituents other than acidity and alkalinity can be evaluated (Chemex labs (1997), Hunter (1997b), Price *et al.* (1997) and Telkwa Coal Project (1997)).

The primary **disadvantages** associated with leaching tests are:

- Test time is lengthy; a minimum of two months is required to conduct one analysis.
- Analysis is expensive.
- Long-term predictable capability of leaching tests is uncertain.
- Data interpretation requires more sophisticated review than the Acid-Base Accounting method (Hunter, 1997b).

One of the major weaknesses of kinetic test interpretation is the lack of long-term data. Although tests are now generally run for significantly longer periods of time than in the recent past, the usual test duration of months or even 1 - 2 years, does not simulate the behaviour of a waste component in time frames often measured in years or tens of years. Assumptions, therefore, have to be made that the stability of concentrations and rates observed after a reasonable length of time of testing can be extrapolated into the future (Lawrence and Day, 1997).

Kinetic tests are carried out to determine the weathering characteristics of a sample as a function of time. For a proposed new mine, specific objectives for both the short and long term can include:

- Validation of static test results and classification.
- Determination of the rate of sulphide oxidation/acid generation.
- Determination of the rate of neutralisation depletion.
- Determination of the availability of NP.
- Time to the onset of AMD.
- Evaluation and selection of AMD control methods.
- Prediction of water quality.

For an existing mine where AMD might already be a problem, some or all of the above objectivesalso apply. In addition, it might be necessary to add the following objectives to facilitate the selection of mitigation methods and for the development of a closure plan:

- Evaluation of the extent of oxidation.
- Evaluation of the extent of neutralisation.
- Evaluation of stored reaction products within wastes (Dagenais and Poling (1997), Lawrence and Day (1997) and Mills (1998h)).

Kinetic tests typically involve subjecting a sample of the waste material to periodic leaching and analysis of the drainage. **The most reliable test would be one that replicates exactly the actual field conditions. In practice this is not possible, not only because of the time factor, but also because it is impossible to simulate the physical, chemical, biological, meteorological and other factors associated with an actual dump, tailing impoundment or other mine component**. With respect to the time factor, the difficult choice in designing, performing and interpreting a kinetic test is either to have a test which attempts to approximate actual field conditions, in which case the test will usually be of too short a duration, or to provide accelerated conditions, in which case the test might be unrealistic. In the former case, kinetic tests can often fail to demonstrate the onset of AMD or reach any steady state with respect to oxidation rates, neutralisation rates or water quality (Lawrence and Day, 1997).

Many types of kinetic tests have been documented and these can vary in complexity, duration, cost and the kinds of data obtained. Currently the most popular kinetic test is the humidity cell test. The trend in humidity cell testing is much longer test times. Column tests, which are generally of a larger scale than humidity cells, are also popular (Lawrence and Day, 1997). The procedure is designed to mimic the conditions expected to occur in regraded spoil. Samples are subjected to alternating water leaching and exposure to moist air. It has been indicated that fine-grained pyrite with a large surface area is much more reactive and more likely to produce acidity than coarse-grained pyritic material (Hunter (1997b), Curuccio (1969, 1984) and Caruccio *et al.* (1982)). Caruccio (1984) suggests that Acid-Base Accounting be used as an initial screening test for overburden samples. Leaching tests will more accurately predict drainage quality (Hunter, 1997b).

3.2.1.1 REPORTING FORMAT FOR KINETIC TESTS

Rates of acid generation and sulphide oxidation can be calculated in a number of ways:

- Weight basis (e.g. mg sulphate/kg/week or mg CaCO3 equivalent/kg/week).
- Cumulative basis (e.g. Total mg sulphate/m2/week).

- Surface area (e.g. mg sulphate/m2/week, derived from surface area to weight conversions) (Chemex Labs, 1997).

3.2.2 HUMIDITY CELLS

Humidity cells have become the most popular devices for conducting kinetic tests. Cell designs can vary in the material of construction, geometry and size. A typical cell is constructed of Plexiglas of dimensions 10 cm in diameter by 20 cm in length and has a nominal capacity for 1 kg of rock. The rock sample is typically crushed to - 6 mm and is placed on a perforated plate to permit the flow of air up through the bed of rock. The cell can be provided with a bubbler tube containing water, attached to a tight-fitting lid, through which the exiting air is passed. The bubbler provides a visual check that air is flowing through the cell and allows the operator to achieve a semi-quantitative balancing of airflow through a bank of humidity cells. Dry or humidified air is supplied to the underside of the perforated plate. The temperature of the water in the humidifier should preferably be maintained slightly above ambient to ensure a good supply of humidified air. Leachate, usually distilled water, is added periodically through the lid of the cell. The mode of addition can vary. In some test programs, the water, typically 250 to 500 mL, is added slowly over several hours (percolation leaching). In this method, the valve at the bottom of the cell is open to allow free draining. In other programs, sufficient water can be added to completely submerge the sample for a period of time before the bottom valve is opened to allow draining. In the latter method, the rock sample is sometimes gently stirred during submergence to promote dissolution of reaction products. A scheme for the arrangement of a humidity cell can be seen in Figure 12.

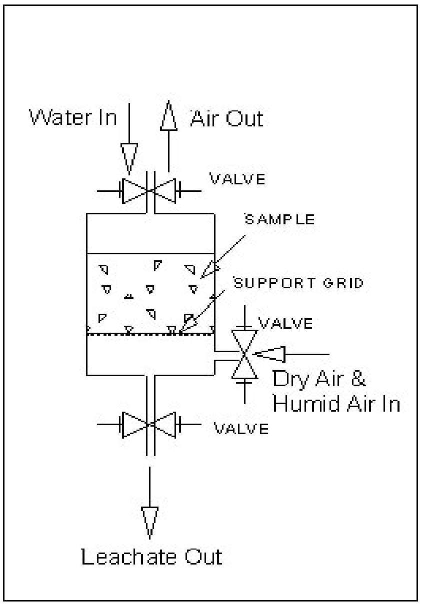


Figure 12. Generic schematic diagrams for the arrangement of a humidity cell (Mills, 1998g).

There are other possible configurations for sub-aqueous test work (Lawrence, 1995). Variable infiltration (water addition) rates can be used to investigate the runoff quality and metal loadings that can be expected seasonally (Lawrence and Day, 1997).

Humidity cells have, in the past, varied considerably in dimensions. However the laboratories servicing the mining industry have now adopted a degree of standardisation. In Designation: D5744-96 Standard Test Method for Accelerated Weathering of Solid Materials using a Modified Humidity Cell (ASTM, 1996), a cell 203mm (8.0 in.) in height by 102 mm (4.0 in.) diameter is specified for material crushed to 100% passing 6.3 mm (crushed core or waste rock and coarse tailings) and a cell 102 mm (4.0 in.) in height by 203 mm (8.0 in.) diameter is specified for material passing 15µm (fine tailings) (Price, 1997), while recommending similar dimensions, states that the dry and humid air flow should be directed across the surface of tailings samples, rather than through the samples from below. In both of the above arrangements the sample mass is 1 kg which typically gives a bed depth of about 80-120 mm in a 102 mm diameter cell and 20 - 40 mm in a 203 mm diameter cell, depending upon sample bulk density. Soregaroli and Lawrence (1998) have reported the use of a 3 kg sample with a 102 mm diameter cell and a 15 kg sample with a 254 mm diameter cell and compared results with those obtained with a 1 kg sample and 102 mm diameter cell (Mills, 1998g). The ASTM method does not specify temperature; only that the temperature of the humidifier must be at 30°C +/-2°C (Bucknam, 1997c).

In a typical test, a 7-day cycle is employed: 3 days of dry air, 3 days of humid air, followed by leaching on the 7th day. On the next day, the next cycle is started. Humidity cell tests should be carried out for as long a time as possible. It is normal for data to be quite erratic over the first few cycles, before consistent results are obtained. This is due to the removal of readily soluble components from prior oxidation and weathering. It is not unusual for humidity cell tests to continue for several months or even more than 1 or 2 years (Lawrence and Day, 1997).

The ASTM Procedure (ASTM, 1996) requires a minimum test duration of 20 weeks, while Price (1997) recommends a minimum of 40 weeks. It is common in Western Canada for humidity cells to be run for periods in excess of two years (104 weeks). It is possible that some tropical areas of the world experience climates similar to that of a humidity cell, but for North American mines the atmospheric conditions of the humidity cell are considerably harsher (Mills, 1998g).

For tailings and other low-permeability materials, the above design is not usually suitable (a) because water might not drain adequately, (b) loss of fines in the drainage and (c) the mechanism of oxidation is not the same as for more permeable waste rock. A larger diameter and shallower cell is preferred because it exposes a greater surface area for reaction. Recent developments in cell design for tailings are taking into account the relationship between sulphide oxidation rate and moisture content. Laboratory cells, which rely only on gravity drainage of leachate, might actually produce lower oxidation rates than in the field, due to a higher retained moisture which reduces air diffusion into the material. Assisted drainage by using a partial vacuum to the underside of the tailing following leaching can assist in reducing moisture contents to field values. The use of dry and humid air through (which is not always possible) or over the surface of the tailings is not necessarily required.

For each cycle, the following parameters should be measured to facilitate calculations and interpretation:

- Volume of leachate added and collected.
- pH.
- Specific conductivity.
- Alkalinity and/or acidity.
- Sulphate.
- Dissolved metal of interest (must include Ca and Mg).

Other parameters that can be measured include:

- Redox potential.
- Weight of cell and contents after each stage of each cycle to determine moisture content of the test sample (Lawrence and Day, 1997).

A typical humidity cell test might employ 500 mL water per week for a 1kg sample. This liquid to solid ratio is much higher than will be experienced for most waste facilities, even in areas of high rainfall. Recent studies on humidity cell protocols have shown that frequency, intensity and duration of simulated rainfall events can have a marked effect on both sulphide oxidation rates and NP depletion rates (Lawrence and Day, 1997).

Humidity cell tests are performed to evaluate the long-term acid-producing potential of mine waste rock, tailings or spent ore. The test simulates accelerated weathering of the sample. This is done by passing moist air followed by dry air through the sample chamber; moist air for three days, followed by dry air for three days and distilled water on the seventh day. The leachate is analysed for pH, conductivity, sulphate, acidity and dissolved alkalinity. This one-week cycle is typically run for 20 weeks. Samples are usually selected to represent the various lithologies at the mine and to represent a range of ABA and/or NP/AP values. In this way, humidity cell results can be used to identify or confirm the AMD risk associated with a range of ABA values. Refinement of the threshold ABA value is often useful for developing material handling plans (Schafer Laboratory, 1997).

A humidity cell test will usually determine *if* a given sample will "go acid", but not *when* the material from which the sample was taken will "go acid" since the operation of the humidity cell has intentionally accelerated sulphide mineral oxidation. Similarly, the accelerated rate of oxidation and acid production will result in an accelerated rate of oxidation products generation as dissolved metals and/or precipitated metal compounds. That is, the metal concentrations in the weekly leachate (wash cycle) are likely to be higher than those generated in the field (Mills, 1998g).

Cravotta stated that he has never obtained a soil, sediment or sludge sample, which did not have some bacteria of interest, regardless of the source of the material. **Unless there is reason to suspect otherwise, one can assume with confidence that a sample will contain the bacteria of interest**. Adding mine water to seed the crushed material may provide extra assurance, but is usually unnecessary. Microbial populations in humidity cells will behave quite differently from those in the field. It cannot be otherwise, since temperature regime, wetting cycles, water chemistry, nutrient supplies, etc. will be different, since these factors are important determinants of microbial populations. This does not necessarily invalidate the test, but it does add a degree of uncertainty in its interpretation (Sobolewski, 1997). The population will change in identity, typically from *T. ferrooxidans* (at pH 2.5) to *L. ferrooxidans/T. thiooxidans* (at pH 1) (Barr, 1997).

Disadvantages

The problem with standardising a leaching test is, that any time you inoculate it with a non-indigenous culture, it leaves open the question of environmental versus biotech, especially if the sample is from an arid mine site which would never see the precipitation that occurs in a humidity cell; therefore local bacteria will also be adapted to dry conditions (Barr, 1997).

Advantages

- The rates of acid generation and neutralisation can be measured in a temperature- and humidity controlled oxygenated environment
- Temporal variations in these rates can be measured.
- Solubilisation of trace elements can be monitored.
- Bacterial influence on kinetic rates can be assessed.
- Various control options such as blending of waste rock can be simulated (Mills, 1998g and Price *et al.,* 1997).
- The test has been widely used in Canada and the U.S.A. and compares favourably with other tests in respect to reliability (Chemex Labs, 1997).

According to Price *et al.* (1997b), the humidity cell is the recommended kinetic test for predicting primary reaction rates under aerobic weathering conditions.

3.2.3 COLUMN TESTS

Column leach tests are usually carried out on a larger scale than humidity cell tests and can be used to observe the effect of control strategies such as water flooding and blending more effectively than the latter method (Lawrence and Day, 1997).

Column test work may be undertaken to determine the kinetic behaviour of waste rock, ore or tailings stored on the surface and exposed to atmospheric weathering (sub-aerial storage), or stored under water cover (sub-aqueous storage). In either case the aim is to monitor water (leachate) quality with time by cyclic (weekly or monthly) sampling. Unlike humidity cell procedures, there is little, if any, standardisation of column test work procedures, allowing considerable flexibility. This flexibility permits column operation to be highly site- or material specific with regard to material particle size and size range (which for waste rock, ore or drill core is usually greater than that used for humidity cell tests, but still less than that of site conditions), sample mass, water infiltration or flow rate and degree of oxygenation. Because of the lack of standardisation of procedures, some regulatory agencies view column test work as supplementary to, or confirmation of, humidity cell test work, rather than an alternative to humidity cell test work. Price (1997) states that trickle leach column tests have the following **disadvantages** (over humidity cells):

1. The primary weathering products may be retained and therefore leachate chemistry cannot be used as a measure of the relative rates of acid generation and neutralisation and of times to mineral depletion.

2. They are run at laboratory temperatures, often with a reduced particle size and without seasonal variations and the extremes of both temperature and precipitation. Consequently, they provide poor analogues for heterogeneous drainage and the secondary mineral precipitation and dissolution, the controlling factors for metal leaching under all but the most acidic pH-values.

3. Without the entire load of primary weathering products, leachate results cannot be used either with geochemical speciation models to predict the extent of secondary precipitation or release, or with field data to predict metal leaching based on the predicted evolution in drainage chemistry (i.e. pH conditions).

The first listed disadvantage appears to ignore the fact that humidity cell tests are intentionally accelerated and cannot be used to predict field rates of acid generation and neutralisation; the second disadvantage is questionable, since column tests are invariably run on coarser material (except for tailings) than humidity cells and can be (and are) run with simulated site seasonal precipitation and temperature variations; the third disadvantage appears to discount the fact that column leachate is produced from a non-accelerated system in which the leachate is in equilibrium with solid oxidation products (Mills, 1998g).

Columns are typically constructed of Plexiglas, PVC, glass, or other suitable inert material and can range in size from 5cm in diameter by 60cm high up to 60cm in diameter by 600cm high or larger for laboratory investigations. Intermediate sizes are probably more typical (Lawrence and Day, 1997). Columns for sub-aerial and sub-aqueous test work are typically 76, 102 or 152 mm (3, 4 or 6 in.) in diameter and from about 1 m to more than 3 m in height. The following photographs show both sub-aerial and sub-aqueous column test work in progress (Mills, 1998g).

3.2.3.1 ACCELERATED KINETIC TESTS

Test methods can sometimes be used in which the conditions of the test are selected to accelerate the rate of weathering of a sample. Examples are increasing temperature to increase oxidation rates; decreasing pH to remove neutralising minerals so that the sulphide oxidation reactions can be studied without delay, and the addition of bacterial cultures, usually in combination with decreasing pH, to enhance sulphide oxidation. However, the popularity of such tests have declined in recent years, since such tests are further removed from reality and results are correspondingly more difficult to interpret. Two of the more popular accelerated kinetic tests are briefly described (Lawrence and Day, 1997).

3.2.3.1.1 BACTERIAL OXIDATION TESTS

Sulphide-oxidising bacteria can exert a major influence on the generation of AMD, particularly when pH-values fall below 3.5, due to higher reaction kinetics and increased solubility of ferric iron. In principle, therefore, kinetic tests in which bacterial activity is significant can provide additional reality to the simulated conditions. It must be noted, however, that the use of bacteria in kinetic testing requires specialised knowledge, and experience is lacking in most commercial laboratories involved in AMD testing. Several studies reported in the literature give conflicting evidence of the role and extent of bacterial action. This is most likely due, in many cases, to poor culture adaptation and to inexperience in growing bacteria and maintaining cultures in a suitable metabolic state for testing purposes.

The most widely used bacterial oxidation test has been the Confirmation Test developed by BC Research. In this procedure, sulphide-oxidising bacterial cultures are used to oxidise pyrite and other sulphides present in a finely ground sample, previously shown to be a potential acid producer in the BC Research Initial Test, under agitated and acidified (pH 2.5) conditions and at an optimum temperature for bacterial activity. Once the reaction is finished (usually after 2 - 4 weeks), an additional sample, equal in weight to the original sample is added in two increments. If sufficient neutralising minerals are present in the sample to raise the pH above 3.5, the sample is classified as a non-acid producer. If the bacteria were able to oxidise sufficient acid so that the pH remains below 3.5, then the sample is confirmed as an acid producer.

A **disadvantage** of this and other tests in which acidified conditions are employed is that the effect of the ability of neutralising minerals to prevent the onset of acid generation at circum-neutral pH is never assessed. Such tests are not, therefore, widely used today (Lawrence and Day, 1997).

3.2.3.1.2 SOXHLET EXTRACTION

The Soxhlet extraction apparatus, used widely by soil scientists to assess the weathering of soils, has been adapted for AMD studies. A Soxhlet extraction apparatus provides a chamber in which a sample is placed and subjected to leaching with condensate produced by the boiling of the leachate in a reservoir. Although the condensate is normally at high temperature, the apparatus can be modified so that the condensate is cooled before contact with the sample. Tests are typically completed in 1 - 2 weeks. Test data are not easy to interpret since the relationship to natural weathering is uncertain. The refluxing action of the procedure changes leachate chemistry significantly, especially with respect to iron, which will precipitate extensively in the high temperature reservoir. The test is not widely used (Lawrence and Day, 1997).

3.2.4 FIELD KINETIC TESTS

Field tests can include:

- Test waste rock piles.
- Small tailings deposits.
- Wall rock leaching.

The emphasis in the following sections is on test waste rock piles. Test tailings deposits are uncommon (Lawrence and Day, 1997).

Other kinetic procedures such as on-site lysimeters, pilot scale kinetic test pads and monitoring of the actual mine components represent a major increase in scale from the procedures described above. As scale increases, test conditions approach those of the operating (or closed) mine, so that these procedures may be better described as "monitoring" rather than "test work". Most of these larger scale options are unavailable to an AMD test work program for a new mine, where quantities of material for test work are usually severely limited (Mills, 1998g).

3.2.4.1 TEST WASTE ROCK PILES

Test waste rock piles are usually set up to determine weathering behaviour under field conditions for comparison with laboratory tests. The test material is usually obtained from mining (either at full- or small-scale) and can therefore provide an indication of actual behaviour that might be expected in a full-scale rock pile. Processes occurring in a rock pile can include:

- Build-up of soluble weathering products due to oxidation of sulphide minerals.
- Release of oxidation products by rainfall (or snowmelt in colder climates).
- Partial or complete neutralisation of acid products due to contact with silicate and carbonate minerals.
- Freezing of the pile during sub-zero conditions.
- Restriction of oxidation by application of covers.

3.2.4.1.1 Application and Limitations

Waste rock test piles are recommended for any prediction project to establish the relationship between weathering rates under laboratory and field conditions. They may be used simply to assess uncontrolled oxidation rates or may be designed to assess control alternatives.

The following limitations should be considered:

1. Initial Characterisation. For larger tests, characterisation of the material prior to testing becomes difficult.
2. Monitoring. Leachate samples need to be collected on a regular basis. If the site is remote, sampling costs may be high.
3. Seasonal Effects. Seasonal effects, particularly in small piles, can be severe, thereby obscuring the other features of interest such as long term decay in release of oxidation products.
4. Duration of Tests. Since the test is conducted under site conditions, the test may take much longer than the same test under laboratory conditions if the site experiences very cool conditions during part of the year .
5. Robustness. As with any field test, the site needs to be carefully protected from damage by extreme climatic conditions and vandalism.
6. Similarity to Full-Scale Rock Piles. It cannot be assumed that the test piles will behave the same as full-scale piles.
7. Testing of AMD control alternatives. Small-scale tests cannot be relied upon to evaluate AMD control alternatives, since duplication of operational conditions is difficult.

3.2.4.1.2 Method

The test material may be obtained from any source. Usually, run-of-mine material from an exploration adit or trench, or an active mine may be used. Several samples of the test material should be submitted for ABA, TIC, metal, size fractions and petrographic determinations. Size fraction analyses can be useful to estimate the relative exposed surface areas of different tests conducted at the same time. Analysis of individual size fractions using ABA may be useful if partitioning of sulphur and NP between the size fractions is suspected.

No standard method for test piles has been described. The test pile is constructed on a liner with a drain layer and a slotted leachate collection pipe wrapped in geo-sock. Leachate is collected in a covered pail equipped with a siphon to prevent the bucket from overfilling. The advantage of this design is that it has been observed to endure for many years without maintenance. The disadvantage is that the conical shape does not allow even distribution of flow through the entire rock mass.

Wooden crib designs are also used. Again, the crib is lined to allow leachate collection. The main advantages of this design are that all rock in the pile receives the same incident precipitation and the slats in the crib sides allow free movement of air into the rock. The disadvantages are that it requires greater construction effort, the design is not as robust as a leach pile and there is probably a limit to the size of the sample which can be contained by the rock.

Neither design is particularly recommended. If the test pad is to be used to evaluate cover material, it should be placed as a thin flat layer rather than a tall cone. The cover will need to extend over the edges of the material to avoid "edge effects".

Precipitation and temperature monitoring are recommended. As a minimum, precipitation should be determined to allow leachate volumes to be estimated. A direct measure of leachate volume is preferred since this allows chemical loads to be calculated. If it is not practical to measure flows directly, they can be estimated from the area of the pad and evaporation. For longer-term projects, a relationship between site precipitation and precipitation at a nearby permanent monitoring station can be developed.

Generally, the leachate should be sampled and analysed at least once a month. The sampling frequency may be increased during periods of high precipitation to evaluate short-term changes. If personnel are on site continually, leachate pH and TDS (or EC) can be monitored weekly and derived relationships between TDS or EC and other parameters used to obtain data for other parameters.

Interpretation of pad leachate may include the following:

- Trend in pH to determine whether acidic leachate was produced and evaluate buffering reactions.
- Recalculation of parameter (sulphate/metals) concentrations as loads (mg/s), on a mass (mg/kg/s) or surface area ($mg/m^2/s$) basis to evaluate trends and determine sulphide and carbonate consumption rates and metal release rates.
- Determination of trends in mole ratios (e.g. $SO_4/(Ca + Mg + 2K + 2Na)$ to evaluate relative rates of oxidation and buffering.
- Testing of mineral saturation using aqueous equilibrium models (e.g. MINTEQ).
- Determination of trends in mole ratios to evaluate changes in buffering mineral reactions (e.g. Ca/Mg).
- Early indications of acid release (other than a transition to low pH) can be indicated by SO4/(Ca+Mg+2K+2Na) ratios increasing from less than 1 to greater than 1.

3.2.4.2 MINEWALL WASHING PROCEDURE ("MINEWALL")

The Minewall Procedure, which has seen limited use to date because it is still in the developmental phase as a procedure, requires the cyclic irrigation of a small (1 m by 1 m), physically isolated, area of exposed pit wall or underground rock exposure and the collection of leachate. Physical isolation is achieved by sealing (with silicone bathroom sealant) a plastic frame (with a horizontal top, two vertical sides and an inclined bottom for leachate capture and collection) to a rock exposure. A polyethylene sheet is used to cover the Minewall assembly during leaching.

The area of exposed rock within the plastic frame is irrigated with 200 mL or more of distilled water. The run-off (leachate) is collected and analysed. The procedure is repeated weekly and results are expressed in µg/square metre/week or mg/square metre/week of anion or cation (Price, 1997).

The procedure is limited by the requirement that the isolated rock area be without fractures, which increase the surface area of the test by an unknown factor (Mills, 1998g).

Studies by Price and Kwong (1997) supports the BC policy of site-specific mine review requiring the consideration of each rock/waste type.

3.2.5 SUMMARY

It is not unusual for kinetic AMD test work to produce results that are inconsistent with ABA results. This can usually be attributed to the fact that ABA tests measure total sulphides, whereas kinetic tests are dependent upon exposed or liberated sulphides. As a consequence, kinetic tests may produce results that indicate that a sample is not net acid-generating when ABA analysis has indicated that the sample is likely to be net acid-generating. This situation most often arises when sulphides such as pyrite and pyrrhotite occur as inclusions finer than 5 µm in size as well as in the form of much coarser grains. In such conditions, the kinetic test has more validity than the ABA test, since the coarser material of a waste rock pile will also contain vast quantities of unliberated sulphide. It is also possible for the situation to be reversed, in that some neutralisation potential measured in ABA tests may not be realised in kinetic tests or in the field because the neutralising minerals are not adequately liberated (Mills, 1998f).

The generation and neutralisation of acid in waste rock piles, tailings and exposed rock and ore in underground mines is often surface area-, not mass-, dependent. Samples from the same deposit and prepared in the same way for humidity cell tests, can vary by an order of magnitude in their specific surface area. In this particular case, metal-leaching rates based on mass, rather than surface area, obtained from the humidity cell tests should not be directly compared with one another. Only when the metal leaching rates are normalised with respect to surface area can comparisons be accepted as valid (Mills, 1998f).

3.3 MODELLING METHODS

Computer models are another approach to the prediction of acid generation. Most of these models incorporate a number of chemical and physical parameters to describe the chemical reactions of acid generation, microbial catalysis and leaching (transport) of the weathering products (Jaynes (1991) Scharer *et al.* (1991) and Hunter (1997a)).

Typical objectives of modelling acid rock drainage are:

1. Prediction of soluble and mobile metal species.
2. Prediction of maximum metal concentrations.
3. Prediction of maximum metal loadings.
4. Prediction of the duration of dissolved metal production.
5. Prediction of concentrations and loadings versus time.
6. Evaluation of decommissioning options using all of the above information (Perkins *et al.*, 1997).

Seven model classes are identified: geochemical database generators, geochemical mass balance models, geochemical phase diagram generators, geochemical aqueous equilibrium models, geochemical mass transfer models, geochemical mass transfer-flow models and empirical/engineering (applied geochemical) models. Each class has a useful role in the assessment of acidic drainage, although no one class meets all requirements. Only the last four classes of models have predictive capability and are therefore of most interest as an aid in AMD decision-making (Perkins *et al.*, 1997).

Aqueous equilibrium models are static. They are used to identify the soluble and mobile metal species, their maximum metal concentrations and their relation to the minerals in mine waste rock.

Mass transfer models are dynamic reaction path models for closed systems that address maximum metal concentrations and their evolution with time.

Mass transfer-flow models are dynamic reaction path models in an open system that addresses the prediction of concentration, load and distance travelled over time.

Empirical/engineering models are best at history matching and have limited predictive capability. They are more appropriate for examining decommissioning options in acid drainage studies.

Input parameters required by these four classes of models include:

FIELD DATA: Water chemistry, Mineralogy, Surface Area, Temperature, Oxygen, Water Balance, Pile Structure, LAB DATA: Column Test, Humidity Cells, DATABASE: Kinetic, Equilibrium Thermo.

Mass transfer models, which address geochemistry in more detail, require more geochemical data and have the best potential for predictable capability in the long term. The major geochemical processes in waste rock piles are:

- Oxidation of sulphides, releasing acid, major and trace metals, and sulphate.
- Precipitation of oxyhydroxides, releasing acid and consuming the more insoluble major and trace metals.
- Dissolution/precipitation of sulphate minerals mediating the dissolved metal concentrations as well as TDS.
- Dissolution of oxyhydroxides, carbonates and silicates, thereby consuming acid. Co-precipitation may also provide a major control on trace element concentrations. Dissolution and precipitation are much more important controls on drainage water quality than ion exchange or adsorption/desorption processes.

Input parameters required for geochemical modelling: The second requirement for quantitative geochemical modelling of waste rock piles is accurate and complete sets of data. Input parameters include water composition, mineralogy, bacterial activity, reactive surface area, temperature, oxygen availability, water availability, waste rock pile structure and composition, humidity and column tests and thermodynamic and kinetic data (Perkins *et al.,* 1997).

Data requirements for most detailed models (from the ICMM):

Climatic:
Monthly mean surface temperature
Monthly precipitation/evaporation/evapotranspiration
Physical:
Surface area, depth
Bulk density, porosity/void volume
Moisture content/saturation level (% void volume)
Particle size distribution
Hydrological:
Hydraulic conductivity (vertical & horizontal)
Infiltration flow
Seepage flow
Water Quality:
Infiltration waters
Background water quality (surface & groundwater)
Porewater quality (with depth)
Seepage quality
Mineralogical:
Detailed mineralogical composition
Estimate of percentage leachable pyrite (sulphide minerals)

Chemical and elemental analysis of solids
Chemical formulae of minerals
Proportion pre-oxidised (easily soluble metals and radionuclides)
Kinetic:
Biological and chemical oxidation rates for sulphide minerals
Weathering rates for silicates and carbonates
Miscellaneous data:
Description of historic as well as current activities
Visual observations reported during field visits
Transport related properties:
Diffusion coefficients
Convective airflow
Thermal conductivity
Temperature measurements with depth
Solid-liquid distribution coefficients (Kd) for metals

It should be noted that according to MEND (1995) "The current waste rock engineering models are the state-of-the-art in geochemical modelling of waste rock piles." Despite this it goes on to say, "**They are clearly insufficient to make detailed predictions of ARD chemistry, as their chemical components are not complete enough. They can however be used for making relative comparisons and for data analysis.**"

The main limitation of geochemical modelling is that a lot of high quality information on both hydrology and geochemistry of a site is often needed to produce useful and reliable results. **With poorer quality data and less information generally available, more assumptions with greater uncertainties are required**. (Alpers and Nordstrom, 2000).

3.4 MANAGEMENT OF AMD

Successful management of AMD requires an understanding of the fundamental principles of AMD and the factors affecting water quality to be able to anticipate the formation, extent and impact of AMD before mining operations start. This will allow the development of operating and closure plans to reduce or eliminate the impact on the environment. For a new mine, a waste management plan can be designed and implemented to prevent the onset of AMD in many cases. At existing mines, developed before AMD management planning was practised, the challenge is to be able to assess the existing wastes and current mining and disposal plans in order to deal with AMD which might already be present and/or predict future AMD occurrences, so that control and closure plans can be developed (Lawrence and Day, 1997).

Although different interpretation schemes have been developed for assessing the risk of AMD using ABA and NP/AP values, the most commonly employed in Canada can be summarised as follows. An ABA value of < -20 ton $CaCO_3$/1000 ton represents a potentially net acid-producing material, while a value > +20 ton $CaCO_3$/1000 ton represents a net neutralising material. Values between -20 and 20 are uncertain and are often the focus of further kinetic testing. A more conservative estimate of the acid-producing potential of a material is based on the NP:AP ratio. A material is considered to have the potential to form acid if the NP: AP < 1 and its risk is uncertain if the ratio is between 1 and 3, although some states and regulatory agencies employ different NP/AP ratios (e.g., Nevada uses NP/AP ratios of 1 to 1.2 as uncertain) (Schafer laboratory, 1997). In BC's proposed guidelines for AMD prediction programs, reported by Price and Errington (1994), material is considered to be uncertain in their acid-producing potential if the NP/AP ratio is less than 4.

There are numerous successful strategies for controlling AMD at mine sites. These strategies involve identification of potential acid-generating material, application of engineering design measures to reduce or eliminate the generation or migration of AMD and finally, development of monitoring programs to identify potential AMD risks and to evaluate the effectiveness of the engineered designs (Schafer Laboratory, 1997). In many studies it has been assumed that acid-generating and -neutralising reactions occurring within waste piles are similar to those in slimes/slurry. There are, however, many physical and chemical differences between the two systems that result in a difference in AMD processes (Morin *et al.,* 1991).

Pyrite oxidation can be significantly reduced by complexing/precipitating Fe^{3+}, inhibiting Fe^{3+} production and depriving the system of oxygen (Jaynes *et al.*, 1984 and Scharer *et al.*, 1991).

It is therefore necessary to understand the basic chemistry of AMD. This would enable one to better understand all the methods being described that are/were used in acid-base accounting in the prediction of the acid-base potential for a mining area.

Correct removal and placement of the waste to minimise oxidation and treatment can then be made. To do this, geochemical information of the samples is necessary. The important parameters to determine for waste are its potential to turn acid, the metals that will be leached, the potential that is available to neutralise the acidity, the mass of acid and base that are available for the site and the time needed for the reactions to take place. This will determine the way the waste is going to be handled during development, operation, closure and post closure/remediation so that the environmental impact would be kept to a minimum.

4 THE DEVELOPMENT OF ABATE

In the previous sections, the general methods of acid-base prediction were briefly discussed. In the section to follow the methods that are proposed for use in South Africa are discussed. This section will highlight the recommendations and findings for four subsections: Static methods, kinetic methods, field observations and geochemical modelling.

A Specialist Workshop, to which the most important role players in the field were invited, was held at the WRC on 15 March 2000. The feedback from the group was positive and supportive of the progress and approach of the project. Appendix 2 lists the participants at this workshop and comments/issues regarding the project. Where possible, issues raised by these specialists in the field have been addressed.

Although the project has been abbreviated as the Acid-Base Accounting (ABA) project, the project aims are to define a suite of drainage prediction tools, applicable to South African conditions. The result is that a new acronym, **ABATE (from Acid-Base: Accounting, Techniques and Evaluation),** has been defined to include **all these methods**. This prevents any confusion arising from the use of the term ABA, since most people associate ABA with the static test component of drainage chemistry prediction.

The key questions in most prediction programs are:

- Is there a potential for AMD generation?
- Will the potential for acid generation be realised?
- When will the AMD be generated?
- How much AMD will be generated?
- For how long will AMD be generated?
- What will the water quality be?
- Will control measures work?
- Will the mine remain in compliance?

No single method can be used to answer all these questions. In opencast spoils this is an even greater problem due to the tremendous heterogeneity. As Rose and Cravotta (1998) state: “The chemical environment within spoil and consequently, water quality in unsaturated and saturated spoil commonly exhibit spatial and temporal variability. Because of the small dimensions of the varying chemical environments, thorough characterisation of chemical conditions (pH, O_2, Fe^{3+}, etc.) in unsaturated spoil may not be possible. The resulting drainage is generally a mixture of fluids from a variety of dynamic micro-environments within the spoil, so that prediction of discharge water quality is difficult and imprecise.” The **methods and detail of application are strongly dependent on the objectives of investigation and the conditions found on site**. It is therefore proposed that all methods relevant to the objective are used in an integrated manner (Refer to the Prediction Wheel (Figure 2) given previously). Section 9 gives case studies which include components of ABATE.

5 STATIC METHODS in SOUTH AFRICA

"*Those who must predict post-mining water quality sometimes debate which of the predictive tools should weigh the heaviest. An appropriate answer to the debate is 'all of them'* "(Kania, 1998).

5.1 Introduction to Static Methods

Generally when Acid-Base Accounting is referred to, the so-called static methods are involved. These are **screening methods** to determine the difference between acid-generating capability and acid-neutralising potential of a particular sample. Static tests are typically simple and inexpensive procedures to prove a preliminary assessment of the potential of a waste or other mine component to generate AMD. They are primarily intended to **examine the balance between the acid-producing and acid-consuming components of a sample**.

5.1.1 ABA TERMINOLOGY

- AP (Acid Potential) = S% x 31.25
- NP (Neutralisation Potential) - the capacity of a sample to consume acid
- NNP (Net Neutralising Potential) = NP - AP
- NPR = NP: AP

Units: Usually kg of $CaCO_3$ equivalent of net neutralisation potential per ton of rock

5.1.2 CONSIDERATIONS, ADVANTAGES AND LIMITATIONS OF ACID-BASE ACCOUNTING

Acid-Base Accounting is often a first or second step in determining mine drainage chemistry. It has been used very widely but it is important to point out that although it can be used very fruitfully, particularly in classifying samples into potentials for acid generation, there are several factors to consider.

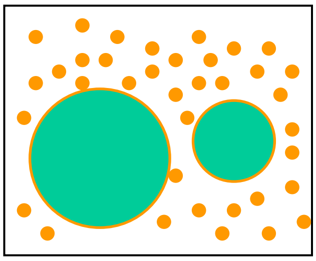
The principal **advantages of ABA** are the following:

- They are relatively cheap.
- Interpretation is based on decades of international research/experience.
- Methods of interpretation are clear and well-established.
- Results are obtained quickly.
- Correlation to field has been shown by case studies (local and abroad).

The widespread use of static tests in AMD prediction has been justified on the basis of historical and generally successful applications to North American coalfields. (Jambor, Dutrizac and Chen, 2000). Overall the static test can be regarded as a first screening level for mine drainage prediction, which provides a very good indication of acid-generating potential. Nevertheless, for the prediction of potential AMD, it is concluded that the carbonate NP provides the most realistic assessment of whether a rock or suite of rocks will be acid-generating. Most non-carbonate minerals can participate in the attenuation of acidity, but only to a modest degree and only in the longer term, after an AMD scenario has already developed (Jambor, Dutrizac and Chen, 2000).

Since static tests involve only single analyses and the procedures are simple, they are rapid and relatively inexpensive. Thus, although the amount of information provided by kinetic tests exceeds that of static tests, the latter are much more widely used in terms of numbers of tests conducted.

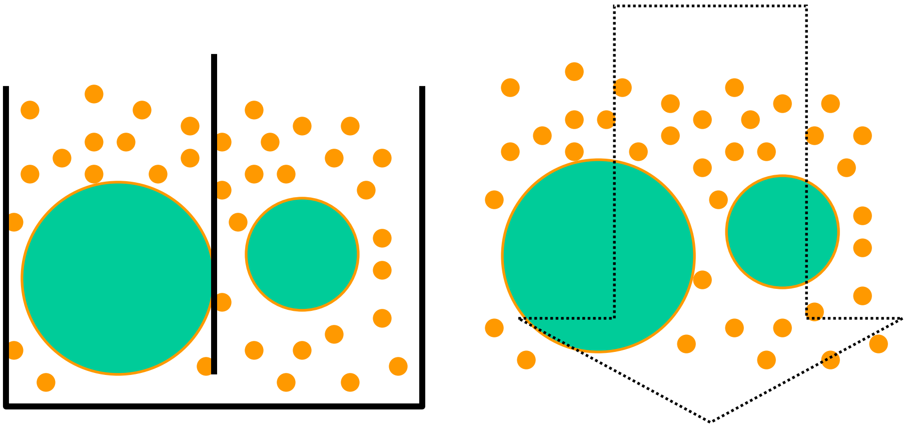
The figure below illustrates some of the factors that impede the extrapolation of ABA results to the field situation through uncertainty.



Possible that:

$CO_3^{2-} > S^{2-}$ in ABA

$CO_3^{2-} < S^{2-}$ in practice



The figure above shows that in the ABA test the rock is crushed; thus all the constituents can react relatively easily. The reactions are also regarded to be virtually instantaneous. In the field situation shown to the right, the kinetics and distribution of the system will determine how the minerals react. This could be very different to that predicted in the laboratory. This approach is analogous to that of an equilibrium approach used in classical chemistry - the tests provide an indication of the likely end point in the system with no concern about how this end point is reached.

The **limitations of ABA** are thus the following (most of these limitations also apply to several other methods):

- It only provides a possibility of occurrence.
- Reaction rates are ignored. (ABA generally tests the fast reacting species; slow reacting neutralising species will usually not prevent acidification. See comments by Jambor *et al.* (2000) above).
- Assume instant availability of reactive species. (However, nearly all rock samples lacking carbonates (which are fast reacting thus instantly available) or not of dunite composition (predominantly olivine + serpentine) have insufficient NP to be classifiable as “not potentially acid-generating” if the minimum limit for this category were to be set at, for example, 20 kg CaCO3 equivalent/tons of material (Errington, 1991).
- Simple reaction stoichiometry is assumed.
- Size effects are ignored (Limestone particles of greater than 6.4 mm are coated with precipitates and are only 20% utilised when acid conditions are in evidence, (Scharer *et al.*, 2000). However, from this paper it is clear that if a 4:1 NPR is used then only 10% fines is required for the system to react as expected. From the trenches dug in the spoils a > 10% fines ratio is a valid assumption in South African conditions, therefore in spoils this limitation is a minor consideration).
- Extrapolation to the field is uncertain when volumetric calculations cannot be made.

Despite all these limitations ABA is a very important component of the ABATE strategy. It has been used widely across the world and the interpretations methods and test methods are well-established. Acid-Base Accounting and other static tests only provide initial assessment of the potential of mining wastes to produce AMD, but the methods are and will be widely used to get an overall view of the potential for a specific site.

5.2 SUGGESTED METHODS

The following are the suggested methods for acid-base accounting:

- Paste/Initial pH and solution products.
- Acid Potential using hydrogen peroxide or Leco furnace.
- Oxidation products analysed, when using he H_2O_2 method.
- Neutralising Potential using sulphuric acid.

The recommended methods are discussed in detail in Section 3.1, and brief supporting evidence for their selection will be outlined below.

5.2.1 PASTE/INITIAL pH

It is suggested that a distinction be drawn between the field determination of pH on rock samples and those in the laboratory. Thus it is recommended that the term ”paste pH” be used for field determinations and “initial pH” for those in the laboratory.

It is recommended that the 1:10 ratio of sample to water, measured after 24 hours, be used. This allows a more realistic determination of the current pH and also allows solubility reactions to be more complete than an instantaneous or 10 minute measurement. The 1:10 ratio is preferred to the 1:1 or 1:2.5 ratios since the supernatant can also be used to determine the water-soluble elements. Price and Kwong (1997) also state that they use a 1:10 ratio for determining water-soluble elements.

This pH-value indicates the immediate acidic or basic characteristics of the sample and could indicate if acid generation has already been initiated. Most of the other authors use the method as described by Sobek *et al.* (1978) with modifications by Page *et al.* (1982). A paste is prepared in the ratio of 1 g soil:1 g deionised water, stirred for 5 seconds, left to stand for 10 minutes and the pH taken of the slurry. In the method prescribed by the Soil Science Society of South Africa (1990) the ratio is 1 g soil:2.5 g deionised water, 5 seconds stirring, stirred again after 50 minutes and allowed to stand for 10 minutes whereafter the pH is determined.

The initial pH of samples recommended is determined with a ratio of 1 g:10 g deionised water. After addition of the water, the sample is stirred for 30 minutes and left overnight. The pH is determined after 24 hrs. Miller *et al.* (1997) use a ratio of 1 g sample:2 g deionised water. This was not included in this study.

In this experiment, all three ratios of 32 different samples were prepared and treated as described by the Sobek (1978), Soil Science (1990), and the recommended method. The values obtained were for a 10-minute period as well as a 24 hr period. Only for the 1:10 ratio was the pH determined after 60 minutes as well.

The results are given in Figure 13 to Figure 15.

In all these figures the following codes are used to differentiate lithologies:

CODE	DSC	MDS	SNDS	SHLE
Description	Discard	Mudstone	Sandstone	Shale

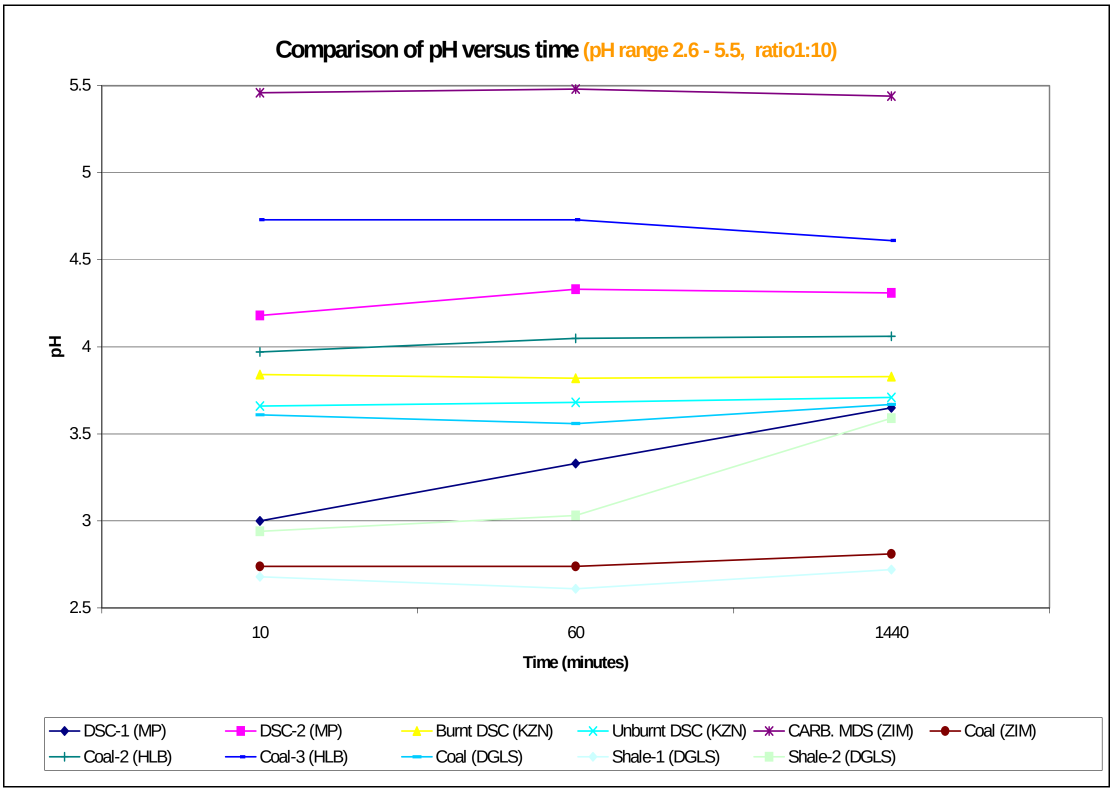


Figure 13. Graph showing the differences/similarities in the lower pH-range after 10 minutes, 60 minutes and 24 hours for the ratio 1:10 (Initial pH).

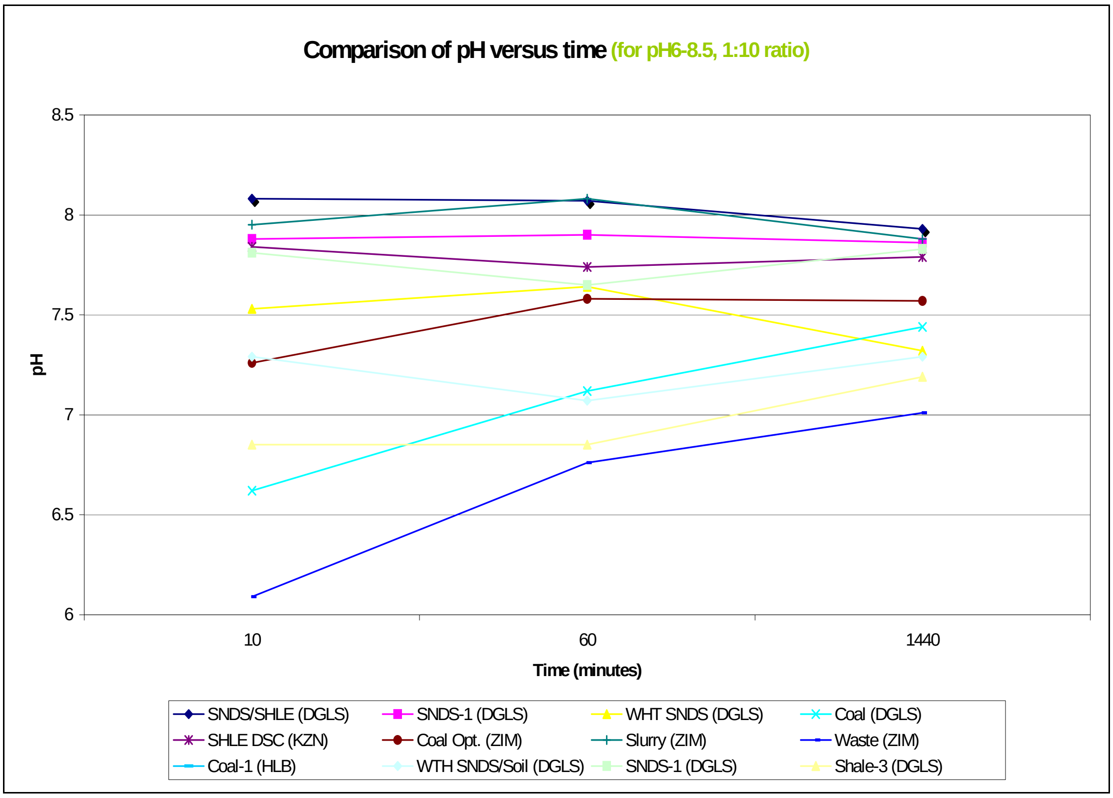


Figure 14. Graph showing the differences/similarities in the neutral pH-range after 10 minutes, 60 minutes and 24 hours for the ratio 1:10 (Initial pH).

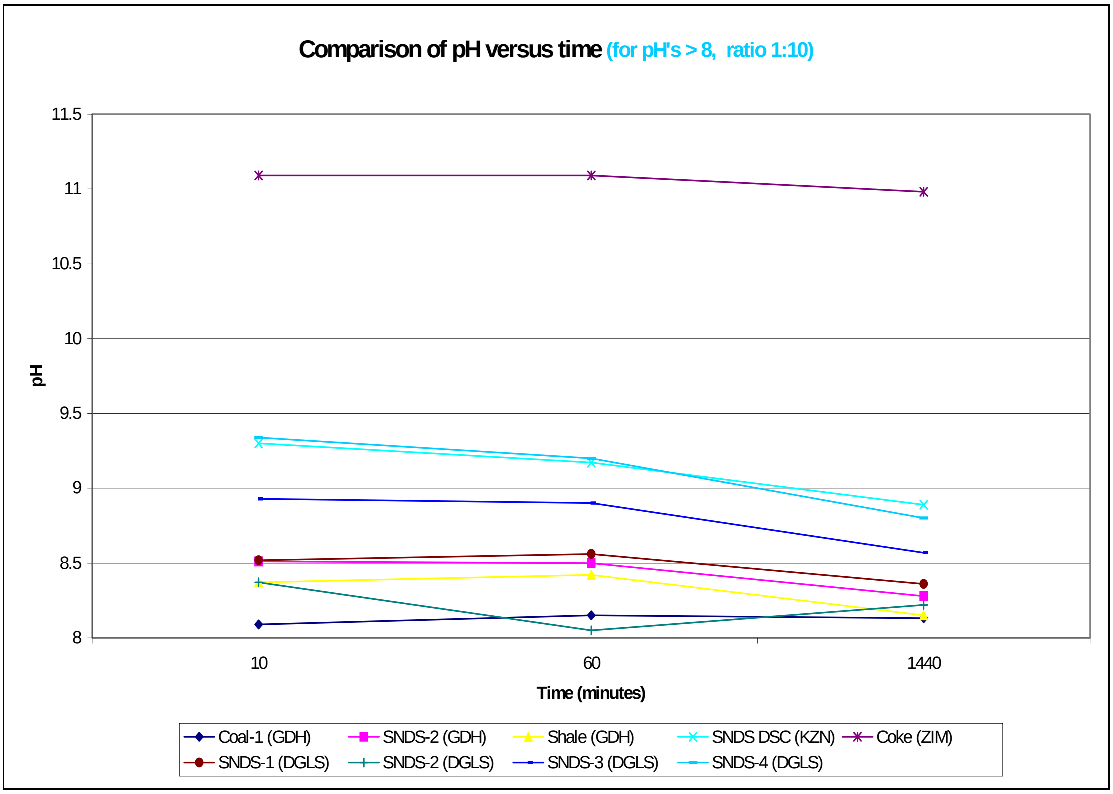


Figure 15. Graph showing the differences/similarities in the higher pH-range after 10 minutes, 60 minutes and 24 hours for the ratio 1:10 (Initial pH).

The values for the 1:10 ratio after 60 minutes did not show a significant trend either way and it was decided to rather compare paste pH, Soil Science pH en starting pH with time. From this it is clear that the pH after 60 minutes is a transition between 10 minutes and 1440 minutes and therefore no further mention of the 60 minute time will be made.

In the following graphs (Figure 16 to Figure 20) the pH's for 10 minutes and 24 hours for each of the three ratios are plotted.

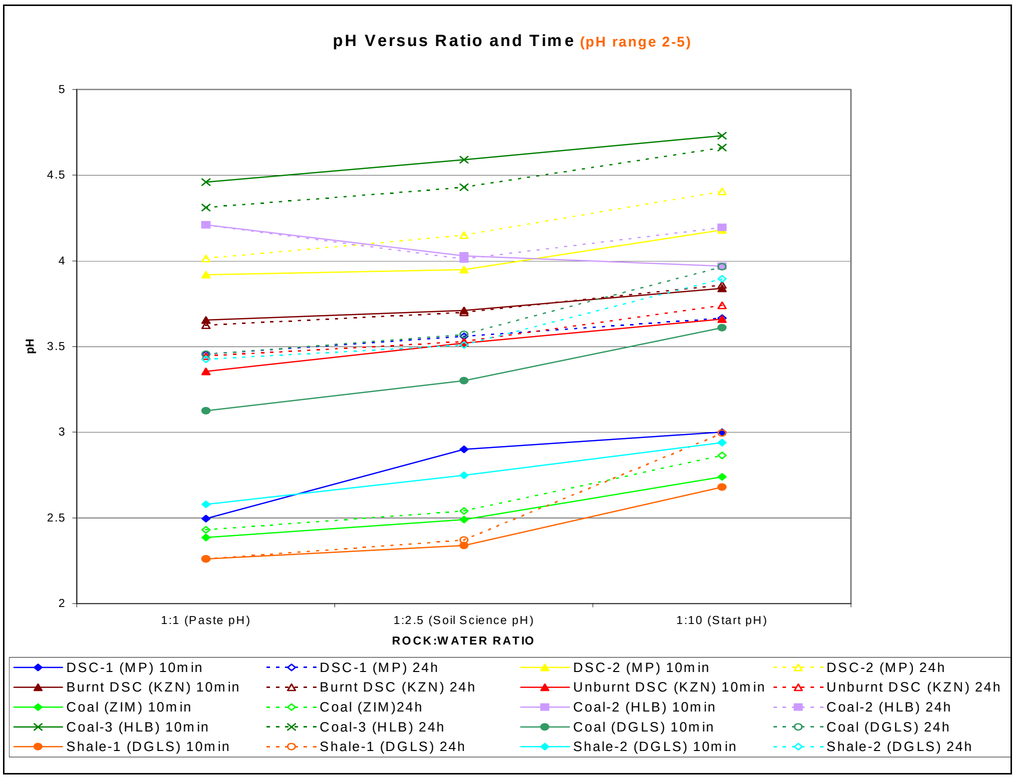


Figure 16. pH versus Ratio over Time (pH-range 2-5).

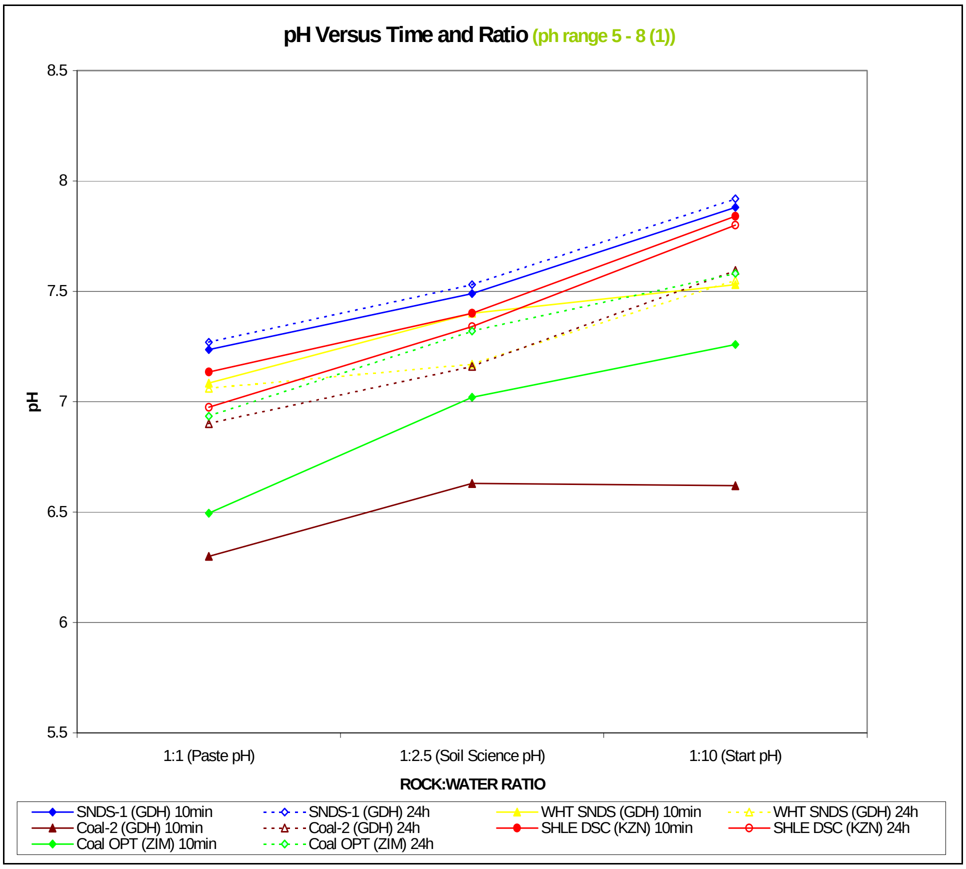


Figure 17. pH versus Ratio over Time (pH-range 5-8(1)).

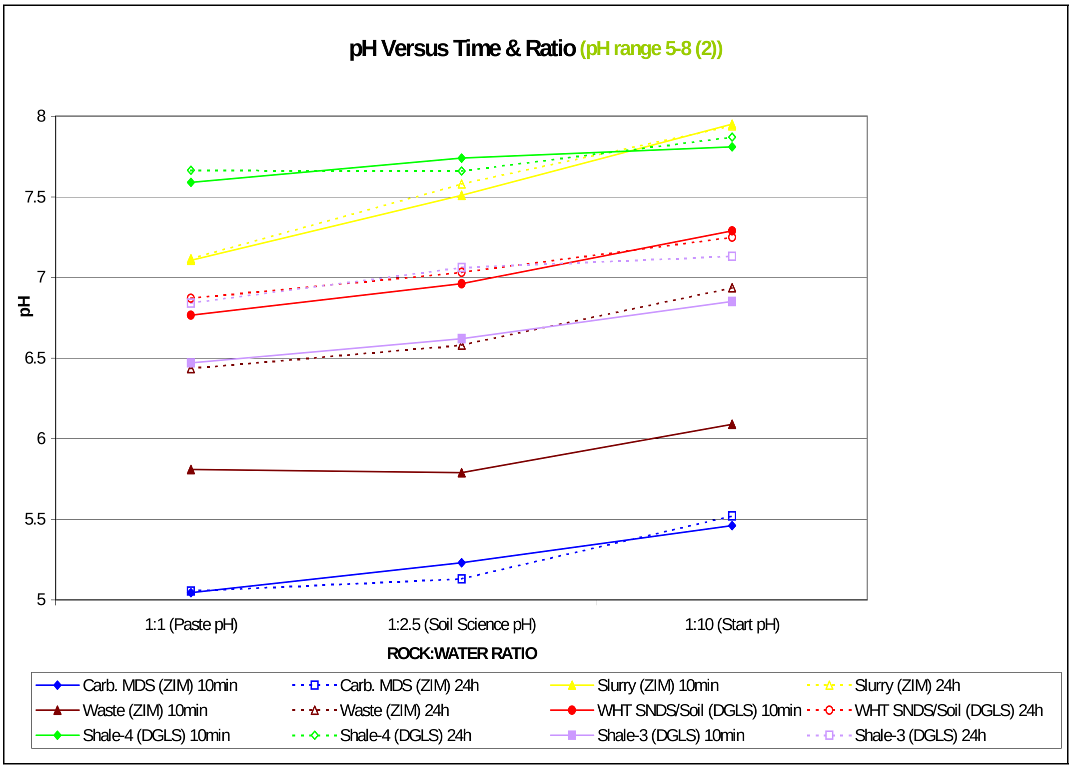


Figure 18. pH versus Ratio over Time (pH-range 5-8(2)).

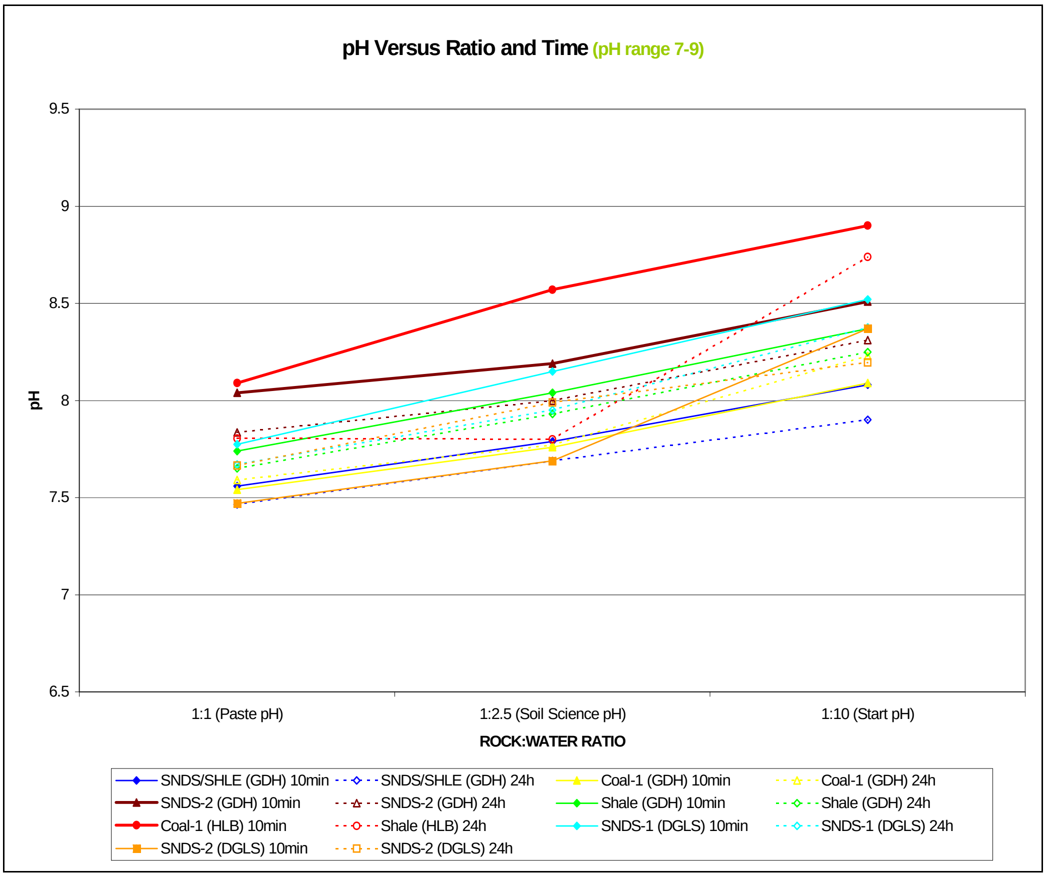


Figure 19. pH versus Ratio over Time (pH-range 7-9).

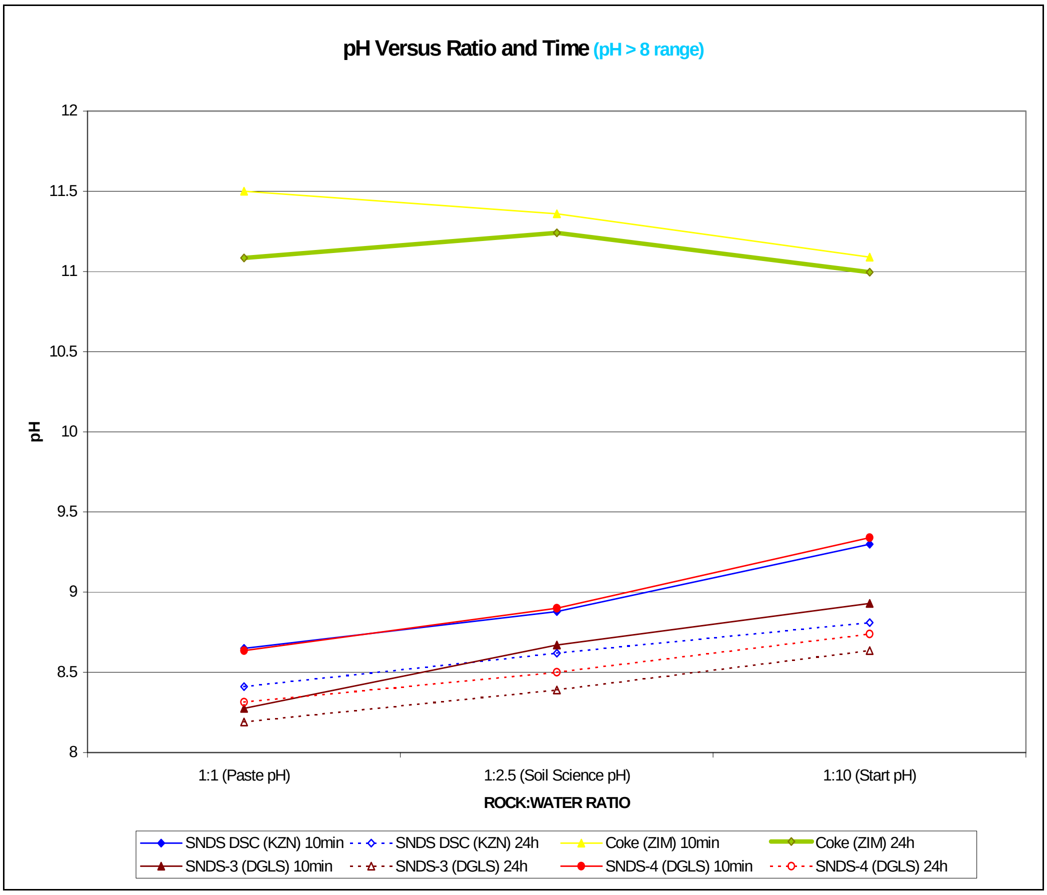


Figure 20. pH versus Ratio over Time (pH > 8).

The pH's obtained in the 1:10 ratio give higher values for all samples both after 10 minutes and 24 hours. There is an exception for the Coke sample where the pH of the 1:10 ratio is lower than that for the other two ratios tested. There is no consistency in whether the 24 hr measurements are higher or lower than those of the 10 min samples. Overall, there is not a very big difference in obtaining the initial pH after 10 minutes or 24 hours and neither is the difference in ratio of any significance. It is recommended that the 1:10 ratio after 24 hours be used, so that the supernatant can also be used to determine the water-soluble elements.

The graphs show that the variation in ratio does not yield a very great difference in measured pH. The 1:10 ratio is more versatile since the supernatant can be analysed for soluble elements.

5.2.2 NEUTRALISING POTENTIAL

H_2SO_4 (0.06N) is added to pulverised rock samples. The pH of this slurry must be below 2.5 after 24 hours, before back titration to a pH of 7 is done with NaOH (0.06N). If the pH is >2.5, more H_2SO_4 is added and the sample left another 24 hours for reactions to complete. The bulk neutralising potential obtained from acid titration is often a good indicator of neutralising capacity above 10 kg/t $CaCO_3$ (Morin and Hutt, 2000), thus the method is justified for most cases.

This method is a variation of established methods (a modification of Lawrence *et al.,* 1997, a modified Sobek method). The advantages of this method are that it does away with the difficult to apply "fizz" test. This will allow for a more consistent application of the method and more reproducible results. Sulphuric acid is chosen for several reasons:

- Results are comparable to HCl (see graph below).
- It is the acid reacting in natural AMD processes.
- It is more stable than HCl; thus there are fewer problems with maintaining standard solutions.
- Dilute HCl sometimes does not react with certain neutralising minerals, whereas sulphuric acid is more likely to do so.

The pH 7 variation from the Lawrence *et al.* pH 8.3 again yields very minor differences in results, but it is felt that since the intention is to obtain *neutralisation* potential, pH 7 is a more realistic end point than a pH of 8.3. Furthermore the pH end point of 7 corresponds to the EPA/Sobek method and is thus widely accepted.

The 24-hour period allows for slower neutralisation reactions to be more complete and thus results in more accurate determinations. It is also felt that with this method, the siderite correction, which needs to be taken into account in certain instances, is allowed for. The use of a 24-hour rather than a longer period is justified since solutions which have not acidified after this period under the conditions of the test are unlikely to acidify over a longer period. Therefore the acid addition will also need to be done after a longer period.

5.2.2.1 HCl VERSUS H_2SO_4 IN DETERMINING THE NEUTRALISING POTENTIAL

Most other authors (Sobek *et al.* (1978) and Lawrence and Wang (1997)) state that they use HCl, which they add to the pulverised sample to bring the pH down to under 2.5, in the determination of the neutralising potential of a sample. HCl is a monoprotic acid, but is not as stable as the diprotic acid H_2SO_4 (Purcell, 1998). HCl is usually used to prevent the precipitation of sulphate minerals (the chlorides are generally less likely to form precipitates) but since the sulphuric acid is reacting in the field this is considered a less realistic representation of the situation.

In order to test the effect of using sulphuric as opposed to hydrochloric acid, duplicate samples of the 32 sample batch were weighed, HCl added to one and H_2SO_4 to the duplicate sample. Samples were stirred (30 minutes) and left overnight at 25°C for acid digestion. Back-titration with standardised NaOH was done to a pH of 7 and terminated only when the slurry was stable after 24 hours.

The following graph (Figure 21) shows a regression coefficient of 0.9971. There is thus no difference in either acidifying the pulverised sample with HCl or H_2SO_4. Since H_2SO_4 is more stable than HCl and AMD mainly consists of H_2SO_4 and not HCl, it is more advantageous to use sulphuric acid in the determinations. The use of sulphuric acid provides a better simulation of field conditions than hydrochloric acid for the Base Potential determination (Bruynesteyn (1984) and Lawrence and Day (1997)).

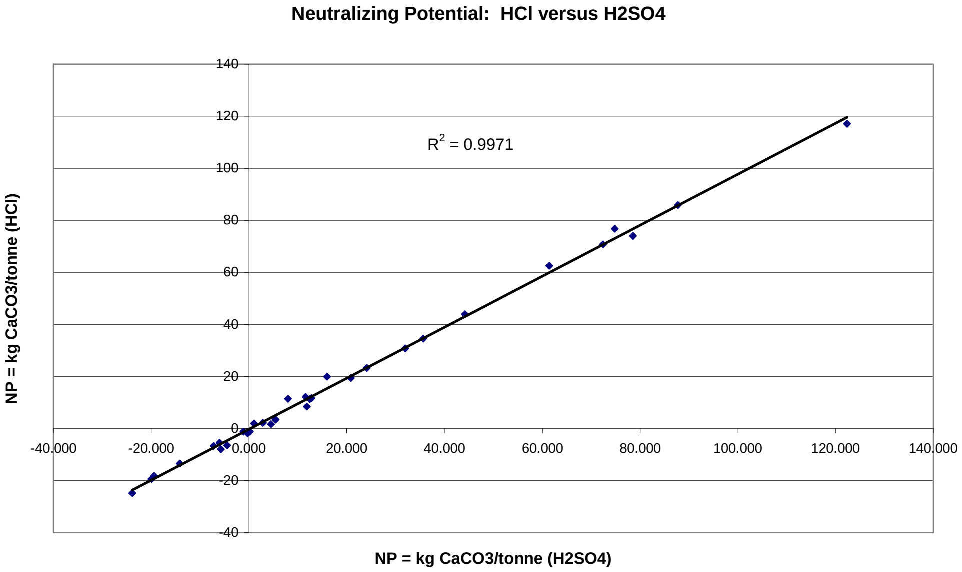


Figure 21. Comparison of HCl and H_2SO_4 for determination of Neutralising Potential.

This is then a modification of the Lawrence and Wang (1997) method for determining base potential.

5.2.2.2 SIDERITE

According to Skousen *et al.* (1997) and others, the content of siderite ($FeCO_3$) must be taken into account when determining base potential. The major reactants and products for the NP digestion and titration, shows that 3 moles of acidity (HCl) (or 1.5 moles of H_2SO_4) and 3 moles of base (NaOH) are consumed and that CO_2 is exsolved. As a result, the overall reaction yields a zero NP for siderite (no net acidity or alkalinity). The recommended method of determining base potential extends over a much longer period than that described by Sobek *et al.* (1978) and is only terminated when the pH is stable at 7 or when the volume 0.06N NaOH added, is less than 0.05 mL over 24 hours, which thus allows for sufficient time for ferrous iron oxidation and subsequent precipitation of ferric hydroxide. Thus, if running the back titration over as long a time as the suggested method, no corrections have to be made for siderite.

The following graphs give visual confirmation of the reasoning outlined above:

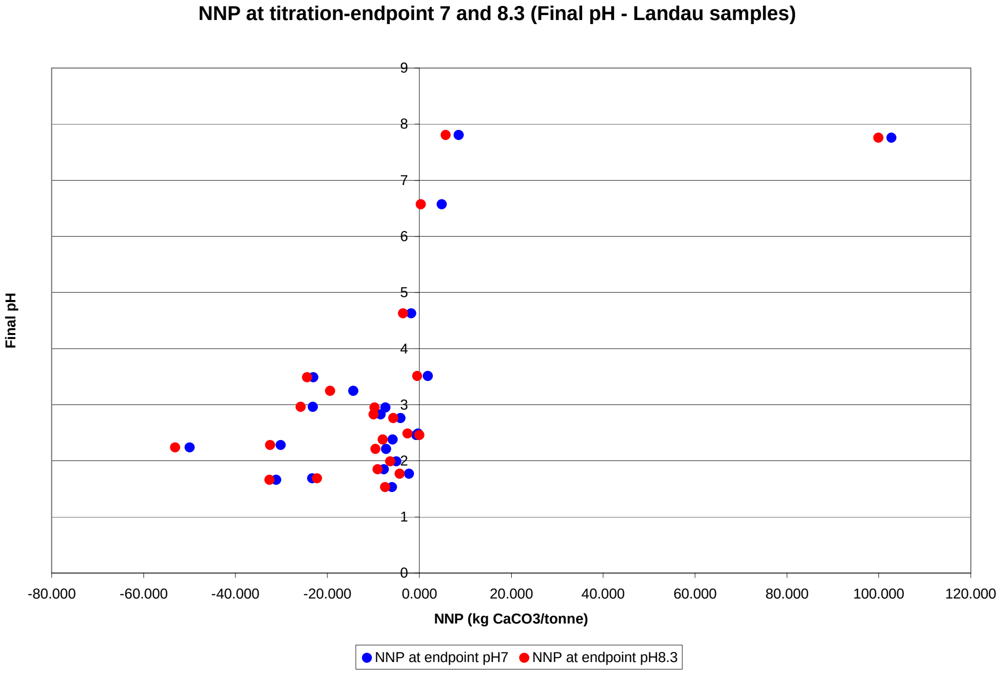


Figure 22. Endpoint pH 7 and pH 8.3 comparison.

5.2.3 ACID POTENTIAL METHOD

A direct determination of acid-producing potential is the rapid pyrite oxidation technique utilising 30% H_2O_2. The actual acid produced during pyrite oxidation by H_2O_2 is termed potential acidity. Pulverised rock samples are used and 30% H_2O_2 is added. This method is based on the Miller *et al.* (1997) Net Acid Generation (NAG) method, with the modification that 30% rather than 15% hydrogen peroxide is used. The reasons for this are that with the more dilute solution, incomplete oxidation can result. The 30% also makes it easier in cases where there is a lot of pyrite present since volumetric limitations are less likely to play a role.

The H_2O_2 method has several potential advantages:

- Only reactive species will oxidise and result in acid generation.
- An immediate indication of the final field pH can be obtained, assuming that optimal acid-generation conditions exist in the field. NAG pH tests confirm that NNP > 20 generally not acid producing and - 20 usually low NAG pH. (Based on a comparison with a limited number of samples it appears that the NAG pH may be able to discriminate AMD risk for “uncertain” samples (Schafer, 2000)).
- Some quality control can be done since resultant pH-values that are low should also have far more acid potential than the neutralising potential.
- The resultant reaction product can be analysed to give an indication of the expected heavy metal content and final water quality which could result.
- The method yields very good reproducibility.

The sections that follow show several of these factors.

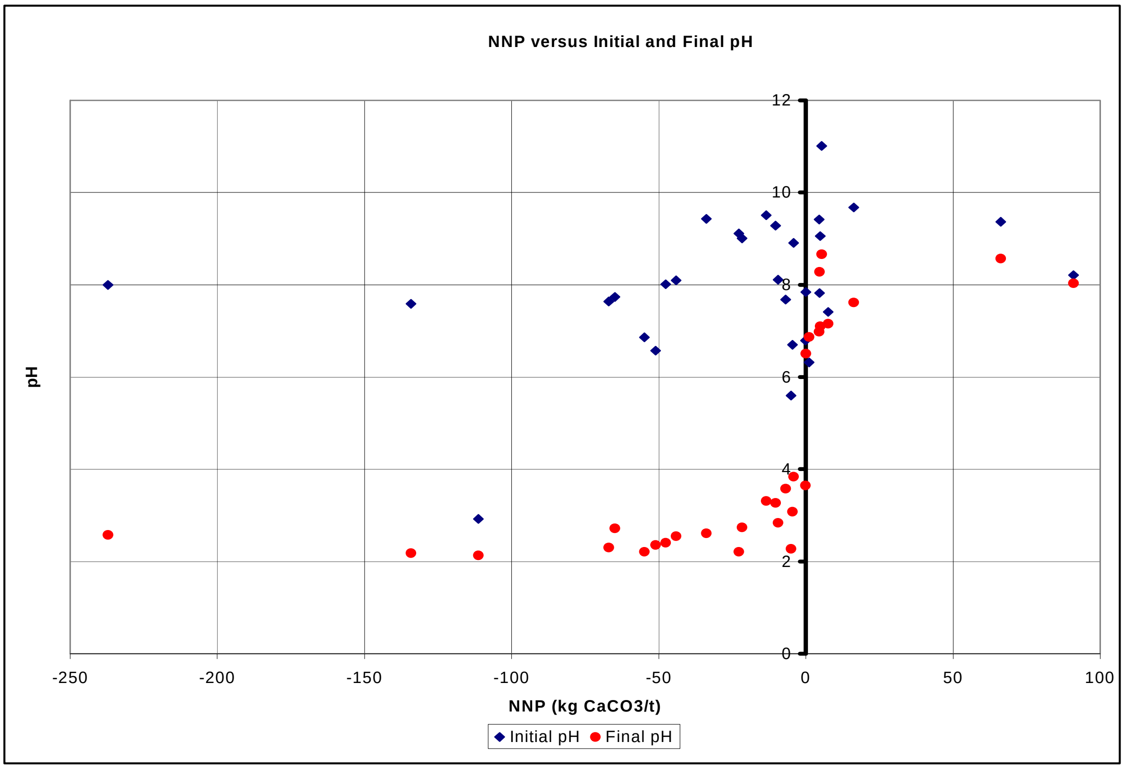


Figure 23. Result NAG test used as quality control.

5.2.3.1 COMPARING 30% TO THE 15% (Miller) H_2O_2 METHOD

This procedure is based on the hydrogen peroxide oxidation procedure developed by Finkelman and Giffin (1986) for determining the pyrite content of coal overburden. Coastech Research Inc. (1989) applied the test as a prediction method to estimate the net acid production from waste rock and tailings.

Evaluation of these test procedures indicates that temperature, concentration of H_2O_2, sample:solution ratio and particle size do not significantly affect the final pH, but can influence the reaction kinetics and amount of acid generated (Krantz, 1993 and Miller *et al.*, 1997).

Miller *et al.* (1994 and 1997) have been developing a simple hydrogen peroxide oxidation procedure for quantifying the acid-generating capacity of a sample. This procedure, known as the net acid generation (NAG) test, provides a direct measure of the net amount of acid produced by a sample. The procedure is simple, low in cost and currently used to identify potentially acid-forming materials at a number of mine sites in Australia, New Zealand, Papua New Guinea and Indonesia.

Test work by Miller *et al.* (1994) indicates that a relationship may exist between the kinetics of the NAG test and the lag period observed in the field. They aim to establish a relationship and then to provide a time factor for use in waste management design. An advantage of the NAG test is that it requires minimal laboratory equipment and can be completed within hours. The suggested method involves oxidation of the sample with 30% H_2O_2 and then determining the sulphate (and other elements) on the filtrate by ICP.

According to the method of Miller *et al.* (1997), 250 mL of 15% H_2O_2 is added to a 2,5 or 1,0 g pulverised sample. Several samples were oxidised with 30% H_2O_2 and the AP determined on the sulphate content of the supernatant while the NAG was determined to pH 4.5 (Miller *et al.,* 1997) and pH 7 on both the slurry and filtrate.

Table 6. NAG (pH 4.5 and 7) values on filtrate and slurry and AP values on filtrate.

Sample	Final pH	NAG pH 4.5 (kgCaCO3/t) On filtrate	NAG pH 7 (kg CaCO3/t) On filtrate	AP (Open) - ICP 30% H2O2 (kg CaCO3/t)	AP (Closed) - ICP 30% H2O2 (kg CaCO3/t)
Discard-1 (MP)	1.7	262	280	258	517
Coal (DGLS) 196/3	2.3	17	21	39	78
SNDS (DGLS) 196/4	2.33	12	14	30	60
Shale-2 (DGLS) 196/5	2.06	99	109	119	238
SNDS (DGLS) 196/6	2.47	5	6	9	18
Shale (DGLS) 196/7	2.37	12	17	24	49
Coal (DGLS) 196/10	2.28	16.2	22	24	48
Coal (DGLS) 196/13	3.04	1	9	21	41
Coal (DGLS) 196/14	2.31	12.4	18.1	32	64
Shale(Shale DGLS) 161/2	2.01	39	49	53	106
SNDS (DGLS)161/6	2.57	7	24	31	62
Coal (DGLS) 161/7	2.37	15	21	37	73
Coal (DGLS)161/10	2.7	4	8	38	76

Sample	Final pH	NAG pH 4.5 (kg CaCO3/t) On slurry	NAG pH7 (kg CaCO3/t) On slurry	AP (Open) - ICP 30% H2O2 (kg CaCO3/t)	AP (Closed) - ICP 30% H2O2 (kg CaCO3/t)
Coal (DGLS) 62/4	3.47	0.3	5	26	53
Coal (DGLS) 62/6	2.42	7	12	17	34
Coal (DGLS) 62/9	2.63	10	14	53	106
Coal (DGLS) 62/11	2.61	5	12	19	38
Discard (Witbank)	2.08	250	274	208	416
Discard-1 (MP)	1.7	236	247	258	517
Discard-2 (MP)	1.82	45	69	59	118
Discard (Witbank)	2.08	138	149	208	416
Shale-2 (DGLS)	2.06	101	109	119	238
Coal (DGLS)	2.3	68	72	78	155
Shale-1 (DGLS)	2.3	37	48	52	103
Coal Opt Area (ZIM)	2.18	32	50	77	153
Coal Chaba (ZIM)	2.13	51	72	50	100
Slurry (ZIM)	2.21	40	45	44	89

Miller's (1997) method titrates the slurry to a pH of 4.5; the difference if titrated to a pH of 7 was investigated to compare the methods. From these results there is not much difference between the NAG at pH 4.5 and 7, except for the low (<20) values. No titrations were done on the slurry samples with these low NAG values.

The NAG values obtained are in the same order as the AP (open systems) and thus this method is validated with that used by Miller *et al.* (1997). In mines, conditions tend more to the closed system and that is why we use the latter.

The same quantity of H_2O_2 was added, but in the form of 30% H_2O_2. The total quantity (125mL, 30%) was added in 5mL shots and at once, to evaluate the method of adding the oxidising solution.

5.2.3.1.1 INFLUENCE OF TITRATION TO FILTRATE AND SLURRY

In the method by Miller, titration is done for the whole sample (slurry) without filtration. For analysis on the ICP, we need to filtrate the sample; titration was thus also done on the filtrate to compare to the described method. Triplicate samples were done for both samples and the results are summarised in Table 7.

Table 7. Summary of NAG values on filtrate and slurry.

SAMPLE	NAG (kg $CaCO_3$/t)
Discard-1 (MP)	
On slurry	224
On filtrate	256
Shale-2 (DGLS)	
On slurry	98
On filtrate	101

According to these results, there is no significant difference between titration to either the slurry or the filtrate. One should not expect differences, because the sample has been fully oxidised and would not take part in the neutralisation step.

5.2.3.1.2 BOILING OF SAMPLE

In the method described by Miller *et al.* (1997), the sample is boiled after oxidation. On the samples tested (NAG pH<2,5), there was no significant difference in the kg SO4/ton obtained, whether the samples were boiled or not, after completion of the oxidation. The method described by Miller *et al.* (1997) was completed up to the point before NaOH is added to the sample and sulphate and iron were determined (ICP) on the filtrate. The results are shown in Table 8.

Table 8. Influence of Boiling on determining the Acid Potential.

Sample	Fe (kg/t)	SO_4 (kg/t)	SO_4 (kg/t) Duplicate	AP as $CaCO_3$ (kg/t)
Discard-1 (MP)				
15% H_2O_2, succession + Boil	64	258		269
15% H_2O_2, succession - Boil	88	279	287(- Boil)	291
15% H_2O_2, once + Boil	63	243	269(- Boil)	253
30% H_2O_2, succession + Boil	81	263		274
Shale-2 (DGLS)				
15% H_2O_2, succession + Boil	21	107		111
15% H_2O_2, succession - Boil	34	106	114(- Boil)	110
15% H_2O_2, once + Boil	21	103	97 (- Boil)	107
30% H_2O_2, succession + Boil	23	111		116

Boiling the sample after oxidation can reduce excessive effervescence, but this is usually not a problem in samples with a low final pH. It can be used successfully for samples with a medium to high final pH. Boiling does not make a difference to the AP (kg SO4/ton) of the sample. It is important to bring the volume loss into consideration. From these results, it is also clear that adding the peroxide once does not result in oxidation as efficiently as when the peroxide is added in succession.

5.2.3.1.3 DISCOLOURING OF ACIDIFIED SAMPLES

The acidified filtrate tends to discolour after some time (a week and more). The question is: what is causing this discolouring (Orange/yellow => colourless)? The following table (Table 9) summarises some of the main elements obtained after immediate and a time lapse for analysis.

Table 9. Immediate versus Time delay for analysis of filtrate.

Sample	Fe	Fe	SO_4	SO_4	Al	Al	Mn	Mn	Zn	Zn
Shale-2 (DGLS)	Imdt	Time	Imdt	Time	Imdt	Time	Imdt	Time	Imdt	Time
15% H2O2, succession	30	30	114	111	0.37	0.28	0.26	0.15	0.05	0.04
15% H2O2, once	14	14	97	102	0.27	0.27	0.26	0.15	0.04	0.04

From this table it can be seen that there will be no influence on the AP determined, but manganese seems to be the element that tends to be lower after some time in the acidified supernatant.

5.2.3.2 COMPARING LECO %S WITH 30% H_2O_2 %S

The Leco furnace is widely used for determination of total sulphur in a sample. This is often the best indication of potential acidity rather than trying to determine all the different sulphur species (organic, sulphate, sulphide etc.) (Kania, 1998). There is a good correlation between the Leco methods and the hydrogen peroxide method, as shown in the graph below (Figure 24).

Total S, as determined by a Leco furnace will overestimate the acid potential if a significant amount of sulphate S, organic S or other non-pyritic forms occur in the sample. 50 samples were selected and split. Part of the samples was analysed by LECO and the other by the 30% H_2O_2 method. The results obtained from both methods are shown below.

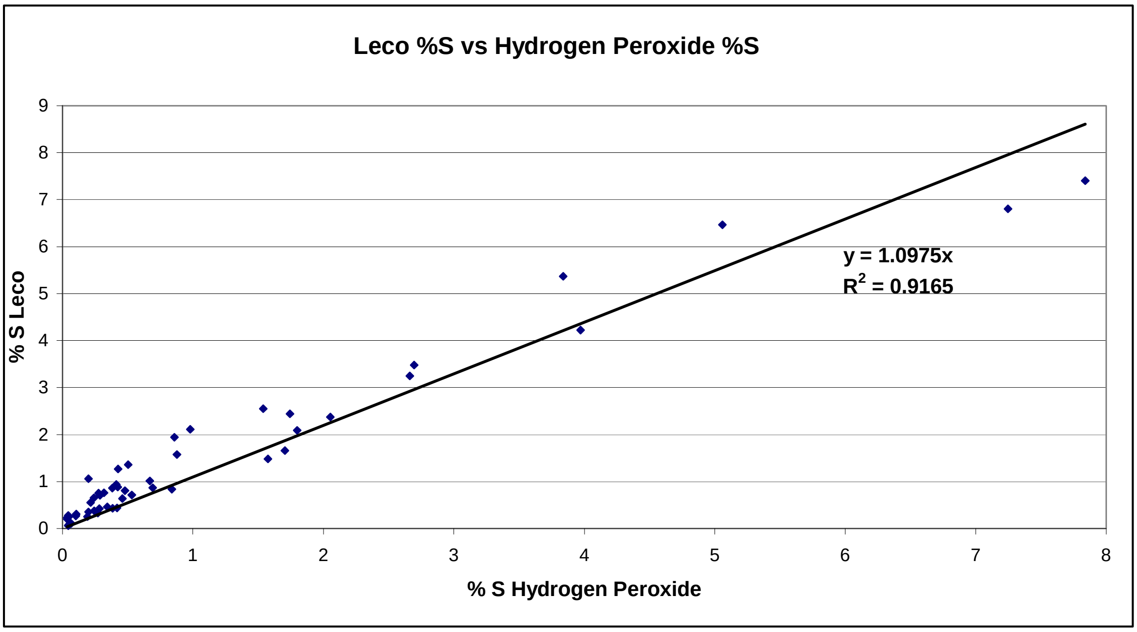


Figure 24. Comparison of percentage Sulphur determined by the Leco analyser and the 30% H_2O_2 method.

From this regression graph, H_2O_2 gives higher %S for values of over 5% and at values lower than 5%, the values obtained by the Leco are higher than those obtained with the peroxide method. For the most common values of coal overburden in South Africa it would seem that the Leco S is generally higher than that determined by the hydrogen peroxide method. A probable explanation is that a proportion of the total S is not reactive. This is included in the Leco total S determination, but not mobilised by the hydrogen peroxide oxidation. This unreacted sulphur is not likely to contribute to the acidity under the natural oxidative processes. It is therefore felt that the hydrogen peroxide method should provide a more realistic determination of the reactive sulphur species, which can potentially generate acidity.

Overall, the values obtained by the 30% peroxide method compare well with those obtained from the Leco analyser. This can be seen from the regression of almost 92% between these two methods.

As stated by Hunter (1997b), sulphur fractionation studies of some overburden material have shown that about half of the total sulphur is present in organic forms and that acidity is being produced that cannot be accounted for by the pyrite (sulphide S was used to determine the AP) and the organic sulphur that was present, giving additional acidity after oxidation processes in the mine were completed. Thus, complete peroxide oxidation will include the attributions of all species that might be acid-forming in the waste rock.

5.2.3.3 GASES RELEASED BY THE PROCESS

Gases that are released during peroxide oxidation are H_2S, CO and SO_2. These parameters were measured on 10 samples at the Technikon Free State with an Oldham MX-21 Multi-gas detector. This can be because of the reaction of the formed sulphuric acid with pyrite as described by Levinson (1974):

$FeS_2 + H_2SO_4 \Leftrightarrow FeSO_4 + H_2S + S$

5.2.3.4 REPEATABILITY

Ten samples were weighed in duplicate and peroxide (30%) was added. From the following regression graphs for Iron and Sulphur, it is clear from Figure 25 and Figure 26 that the repeatability of this method is acceptable.

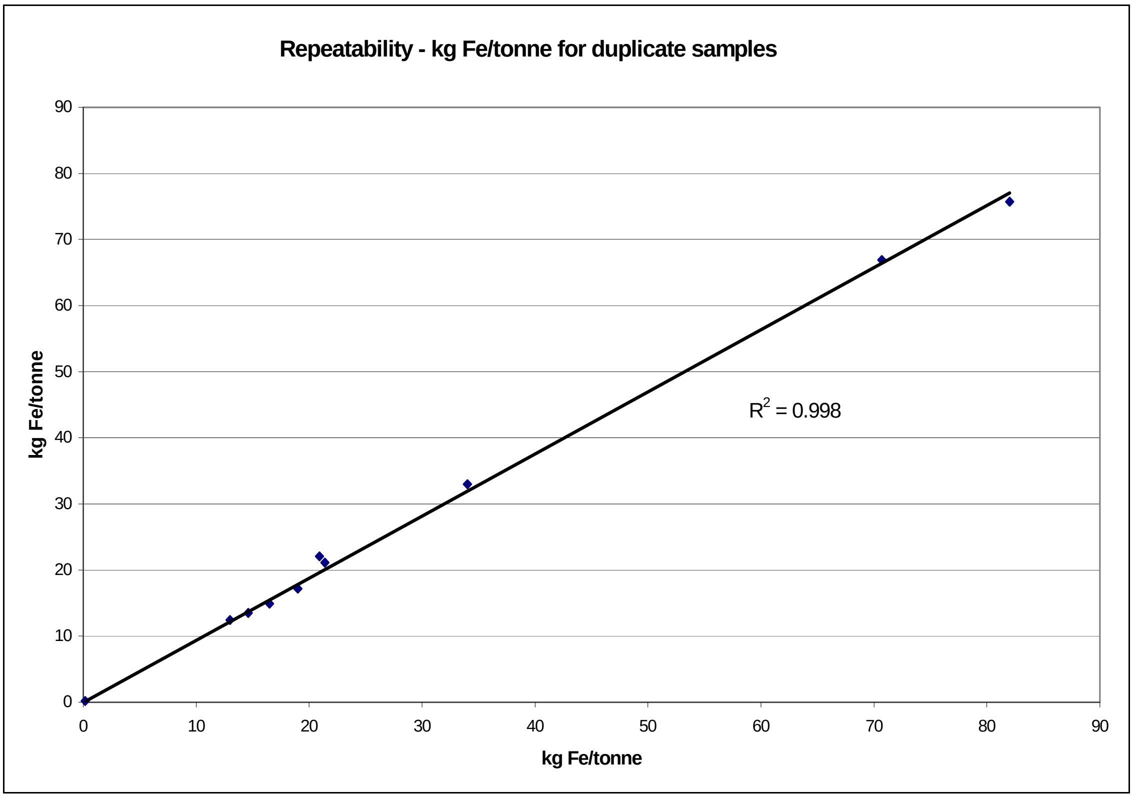


Figure 25. Comparison of Fe obtained for duplicate samples to show repeatability.

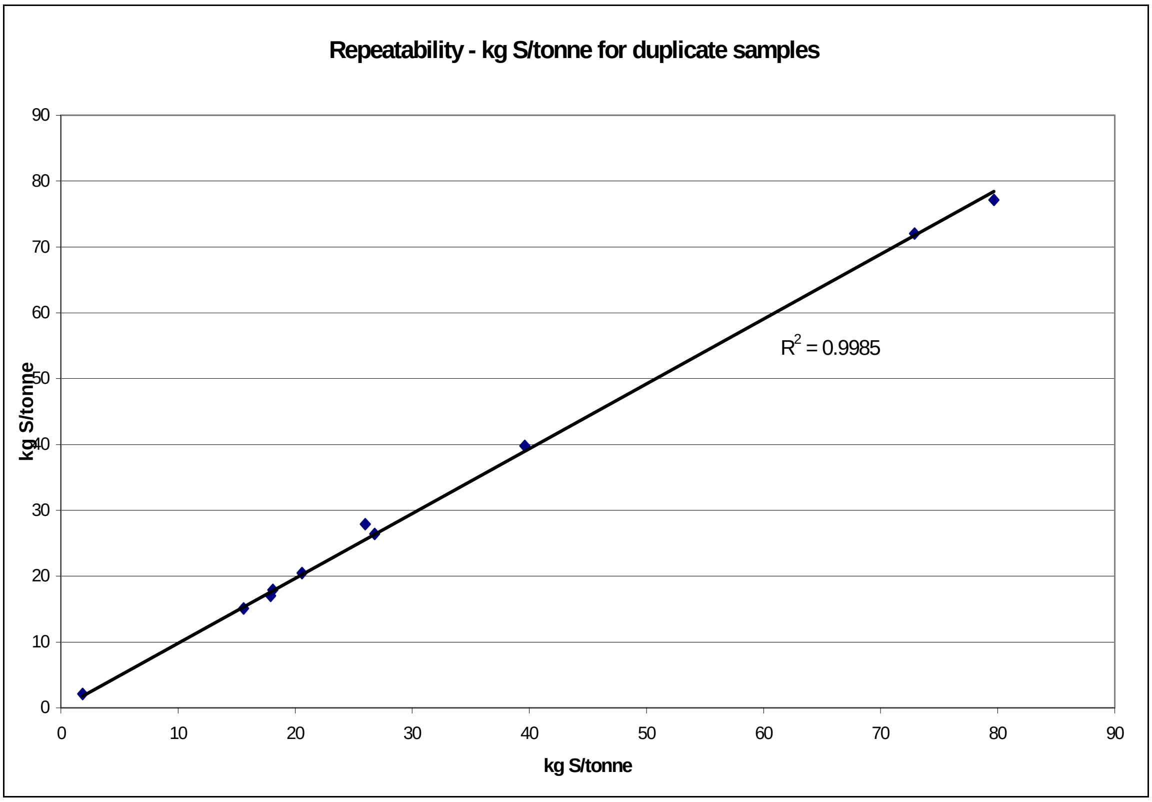


Figure 26. Comparison of S obtained for duplicate samples to show repeatability.

5.2.3.5 ACID LEACHABLE METALS

Price and Kwong (1997) used the following for leaching tests:

1. Distilled water leach: Mixture of the sample and distilled water (ratio of 1:10) was shaken for one hour and the centrifuged and analysis was done by ICP on the supernatant.
2. Dithionite-citrate extraction: Iron oxides were removed by this. Analysis of the extractant was by ICP. The results indicate that elements are strongly sorbed to iron oxides and potentially susceptible to remobilisation upon the destruction of the iron oxide hosts under reducing or strongly acidic conditions.
3. Dilute acid leach: Leaching was by 0.1N HCl and analyzed by ICP. The results provide a measure of expected metal releases if acidic drainage was to occur.
4. Strong acid leach: Aqua regia was used and showed the maximum metal release under extremely oxidising and acidic conditions; conditions which may not be readily realised in the natural environment.

Since Step 1 is a routine analysis in most laboratories and Step 4 is notnatural environmental conditions, the following were compared: 0.06N Sulphuric and hydrochloric acid and the filtrate (AMD) obtained from Discard -1 sample after oxidation with H_2O_2.

Two samples with fairly high initial pH were chosen:

- A coke sample - pH 10.98 and
- An interbedded Sandstone sample - pH 8.57.

The results are summarised in Table 10.

Table 10. Constituents released (kg/t) using different leaching solutions on two alkaline samples.

Samples	Al	As	B	Ba	Be	Ca	Cd	Cr
Coke + 52mL H_2O_2 filtrate	0.45	0.0018	0.11	0.0035	0.0001	3.71	0.0002	0.0041
Coke + 40mL H_2SO_4	0.43	0.0009	0.23	0.0023	0.0000	3.71	0.0001	0.0067
Coke + 40mL HCl	0.46	0.0008	0.14	0.018	0.0000	4.02	0.0001	0.0048
Interbedded SNDS + 90mL H_2O_2 filtrate	0.60	0.0057	0.076	0.0026	0.0004	15.58	0.0002	0.0014
Interbedded SNDS + 40mL H_2SO_4	0.66	0.0008	0.018	0.0022	0.0003	19.72	0.0002	0.0050
Interbedded SNDS + 40mL HCl	0.62	0.0006	0.045	0.14	0.0004	19.27	0.0002	0.0049

Samples	Co	Cu	Fe	K	Li	Mg	Mn	Mo
Coke + 52mL H_2O_2 filtrate	0.0063	0.011	16.27	0.096	0.0084	0.0000	0.16	0.0002
Coke + 40mL H_2SO_4	0.0019	0.0053	5.30	0.081	0.013	0.11	0.16	0.0001
Coke + 40mL HCl	0.0019	0.0059	5.42	0.069	0.0089	0.13	0.17	0.0001
Interbedded SNDS + 90mL H_2O_2 filtrate	0.0104	0.0097	6.72	0.34	0.0084	6.44	0.18	0.0008
Interbedded SNDS + 40mL H_2SO_4	0.0024	0.0034	17.61	0.24	0.0053	8.19	0.29	0.0000
Interbedded SNDS + 40mLHCL	0.0023	0.0033	14.62	0.26	0.0046	7.99	0.23	0.0000

Samples	Na	Ni	Se	Sr	Pb	V	Zn
Coke + 52mL H_2O_2 filtrate	0.20	0.017	0.0004	0.011	0.0033	0.0016	0.022
Coke + 40mL H_2SO_4	0.14	0.0049	0.0007	0.015	0.0032	0.0017	0.018
Coke + 40mL HCl	0.15	0.0037	0.0003	0.018	0.0052	0.0016	0.018
Interbedded SNDS + 90mL H_2O_2 filtrate	0.28	0.027	0.0009	0.039	0.0014	0.0004	0.034
Interbedded SNDS + 40mL H_2SO_4	0.13	0.0032	0.0002	0.039	0.0016	0.0074	0.016
Interbedded SNDS + 40mL HCl	0.14	0.0029	0.0006	0.048	0.0034	0.0072	0.017

More Ba is in solution with the HCl than with either the H_2SO_4 or the H_2O_2 supernatant (AMD solution), because $BaSO_4$ tends to precipitate. Much more Co and Cu are released and in solution with the AMD solution. Ag, Mo and V in the sandstone experiment are negative, because it may have formed complexes. There is not that much difference between the three solutions used. Thus, use H_2SO_4 instead of HCl as described by other authors (Price and Kwong, 1997). The use of sulphuric acid provides a better simulation of field conditions than hydrochloric acid.

Enough acid should be added to let the pH of the sample drop <2.5. Determining elements on samples that did not turn acid after oxidation, does not give any information about the potential toxicity of what that mineral might be released if it comes into contact with acidic mine drainage. This can be seen if the values obtained on non-acidic samples are compared to the same sample leached with H_2SO_4 and AMD. Table 11 illustrates these findings.

Table 11. Constituents released (kg/t) by peroxide oxidation and leaching with acid and AMD.

Sample	Final pH	Al	Ba	Ca	Cr	Co
Coke + H_2O_2	8.66	0	0	1.46	0.0008	2.5E-05
Coke + H_2SO_4	<2.5	0.43	0.0023	3.71	0.0067	0.0019
Coke + H_2O_2 filtrate	<2.5	0.45	0.0035	3.71	0.0041	0.0063
Interbedded SNDS + H_2O_2	7.59	0.0012	0.0014	1.76	0.0009	0.0002
Interbedded SNDS + H_2SO_4	<2.5	0.66	0.0022	19.72	0.0050	0.0024
Interbedded SNDS + H_2O_2 filtrate	<2.5	0.59	0.0026	15.58	0.0014	0.010
Sample	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Coke + H_2O_2	4.3E-05	0.0017	0.0017	4.6E-05	5.8E-05	0
Coke + H_2SO_4	0.0053	5.30	0.16	0.0049	0.0032	0.018
Coke + H_2O_2 filtrate	0.011	16.27	0.16	0.017	0.0033	0.022
Interbedded SNDS + H_2O_2	3.5E-05	0.0032	0.0004	0.0003	0	0.0002
Interbedded SNDS + H_2SO_4	0.0034	17.61	0.29	0.0032	0.0016	0.016
Interbedded SNDS + H_2O_2 filtrate	0.0097	6.72	0.18	0.028	0.0014	0.034

Constituents not released after oxidation, increase 5- to 3000-fold under acidic conditions.

Additional acid leachable constituents were tested on the samples submitted for ABA and subsequent humidity cells. These comparisons again showed the significant increase in leaching with acidification for all samples.

The results from these determinations are given in Table 12 and Table 13. The marked increase in leached parameters under highly acidic conditions is again evident. The exception is the sample with a very high acid potential that acidified markedly due to the hydrogen peroxide oxidation. Constituents released during oxidation were generally of the same order or higher than those found after the acid digestion. The conclusion that can be drawn is that the analysis of the supernatant in the oxidation test provides a good measure of the potential metal release from a sample. **For samples that do not acidify markedly, acid digestion is recommended to provide an indication of potential metal release, should the system acidify**. Where any material is to be placed adjacent or below acid-generating material, determination of acid leachable metals is essential to provide an indication of the mobilisation that will occur.

Table 12. Constituents released during complete oxidation in kg/t.

Samples	1A	AH	SH	SS	OS	OSH
Final pH	2.15	1.99	2.31	2.49	2.30	2.36
Ag	4.2E-05	1.7E-05	4.4E-06	1.0E-04	2.9E-05	3.8E-05
Al	1.4E+00	1.3E+00	3.2E+00	1.7E+00	2.4E+00	2.9E+00
B	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
Ba	1.5E-03	2.5E-04	3.7E-04	2.1E-03	7.3E-04	1.1E-03
Ca	6.5E-01	6.3E-01	1.7E+00	1.2E+01	1.3E+00	1.9E+00
Cd	1.4E-04	1.2E-04	3.1E-04	1.0E-04	5.3E-05	2.5E-04
Cr	2.9E-03	4.5E-03	3.5E-03	7.0E-03	1.9E-02	4.9E-03
Co	7.7E-04	4.4E-03	7.6E-03	1.5E-03	2.1E-03	5.8E-03
Cu	1.1E-02	7.7E-03	2.1E-02	3.6E-03	7.5E-03	1.0E-02
Fe	1.4E+01	3.6E+00	1.4E+00	9.2E+00	5.6E+00	7.5E+00
K	7.4E-02	2.1E-01	4.7E-01	5.0E-01	6.2E-01	6.5E-01
La	1.5E-03	2.5E-04	7.6E-04	7.7E-04	4.8E-04	9.6E-04
Mg	3.2E-01	4.7E-01	5.1E-01	4.4E+00	5.5E-02	1.4E+00
Mn	1.1E-02	6.4E-02	2.3E-02	1.6E-01	6.1E-02	1.0E-01
Mo	1.6E-07	0.0E+00	0.0E+00	0.0E+00	5.4E-06	0.0E+00
Na	2.5E-01	1.8E-01	1.6E-01	1.4E-01	4.1E-02	2.0E-01
Ni	6.2E-03	1.6E-02	1.1E-02	3.0E-03	9.4E-03	9.1E-03
Sb	0.0E+00	6.2E-05	9.2E-06	1.6E-04	1.1E-04	1.5E-04
Se	6.5E-06	1.6E-04	1.3E-04	0.0E+00	0.0E+00	2.8E-05
Sr	2.9E-03	8.0E-03	1.5E-02	2.9E-02	2.7E-02	3.3E-02
Pb	1.1E-03	1.4E-03	3.2E-04	1.6E-03	3.9E-04	8.0E-04
V	1.8E-03	3.5E-03	6.1E-03	4.5E-03	3.9E-03	5.3E-03
Zn	2.4E-02	3.2E-02	3.4E-02	1.1E-02	9.7E-03	2.8E-02
SO4	68.6	0.0	0.0	0.0	0.0	0.0

Table 13. Constituents released acidification in kg/t.

Samples	1A	AH	SH	SS	OS	OSH
Final pH	2.10	6.59	2.61	6.99	2.42	3.13
Ag	1.5E-04	0.0E+00	0.0E+00	0.0E+00	2.6E-05	9.0E-05
Al	6.2E-01	1.8E-02	5.0E-01	2.5E-03	7.0E-02	9.8E-02
B	2.1E-02	8.8E-04	2.0E-03	0.0E+00	4.5E-03	2.7E-03
Ba	-3.6E-04	4.0E-04	1.8E-02	1.7E-03	3.8E-04	1.9E-03
Ca	7.2E+00	1.8E-01	4.6E-01	1.2E+00	5.0E-01	9.2E-01
Cd	4.5E-04	4.8E-04	3.9E-03	4.0E-05	0.0E+00	3.2E-04
Cr	4.7E-03	1.3E-03	1.5E-03	3.8E-04	1.6E-03	2.1E-03
Co	8.5E-03	4.8E-04	3.9E-03	4.0E-05	1.6E-03	1.0E-02
Cu	2.3E-02	5.8E-04	1.7E-02	2.2E-04	1.5E-02	2.2E-02
Fe	2.4E+01	5.6E-03	5.3E-01	8.0E-04	2.2E+00	1.2E+00
K	7.4E-02	1.8E-01	2.3E-01	1.5E-01	5.2E-02	1.7E-01
La	2.1E-03	0.0E+00	0.0E+00	0.0E+00	1.3E-04	6.1E-05
Mg	4.4E+00	1.2E-01	1.6E-01	4.8E-01	7.4E-02	8.8E-01
Mn	2.4E-01	5.4E-03	5.9E-03	3.0E-03	2.3E-02	8.1E-02
Mo	1.4E-04	9.4E-04	6.0E-04	2.0E-04	1.1E-04	5.3E-05
Na	8.0E-02	2.6E-01	1.8E-01	1.2E-01	7.2E-02	1.6E-01
Ni	3.7E-02	0.0E+00	5.1E-03	0.0E+00	3.4E-02	2.1E-02
Sb	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
Se	5.4E-04	5.4E-04	4.2E-04	0.0E+00	1.5E-04	4.4E-04
Sr	1.3E-02	1.8E-03	3.8E-03	4.2E-03	4.2E-03	2.0E-02
Pb	3.8E-03	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
V	7.4E-03	0.0E+00	7.0E-04	0.0E+00	9.8E-04	0.0E+00
Zn	1.2E-01	1.6E-03	2.7E-02	5.0E-04	2.1E-02	5.8E-02
SO4	126.7	0.9	1.2	1.6	13.8	9.7

The graph below (Figure 27) illustrates this graphically for several more common constituents.

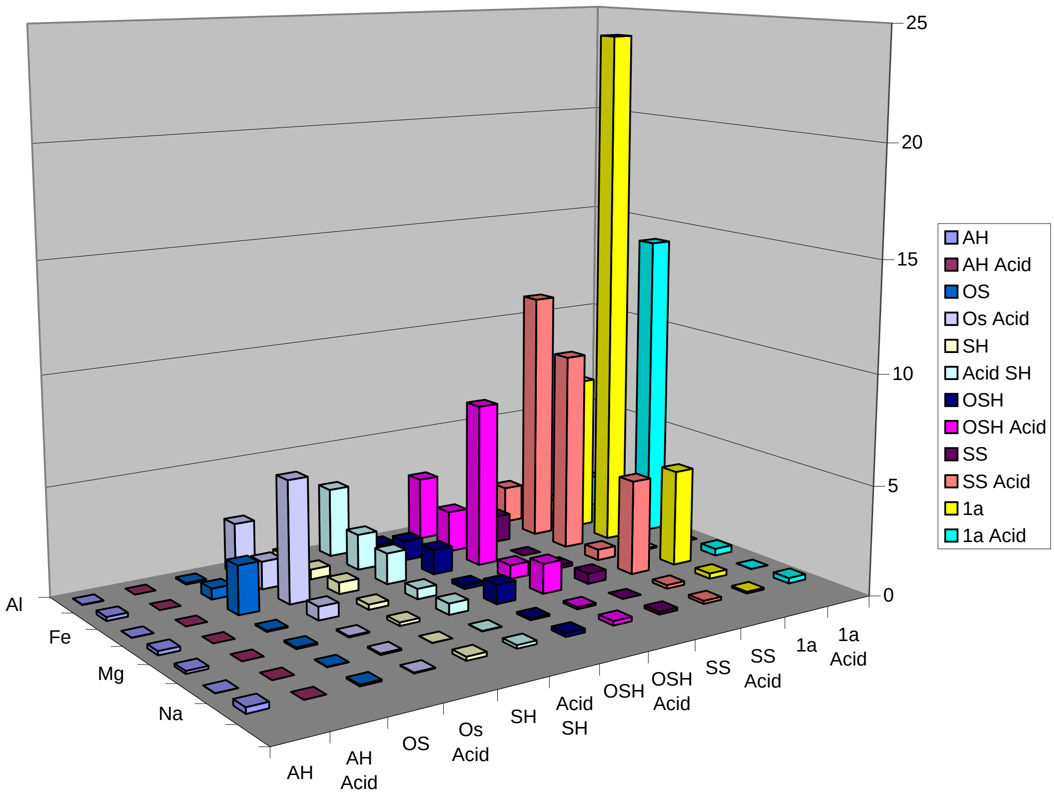


Figure 27. Comparison of constituents released in complete oxidation and acid digestion.

5.2.3.6 CONCLUSION

This section has detailed the findings from an evaluation of suggested ABA methods. Form this suggested methods for doing ABA in South Africa have been determined.

The results show that the proposed South African static test methods compare to those used by internationally accepted methods. The methods have been thoroughly tested and compared to find those most applicable to local coal mines. The improvements suggested to the methods are all shown to be justified and should result in more consistent application of the methods in South Africa.

These methods can thus be used with great certainty and success for the screening of waste rock in the coal mines of Southern Africa.

5.2.4 SCREENING CRITERIA

One of the major advantages of static tests is that fairly well-defined sets of screening criteria have been developed to interpret these tests. Although these criteria can sometimes provide slightly contradictory interpretations, their combined use can lead to good classification of tested samples into classes or non-acid-generating to acid-generating, with a slight grey area in between. ABA criteria should be determined on a site-specific basis, reflecting reaction rates of the acid-generating and acid-neutralising minerals at the particular site (Morin and Hutt, 1994). The researchers agree with this sentiment but feel that until there is a large enough, comparable Acid-Base Accounting database in South Africa that the international criteria should be used.

The criteria to be used are the following:

- Net Acid Generating Test (NAG) pH.
- Net Neutralising Potential (NNP).
- Neutralising Potential Ratio (NPR).
- % S & NPR.

A brief description of each set will be given in the sections below.

5.2.4.1 NET ACID GENERATING TEST (NAG) pH

This set of criteria is based on the final pH obtained in the NAG test. These subdivisions are slightly arbitrary and can serve as a rough guideline but not as stand-alone criteria in categorising the samples.

Final pH in NAG Test	Acid Generating Potential
> 5.5	Non-acid-generating
3.5 to 5.5	Low risk acid-generating
<3.5	High risk acid-generating

The 5.5 upper limit is derived from the carbon dioxide/pure water equilibrium pH of 5.69. Any sample tested with deionised water commonly used in laboratories requires this value to be used as reference rather than a theoretical neutral pH of 7.

5.2.4.2 NET NEUTRALISING POTENTIAL (NNP)

The use of NNP most often leads to uncertainties. The reason for this is that research and experience have shown than there is a range from -20 to 20 kg/t CaCO3 where the system or sample can either become acidic or remain neutral. However, when used in conjunction with the other criteria, this uncertainty can often be resolved.

Where Net Neutralising Potential (NNP) =

Neutralising Potential (kg/ton CaCO3)- Acid Generating Potential (kg/ton CaCO3)

The criteria are as follows:

If NNP =NP-AP <0 The sample has the potential to generate acid

If NNP =NP-AP >0 The sample has the potential to neutralise acid produced

More specifically any sample with NNP<20 is potentially acid-generating and any sample with NNP > -10 might not generate acid.

5.2.4.3 NEUTRALISING POTENTIAL RATIO (NPR)

Guidelines for screening criteria based on ABA (from Price *et al.,* 1997b).

POTENTIAL FOR ARD	INITIAL NPR SCREENING CRITERIA	COMMENTS
Likely	<1:1	Likely AMD generating
Possibly	1:1 - 2:1	Possibly AMD generating if NP is insufficiently reactive or is depleted at a faster rate than sulphides
Low	2:1 - 4:1	Not potentially AMD generating unless significant preferential exposure of sulphides along fracture planes, or extremely reactive sulphides in combination with insufficiently reactive NP
None	>4:1	No further AMD testing required unless materials are to be used as a source of alkalinity

The criteria above can also be plotted to give a visual indication of the likelihood of acid generation as shown in Figure 28 below.

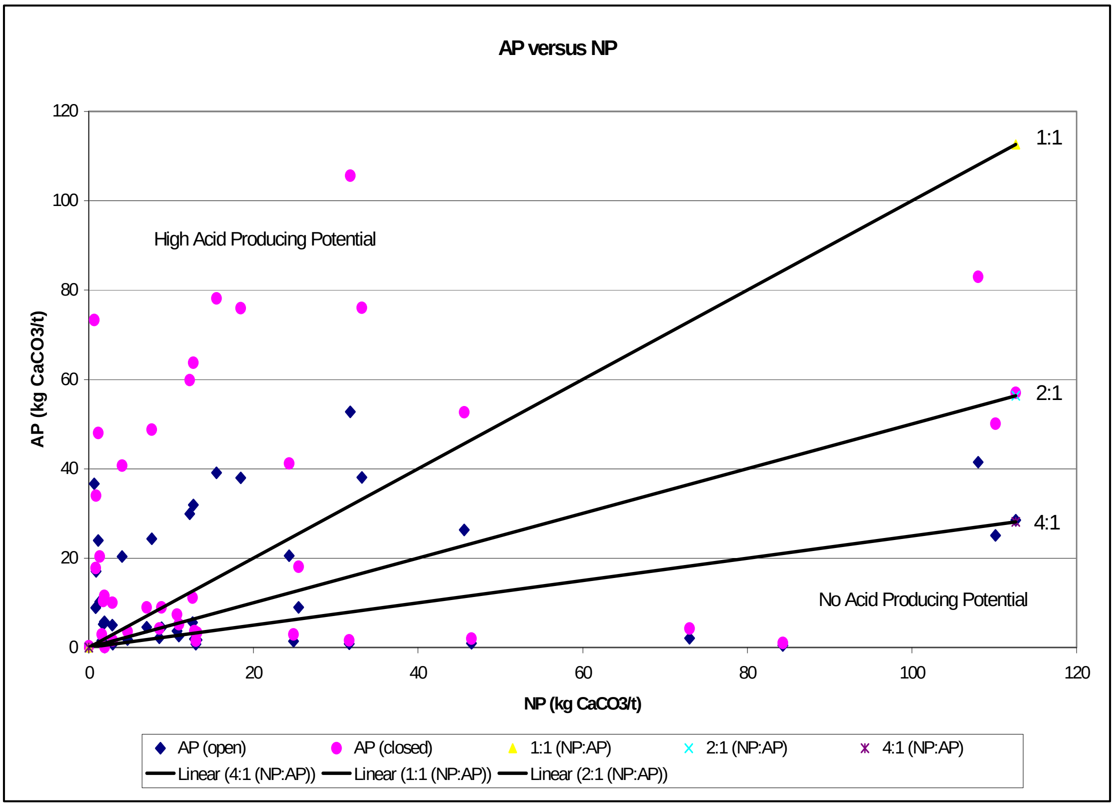


Figure 28. Plot showing different categories of acid-generation potential based on NPR.

5.2.4.4 % S AND NPR

A set of rules, which has been derived based on several of the factors calculated in ABA, was reported by Soregaroli and Lawrence (1998). It has been shown that for sustainable long-term acid generation, at least 0.3% sulphide - S is needed. Values below this can yield acidity but this is likely to be only of short-term significance. Using this fact and the NPR values, another set of rules can be derived ,as follows:

1.Samples with less than 0.3% sulphide-S are regarded as having insufficient oxidisable Sulphide-S to sustain acid generation.

2.NPR ratios of >4:1 are considered to have enough neutralising capability.

3. NPR ratios of 3:1 to 1:1 are considered inconclusive.

4. NPR ratios below 1:1 with sulphide-S above 0.3% are potentially acid-generating.

This can again be graphically evaluated, with the red block showinghigh likelihood of acid generation, the green low and the grey region is uncertain. Samples would only plot in the white region if a high S value occurs in a rock with very high neutralising capabilities (See Figure 29).

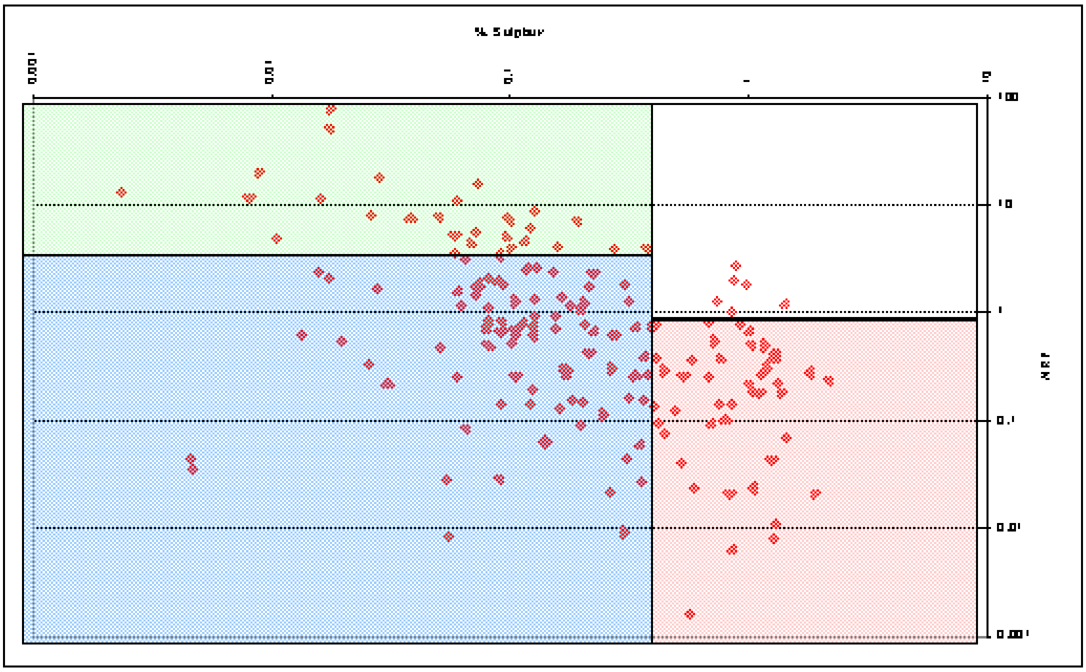


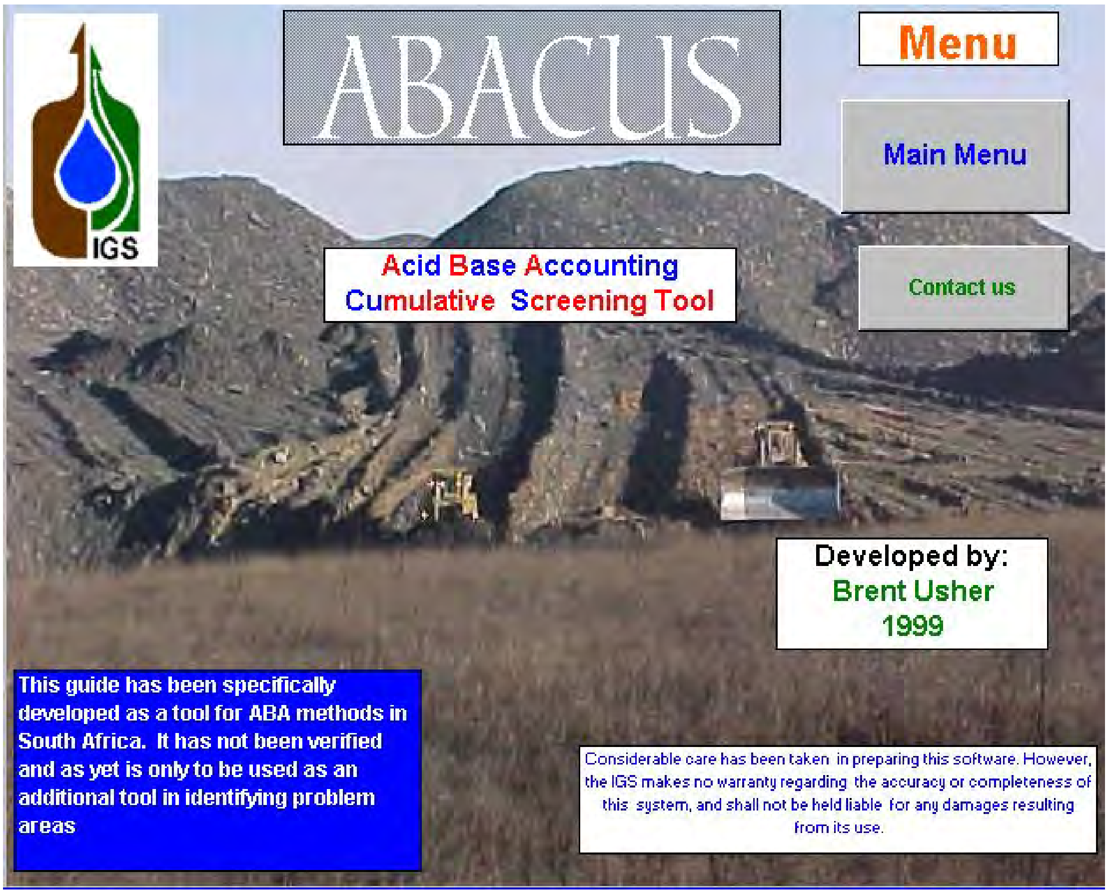
Figure 29. Evaluation plot using %S and NPR to differentiate samples.

5.2.5 REPORTING

It is recommended that all results be reported in units of kg/ton rock. All the ABA results should be expressed in units of kg/ton $CaCO_3$ for standardisation. It is recommended that one of two formats be used; either the ABACUS tool described below or the WISH format.

5.2.6 INTEGRATING THE CRITERIA

In order to be consistent with the application of criteria, a simple Excel-based tool called " Acid-Base Accounting Cumulative Screening tool" or ABACUS has been developed. This tool applies all the rules outlined above and incorporates several of the graphical presentations. It is felt that this will assist both the practitioners and regulators to get consistent application and interpretation of the rules associated with ABA.



This guide has been specifically developed as a tool for ABA methods in South Africa. It has not been verified and as yet is only to be used as an additional tool in identifying problem areas

Considerable care has been taken in preparing this software. However, the IGS makes no warranty regarding the accuracy or completeness of this system, and shall not be held liable for any damages resulting from its use.

Figure 30. ABACUS entry screen.

The tool is very simple and is menu/button driven, with macros programmed to guide the user and lead users to the correct interpretation.

The inputs required are the following:

- Sample number.
- Neutralising potential.
- Acid Potential or % S.

Based on these the following will be given:

- Open system NNP.
- Closed system NNP.
- Net Neutralising Ratios (NPR).
- Interpretations based on the screening criteria discussed in the preceding section.
- Interpretive graphs will be automatically generated.
- Additionally, another concept has been incorporated, namely that of an ABA index. This index uses all the values obtained from different tests and ratios calculated to provide a universal value to interpret the data. This ABA index will need to be evaluated over time and the factors assigned to each type of

test reassigned. Currently the values used are arbitrarily assigned but it has been tested for sensitivity and output generated with various real and hypothetical values.

- Conversion to a WISH compatible data sheet.

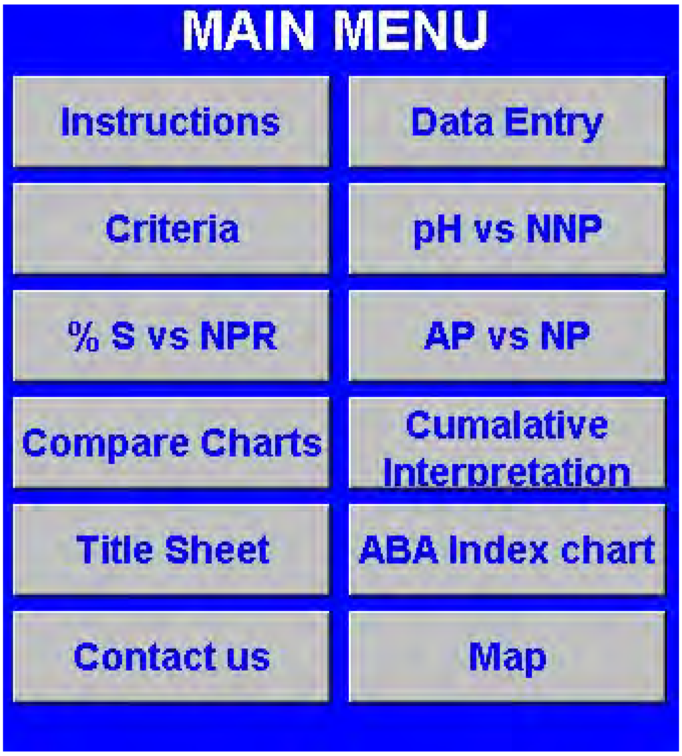


Figure 31. Menu for ABACUS.

The system can accommodate the volumetric calculations, in cases where depth specific information is available for the area under investigation. Application of such volumetric calculations is given in Section 9.2.2.3.

5.3 MINERALOGY

The mineral composition of a sample will ultimately determine the contribution of different species in the system as a whole. Particularly where more detailed assessments are required and geochemical modelling is used, mineralogical determinations are a vital component in the evaluation. Mineralogical determinations therefore form an integral part of the ABATE strategy.

5.3.1 XRD

X-ray powdered diffractometry was completed on untreated and 30% H_2O_2 treated samples.

The minerals that dissolve due to the oxidation (marked with -2) are summarised in Table 14. All pyrite, dolomite, siderite and calcite are removed during oxidation, indicating complete oxidation procedures.

Table 14. XRD results on 30% H_2O_2 treated (-2) and untreated samples.

Sample		Quartz	Pyrite	Calcite	Dolomite	Siderite	Kaolinite
DSC-1 (DGLS)	A	+	+				+
DSC-1 (DGLS) - 2	A2	+	-				+
DSC-2 (DGLS)	B	+	+				+
DSC-2 (DGLS) - 2	B2	+	-				+
COAL (LND)	C	+					
COAL (LND) - 2	C2	+					
DSC (Witbank)	D	+	+	+			+
DSC (Witbank) - 2	D2	+	-	-			+
Shale-2 (DGLS)	E	+	+			+	+
Shale-2 (DGLS) - 2	E2	+	-			-	+
Coal (DGLS)	F	+	+				
Coal (DGLS) - 2	F2	+	-				
Shale-1 (DGSL)	G	+	+				
Shale-1 (DGSL) - 2	G2	+	-				
Coal Opt Area (ZIM)	H	+	+	+	+	+	
Coal Opt Area (ZIM) - 2	H2	+	-	-	-	-	
Coal Chaba (ZIM)	I	+	+				+
Coal Chaba (ZIM) - 2	I2	+	-				+
Slurry (ZIM)	J	+	+	+			+
Slurry (ZIM) - 2	J2	+	-	-			+

Sample		Muscovite	Albite	Anorthite	Illite	Montmorillite
DSC-1 (DGLS)	A					
DSC-1 (DGLS) - 2	A2					
DSC-2 (DGLS)	B					
DSC-2 (DGLS) - 2	B2					
COAL (LND)	C		+		+	
COAL (LND) - 2	C2		+		+	
DSC (Witbank)	D	+		+		
DSC (Witbank) - 2	D2	+		+		
Shale-2 (DGLS)	E					
Shale-2 (DGLS) - 2	E2					
Coal (DGLS)	F					
Coal (DGLS) - 2	F2					
Shale-1 (DGSL)	G					
Shale-1 (DGSL) - 2	G2					
Coal Opt Area (ZIM)	H					
Coal Opt Area (ZIM) - 2	H2					
Coal Chaba (ZIM)	I				+	
Coal Chaba (ZIM) - 2	I2				+	
Slurry (ZIM)	J				+	+
Slurry (ZIM) - 2	J2				+	+

5.3.1.1 X-RAY DIFFRACTION/FLUORESCENCE INVESTIGATION OF ROCK SAMPLES USED IN KINETIC TESTS:

5.3.1.1.1 INTRODUCTION

Seven rock samples, representing the initial samples used in the kinetic tests (See Section 6.3) were submitted to the Geology Department of the UFS, with the request that they be investigated mineralogically and chemically.

5.3.1.1.2 METHOD OF INVESTIGATION

Some of the samples were already finely ground while others were chip samples. In order to do an X-ray diffractometric investigation of the samples, the latter were also crushed and ground to a grain size of minus 50 micron for semi-quantitative X-ray diffraction analyses. The powdered samples were analyzed with a Siemens D-5000 X-ray diffractometer using monochromatic CuKα-radiation and the PC-PDF2 computer programme for mineral identification.

5.3.1.1.3 XRF RESULTS (as reported by the Geology Department , UFS)

Major Element Analysis in wt %

Table 15. Results of XRF determination on samples for kinetic testing .

	OSH	OS	1A	2A	ALT 1	SS1	SH1
SiO_2	49.54	88.75	51.93	50.11	70.52	76.47	49.23
TiO_2	0.9	0.36	0.97	0.95	0.98	0.46	1.08
Al_2O_3	20.77	5.4	18.61	18.17	16.51	10.65	26.5
Fe_2O_3	6.12	1	8.47	8.93	0.84	1.75	1.77
MnO	0.09	0.02	0.06	0.06	0.02	0.03	0.02
MgO	1.02	-0.11	1.12	1.21	0.05	0.66	0.53
CaO	0.33	0.18	0.83	1.04	0.07	1.49	0.27
Na_2O	0.18	0.17	0.16	0.16	0.19	0.62	0.15
K_2O	2.25	1.74	2.84	2.78	1.98	3.19	1.52
P_2O_5	0.13	0.15	0.12	0.13	0.05	0.05	0.25
H_2O^-	0.93	0.12	0.37	0.49	0.34	0.1	0.83
LOI	17.41	2.1	14.58	15.56	8.5	4.08	17.48
Total	99.67	99.88	100.06	99.59	100.05	99.55	99.63

Table 16. Trace Element Analyses in parts per million.

	ALT 1	OSH	OS	SS1	2A	1A	SH1
Rb	59	108	36	95	112	113	77
Sr	97	249	111	146	125	120	368
Y	21	41	0	11	38	37	46
Zr	446	235	79	183	320	326	250
Nb	14	15	0	7	17	17	17
Cu	10	29	0	0	18	19	45
Zn	77	130	18	40	135	132	129
Ni	45	49	27	9	32	32	67
Co	4	22	2	4	19	19	14
Cr	100	110	106	45	93	94	105
V	128	158	31	26	114	121	207
SC	13	22	2	7	22	18	33
Ba	445	939	458	790	843	873	760

5.3.1.1.4 XRD RESULTS

5.3.1.1.4.1 EXPLANATION OF SEMI-QUANTITATIVE XRD TERMINOLOGY:

The terminology used to describe the semi-quantitative composition of the samples in the text is as follows:

Dominant:	(> 40 volume percent)
Major:	(10 to 40 volume percent)
Minor:	(2 to 10 volume percent)
Accessory:	(1 to 2 volume percent)
Rare:	(< 1 volume percent)

5.3.1.1.4.2 RESULTS:

The X-ray diffractometric results of the seven samples are as follows:

Sample SSI: X-ray diffractometry reveals **quartz** to be the dominant phase with major quantities of potassium feldspar, **microcline** and minor quantities of the chlorite mineral **ferroan clinochlore** and the mica **muscovite.** According to the mineralogical composition, the sample could be an impure feldspathic sandstone or quartzite.

Sample OSI: The dominant mineral is **quartz** with minor quantities of potassium feldspar, **microcline** and accessory amounts of the chlorite mineral **ferroan clinochlore.** According to the mineralogical composition, this sample could be a relatively pure sandstone or quartzite.

Sample SHI: X-ray diffractometry reveals the chlorite mineral, **ferroan clinochlore** to be the dominant phase with major quantities of **quartz,** minor to accessory potassium feldspar (**microcline**) and the mica **muscovite,** as well as accessory to rare quantities of the sulphide **pyrite.** According to mineralogical composition, this rock could represent a shale.

Sample OSH: The X-ray diffraction pattern indicates that the sample constitutes major quantities of **ferroan clinochlore** and **quartz** with minor amounts of potassium feldspar **microcline** and **muscovite** mica. **Pyrite** forms an accessory to rare constituent. This rock is most probably a shale.

Sample 2A: This sample consists of major amounts of the chlorite mineral **ferroan clinochlore** and **quartz.** **Microcline** constitutes minor to major quantities, while **muscovite** mica forms a minor component. The sulphide **pyrite** forms an accessory constituent. According to mineralogical composition, this rock could also be shale.

Sample 2A: X-ray diffractometry reveals the sample to be very similar to the previous two samples, constituting major quantities of **ferroan clinochlore** and **quartz,** minor amounts of the feldspar **microcline** and **muscovite** mica. **Pyrite** occurs in accessory amounts. This rock is most probably shale, similar to the previous two.

Sample ALTI: **Quartz** constitutes the dominant mineral phase in this rock, with major amounts of **ferroan clinochlore,** minor quantities of **microcline** and accessory **muscovite.** This rock could probably represent an impure feldspathic quartzite.

The results from the ABA and humidity cell tests compare well with the determinations given above, verifying the usefulness of all these components of ABATE.

5.4 DETERMINATION OF pH BUFFERING OF DIFFERENT MINERALS

In section 2.3, the buffering capability of various minerals is referred to. The tabulated buffering levels of different minerals are often somewhat misleading.

Neutralisation of acid generated by AMD processes occurs due to (Hodgson and Krantz, 1995):

1. The alkalinity of the water itself.
2. Minerals contained within the spoil (Carbonates, Clay minerals).

This section will explore some of these aspects in more detail to elucidate some of the most important considerations and clarify certain misconceptions, which exist.

5.4.1 ALKALINITY

Alkalinity refers to a *solution's* ability to neutralise acid. The main source of alkalinity in naturally occurring groundwater is carbonate dissolution. The solubility of carbonate minerals in pure water is relatively low. However, the dissolution is substantially increased in the presence of carbon dioxide according to the reaction (Loewenthal, 1984):

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3$$

An illustration of this phenomenon is shown below in Figure 29 :

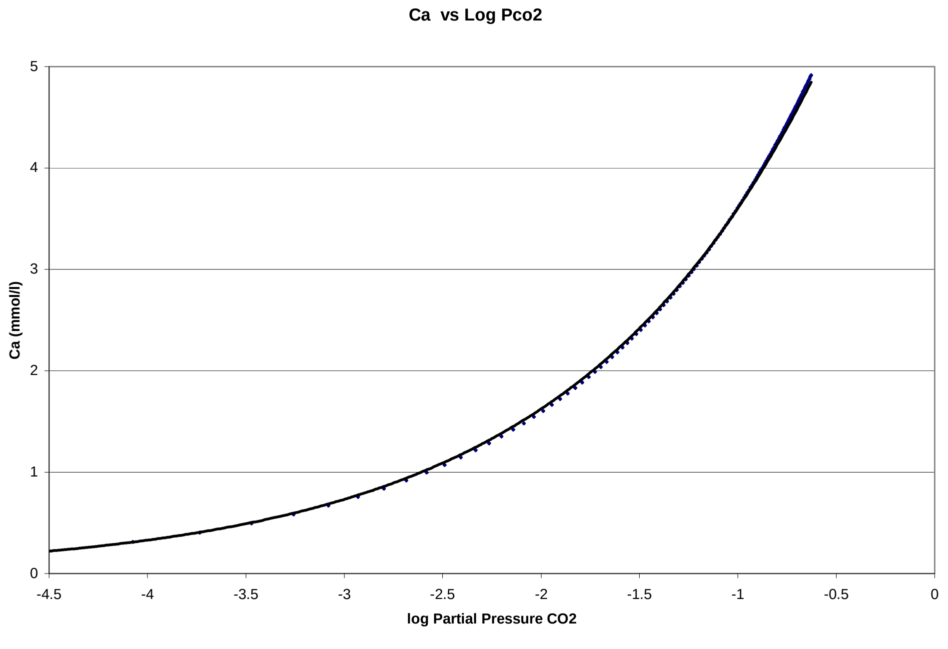


Figure 32. Calcite dissolution as a function of Pco_2.

With an increase in partial pressures of CO_2 more calcite dissolves and consequently the alkalinity will also increase (Figure 33). However, increased Pco_2 does not directly cause an increase in alkalinity, as has been implied in certain publications (e.g.

Hodgson and Krantz, 1995). The increased solubility results in more bicarbonate in the water, increasing the alkalinity.

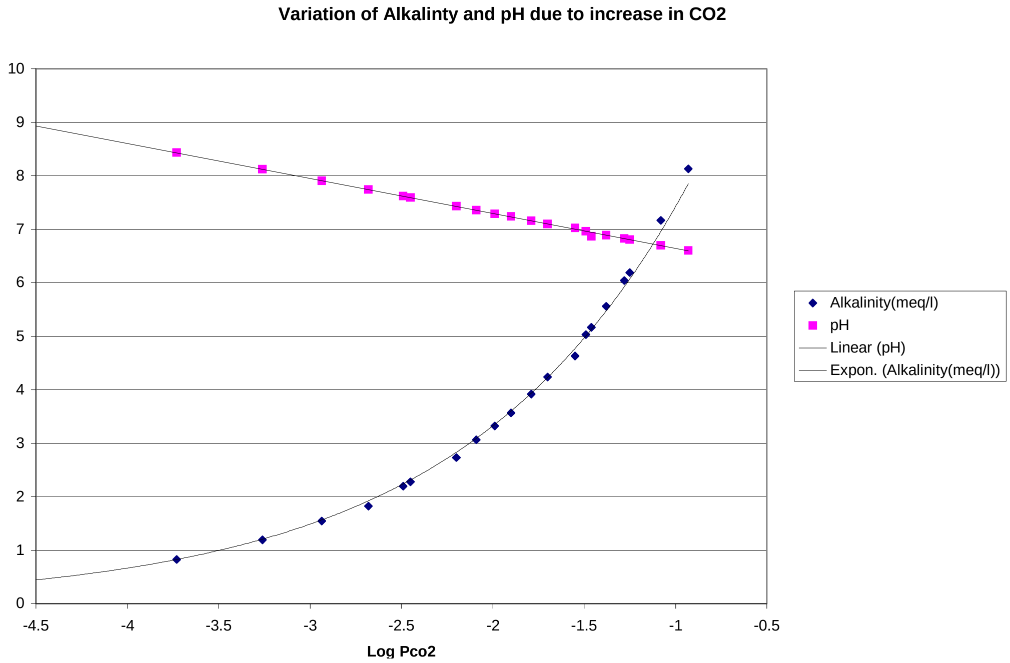


Figure 33. Variation of Alkalinity and pH as function of calcite dissolution at varying Pco_2.

It has been reported that the increased alkalinity is due to the dissolution of CO_2, due to the increased partial pressure and the expected Henry's Law response:

$$CO_2 + H_2O = H_2CO_3^*$$

The amount of $H_2CO_3^*$ that is formed is a function of the pCO_2 pressure within the spoil.

$$H_2CO_3^* = H^+ + HCO_3^-$$

The $H_2CO_3^*$ dissociates to form bicarbonate which, it has been argued, causes the alkalinity of the water. (Hodgson and Krantz, 1995).

This argument is not appropriate for alkalinity. Borate, ionised silicic acid, bisulphide, organic anions, hydrogen ion and hydroxyl ion are all species that could add to the alkalinity of water. In most natural waters they are, however, present in concentrations that are very small compared to bicarbonate and carbonate (Drever, 1997). Under these circumstances,

$$\text{Alkalinity} = mHCO- + 2mCO_2$$

This is also the *carbonate alkalinity.* In most natural waters, carbonate alkalinity and total alkalinity are almost equal and therefore carbonate alkalinity is conservative (Drever, 1997).

Alkalinity is independent of PCO_2, because neither the PCO_2 nor the uncharged species H_2CO_3 is involved directly in the charge balance equation. Although an increase in PCO_2 will cause an increase in HCO_3-, the reaction is either (Drever, 1997):

$$CO_2 + H_2O + CO_3^{2-} = 2HCO_3^-$$

or

$$CO_2 + H_2O = H^+ + HCO_3$$

In the first case, the alkalinity gained by increasing $mHCO_3$- is exactly balanced by the alkalinity lost by decreasing mCO_3-. In the second case, the increased HCO- is exactly balanced by H^+ so the net effect on alkalinity is zero. Thus the increase in alkalinity due to the variation in Pco_2 is due to the increased carbonate mineral dissolution.

5.4.1.1 FURTHER INFLUENCES OF Pco_2

The buffering level of any of the carbonate minerals present in the spoils is dependent on the partial pressure of carbon dioxide present. Thus this must be considered when determining/reporting on minerals responsible for maintaining the pH at a specific level in areas affected by mining. The simulation was done using the geochemical modelling code PHREEQC (Parkhurst and Appelo, 1999).

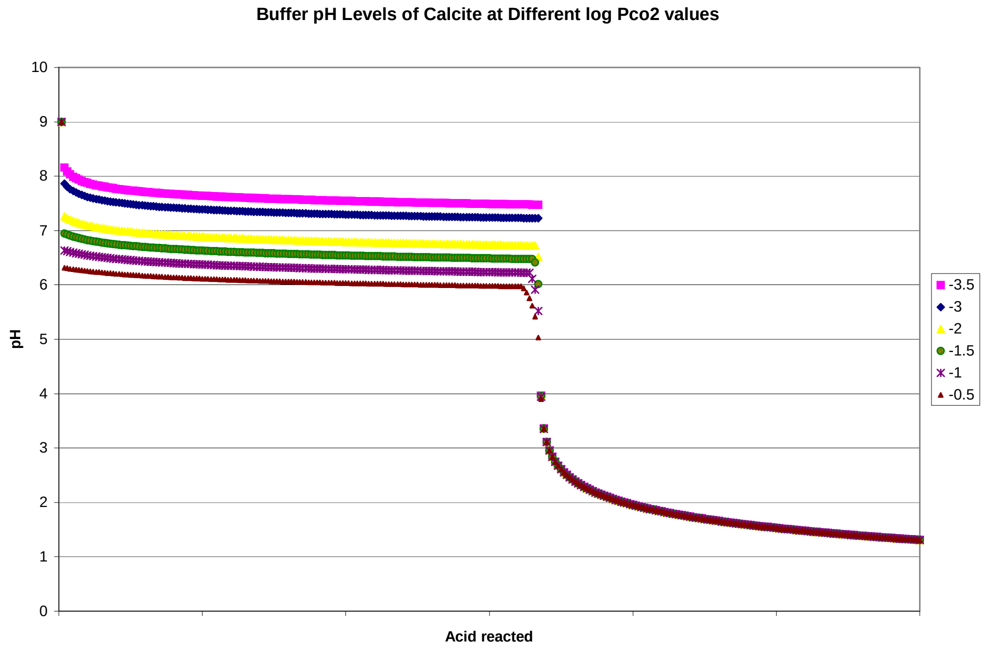


Figure 34. Calcite buffering level as a function of Pco_2.

Figure 34 above shows how, **under different Pco_2 conditions, the buffer level can vary up to two pH units. This is very important in interpreting conditions on site.**

In mining waste facilities such as exposed tailings impoundments and waste rock piles, depending on factors such as carbonate contents, sulphide contents, sulphide oxidation rates, gas exchange rates between pore gas and the atmosphere, the CO_2 partial pressure could vary in the range of 0 - 3 orders of magnitude higher than that of the atmosphere, i.e., in the range of 0.0003 to 0.3 atm. Assuming equilibrium conditions, the fact that most pore water or leachate pH observed in carbonate-containing waste materials are within the range of 6.5 - 8.5 implies, a pore gas CO_2 partial pressure ranging from 0.0003 to about 0. 1 atm. (Li, 2000).

5.4.2 CONTRIBUTION OF INDIVIDUAL SPECIES

Several minerals are credited with the ability of causing buffering, in some cases, or consumption of produced acidity. The carbonates are often credited with having the greatest influence, however it is clear in that terms of acid consumption several of the other minerals can be regarded as numerically greater consumers of acidity per mole.

Some examples are (reactions generated by *RXN*, part of the Geochemists Workbench, Bethke, 1996):

Diopside ($CaMgSi_2O_6$) + $4*H^+$ = $2*H_2O$ + Ca^{++} + Mg^{++} + $2*SiO_2$ (aq)

Anorthite(Ca-feldspar/ $CaAl_2Si_2O_8$) + $8*H^+$ = $4*H_2O$ + Ca^{++} + $2*Al^{+++}$ + $2*SiO_2$(aq)

Albite (Na-feldspar/$NaAlSi_3O_8$) + $4*H^+$ = $2*H_2O$ + Na^+ + Al_{+++} + $3*SiO_2$ (aq)

Calcite ($CaCO_3$) + H^+ = Ca^{++} + HCO_3^-

Gibbsite ($AlOH_3$) + $3*H^+$ = $3*H_2O$ + Al^{+++}

Kaolinite ($Al_2Si_2O^5$ $(OH)_4$) + $6*H^+$ = $5*H_2O$ + $2*Al^{+++}$ + $2*SiO_2$ (aq)

Shown in Figure 35 below is the relative acid consumption capacity of some of the minerals listed above and also the expected buffering levels of the different minerals as determined by PHREEQC (Parkhurst, *et al.,* 2000). The assumption implicit in this figure is that the acid generation is constant and that it is added at a rate that is slow enough for equilibrium to be attained by each acid-consuming mineral. In section 8.2.3 the kinetic response to a similar situation is given. This will indicate the inherent danger of disregarding the likely kinetic chemical response of the system.

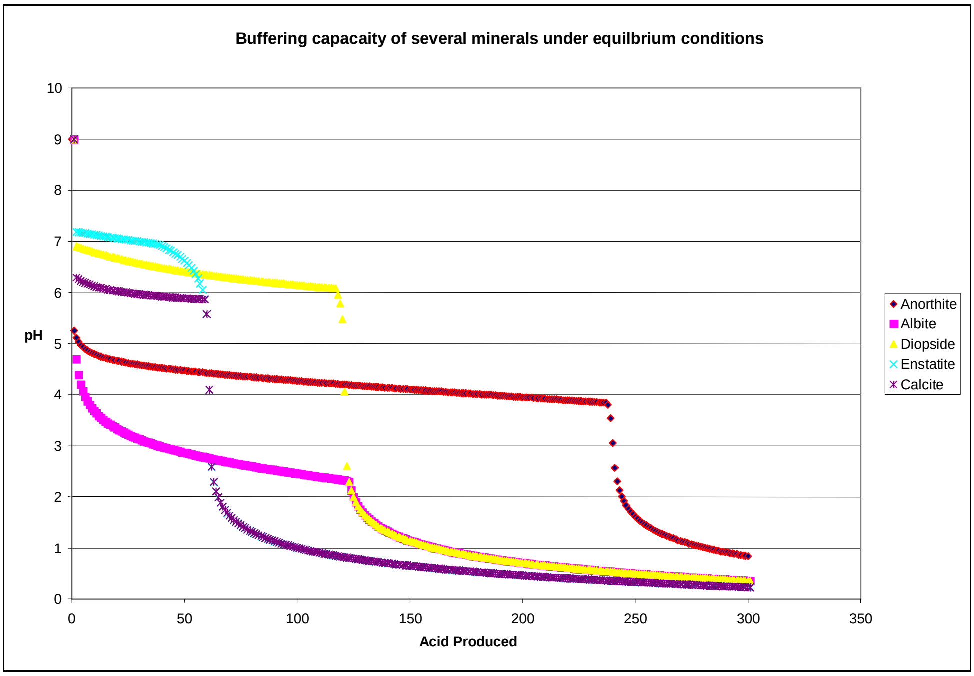


Figure 35. Equilibrium buffering levels of different minerals in an open system.

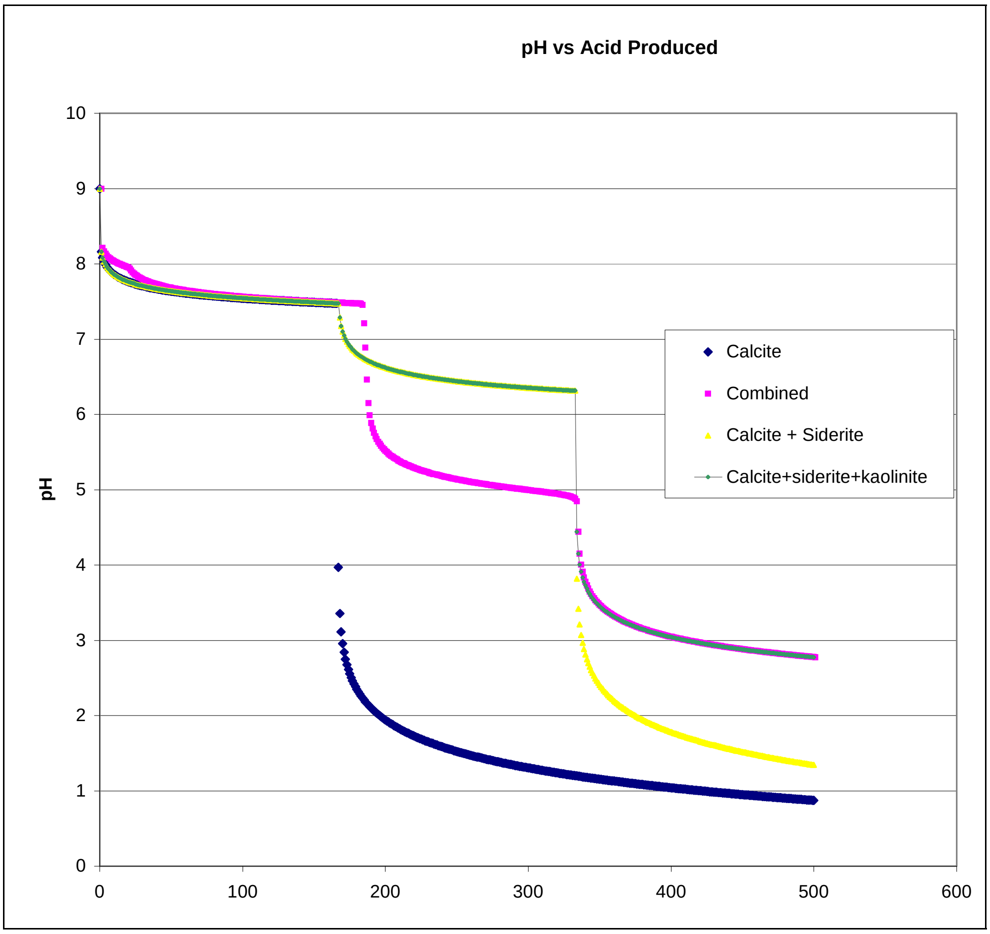


Figure 36. Combined buffering profile of equivalent amounts of different common minerals.

An assessment was also done in the laboratory using an automated titrator, to verify the buffering levels reported in many publications. The results from these determinations showed that buffering pH levels of pure mineral phases were dependent on the rate of acidification. Generally at the high (relative to field conditions) rates of acidification the buffer levels obtained for various minerals were lower than those reported in these tables. Comparison between the laboratory-determined values and PHREEQC simulations showed that these minerals were reacting as could be expected in an open system. The determinations were mostly done over a 24-hour period with minuscule incremental additions of sulphuric acid (to simulate field conditions).

The results of the tests and the corresponding PHREEQC simulations are contained in Appendix 3.

6 KINETIC TESTS

6.1 LABORATORY KINETIC TESTS

Acid-Base Accounting procedures are used as a screening process to categorise materials into potentially acid-generating, potentially non-acid-generating and uncertain groups. **For material where the potential for acid generation is uncertain or rates of reaction are required, kinetic test work is performed to attempt to define acid generation characteristics**. The term 'kinetic' is used to describe a group of test work procedures wherein the acid-generation (and metal solubilisation and transport) characteristics of a sample are measured with respect to time (Mills, 1998g and Chemex labs, 1997).

Oxidation rates of sulphidic mine wastes measured at a range of scale sizes have been collected from a number of sources. The results suggest that **well-designed laboratory columns, under controlled conditions, provide comparable information to that obtained from field test piles on oxidation rates** (Bennet, Comarmond and Jeffrey, 2000). The rates of pyrite oxidation by oxygen in moist air are comparable to the rates of pyrite oxidation by ferric iron in solution (Jerz and Rimstidt, 2000) so that an idea of the order of magnitude of oxidation can be found for an already acidified system which is submerged. These tests can therefore be used as valuable tools in the ABATE strategy to predict drainage water quality.

6.1.1 INTRINSIC OXIDATION RATE FROM KINETIC TESTS

Bennet *et al.* (2000) describe the use of humidity cells to provide the rates of reaction. They define a concept of intrinsic oxidation rate to describe a system's reaction kinetics. The intrinsic oxidation rate (IOR) is the rate of oxidation of material in a system (column, stockpile, dump) under the particular conditions which pertain to that point. The IOR is a **function of many variables such as oxygen concentration, sulphide sulphur concentration, temperature, pH, pyrite morphology, microbial ecology** etc. and is time dependent. Since it is currently impossible to predict the IOR function by measuring individual material characteristics, the only other approach is to measure the oxidation rate itself, either of samples in the laboratory or in the field. Laboratory measurements can be designed to provide the functional dependence of the IOR on any of the variables, which are judged to be important (Bennet, Comarmond and Jeffrey, 2000). This is essentially what these tests hope to achieve.

6.1.2 ADVANTAGES, DISADVANTAGES AND USES

The main **advantages and disadvantages** of kinetic tests are discussed in Section 3.2:

Kinetic tests are carried out to determine the weathering characteristics of a sample as a function of time. Thus specific objectives for both the short and long term can include:

- Validation of static test results and classification.
- Determination of the rate of sulphide oxidation/acid generation..
- Determination of the rate of neutralisation depletion.

- Determination of the availability of NP.
- Time to the onset of AMD.
- Evaluation and selection of AMD control methods.
- Prediction of water quality.

For an existing mine where AMD might already be a problem, some or all the above objectives also apply. In addition, it might be necessary to add the following objectives to facilitate the selection of mitigation methods and for the development of a closure plan:

- Evaluation of the extent of oxidation.
- Evaluation of the extent of neutralisation.
- Evaluation of stored reaction products within wastes (Dagenais and Poling (1997), Lawrence and Day (1997) and Mills (1998h)).

Kinetic tests typically involve subjecting a sample of the waste material to periodic leaching and analysis of the drainage. The most reliable test would be one that replicates exactly the actual field conditions. In practice this is not possible, not only because of the time factor, but also because it is impossible to simulate the physical, chemical, biological, meteorological and other factors associated with an actual dump, tailing impoundment or other mine component. With respect to the time factor, the difficult choice in designing, performing and interpreting a kinetic test is either to have a test which attempts to approximate actual field conditions, in which case the test will usually be of too short a duration, or to provide accelerated conditions, in which case the test might be unrealistic. In the former case, kinetic tests can often fail to demonstrate the onset of AMD or reach any steady state with respect to oxidation rates, neutralisation rates or water quality (Lawrence and Day, 1997).

Many types of kinetic tests have been documented and these can vary in complexity, duration, cost and the kinds of data that can be obtained.

The following list shows different categories of tests:

1. Humidity cells.
2. Column tests.
3. Accelerated biological oxidation tests.
4. Field tests.
5. Specialised test apparatus.

The most popular kinetic test is the humidity cell test. Therefore, this type of test formed the focus of the kinetic testing research in this project.

6.1.2.1 REPORTING FORMAT FOR KINETIC TESTS

Rates of acid generation and sulphide oxidation can be calculated in a number of ways:

- Weight basis (e.g. Mg sulphate/kg/week or mg CaCO3 equivalent/kg/week).
- Cumulative basis (e.g. Total mg sulphate/m2/week).
- Surface area (e.g. mg sulphate/m2/week, derived from surface area to weight conversions) (Chemex labs, 1997).

6.2 HUMIDITY CELLS

Internationally, humidity cells have become the most popular devices for conducting kinetic tests. Locally the usage has, unfortunately, been very limited. Cell designs can vary in the material of construction, geometry and size. A typical cell is constructed of Plexiglas of dimensions 10cm diameter by 20cm in length and has a nominal capacity for 1kg of rock. The rock sample is typically crushed to -6mm and is placed on a perforated plate to permit the flow of air up through the bed of rock. The cell can be provided with a bubbler tube containing water, attached to a tight-fitting lid, through which the exiting air is passed. The bubbler provides a visual check that air is flowing through the cell and allows the operator to achieve a semi-quantitative balancing of airflow through a bank of humidity cells. Dry or humidified air is supplied to the underside of the perforated plate. The temperature of the water in the humidifier should preferably be maintained slightly above ambient to ensure a good supply of humidified air. Leachate, usually distilled water, is added periodically through the lid of the cell. The mode of addition can vary. In some test programs, the water, typically 250mL to 500mL, is added slowly over several hours (percolation leaching). In this method, the valve at the bottom of the cell is open to allow free draining. In other programs, sufficient water can be added to completely submerge the sample for a period of time, before the bottom valve is opened to allow draining. In the latter method, the rock sample is sometimes gently stirred during submergence to promote dissolution of reaction products. A scheme for the arrangement of a humidity cell can be seen in the figure below (Figure 37).

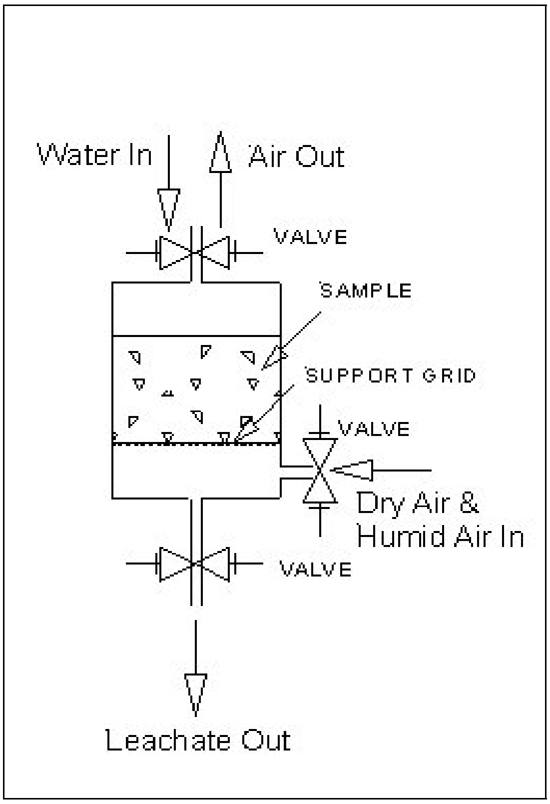


Figure 37. Generic schematic diagrams for the arrangement of a humidity cell (Mills, 1998g).

At the IGS, humidity cells with the following construction (Figure 38) are currently used.

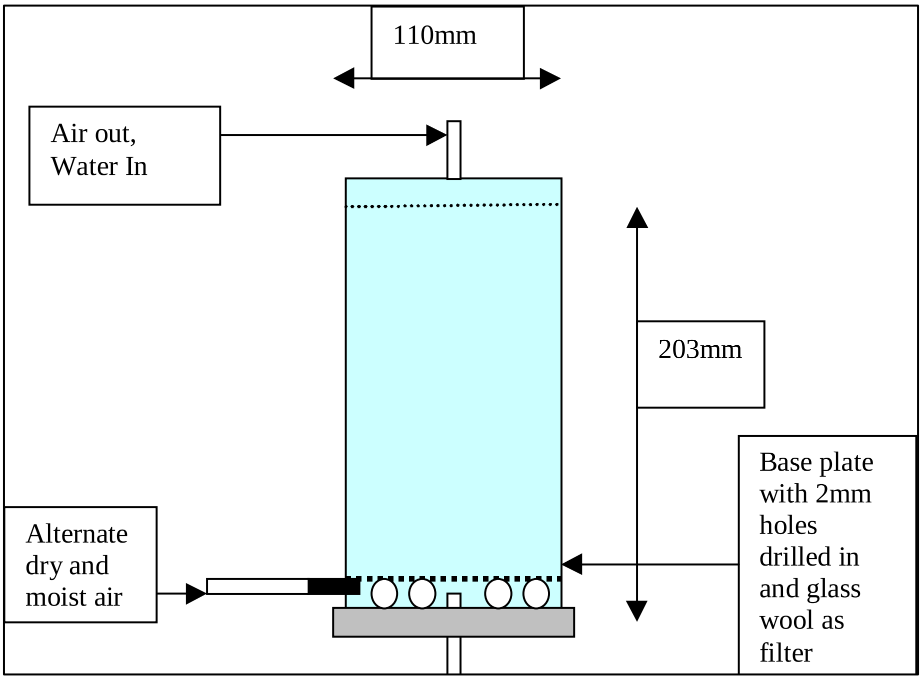


Figure 38. Humidity cell configuration used at the IGS.

For each cycle, the following parameters should be measured to facilitate calculations and interpretation:

- Volume of leachate added and collected.
- pH.
- Specific conductivity.
- Alkalinity and/or acidity.
- Sulphate.
- Dissolved metal of interest (must include Ca and Mg).

Other parameters that can be measured include:

- Redox potential.
- Weight of cell and contents after each stage of each cycle to determine moisture content of the test sample (Lawrence and Day, 1997).

A typical humidity cell test employs 500 mL water per week for a 1 kg sample. Humidity cell tests are performed to evaluate the long-term acid-producing potential of mine waste rock, tailings or spent ore. The test simulates accelerated weathering of the sample. This is done by passing moist air followed by dry air through the sample chamber; moist air for three days, followed by dry air for three days and distilled water on the seventh day. This one-week cycle is typically run for 20 weeks according to the ASTM standard. Samples are usually selected to represent the various lithologies at the mine and to represent a range of ABA and/or NP/AP values. In this way, humidity cell results can be used to identify or confirm the AMD risk associated with a range of ABA values. Refinement of the threshold ABA value is often useful for developing material handling plans (Schafer Laboratory, 1997).

6.2.1 BACTERIAL ADDITION TO CELLS

Cravotta (1995), states that he has never obtained a soil, sediment or sludge sample which did not have some bacteria of interest, regardless of the source of the material. Unless there is reason to suspect otherwise, one can assume with confidence that a sample will contain the bacteria of interest.

6.3 RESULTS OBTAINED

The IGS has attempted to construct standardised humidity cells from readily available and cost-effective materials. Use has been made of regular PVC piping with supporting grids made from Perspex or PVC discs with holes drilled in. Connections and nozzles for the system have been obtained from shops selling garden irrigation equipment and pet shops selling fish tank components. The emphasis throughout has been to generate reproducible results in a cost-effective manner and to investigate and compare different methodologies.

The figures below show the construction, array and equipment used in the IGS system by making use of a simple structure and readily available material, it is felt that the cells will have widespread use and application.

Figure 39. An IGS humidity cell, left and right an array of cells set up at the IGS.

Figure 40. Interior of cell shown without and with sample in cell.

In a typical test, a 7-day cycle is employed: 3 days of dry air, 3 days of humid air, followed by leaching on the 7th day. On the next day, the next cycle is started. Humidity cell tests should be carried out for as long a time as possible. It is normal for data to be quite erratic over the first few cycles before consistent results are obtained. This is due to the removal of readily soluble components from prior oxidation and weathering. It is not unusual for humidity cell tests to continue for several months or even more than 1 or 2 years (Lawrence and Day, 1997).

Figure 41. Modified humidifier components: A fish tank heater, left and a 20 litre drum with fish aerator and tubing, right.

Table 17 below shows the static ABA done on the samples used for kinetic testing. These mostly fall into the uncertain range, according to the criteria discussed previously, with the first sample tested to ascertain whether an acid-generating sample according to ABA would acidify in a cell.

Table 17. ABA results for samples used in kinetic tests.

Cell	Initial pH	Final pH	Acid (Open)	Acid (Closed)	Base	NNP (Open)	NNP (Closed)
Cell1/2(Shale)	7.61	2.10	131.90	263.90	24.10	-107.9	-239.8
OSW / OSA Sandstone Normal/Humid	6.66	2.42	14.40	28.70	1.5	-12.9	-27.3
OSHW / OSHA Shale Normal/Humid	7.75	3.13	10.10	20.10	5.9	-4.1	-14.2
ALT (Alternating SS/SHLE) Cell/Tray	7.55	6.59	0.90	1.79	2.91	2.09	1.12
SH (Shale) Cell/Tray	6.88	2.61	1.29	2.58	1.71	0.41	-0.88
SS(Sandstone) Cell/Tray	8.40	6.99	1.69	3.38	38.37	36.71	35.02

A crucial question in humidity cell testing is that of repeatability. Duplicate samples have been used in certain cases to evaluate the repeatability of the procedures. The results from the longest running cells show that, despite weekly variation, the overall trend in duplicate cells is very similar. The results shown in the graphs which follow show the relative reaction rate of each sample. This supports the fact that meaningful results can be obtained from the cells and that the standardisation of the procedure has merit.

Figure 42. Repeatability .

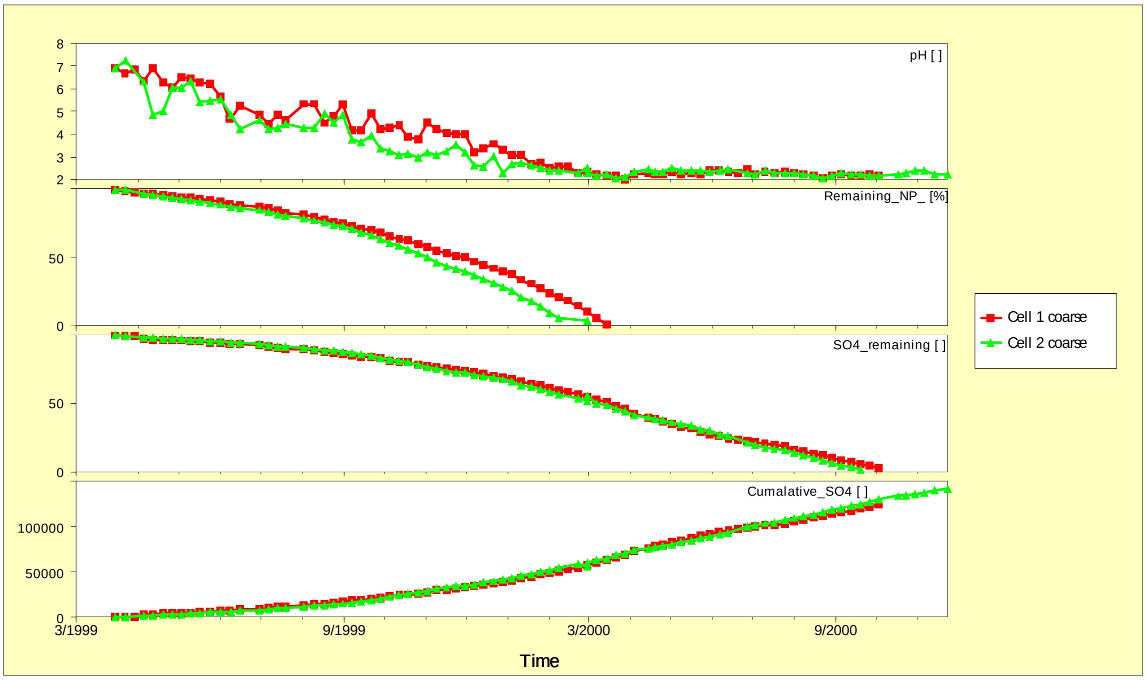


Figure 43. Comparison duplicate cells'cumulative sulphate production, remaining S and NP depletion.

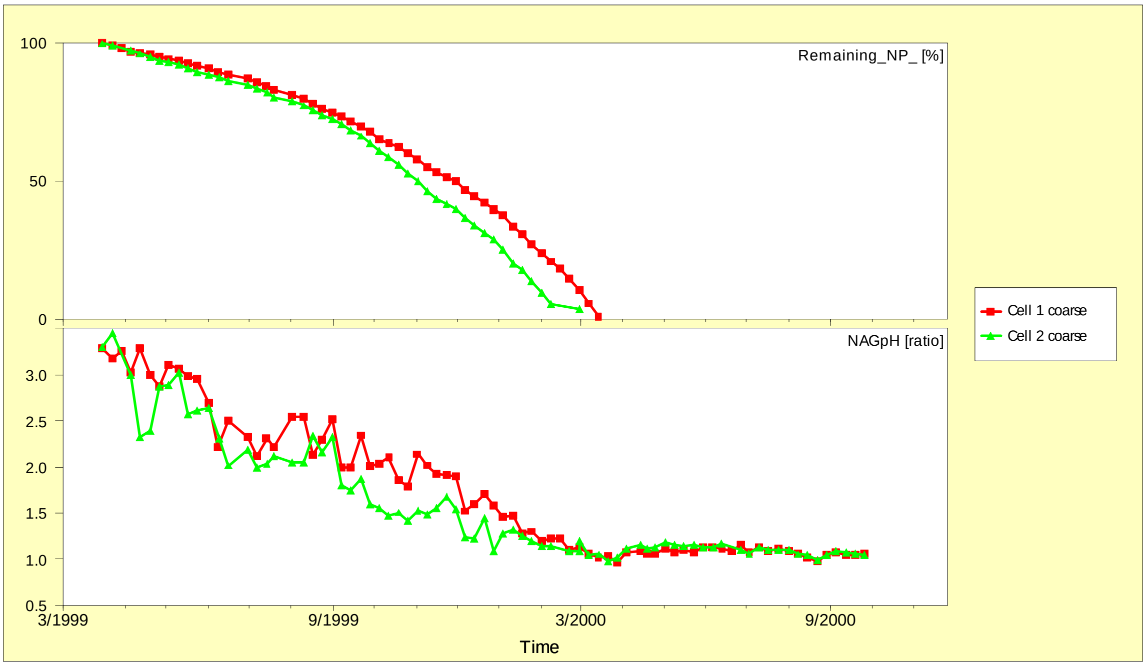


Figure 44. Comparison between ratio of NAG/final pH and outflow pH with time.

Figure 45. Duplicate cell's metal production rates compared to pH.

It is clear from the figures above that **these cells can provide repeatable results**. This is shown by the excellent match between the duplicate cells, as far as evolution of the contaminant release and pH-profile is concerned.

Figure 43 given above shows the depletion of neutralisation capacity over time. The cumalative increase in sulphate and depletion of overall SO_4 capabilty are also indicated. This depletion shows that the cells have almost run to completion and have yielded most of the sulphates available from the pyrite generation.

Figure 44 shows a very interesting phenomenon, indicating that the **theoretical neutralising capacity** is depleted at approximately the same time as the pH reaches the final oxidised NAG pH. It can be seen that the oxidised NAG pH:pH ratio also indicates the good correlation between the static and kinetic methods. The depletion of all neutralising capacity provides a verification of the acid-potential method suggested as standard method to be used, as the obtained final pH and the depletion of the neutralisation capabilty coincide where the humidity cell pH and the NAG value coincide.

This would lead to the erroneous assumption that the reaction sequence has been completed. However, it is evident from Figure 45 and Figure 47 that it is at this point that the metal leaching really begins. For all the metals shown in these figures it is clear that a significant amount of the metal loading is only released at this point. Termination of the humidity cell prior to this would therefore lead to a skewed perception of the likely metal release rates/capacity in the field.

It is interesting to compare these curves to theoretical metal solubilty curves as shown in Figure 46 below. It is clear that the release of the metals is, as expected, largely pH-controlled. However, from purely solubility considerations, elevated metals would be expected sooner for several of the metals shown; the implication is that there is a delaying mechanism that needs to be overcome before the metals are released. It is suspected that this could be due to grain size bufferring phenomena.

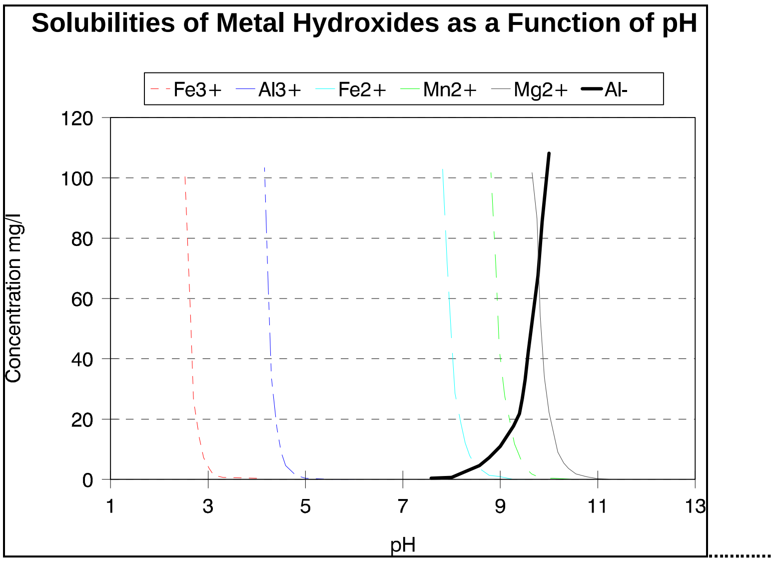


Figure 46. Solubility of selected metal hydroxides as a function of pH.

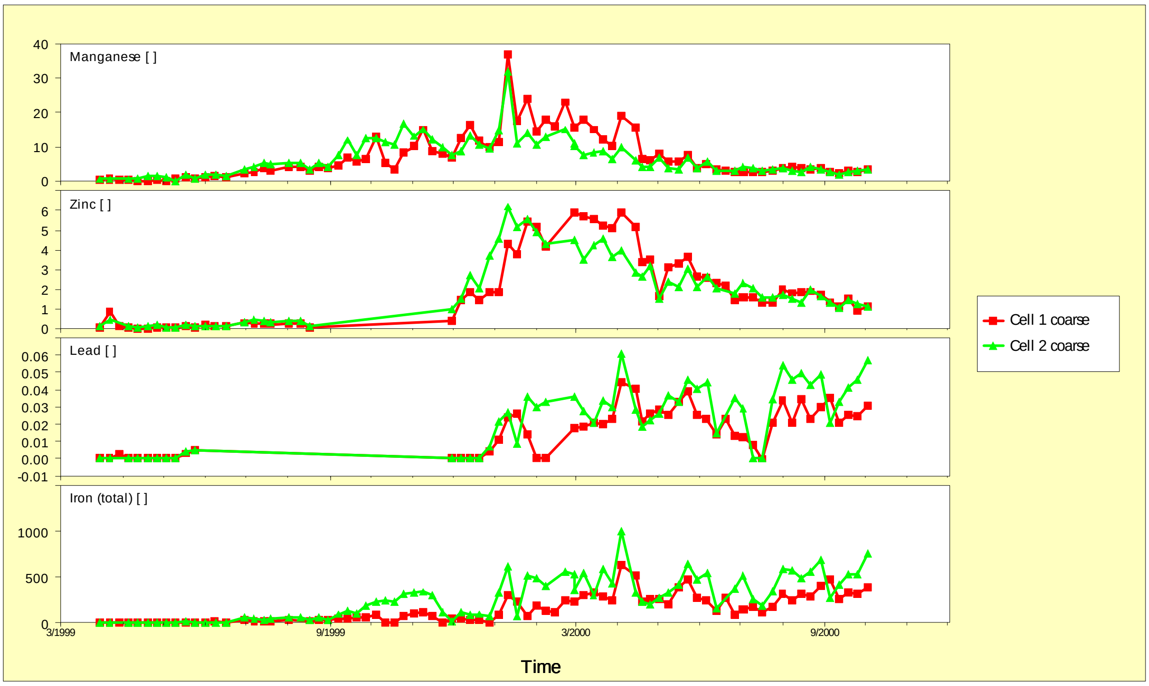


Figure 47. Correlation between iron concentration and that of other metals.

The correlation between iron and the other metals indicates the metal solubilisation phenomenon via iron, as discussed in section 2.2.2.1.

Several authors have proposed the use of kinetic tests for investigating the most important controls on the rates of production. As part of this project the influence of humidity was included. The rate of pyrite oxidation increases with increasing relative humidity. (Jerz and Rimstidt, 2000). Duplicate core samples from a sandstone and shale horizon were subjected to slightly different test conditions. One set (termed “Normal”) used the ASTM suggested cycle of three dry and three humidified air days, while the duplicate set (termed ”Humid”) was subjected to a cycle of one day of dry air and five days of humidified air. Initially the intention was to use a six-day humidified air routine but the experience from the first few weeks suggested that the cells were semi-saturated after the leaching cycle. A day of dry air was therefore used to remove excess moisture content before the humidified air cycle was initiated.

Figure 48 below shows the response of the sandstone sample to the contrasted methodologies. It can be seen from this figure that although the trend appears to be similar there is a slight acceleration in the production rate in the humid air set-up. The accelerated acidification also produces elevated metal loading, as can be seen from Figure 51. The humid cell releases these metals while the standard protocol would still suggest that metal release is unlikely after a period of a year. The consequences of such an error in interpretation would be disastrous in the planning of long-term remediation and containment strategies for a mine. This agrees well with research conducted internationally on this aspect.

The depletion in NP as a result of the more humid conditions is also clear. Over the period of testing shown, the theoretical neutralisation potential remaining in the sample is approximately 20% whilst that of the normal cycle is much higher at around 60% of the original.

One might conclude that the humid protocol is more appropriate since it heightens the “acceleration” of the rates. This would probably be appropriate for tropical regions, but is not considered realistic for conditions in the South African coalfields.

A very significant finding from this set of cells is that, despite the very low acid potential and “uncertain” NNP value, the cells have acidified. This ties in with the very slight negative NNP determined by the ABA and lends credence to the ABA results.

Figure 48. Comparison. Alternating dry vs. continuous humidified air.

Figure 49.Comparing humid vs. normal cycles, showing more rapid depletion in NP and quicker acidification (sandstone).

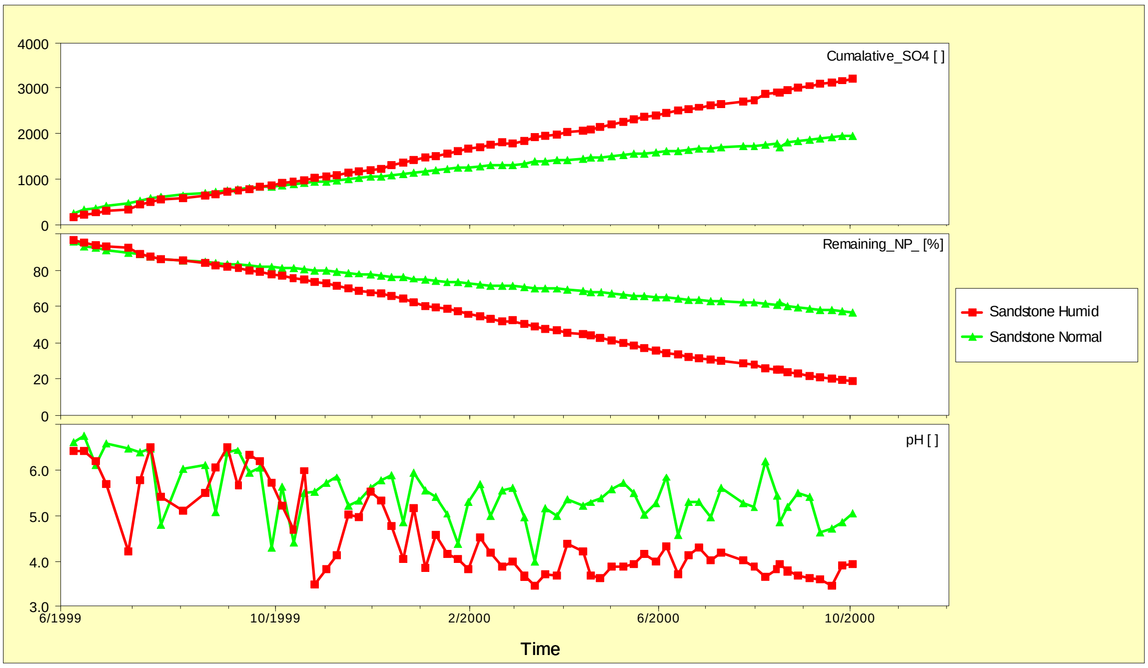


Figure 50. Comparing humid vs. normal cycles, showing higher SO_4 production, more rapid depletion in NP and quicker acidification.

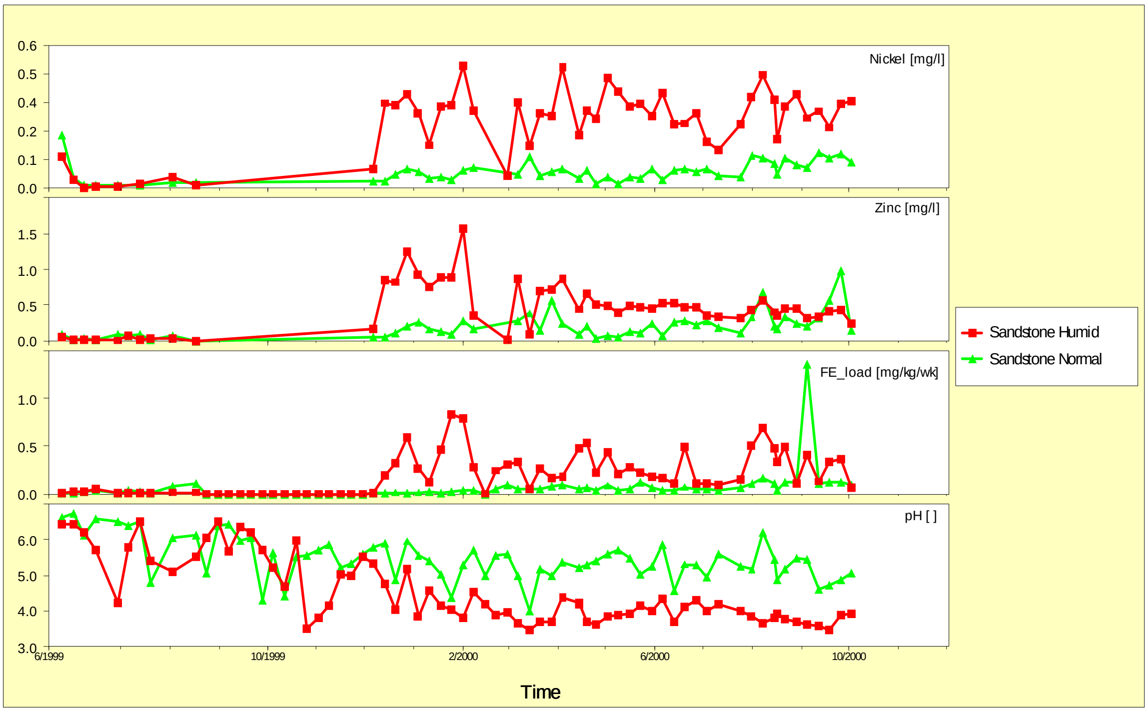


Figure 51. Comparison between metal loadings for humidified and normal cycles in sandstone.

Duplicate humidified and normal protocol testing was also done on shale samples. After more than a year of testing, the shale sample shows that the two protocols mirror one another more closely than the sandstone sample. The release rates from the shale samples in the extended humidified protocol shows greater NP depletion, implying that the onset of acidity should be earlier for the humid air protocol.

The problem of what time period to allow for humidity cell testing is again highlighted here. The standard 20 week period as outlined with the ASTM regulations would provide none of the key answers required and thus an extended period of more than a year would be needed in this case. The greatest uncertainty lies in trying to determine this time period and as can be seen from these four cells, this cannot be determined at the outset of the project.

The shale samples remained fairly alkaline throughout the testing period. The ABA data suggest that this cell should in time acidify. The NNP value for an open system is, however, only very slightly negative (Table 17) and within the so-called grey zone. Kinetic testing in this case suggests that the reaction rate of the system is very slow and that if depletion does eventually occur, it would be minimal. A crucial question would therefore be that of what minerals could possibly be causing this buffering.

The mineralogical determination (Section 5.3) on this sample, shows no clear carbonate phases that could be buffering the system. An assessment was, however, made of the saturation indices of different minerals to find possible buffering phases.

An assessment of the Saturation Indices (SI values) was done for dolomite, calcite and gypsum. The methodology used was to approximate the ionic strength from the analysis of each week’s leachate, using the Guntelberg approximation to yield the activity co-efficient and then calculating the ion activity product from this. The results were compared to those from PHREEQC and were found to be within approximately 10% and therefore appropriate for the use in indicating any mineralogical control on the observed outflow chemistry. For this shale sample, it was clear that the trace amounts of calcite/dolomite present were sufficient to buffer the system under the influence of open system carbon dioxide. The graph below, showing the pH, alkalinity and dolomite saturation shows that where the pH is at its maximum the system is at equilibrium with these carbonate species (seemingly due to the increased mobilisation of calcium) which effectively buffer the system. The mobilisation rate for this sample is fairly low, suggesting the sample would contribute very little to the overall load in the field.

The comparison of the saturation state of all the cells showed that the flushing rates in all the cells were high enough (no minerals repeatedly at saturation). Gypsum, regarded as a very likely secondary mineral to form from pyrite oxidation in the presence of calcium carbonates, is shown as an example in Figure 55 for all the cells and Figure 56 for the cells that produced the most sulphate. Evaluation using PHREEQC shows that for several cells, particularly 1a and 2a, the iron species are often oversaturated. It is not clear if this is due to the inability of geochemical speciation models to accurately handle these values, as reported by Williams and Smith (2000), for iron species due to the slow kinetics of formation, or due to real supersaturation.

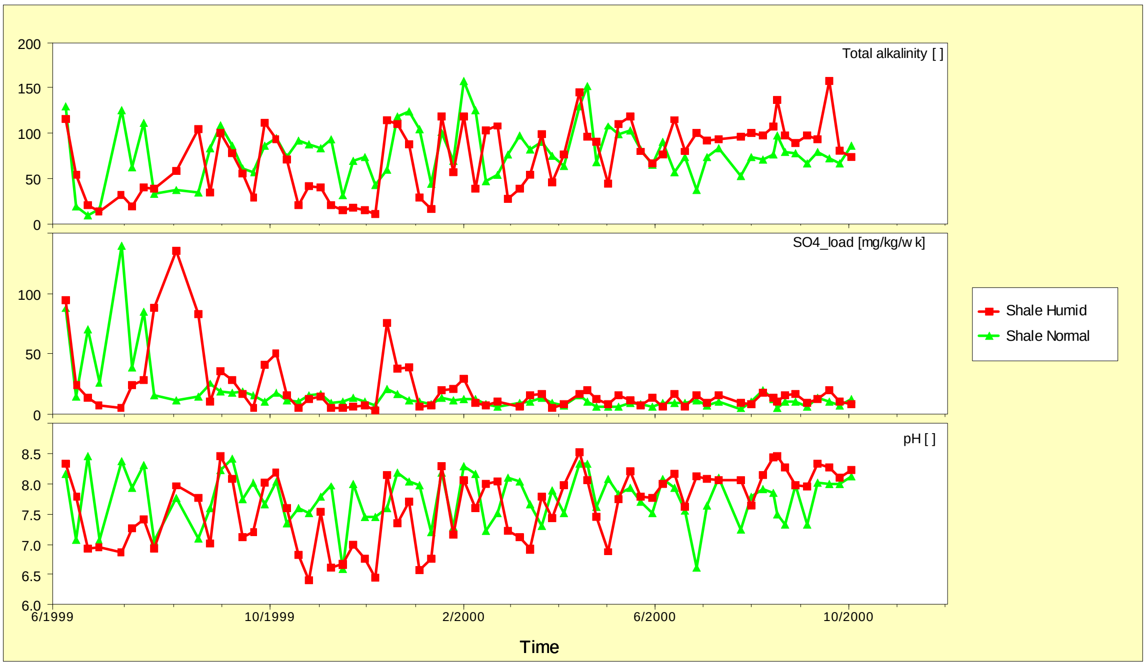


Figure 52. Comparison of the two protocols for the shale sample.

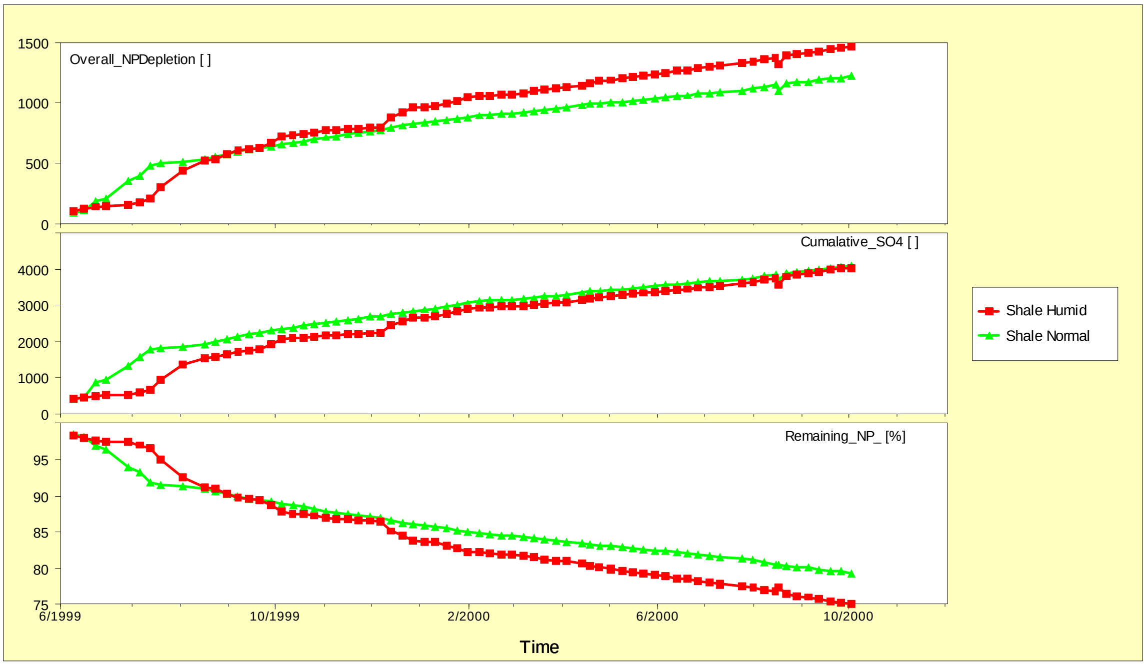


Figure 53. Comparison of the two protocols for the shale sample, showing very slightly higher leaching for the humid protocol.

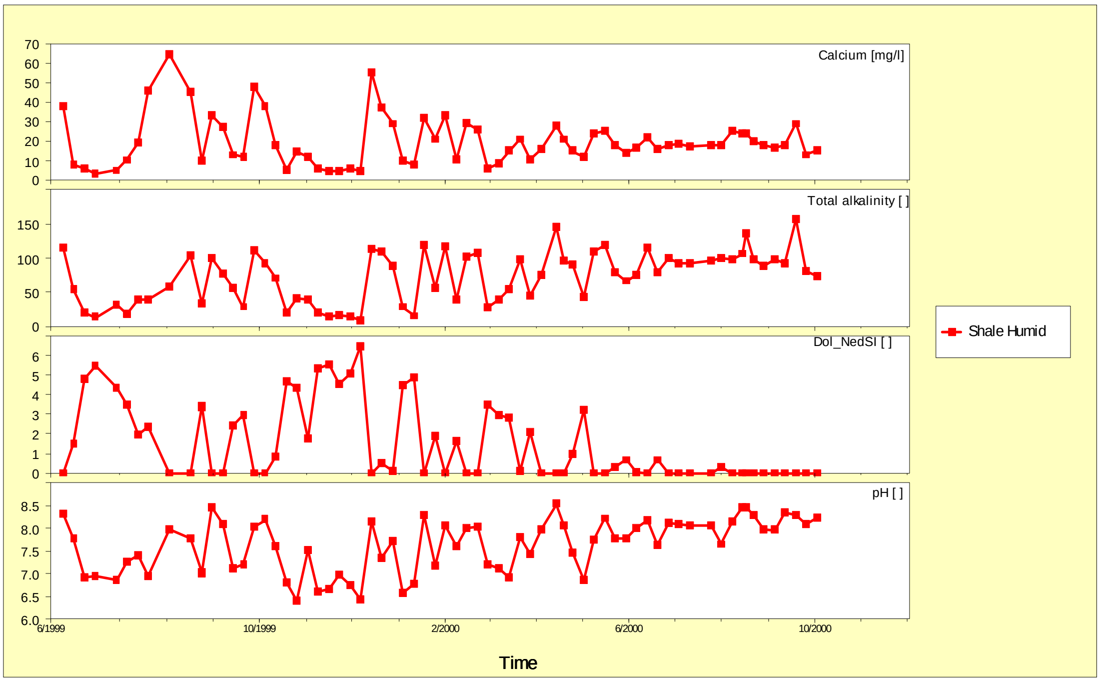


Figure 54. Comparison of observed pH, alkalinity, calcium and the saturation index of dolomite.

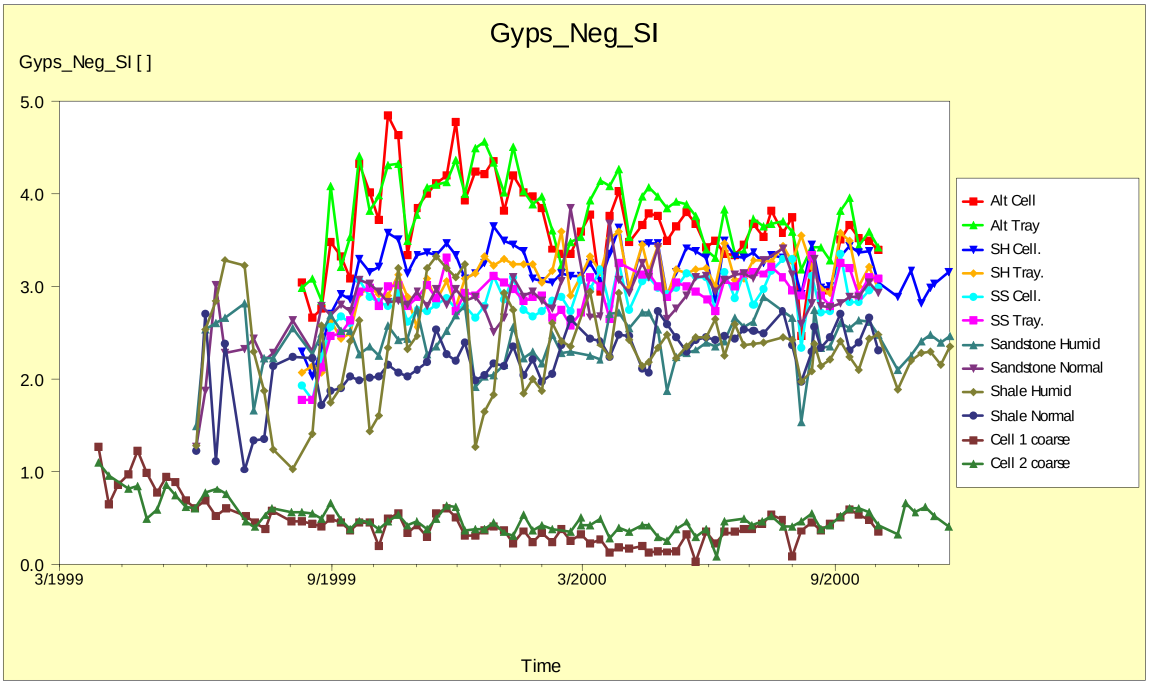


Figure 55. Gypsum Saturation for all cells.

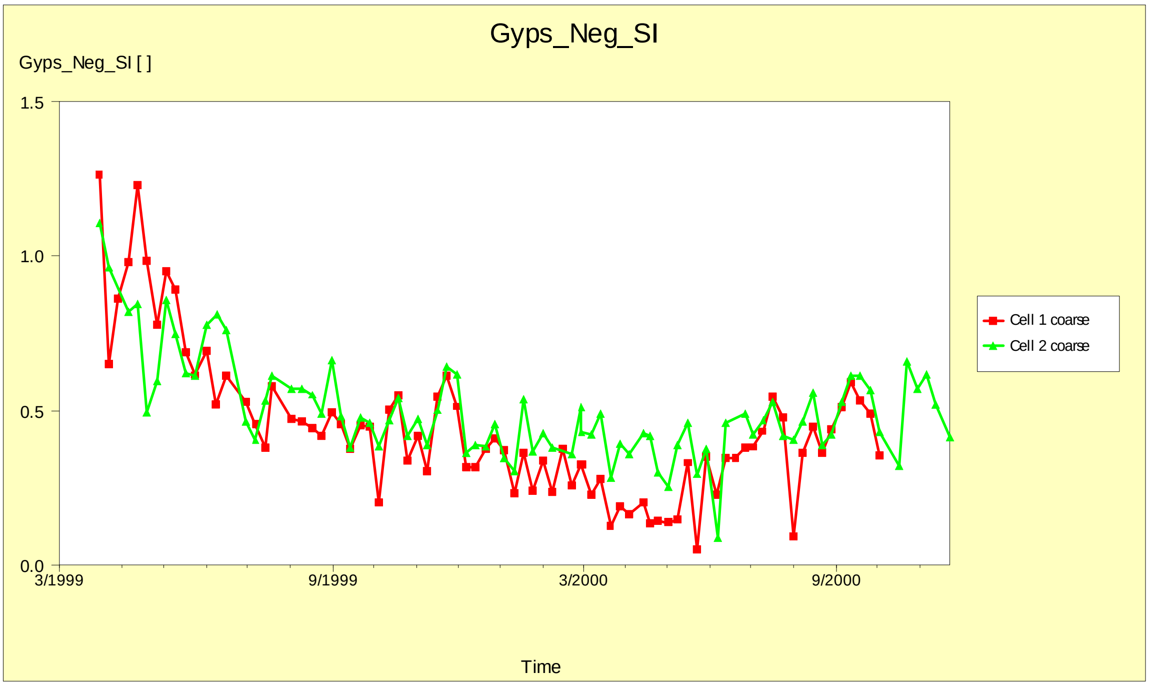


Figure 56. Gypsum saturation for cells 1 and 2, showing that saturation is never reached.

As part of the project, the use of aerated trays was also researched (Figure 57). In these trays, duplicate samples for certain humidity cells have been placed. The samples are sprayed with a water bottle each morning and evening and the surface area is such that most of the sample is exposed to the atmosphere. The reaction sequence in these trays is compared with that in the cells to test effectiveness. It is felt that if these trays yield relatively good results, they can be employed with great success, due to their simplicity and cost-effectiveness.

Figure 57. Aerated Trays used as alternative to humidity cells.

The trays were an attempt to scale the rigorous humidity cell methodology down to an affordable and time-effective method. The trays used for this investigation are constructed of plastic and cost less than R20 each. The most important consideration in their construction is that they should be chemically inert and have a large surface area to hold the required sample size in a single layer. Thus the amount of surface area exposure to oxygen is maximised.

Duplicate samples where tested in humidity cells constructed as above and operated according to the three-day dry/three-day humid air protocol. The protocol followed for these trays was as follows:

- One kilogram sample was used.
- Day one: leach with 500 mL of deionised water.
- Allow to stand for one hour and then decant into sample container.
- For four days keep samples moist by application of dionised water via spray bottle.
- Allow two days for drying and reaction with only oxygen.
- Repeat.

The trays were kept in the same temperature controlled facility as the humidity cells with a temperature maintained at approximately 30 °C.

The results from these "aerated trays" show close replication to those obtained from the more conventional cells. There is thus a potential of using this methodology which is less capital and labour intensive to obtain equivalent results to those obtained by more conventional humidty cell methods. The results from the cells are also in line with the ABA done on these samples.

Figure 58. Comparison: Humidity cell vs. aerated tray for major constituents (sandstone).

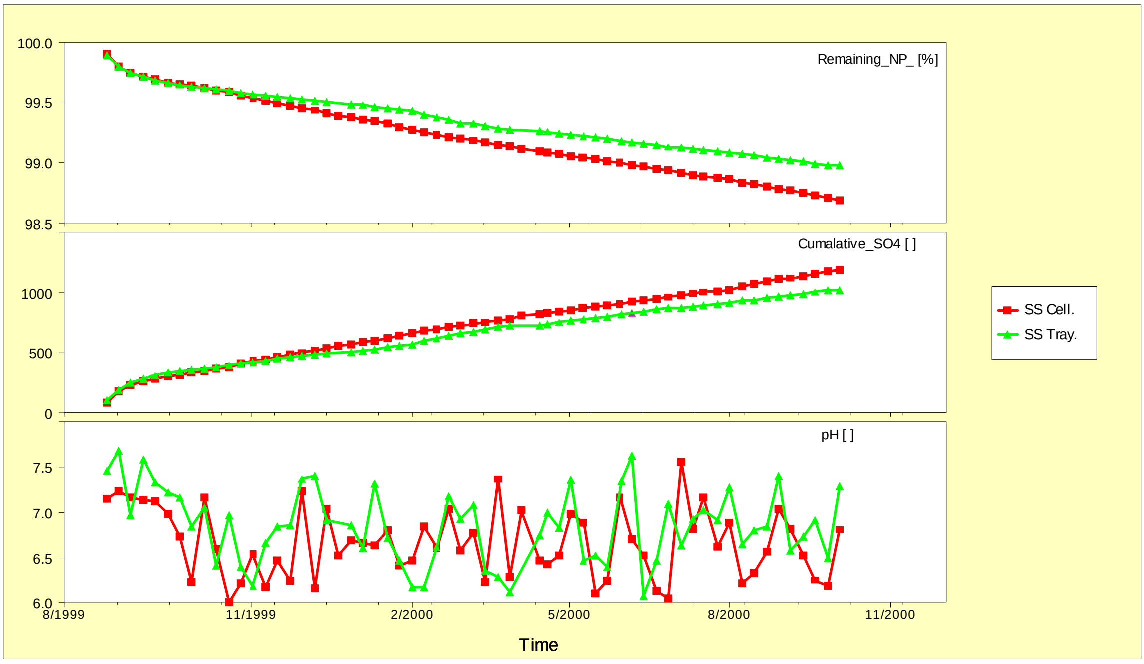


Figure 59. Comparison: Humidity cell vs. aerated tray for sulphate produced and remaining NP vs. pH(sandstone).

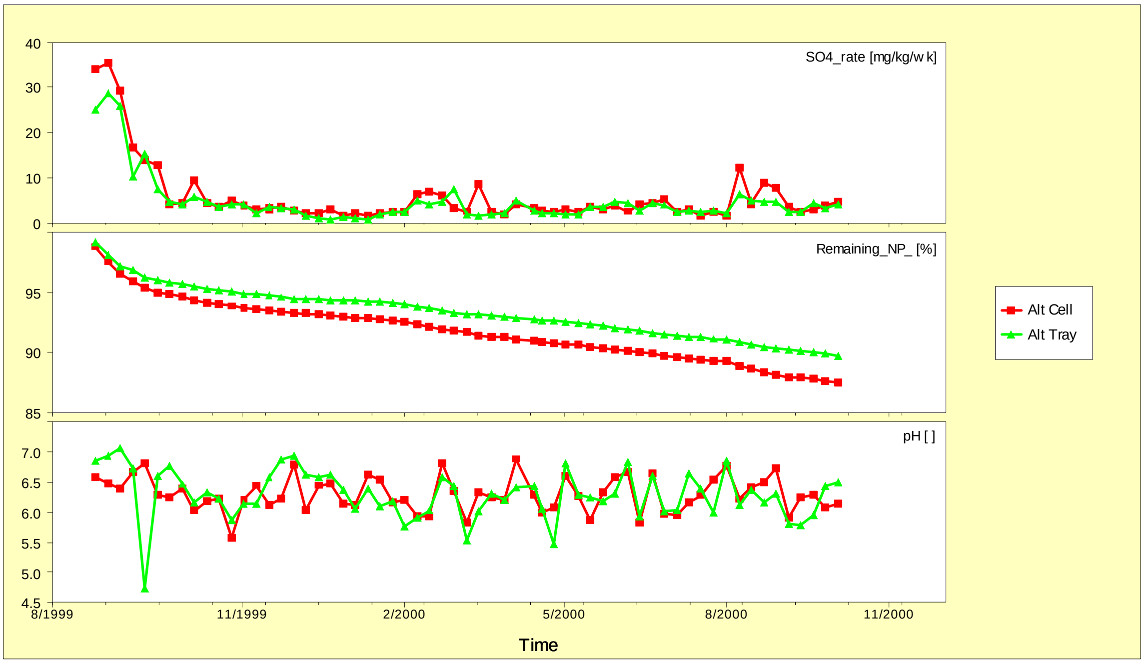


Figure 60. Comparison: Humidity cell vs. aerated tray (Alternating sandstone/shale cell).

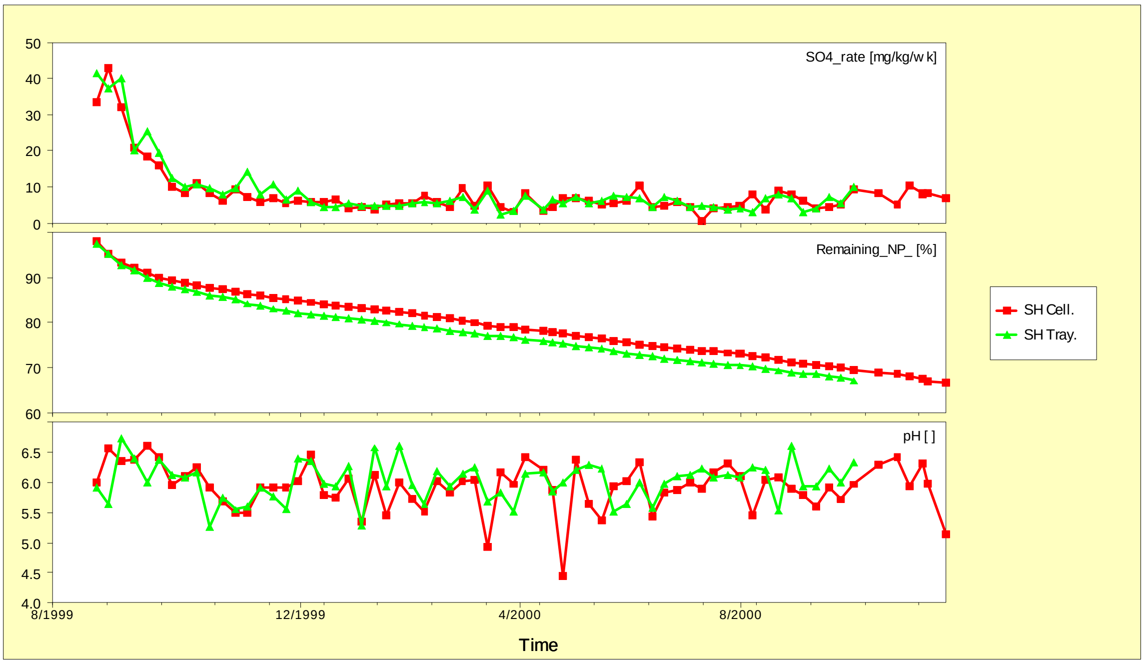


Figure 61. Comparison: Humidity cell vs. aerated tray for major constituents (shale cell).

The time period for which the cells should be operated and the number of cells required to give meaningful results are very important. The ASTM Procedure (ASTM, 1996) requires a minimum test duration of 20 weeks, while Price (1997) recommends a minimum of 40 weeks. It is common in Western Canada for humidity cells to be run for periods in excess of two years (104 weeks). It is possible that some tropical areas of the world experience climates similar to that of a humidity cell, but for North American mines the atmospheric conditions of the humidity cell are considerably harsher (Mills, 1998g). Morin and Hutt (1999) published a paper on the question of time and quantity. Their findings can be summarised as follows:

How long?

- Used extensive database of kinetic tests.
- Need long-term stability of cells.
- Usually 20 weeks insufficient; 1 year minimum.
- Only 50% complete after 1 year.
- Testing period cannot be determined *a priori.*

How many cells?

- Tested 7 mines with 12 - 40 cells.
- If sulphate production rates are low, 12 or less are sufficient.
- At high SO_4 production rates 36 may be too few.

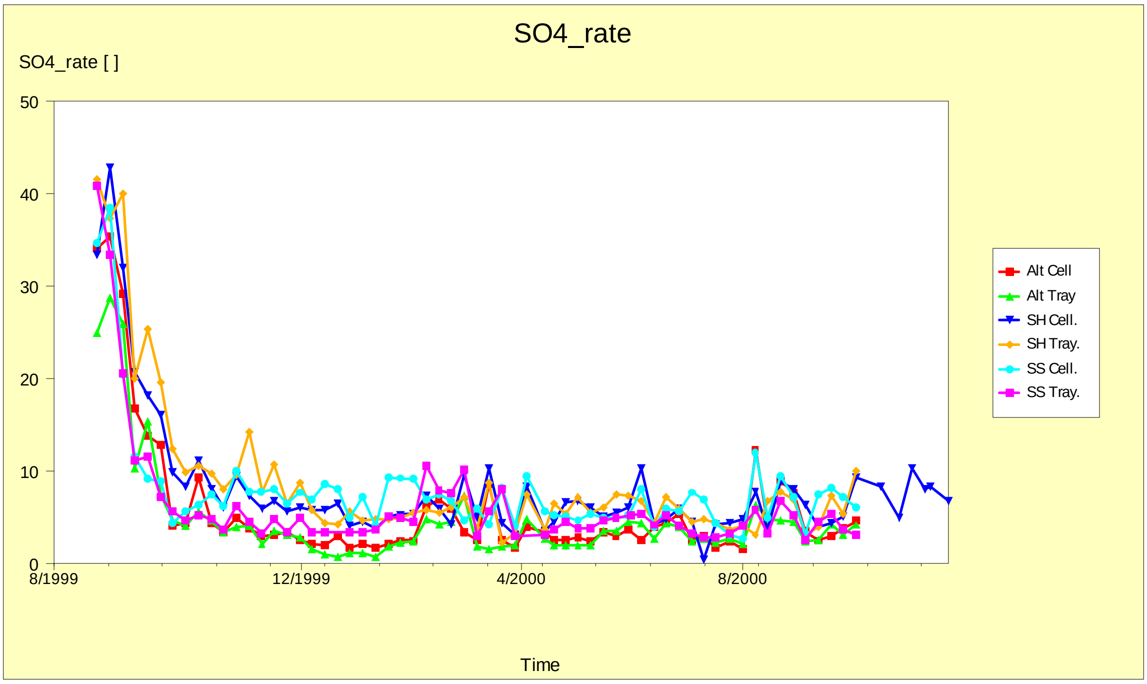


Figure 62. Sulphate production rate for all the core samples tested for conventional and aerated trays.

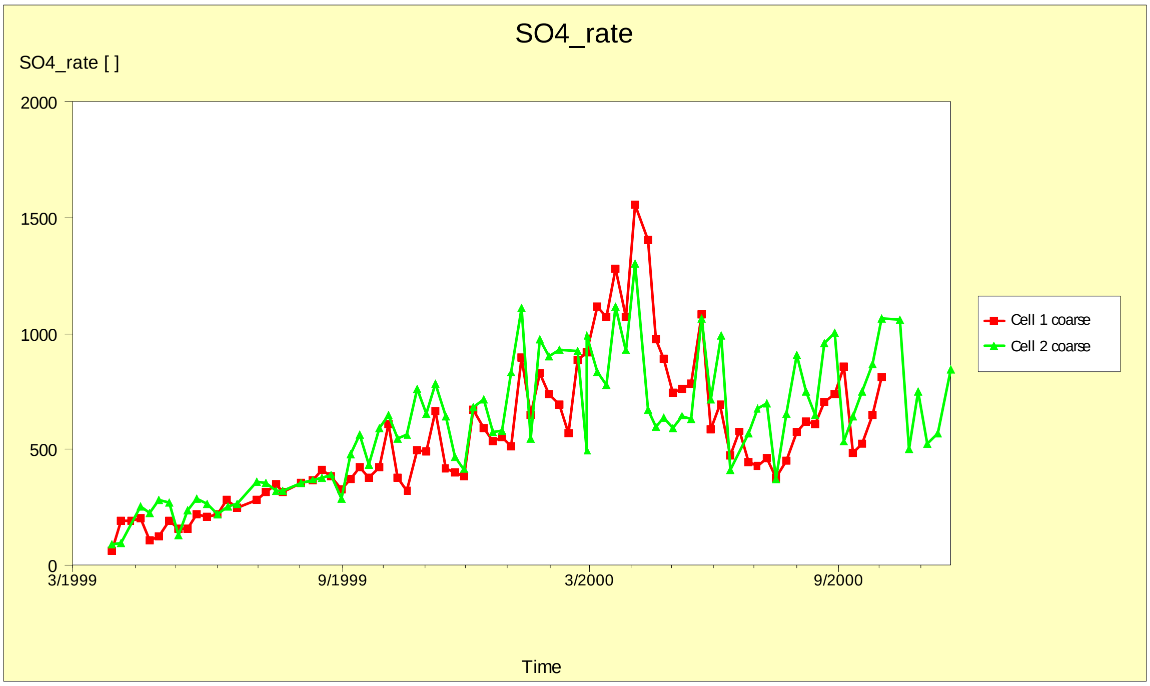


Figure 63. Sulphate production rate for the shale samples.

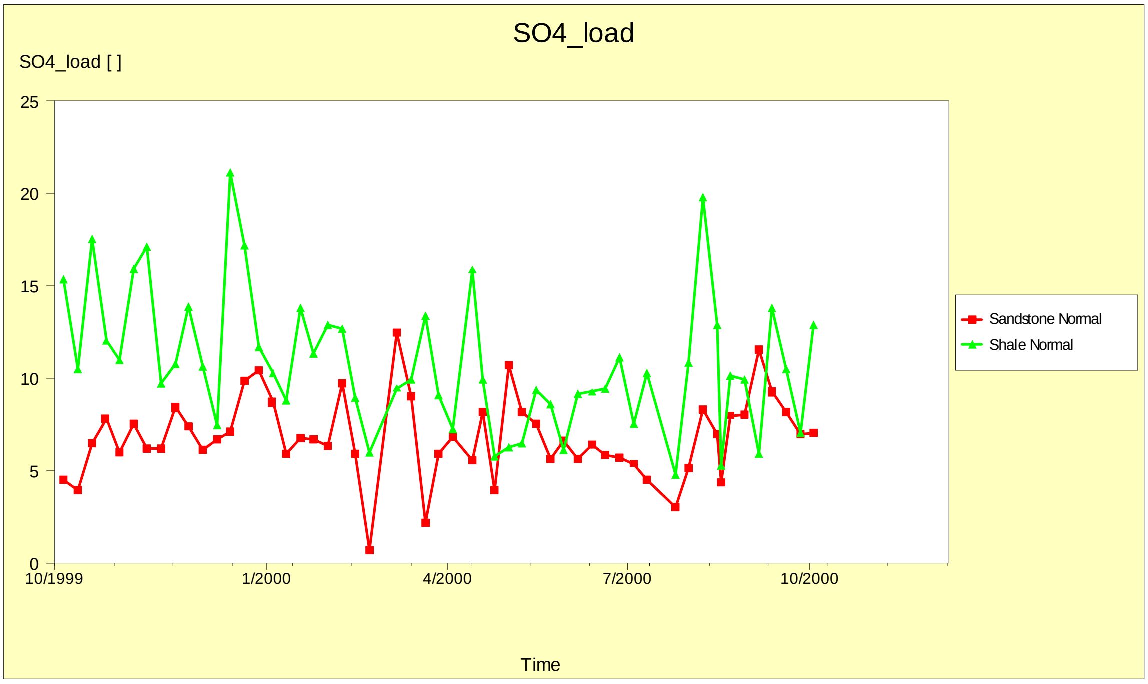


Figure 64. Sulphate production rate for the conventional humidity cells in the humid vs. normal test.

The preceding figures (Figure 62 to Figure) show the sulphate production rate. These rates provide a good indication of the rates in the field for conditions where moisture and oxygen are available, or under submerged conditions where ferric iron is the oxidant. (The rates of pyrite oxidation by oxygen in moist air are comparable to the rates of pyrite oxidation by ferric iron in solution, Jerz and Rimstidt (2000)). It is clear that for the core samples the rates obtained are extremely low (in the order of 10 mg/kg/week), with the majority of the sulphate flushed out within the first portion of the testing period, most likely as a result of the flushing out of accumulated secondary products in these samples.

The end portion (stabilised) rate from sandstone and shale samples evaluated against the humid protocol shows that the shale sulphate production rate is at an average of 11 mg/kg/week with a standard deviation of 3.7, while the sandstone is lower at a sulphate production rate of an average of 6 mg/kg/week for the stabilised period, with a standard deviation of 2.2.

The shale samples running the longest and tested for repeatability yield a far higher rate of 740 mg/kg/week with a standard deviation of 220 for the last 8 months.

The final set of tests was done on “raw” spoil samples. Six sets of duplicate tests were done using the standard humidity cell method and another variation on the aerated trays. For these tests the sample obtained from the test pits dug in the spoils were subdivided and, without sorting, 1 kg samples were placed in the humidity cells and aerated trays respectively.

The trays were placed in incubators at the Department of Microbiology/Biochemistry, UFS, usually used for the enhancement of bacterial growth under controlled conditions. The temperature in the incubator was set at 31°C. Water bowls were placed in the incubator and the trays sequentially varied with relation to these bowls, to ensure a relatively even distribution of humidity in each tray over time. The tests were all run for the 20 week period designated by the ASTM. Table 18 gives the ABA results from these samples.

Table 18. ABA results for spoils.

Samples	Initial pH	Final pH	Acid (Open)	Acid (Closed)	Base	NNP (Open)	NNP (Closed)
A	7.52	2.92	7.24	14.48	6.06	-1.18	-8.42
B	7.35	2.86	8.03	16.07	5.98	-2.06	-10.09
C	7.53	2.85	4.70	9.40	4.94	0.24	-4.46
D	5.69	2.63	30.78	61.55	5.54	-25.24	-56.01
E	7.25	3.06	41.09	82.18	10.22	-30.87	-71.96
F	5.63	2.72	1.48	2.97	0.55	-0.93	-2.42

The results from the kinetic tests are given in the figures below.

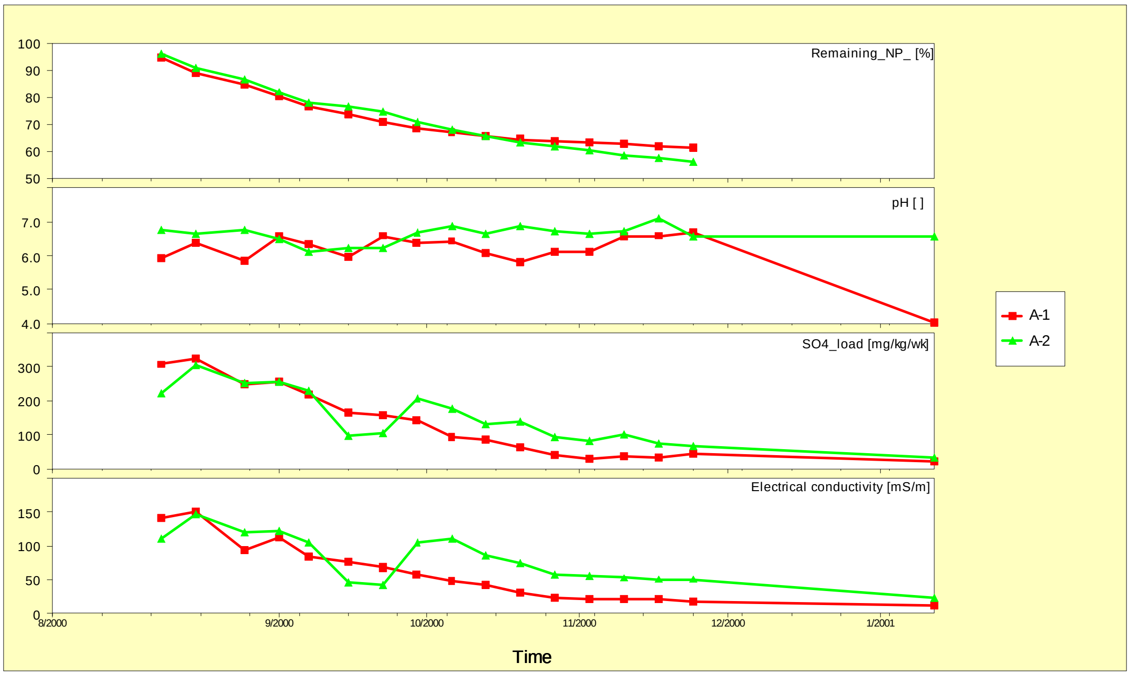


Figure 65. Results from spoil sample A, from the different methodologies.

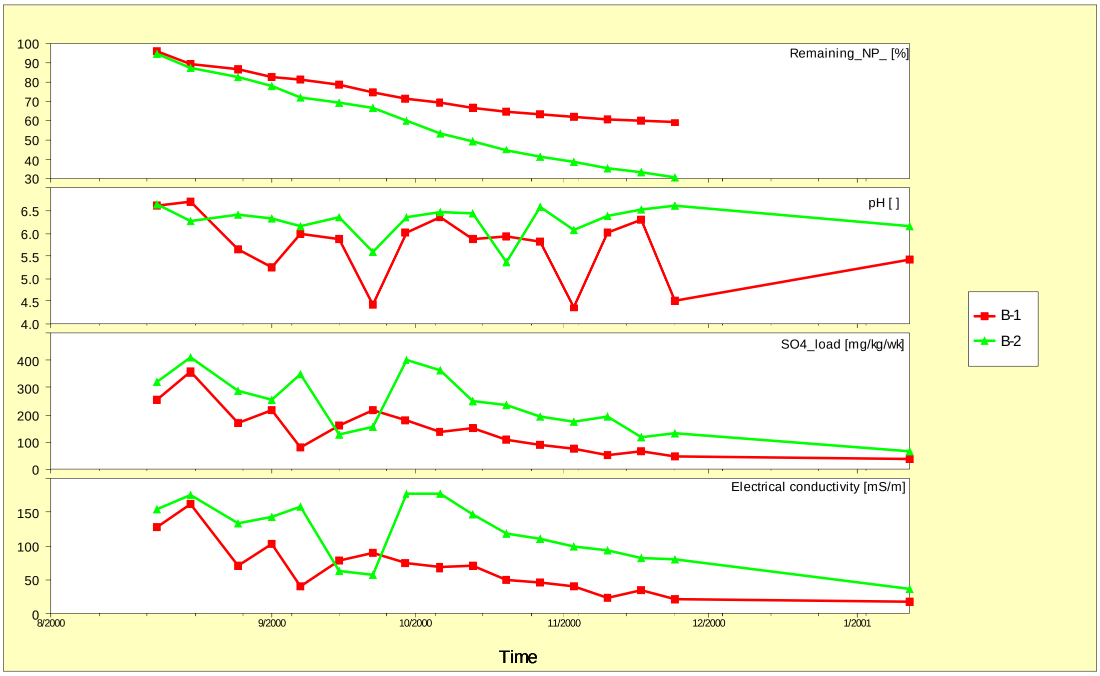


Figure 66. Results from spoil sample B, from the different methodologies.

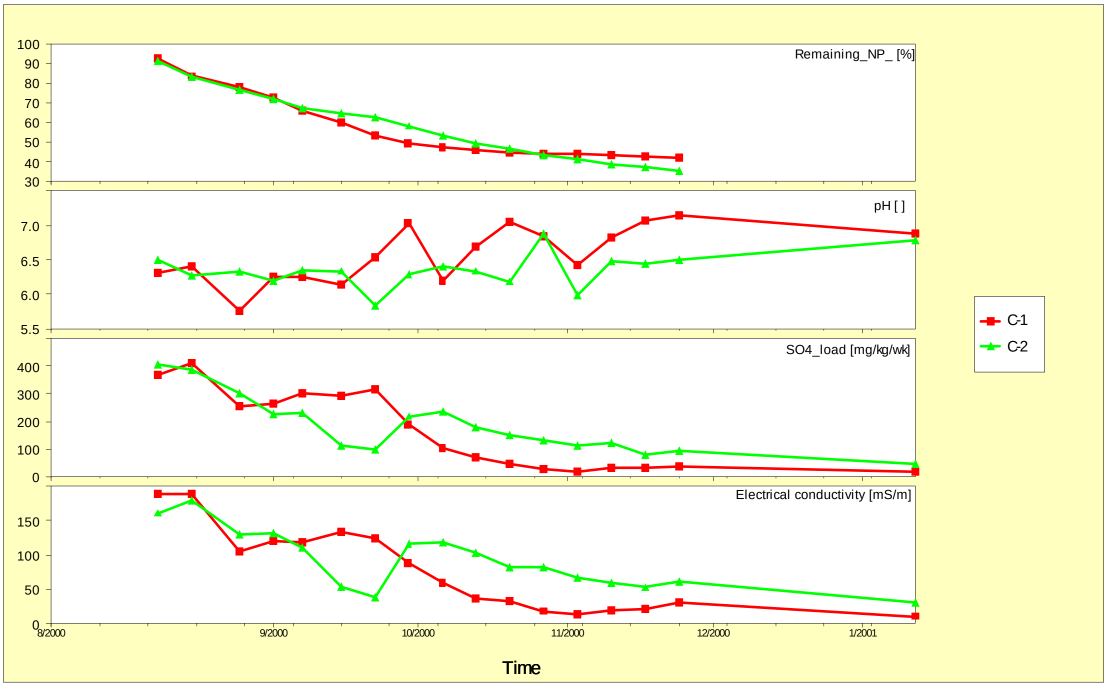


Figure 67. Results from spoil sample C, from the different methodologies.

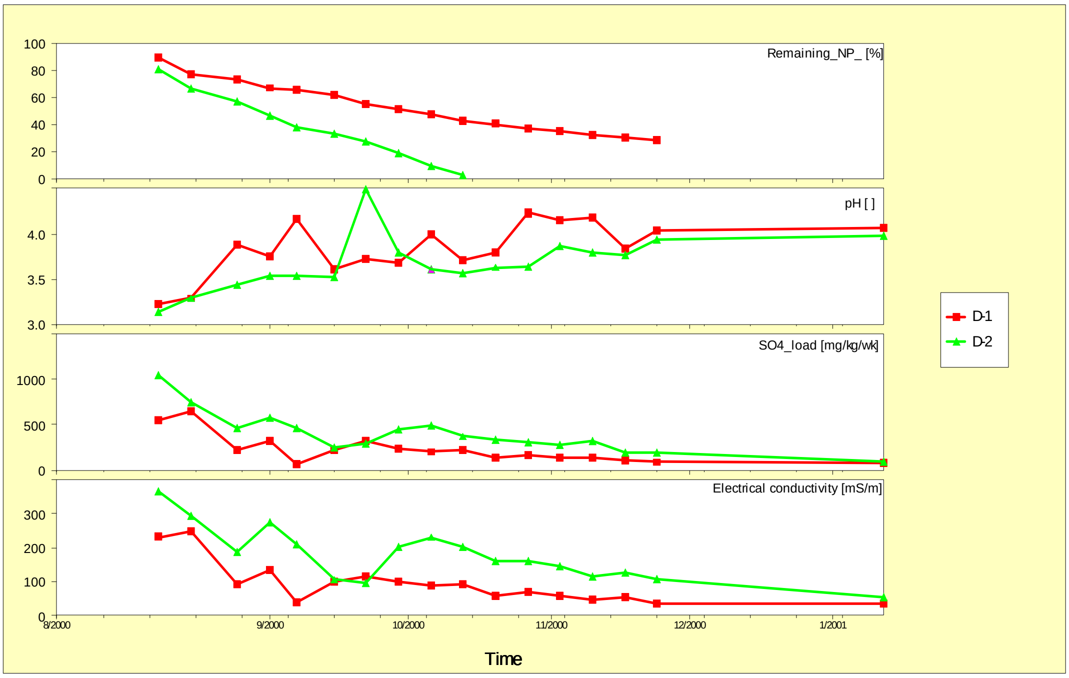


Figure 68. Results from spoil sample D, from the different methodologies.

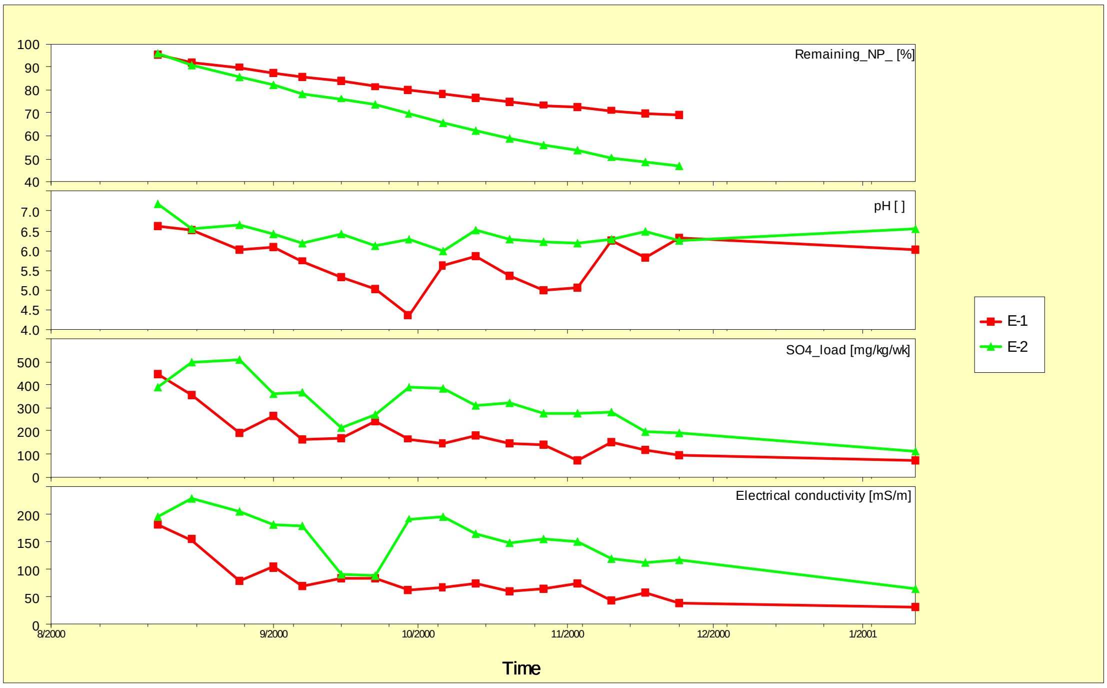


Figure 69. Results from spoil sample E, from the different methodologies.

Figure 70. Results from spoil sample F, from the different methodologies.

Figure 71. Incubator used for trays.

The 12 sets of results show that the standard methodology and the modified methodology using the trays give comparable results. Furthermore the ABA results tie in very well with the results obtained for each spoil sample. Only two samples, D and E, would fall into the category of definite acid-generators according to the NNP criteria.

However, for all of these cells the NNP is below 0.5. Thus the fact that acidification is evident is to be expected, which is again in line with static ABA testing.

Advantages of humidity cells

- The rates of acid generation and neutralisation can be measured in a temperature- and humidity controlled oxygenated environment.
- Temporal variations in these rates can be measured.
- Solubilisation of trace elements can be monitored.
- Bacterial influence on kinetic rates can be assessed.
- Various control options such as blending of waste rock can be simulated (Mills, 1998g and Price *et al.,* 1997).
- The test has been widely used in Canada and the U.S.A. and compares favourably to other tests with respect to reliability (Chemex Labs, 1997).
- According to Price *et al.* (1997b), the humidity cell is the recommended kinetic test for predicting primary reaction rates under aerobic weathering conditions.

6.3.1 OBSERVATIONS FROM THE INTERNATIONAL KINETIC DATABASE

The International Kinetic Database (MDAG, 2000) was consulted to identify trends observed in humidity cells operated worldwide. Morin and Hutt (1999, 2000) used the data contained in this database extensively for publications, to highlight some common features arising from humidity cells. The database obtained and used for the interpretations below was from 64 mines and 475 cells.

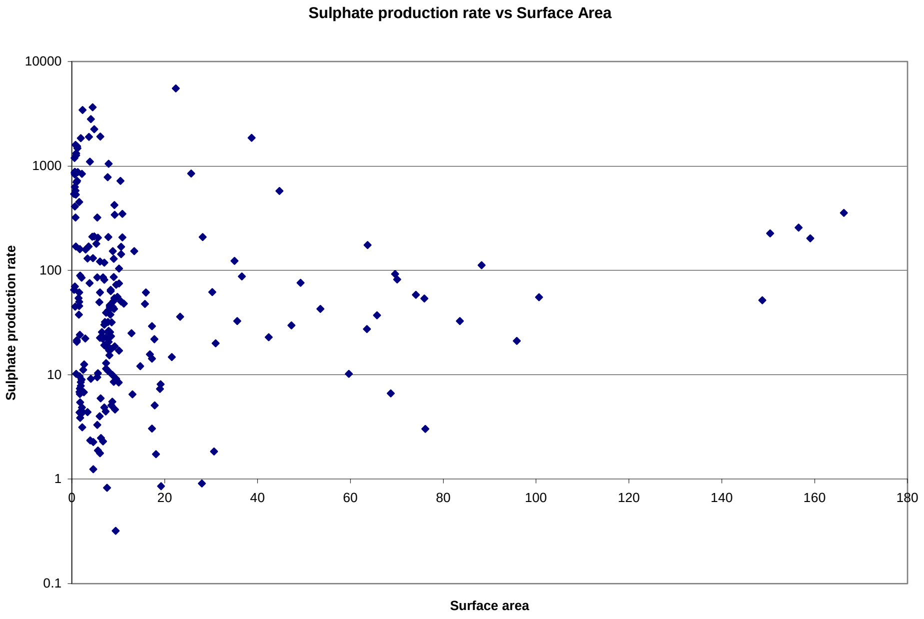


Figure 72. Surface areas vs. sulphate production rate.

Figure 72 above shows the relationship between the average surface area in the cells and observed sulphate production. It is apparent that greater surface areas do not necessarily yield greater amounts of sulphate and that the range of surface areas varies from very low (i.e. larger fractions) to very fine material. Hollings *et al.* (2000) also found no correlation between grain size and sulphate release rate in humidity cells to extrapolate rates to the filed. In addition there was no correlation between grain size and oxygen consumption. This poor correlation is interpreted to be the result of low sulphur content, but may be a more widespread phenomenon. From theoretical considerations one would expect the higher surface areas to yield far greater quantities of product per week, but this is not necessarily the case.

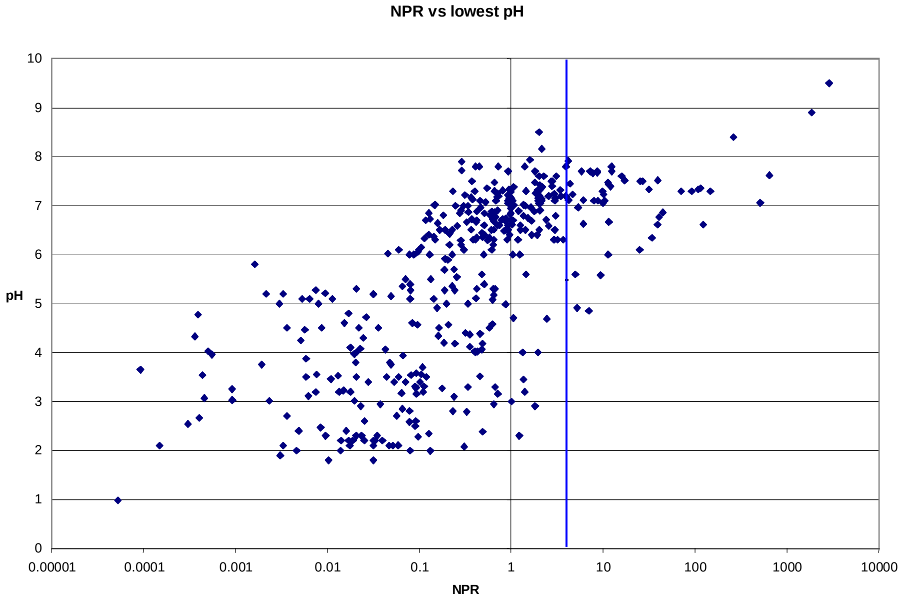


Figure 73. NNP vs. lowest pH.

The Net Neutralising Potential Ratio against the lowest recorded pH yields some interesting observations. Ratios of less than one are assumed to yield acidic waters over time according to the theoretical considerations, while a “safety criteria” of 4:1 (shown on Figure 73) is often set to ensure that acidity does not occur. The plot shows that the 4:1 ratio appears to be very effective in eliminating samples that will become acidic in time. It can also be seen that several samples in the NPR range of 1 to 4 become acidic over time and that many samples do not appear to acidify even when the NPR ratios are below 1. This latter point can be misleading as a large proportion of these cells were probably run for the minimum period of 20 weeks and were consequently terminated prematurely.

Figure 74 below shows the relationship between the sulphate production rate and the acidity produced. There does appear to be some correlation between the two as would be expected from the oxidation of the sulphides present, but other factors, such as secondary mineral formation, play a large role in many of the observed values, thereby yielding a very poor correlation between the two parameters.

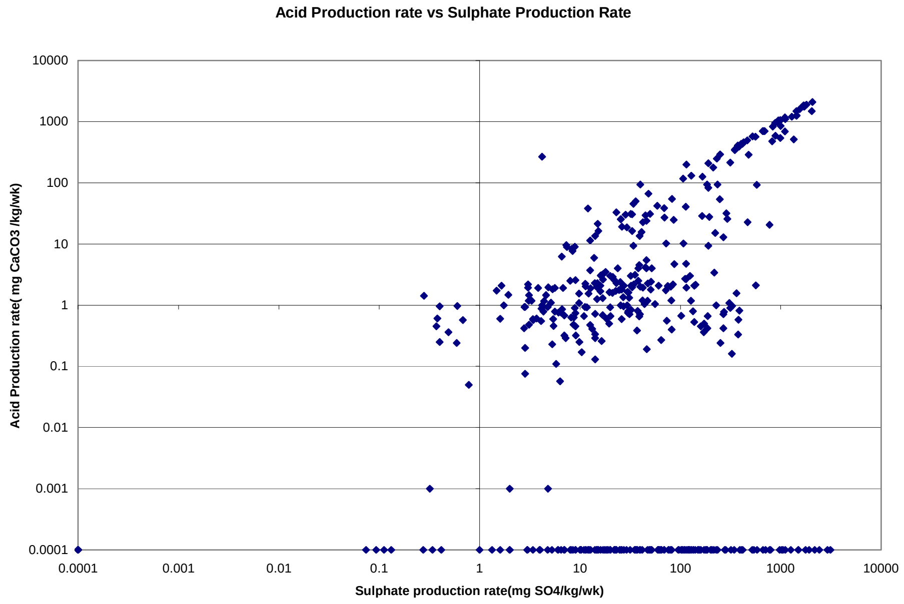


Figure 74. Acid production rate vs. sulphate production rate.

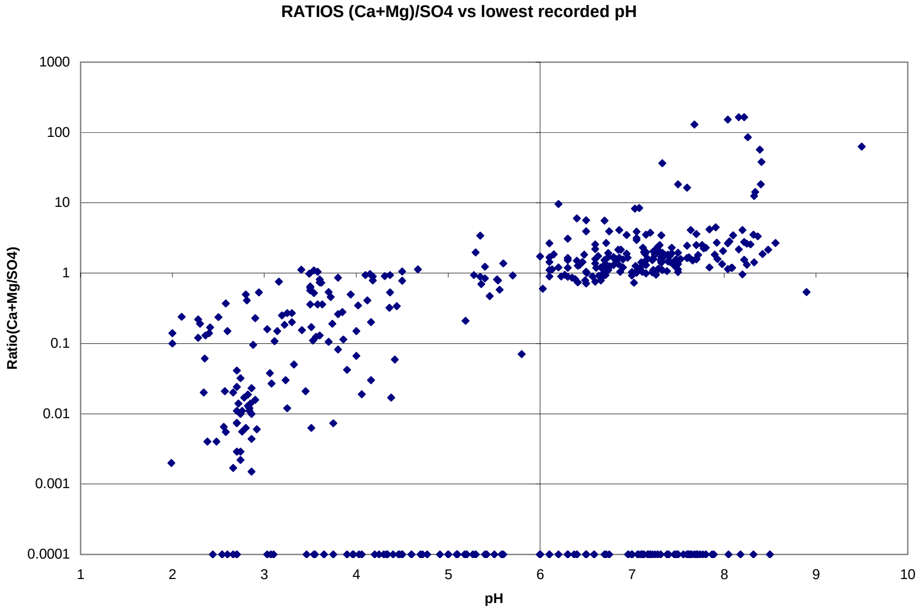


Figure 75. "Base cation/acid anion ratios" vs lowest pH.

The relationship between the ratio of calcium and magnesium to sulphate against the lowest recorded pH shows that as long as there is an equivalent amount or more of calcium and magnesium being produced, the drainage from the humidity cells is near neutral (Figure 75). In most cases, once the sulphate exceeds these two cations, there appears to be an onset of acidity. This has meaningful implications for the interpretation of observed values at mines and can possibly act as an early warning mechanism.

Use of this ratio was also made in the evaluation of the kinetic tests done as part of this project. The depletion of this ratio in the cells that acidified over the testing period indicates that this ratio could be a very useful indicator to predict the onset of acidification (Figure 76).

Figure 76. Comparison of "Base cation/acid anion ratio" vs. pH and Remaining Neutralising Potential on humidity cell.

A defunct mine where acidification has already occurred was used to further explore this phenomenon and this again showed a good correlation between the low pH and the depleted calcium + magnesium against sulphate ratio. Figure 77 clearly shows that the acidified samples all have ratios of below 1 and, in most cases, below 0.8. This illustrates the field applicability of this ratio as monitoring and evaluation tool.

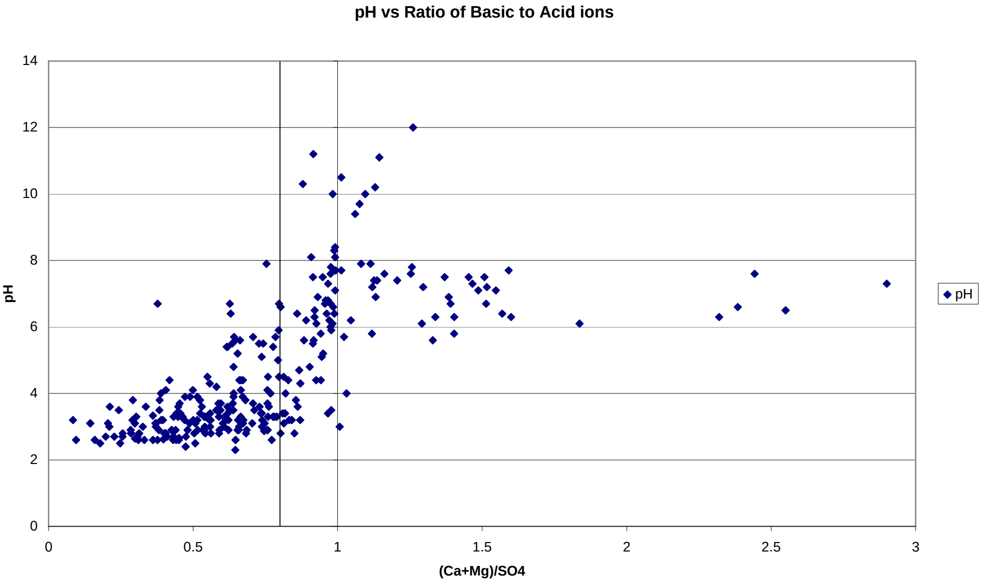


Figure 77. Comparison of "Base cation/acid anion ratio" vs. pH at defunct coal mine.

The figure below (Figure 78) shows that there is some correlation between % S and the eventual sulphate production rate. However, the importance of other minerals, availability of the sulphides and several other effects also clearly play a very important role, since very high sulphides do not necessarily yield extraordinarily high sulphate production rates. When making any deductions from these graphs, it must be assumed that the cells have been constructed and operated to optimise conditions for sulphide oxidation; thus this latter observation is very important, particularly when trying to extrapolate values to the field by empirical methods or modelling. Higher S percentages should yield higher rates if the grain size is similar.

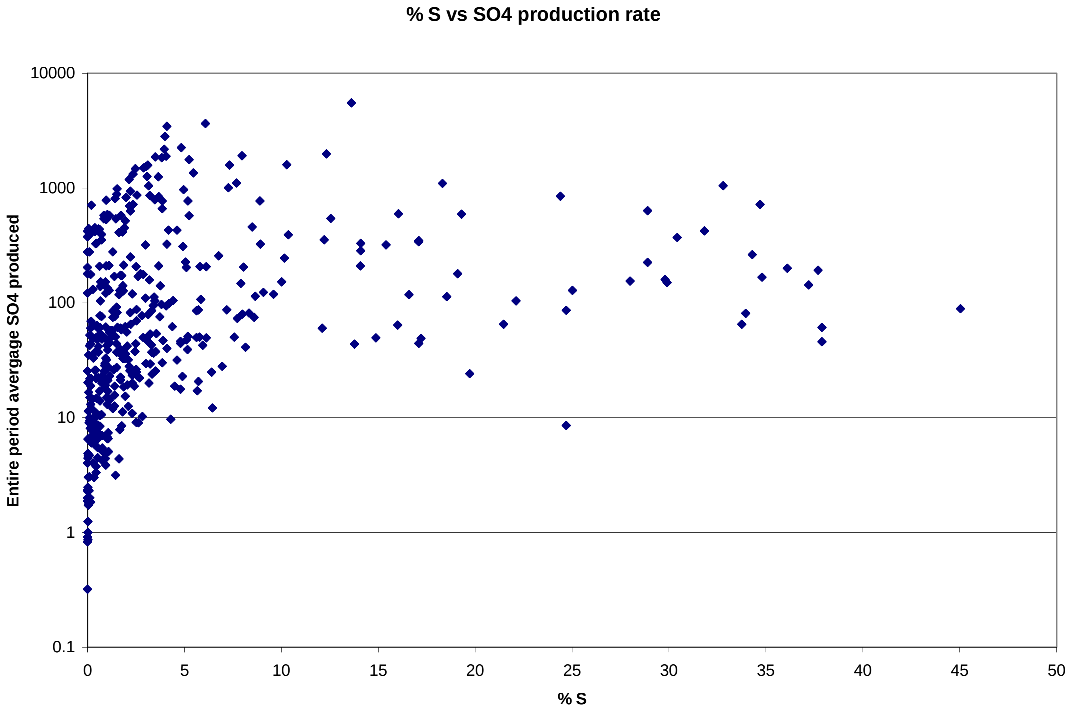


Figure 78. % S vs. SO4 production rate.

There appears to be a very weak correlation between the total sulphide present and lowest recorded pH (Figure 79).

At extremely low values (below 0.1 %) the majority of lowest recorded pH-values are non-acidic. However, if one considers the 0.3% criteria suggested by Lawrence and Soregali (1996) it is clear that in the range of 0.1% to 0.3% there are several cells which yield acidic discharge at some point in the operation. Unfortunately, this database only gives the highest and lowest pH and it is thus not possible to verify if the lowest pH-values were sustained for a period of time or only a brief phase in the cells' hydrochemical evolution.

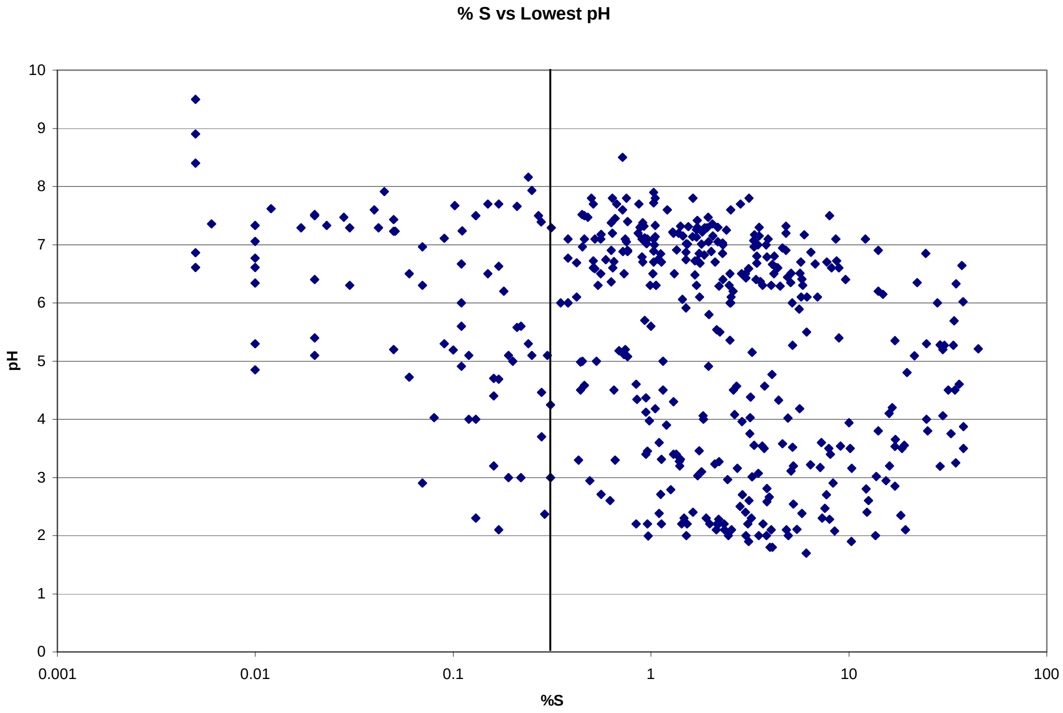


Figure 79. % S vs. lowest recorded pH.

6.4 CONCLUSIONS

Humidity cells are excellent kinetic teststo supplement static ABA. Their advantages are that they can supply rates of reaction and can provide a better assessment of on-site rates. Research by several authors has shown the sulphate production rate to be an accurate assessment of the sulphide oxidation rate where high enough flushing rates are maintained to prevent secondary mineral precipitation.

Hornberger and Brady (1998) give the following, as general principles of kinetic test design and performance and as guidelines of the major factors to be considered:

1. The size, shape and structure of the kinetic test apparatus should be as simple as is practicable, given that multiple arrays of these devices may be needed to concurrently test multiple rock samples from a proposed mine site. The apparatus may need some complexity to allow fluids and gases (i.e. oxygen and carbon dioxide) to enter, circulate through and exit the apparatus.

2. The dimensions of the kinetic test apparatus should be in proportion to the particle size distribution and volume of the rock sample to be tested, so that there are no adverse interactions (e.g. airlocks or other testing artifacts) between the sample and its container. For example, with a columnar shaped apparatus, the inside diameter of the column should be

at least several times greater than the largest particle diameter within the volume of rock samples.

3. The goals of sampling for kinetic testing should be to obtain rock samples that are representative of the physical (i.e. particle size distribution) and chemical (i.e. mineralogic composition) characteristics of the consolidated overburden strata, backfilled mine spoil or waste dump to be simulated in the test.

4. Multiple lithologic units should not be combined in the same kinetic test apparatus, in composite samples, or especially not in layers, unless the potential acidity or alkalinity of the individual lithologies has already been accurately and unequivocally determined from similar kinetic tests, static tests or equivalent geochemical information.

5. The volume of influent water minus the volume of water consumed during the kinetic test determines the volume of effluent water or leachate. These volumes of water should be properly proportioned to the volume of rock sample and should generally not exceed 1:1 and preferably 0.5 L water to 1 kg sample.
6. Rock samples in kinetic tests should usually not be in a completely saturated condition for the duration of the test, because pyrite oxidation rates will be greatly diminished.
7. Samples should not be agitated excessively once the test is underway. Test protocols which disrupt the oxidising environment, such as shaking the cells, high addition of acidic water and extreme wetting and drying cycles create an oxidising environment that more closely represents field conditions and are therefore recommended (Frostad and Lawrence, 2000).

8. The pore gas composition within the kinetic test apparatus should be similar to that within reclaimed surface mine spoil, particularly to have a partial pressure of carbon dioxide sufficient to facilitate the dissolution of carbonate minerals.

9. Iron-oxidising bacteria must be present and relatively abundant within the kinetic test apparatus, if the test conditions and results are expected to be representative of pyrite oxidation potential in the mine environment. There is no need for inoculation as several authors have shown that the bacteria are generally present or that the bacteria only have a transient, unnatural effect (Cravotta (1997), Morin and Hutt (1997)).

10. Maintain temperature conditions between 20°C and 40°C during the test to provide optimum conditions for a healthy bacteria population.

Based on these principles and the findings in this project the following is recommended:

- Humidity cells should be used as method of choice for laboratory kinetic tests.
- The standard methodology should be as follows:
    1. Set an apparatus with dimensions similar to those given in the section above or scaled up proportionally when greater mass/particle size is to be used.
    2. Use appropriate methods to maintain the temperature of these tests at 30°C.
    3. Leach with deionised water, collect and analyse for pH, sulphate, alkalinity and the parameters of choice (with Fe, Mg and Ca as minimum).
    4. Pass air through on a cyclic dry/humidified cycle for three days each.
    5. Leach with deionised water on the seventh day, using flushing volumes of half that of the test sample, collect leachate and analyse.
    6. Determine rates of production for all the parameters of choice, together with rates of NP and AP depletion. Report in terms of mass product/mass sample/time period.

Detailed methodologies are given in the accompanying guide to the methods.

This project and others elsewhere, have shown that very simple methods can supply equivalent information. However, where deviation of the above guidelines is applied, it is recommended that duplicate humidity cells be used as reference to demonstrate that the modified method yields the same results. This is also proposed where a variation on the standard test is done to establish the influence of a particular management option. In summary thus, the standard humidity cell method should be used as far as possible and where deviating from it duplicate standard methods should be done for purposes of evaluation.

The ideal kinetic test for the prediction of mine drainage quality will be:

(a) practical to construct and operate.

(b) of reasonable time and cost requirements to encourage widespread acceptance and use.

(c) representative of the physical, chemical and biological conditions of the mine environment (i.e. in conformance with the preceding 8 principles).

(d) readily interpretable due to the capability of producing the range of acidity, alkalinity, sulphate and metal concentrations found in acidic and alkaline mine drainage.

As a final point the views of Hornberger and Brady (1998) as far as standardisation of the methodology is briefly discussed. These authors feel that two major advantages of developing standard kinetic procedures are that almost everyone, especially for mine permitting purposes, would be using the same test procedures (which facilitates data comparison and database building) and that scientific and legal controversies between government and industry users of prediction techniques over interpretations of the test results and accuracy of the predictions would be substantially reduced.

In summary the following points are pertinent to kinetic testing:

Factors to be borne in mind include:

- The scale up of kinetic test results to field scale and long periods is often problematic.
- Type of test and equipment should be driven by the environment and answers that are required.
- The length of the testing period is difficult to determine prior to testing.
- From this study **humidity cells are suggested as the kinetic test of choice.**

Humidity cell tests are vitally important within the ABATE strategy since:

- **They provide rates of production** under test conditions.
- **They provide expected reaction sequence**.
- They can be **used to test different influences** on reaction rate.
- They are **short-term tests to determine long-term effects**.
- **Results can be used in geochemical modelling.**

Kinetic tests are the only method of verifying/obtaining much of this data in the predictive program.

7 FIELD METHODS

Field methods are a very important and useful component of the ABATE process. Field measurements provide real data and can add a valuable understanding to the overall interpretation and prediction of the mine drainage chemistry.

The most important field methods suggested are the following:

- Rock sampling.
- Water Sampling.
- Borehole profiling.
- Spoils trenching.

7.1 ROCK SAMPLING

Obtaining representative samples is a vital component of any drainage prediction methodology, since the remaining methods rely on adequate sampling and interpretation of results requires adequate and representative samples. As an analogy the 1 g sample representing 500 tons of material used in ABA can be compared with the testing of 1 apple for a 300 ha orchard (Tarantino, 1998).

Sampling has been broadly subdivided into two different end members with variations in-between. The characteristics of randomly obtained and cored borehole samples are shown below.

Random

- Taken at selected points
- Limited by accessibility
- Unbiased population

Core Boreholes

- Collect data from exploration boreholes
- Get data with depth
- Allow subdivision into broad lithologies

In Figure 80, examples of cores from exploration boreholes and random sampling respectively can be seen.

Figure 80. Examples of core and random samples.

Determining the number of samples to be taken and the representativeness of the sample set are critical considerations.

Guidelines based on area and volumes have been suggested in certain regions overseas (SRK, 1989). Thus for example in Pennsylvania, an average of 1 cored borehole would be required for every 6 - 8 ha to give representative samples and results acceptable to the authorities (Tarantino and Schaffer, 1998). In the 1989 draft guidelines for British Columbia (SRK, 1989) the following graph was given to determine the minimum number of samples to be taken, based on the mass of geologic unit to be sampled (based on data collected by NORECOL Consultants):

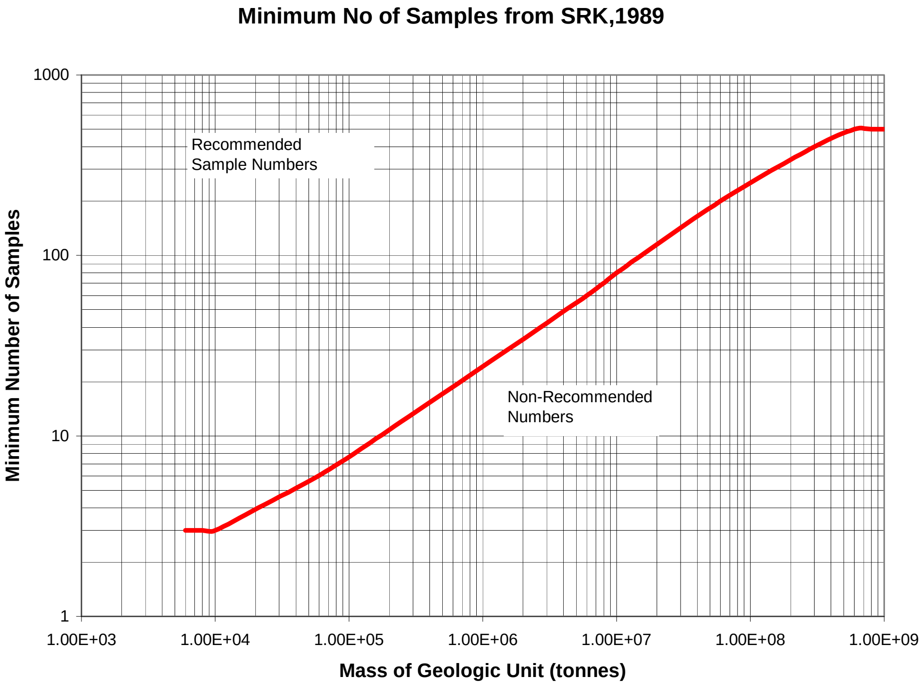


Figure 81. Minimum No. of samples based on mass of Geologic Unit.(from SRK, 1989)

These empirical methods are useful for a preliminary guide; they are, however, based on data from different environments to those encountered locally. It is therefore **suggested that sampling programs are conducted in a stepwise fashion** and that the **representiveness of the sample set be determined**. Once **a more complete database** is available for South African opencast coal mines, analysis of the data should be able to provide a **more generic areal guideline** for sample numbers.

There are several statistical methods to determine the adequacy of sampling. Several of these methods are very intricate and cumbersome in application and the use would be impractical to enforce.

Several parameters pertaining to ABA have normal or lognormal distribution in the field. Examples of these are initial pH (normal in undisturbed strata) and acid potential (log normal). If a population exhibits a normal distribution the following equation can be used to evaluate the number of samples (n) required (Walpole, 1982):

$$n = (Z_{\alpha/2}\sigma / e)^2$$

where Z = the two tailed value of the standardised normal deviate associated with the desired level of confidence.

σ= the preliminary estimate of the standard deviation.

e = the acceptable error (half the acceptable confidence interval).

An example would be for 80% confidence levels (considered at this stage to be the minimum acceptable level), Z=1.26 and the error value (*e*) would be 10% of the determined mean for the sample set.

The error estimate associated with the (preliminary) sample set for each confidence level is largely determined by the number of samples in the set and the observed standard deviation (Walpole, 1982).

$$Z_{\alpha/2}\left(\sigma / \sqrt{n}\right)$$

The following examples will more clearly indicate the concepts.

Table 19 shows two South African opencast mines (with areas of approximately 5000 and 7000 ha) tested using this methodology. The reported values are based on the assessment of several of the ABA parameters.

Table 19. Confidence levels and required number of samples.

Confidence Level *%*	**Mine 1** *N*	**Mine 2** *N*
90	374	443
85	146	173
80	61	72

Table 20 shows the increase in uncertainty at mine 1 as the required confidence level is increased. The parameter selected for illustration is natural or initial pH, which in undisturbed strata exhibits a near normal distribution.

Table 20. Potential error estimate for used number of samples, as required confidence increases.

Mine 1- Initial pH	
Samples	210
Mean	8.29
Std Deviation	1.353
Confidence 99	0.24
Confidence 95	0.18
Confidence 90	0.15
Confidence 85	0.13
Confidence 80	0.12
Confidence 75	0.11
Confidence 70	0.10
Confidence 65	0.09
Confidence 60	0.08
Confidence 55	0.07
Confidence 50	0.06

The figure below visually displays this data

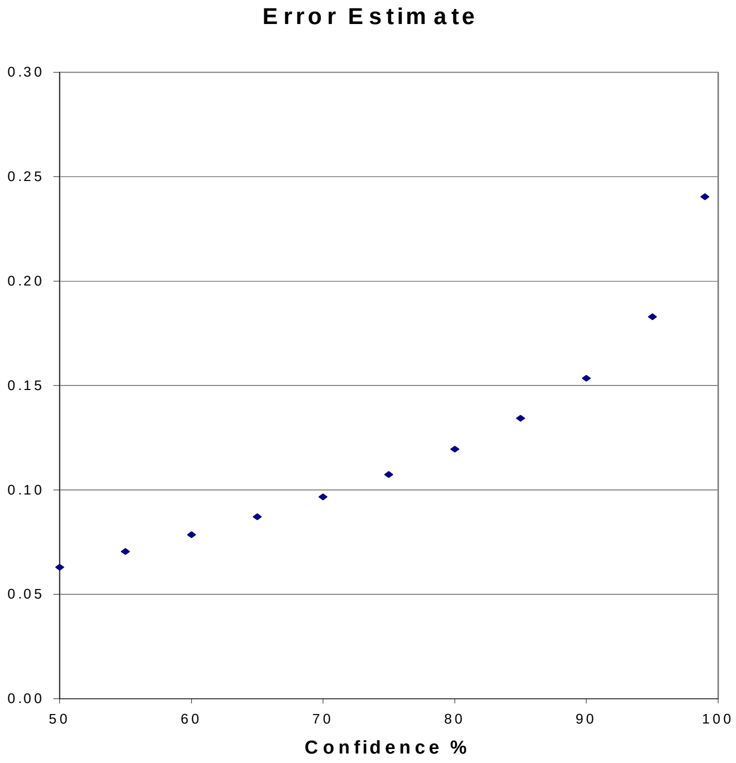


Figure 82. Increase in error with increasing desired confidence level, based on current data set.

It is important to reiterate that these equations are only valid for normal distributions. However, if data can be transformed the equations are still valid, provided the transformation is taken into account for the error estimate (van Zyl, Personal Communication, 2000) An example of this is shown for acid potential at mine site 2 below.

The table and figures below describe the estimated sample size needed based on the available data set on the Acid Potential as obtained from ABA.

Table 21. Required number of samples for Mine1, based on required confidence.

Confidence Level	No of Samples
99	980
95	568
90	402
85	332
80	246
75	213
70	160
65	133
60	107
55	84
50	68

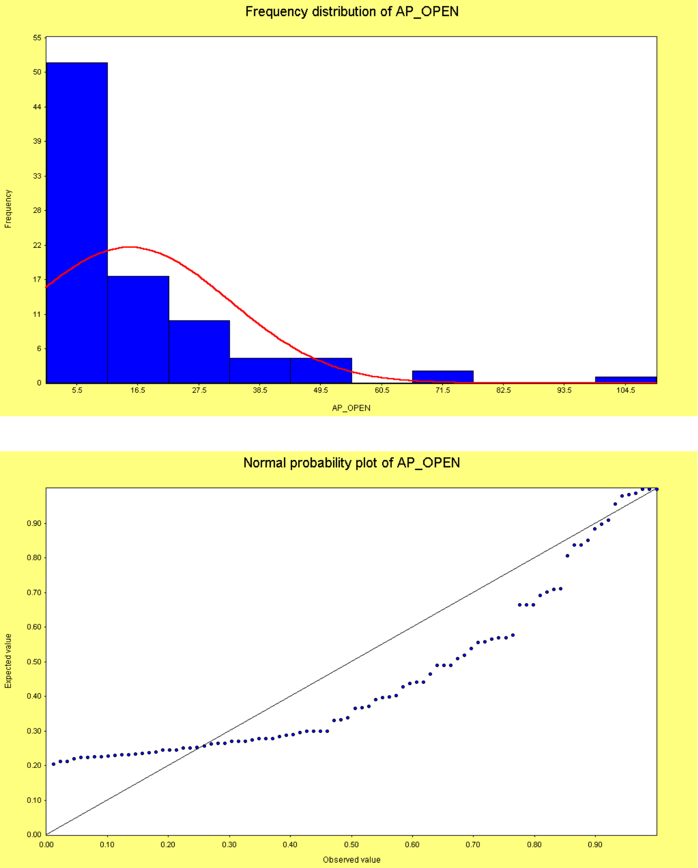


Figure 83. Distribution of AP values and normal probability plot of raw AP data.

It is evident from the preceding figure that the AP data does not represent a normally distributed population. Several parameters in nature follow a log normal distribution and this has also been shown for the sulphide distribution at coal mine sites (Morin and Hutt, 1997).

Log transforming the data yields the following results and distribution. Note that for the estimate of sample adequacy for example 80%, a tenth of the determined mean of the transformed data is again used as acceptable error.

Confidence Level	No of Samples
99	295
95	171
90	121
85	100
80	74
75	64
70	48
65	40
60	32
55	25
50	21

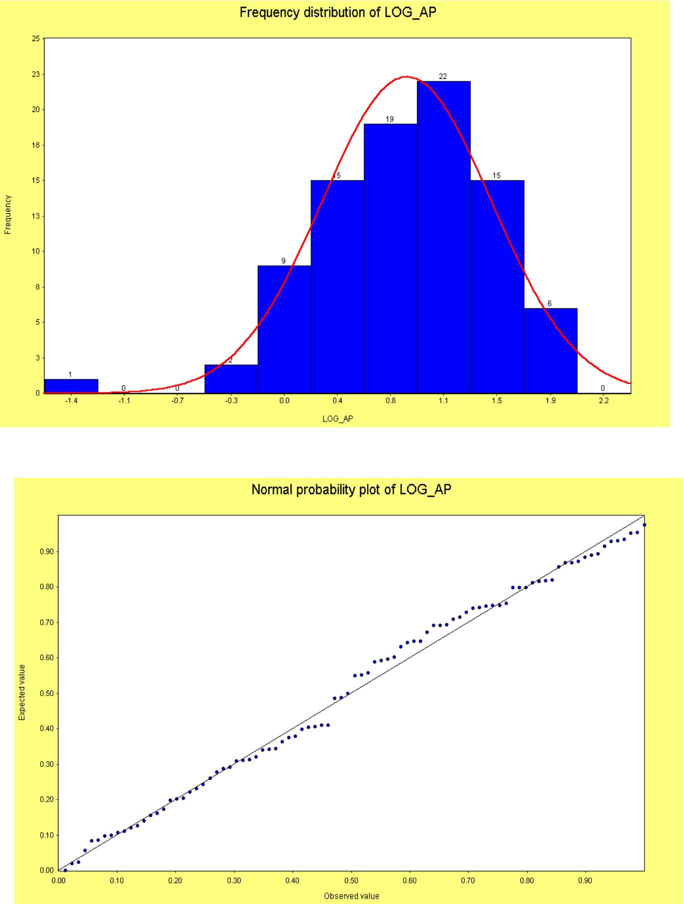


Figure 84. Distribution of values and Normal probability plot of log transformed AP data.

From the above example, it can be seen that the sample size estimate decreases (using 80% confidence level) from 246 to 74 using the transformed data.

It is **suggested that these statistical equations be used to determine sample size adequacy**. Once there is a large enough, reliable South African database for ABA, areal/mass determinations can be made to assist in determining sample size at the outset of a project. Until such a time, stepwise sampling should be done and the sample sets evaluated using these equations. Some research into areal determination of e.g. AP is proposed to find an easy to apply statistical method to infer relationships of sulphide occurrence.

For **existing spoils the situation is more complex**. The occurrence of hotspots has been documented by several authors (e.g. Scharer *et al.* (2000), Hodgson and Krantz (1995), Rose and Cravotta (1998) etc.). Any sampling program to determine the characteristics of the spoil and make predictions as to its behaviour will have to have a high probability of locating the hotspots. Use was made of the public domain software DQO-Pro (Keith *et al.,* 2000) developed for the U.S. EPA. As part of this easy-to-use program, a sub-routine called "HotSpot-Calc" was used to statistically determine the number of samples that would be required to find these hotspots. Using the assumption, based on the evidence gathered from the field work in this project, that these hotspots are between 10 m and 20 m in extent and that they occur as circular features (the most simple case requiring the least number of samples) the sample size and grid spacing for sampling can be determined. If the **confidence required is 80%** then the **number of samples required would be in the order of 7- 25 samples per hectare in spoils themselves**.

7.1.1 CONCLUSIONS

The advantages of high density data modelling for predicting acid drainage from mine waste rock (Scott and Eastwood, 1998) are that it:

- is less sensitive to inaccuracies in interpolation parameters (weighting, search distance and orientation, interpolation distance and degree of smoothing).
- shortens the data projection distance.
- reduces the amount of smoothing possible.
- is more appropriate to the use of smaller block sizes, if that is required.
- reduces the influence of anomalous data.

The linking of geology and Acid-Base Accounting into the waste block model has the following advantages:

- generating cost efficiencies.
- facilitating the calculation of total volumes of problematic waste at an early stage of the mining project.
- reliably identifying the spatial and temporal distribution of waste rock types.
- more accurately predicting the mine waste schedule and timing of problematic waste for better mine planning.

To summarise the findings/recommendations on sampling methods:

- Representivety is very important for the rest of the process.

- Core and random can yield good results.
- Core allows for lithological comparisons.
- Sample size can be estimated from tonnage.
- Sample size can also be based on visual inspection of plots and statistical methods.
- When non-acidity is predicted a higher degree of confidence is required in the data .
- More samples should lead to greater confidence in the data.

7.2 WATER SAMPLING AND *IN SITU* MULTI-PARAMETER PROFILES

Water sampling is the most obvious field method to be included. Ideally long-term monitoring data should be available. This **provides an indication of the system's current behaviour** and can provide **a verification of rates predicted using other methods**. It can also provide an **early warning system** with slight drops in pH indicative of the onset of acidification. Investigations in other countries (e.g. Brady *et al.,* 1998) showed that extrapolation to adjacent sites is possible if the mining method, disposal methods and lithology are similar. Brady (2000) states the case for using such data as follows: "Groundwater chemistry from previously mined areas, when available and used properly, is the **best prediction tool in the tool kit**."

Sampling localities include boreholes, pits, discharge points and surface water. This water sampling is useful since it can be used to:

- give an indication of current acidification,
- provide early warning systems and
- make comparisons with ABA results.

Recommended methods for sampling are contained in several documents such Weaver (1992), Hodgson (1998) (DWA&F Waste Management series) and Karkins (1996). Plumb (1999) details specific requirements for mine contaminant monitoring.

Depth profiling is a particularly useful tool to assist in understanding the system interactions and controls on the water quality. Typically this will entail the measurement of several parameters with depth in a borehole or other water body such as refilling pit. The parameters measured generally included pH, EC, temperature, dissolved oxygen and redox potential. Using all the parameters the hydrochemical description of the system can be improved and correlation with features such as coal seams, the influence of refilling pits etc. can be evaluated. The dissolved oxygen, redox and temperature values can also provide useful information regarding the pyrite oxidation reactions occurring in the immediate environment of the profile.

Profiling is therefore useful to:

- give variation with depth,
- identify stratification,
- observe geothermal influences,
- compare to related features spatially and with depth and
- understand processes occurring.

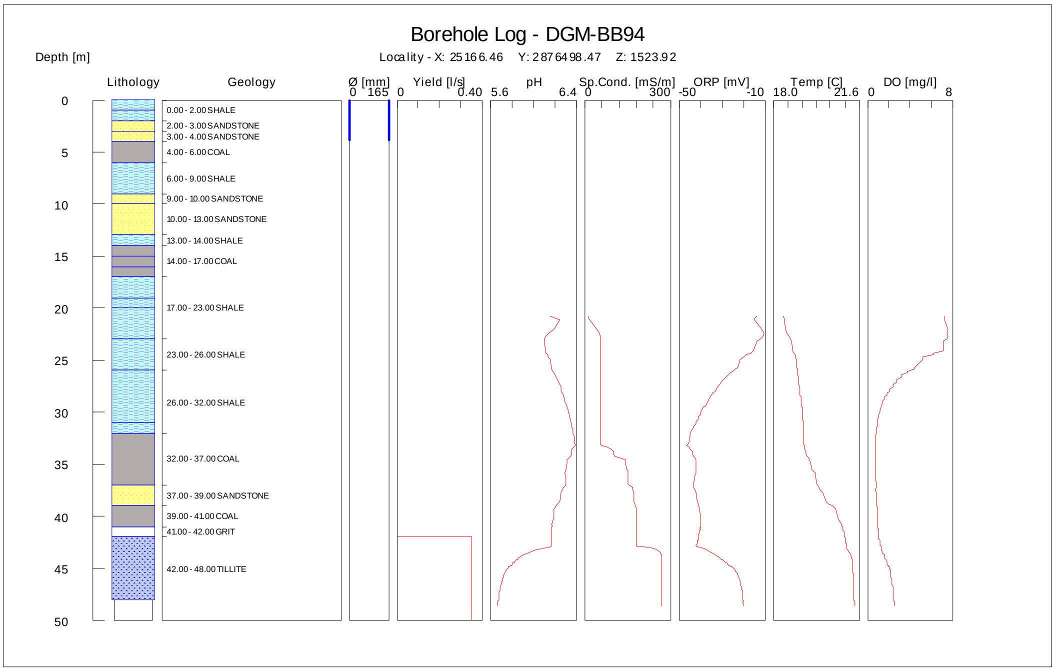


Figure 85. Example of a depth profile and comparison to geology and water strike.

7.3 TEST PITS

An excavator was used to dig the inspection pits to depths in excess of 3 m. The aim was to evaluate the condition of the spoils at different localities at first hand and correlate this information with the hydrochemical logs from below the water table in the pits.

Data collected in each pit included:

- Paste pH-values of the spoil with depth. In most instances, samples were taken just below the topsoil, then at around 1 m depth and at the bottom of the pit, as well as at any horizon where a variation in the spoils was visible.
- The temperature was measured at various depths to give a temperature profile of each hole with depth.
- Samples of each different feature were taken. These were put in airtight plastic bags and stored, so that at any time in the future, tests can be done on these samples.

Figure 86. Excavator and removed spoils in an inspection pit .

- Visual inspection of the exposed sides was done to note any salient features (Figure 86).
- The depth of the topsoil was measured or averaged where a variation existed over the extent of the dug pit.
- The localities of the pits were obtained with a GPS and the relative age of the spoil with respect to mining were noted.

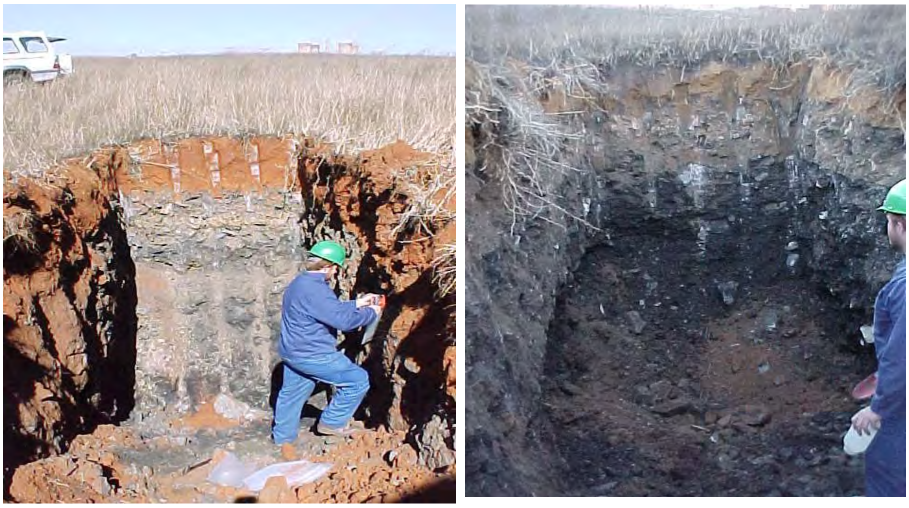


Figure 87. Two profiles - a non-acidic pit on the left and an acidic pit on the right.

The spoils contain various types of material. A proportion of the material has burnt and portions of the dumps are still burning. Along certain sections, coal slimes have often been interdisposed with spoils.

Figure 88. Photographs that show the heterogeneity of the spoil.

It is almost **impossible to distinguish visually between acid spoils and alkaline spoils**, except that weathering may be more conspicuous at acid sites. Vegetation grows prolifically across rehabilitated acid sites, hiding any evidence of the acidity below.

Figure 89. Two examples, showing non-acidic spoils on the left and acidic spoils on the right. Note the thick soil cover at the acidic site.

Figure 90. Surface rehabilitation at the acidic sites.

From observations in the dug pits, it is known that:

- The **hydraulic characteristics of dumps vary greatly**. Areas exist from where salts will mobilise and others where no mobilisation will occur due to moisture retention and evaporative properties of the material.
- The **depth of the topsoil covering varies** greatly.
- Evidence from most of the dug holes suggested that there was **enough water contained in the fine material** in the spoils to support the initiation of acid generation. Once the process is initiated it becomes a self-feeding and accelerating processes which is difficult to curb.
- pH-levels are generally at the buffering level for calcium/magnesium carbonate or below in a few instances. This will be exposed as the rock disintegrates over time. The latter is a very slow process, which could span centuries. It is important to note that only the outer edges of the spoil particles and rock in the unsaturated zone partake in the current chemical reactions. Furthermore, leachate from the upper spoil will become acid before the spoil in the saturated zone below acidifies. The saturated spoil will then progressively acidify by receiving continuous acid seepage from above. The pH-profiles of the spoil water, as discussed under the previous heading, confirm the above conclusions.
- The **depth of soil cover has no apparent impact on the spoil water chemistry**. Oxygen and moisture penetrate into the system, regardless of the thickness of the soil cover.

- Temperatures in the dug pits can be very low at surface, due to the average winter temperature during June. A rapid increase in the spoil temperature with depth is present in most pits and at 3 m, temperatures around 20°C have been recorded. In several of the dug pits, elevated temperatures ranging from 25 - 50°C have been recorded. It is noteworthy that bacteria oxidation of sulphur functions optimally at 30°C. At temperatures significantly higher, chemical oxidation rather than bacterial oxidation becomes the dominant type.
- The conclusion is that acidification of spoils above the water table is relatively rapid because of the skin effect whereby only the outside of spoil particles and rock is oxidised. The drop to a pH of around 6,5 occurs within a year or two after mining. Buffering at this level continues until the base potential on the outside of the particles is exhausted. This may take anything from a few years to decades and cannot be predicted with more accuracy on a cost-effective basis, due to heterogeneity in the spoil. In the long term acidification of most of the spoil is imminent.
- There is not enough evidence to suggest that the spoils become more acidic with age.
- In the acidic holes a very prominent feature was the presence of far deeper roots from the vegetation (grass). It is difficult to predict if the deeper occurrence of these roots causes or is a result of the increased weathering. The latter is considered more likely.
- There are **localised areas of acidification**. These are due to specific optimal microclimates; it seems that mineralogical composition plays a more important role than age of the spoils.

The results from the field observations are presented in Table 22.

Table 22. Results from inspecting pits into the spoil.

Sample No.	Depth (m)	Paste pH	Depth (m)	Degree C	Weathering	Relative age	Depth of topsoil (m)
O1-1	2.50	6.45	0.60	9.7	No	Young	0.55
			2.60	18.3	No		
O2-1	1.00	6.15	1.00	11.2	No		0.90
O2-2	2.00	6.09	2.00	15.1	No		
O2-3	3.00	6.40	3.00	18.3	No		
O3-1	1.10	6.37	0.50	12.7	No		0.75
O3-2	3.10	6.56	1.00	14.8	No		
			3.10	23.8	No		
O4-1	1.50	6.15	0.60	10.2	No		0.55
O4-2	2.80	6.72	1.80	13.8	No		
O4-3	2.90	6.93	2.90	19.8	No		
O5-1	1.50	5.97	0.50	7.8	No		0.70
O5-2	3.00	6.18	0.90	10.7	No		
			3.10	17.3	No		
O6-1	1.50	6.45	0.40	9.0	No		0.45
O6-2	3.00	6.90	1.50	11.9	No		
			3.10	18.2	No		
O7-1	0.70	5.92	0.50	19.7	No		0.65
O7-2	3.00	6.68	0.70	26.9	No		
			2.00	39.2	No		
			3.00	55.4	No		
O8-1	1.60	6.00	1.00	14.3	No		1.50
			3.10	26.1	No	↓	
O9-1	0.50	3.28	0.40	12.5	Yes	Old	0.35
O9-2	1.50	5.48	0.80	18.0	No		
O9-3	3.00	5.04	1.00	20.7	No		
			3.00	26.8	No		
Z1-1	0.35	6.23	0.25	7.6	No	Old	0.30
Z1-2	3.00	6.25	1.40	10.4	No	↑	
Z2-1	0.60	6.19	0.20	9.8	No		0.30
Z2-2	1.20	6.33	1.00	10.7	No		
Z2-3	3.00	6.52	1.50	12.6	No		
			2.90	18.7	No		
Z3-1	1.50	6.22	0.60	11.4	No		1.20
Z3-2	2.80	6.34	1.50	13.6	No		
			2.80	18.3			
Z4-1	0.50	3.40	0.60	9.1	Yes		0.30
Z4-2	1.50	5.74	2.60	10.4	No		
Z5-1	0.50	4.44	0.20	10.1	No		0.25
Z5-2	1.50	3.19	1.50	13.7	No		
Z5-3	2.90	3.42	2.90	19.2	No		
Z6-1	1.30	6.77	0.70	7.6	No		0.80
Z6-2	2.90	6.52	1.20	11.8	No		
			3.00	16.5	No		
Z7-1	2.50	6.64	0.30	9.3	No	Young	0.40
			0.60	11.2	No		
			2.80	16.1	No		

7.4 OTHER ON-SITE MEASUREMENTS

Where detailed kinetic and reactive transport modelling is required with a high degree of confidence, some additional parameters also need monitoring and measuring in the field. Bennet (1998) lists the following key parameters for monitoring at AMD sites. He also states that techniques for tailings are well-established but rock dumps, such as spoils, represent more of a problem due to heterogeneity and unsaturated conditions.

The following table outlines the key techniques and their usefulness for understanding the site:

	Key parameter		
Monitoring technique	**Pollutant Production Rate**	**Drainage Flow rate**	**Pollutant Concentration**
O_2 Concentration Profile	X		
Temperature profile	X		
Lysimeters	X	X	X
Drainage monitoring	X	X	X
Piezometers in waste	X	X	X

As is discussed in Section 8.1.1 without these parameters accurate prediction of mine drainage evolution over extended periods into the future is fraught with uncertainty.

7.5 CONCLUSIONS FOR FIELD METHODS

Field methods are vital to understanding acid-generation processes. Their inclusion in the ABATE process is based on the following facts:

- **Most reliable measurements**.
- **Best Kinetic reactor** there is. Morin and Hutt (1997) state, “ Undoubtedly the most valuable and representative kinetic test that can be operated at a minesite is the full-scale operation of minesite components ”.
- **Vital input to geochemical models.**
- Determines the **current situation**.
- Provides **understanding of controls on chemistry**.
- Allows **comparison to ABA**, **kinetic tests and modelling.**
- **Early warning** system.
- Decision on appropriate control measures.

8 MODELLING

As part of the development of the ABATE methods, a short review of geochemical modelling is included. Although this does not pertain directly to ABA, geochemical modelling is increasingly seen as the method of choice for the prediction of long-term drainage from mines.

The section which follows, highlights the advantages, requirements and limitations for geochemical modelling. The question is often posed: "Which is the best modelling tool/package for AMD prediction?" The answer to this is none; each modelling code or method has particular advantages and disadvantages as far as availability, cost, ease of use and inherent assumptions and weaknesses. The only answer is that **the appropriate code or method must be used based on the type of answer required**. By highlighting the usefulness of these models and their basic data requirements, along with the uncertainties involved in geochemical models, the user/researcher will, hopefully, be in a position to select an appropriate modelling method and geochemical modelling code. A full evaluation of several commonly used models for mining application is available at the Internet Service Centre for Mine Related Water Models (http://www.cosmiclink.co.za/iscp/), developed as a result of a WRC-sponsored project. Since a full evaluation of several of the commonly used codes is available here, it was felt that repeating this exercise would be redundant; instead this section provides guidance in terms of the uncertainties, requirements and output from geochemical models.

Computer models are another approach to the prediction of acid generation. Most of these models incorporate a number of chemical and physical parameters to describe the chemical reactions of acid generation, microbial catalysis and leaching (transport) of the weathering products (Jaynes (1991), Scharer *et al.* (1991) and Hunter, (1997a)).

A crucial question is: why should one need to model a system? The following are some reasons:

- Characterise and interpret current contaminant load.
- Environmental assessment (source and receiving environment).
- Predict future contaminant concentrations and loads.
- Assess future treatment needs.
- Compare management and decommissioning options.

To support this, Lichtner (1996) states: "Computer models can provide, if not a direct quantitative description, at least a far better qualitative understanding of the geochemical and physical processes under investigation than might otherwise be possible."

Therefore typical objectives of modelling acid rock drainage include:

- Prediction of soluble and mobile metal species.
- Prediction of maximum metal concentrations.

- Prediction of maximum metal loadings.
- Prediction of the duration of dissolved metal production.
- Prediction of concentrations and loadings versus time.
- Evaluation of decommissioning options using all of the above information (Perkins *et al.*, 1997).

According to the level of detail required, AMD prediction can entail a range of tasks (Li, 2000), listed below in increasing degree of complexity:

1. Predicting whether a waste rock will ever become acid-generating (yes/no).
2. Predicting how soon a potentially acid-generating rock will become acidic (lag time).
3. Predicting the long term trend in acidity loading from a waste rock pile, and
4. Predicting temporal variations in contaminant loading and drainage water quality over time.

The first two can usually be accomplished by laboratory tests, supplemented when necessary by weathering tests.

Task 3 involves collection of input data for the model of choice, including full characterisation of waste rock pile with respect to its chemical and physical properties, meteorological information, etc. The second part is running the model, which can consist of kinetic/equilibrium geochemical and a transport part. Where the reaction products are completely washed out by annual rainfall, this can be accomplished. Where net accumulation within the waste piles cannot be neglected, information on heterogeneity is necessary to predict loading from the pile. At the present time and with currently available models, prediction of long-term loadings is possible, but *uncertainty* associated with prediction results is generally *high* (Li, 2000).

Task 4 is generally impossible to accomplish at this time.

The major geochemical processes in waste rock piles are:

1. Oxidation of sulphides, releasing acid, major and trace metals and sulphate,
2. Precipitation of oxyhydroxides, releasing acid and consuming the more insoluble major and trace metals;
3. Dissolution/precipitation of sulphate minerals mediating the dissolved metal concentrations as well as TDS; and
4. Dissolution of oxyhydroxides, carbonates and silicates, thereby consuming acid. Co-precipitation may also provide a major control on trace element concentrations.

All these processes need accurate data and detailed simulation for a model to begin to approximate the field situation.

There are seven basic model classes; these have been discussed in detail in section 3.3:

1. Aqueous equilibrium models are static models used to identify the soluble and mobile metal species, their maximum metal concentrations and their relation to the minerals in mine waste rock.
2. Mass transfer models are dynamic reaction path models for closed systems that address maximum metal concentrations and their evolution with time.
3. Mass transfer-flow models are dynamic reaction path models in an open system that addresses the prediction of concentration, load and distance travelled over time.
4. Empirical/engineering models are best at history matching and have limited predictive capability. They are more appropriate for examining decommissioning options in acid drainage studies.

Input parameters required by these four classes of models are:

CLIMATIC DATA.
PHYSICAL DATA (e.g. dimensions, porosity, moisture content, particle sizes, preliminary physical modelling).
HYDROLOGICAL DATA (infiltration rates, etc.).
MINERALOGICAL DATA (field descriptions, interpretation of ABA and preparation of mineralogical inputs).
WATER QUALITY DATA (monitoring data).
TRANSPORT-RELATED PARAMETERS
FIELD DATA: Water chemistry, Mineralogy, Surface Area, Temperature, Oxygen, Water Balance, Pile Structure,
LABORATORY DATA: Column Test, Humidity Cells,
DATABASE: Kinetic, Equilibrium Thermodynamic.
Mass transfer models, which address geochemistry in more detail, require more geochemical data and have the best potential for predictable capability in the long term.

The most important however, is the validity of the conceptual model, i.e. does the system behave as suggested by the model and are the simplifying assumptions valid and realistic?

Geochemical modelling can thus be a very useful tool in the ABATE process. The type and intensity of modelling should be determined by the objectives and the field situation. Above all, the appropriate model must be used for the objectives and where long-term predictions of loadings are made, these models should have some field verification to show validity.

8.1.1 UNCERTAINTY IN GEOCHEMICAL MODELLING

Any model is a simplified version of reality based on various assumptions. Apart from the assumptions made to construct the conceptual model, there is a major uncertainty with several input parameters in addition to those highlighted by Li (2000) as described above (Boer, 2000):

- Mineralogy.
- Sulphide minerals (% fines).
- Buffering minerals (carbonates and aluminosilicates).
- Secondary minerals (stored acidity, sorption).
- Proportion of Easily Leachable (pre-oxidised) metals.
- Flows and Quality (infiltration, porewater, seepage).
- Porosity and Moisture Content.
- Kinetics of sulphide oxidation.
- Oxygen Transport (convection, diffusion).

Due to the various assumptions needed for these models, a geochemical model provides not only results but also uncertainty regarding the accuracy of the results. Uncertainty is an integral part of modelling that deserves as much attention as any other aspect of a study (Bethke, 1996). The degree of confidence with which modelling results are used is of vital importance to all the interested parties in mine drainage prediction in South Africa, since the weight given to these results is crucial in determining what the long-term management strategies need to be. To commit large amounts of resources to a particular strategy based on a modelling result in which there is potentially an accumulation of uncertainty in several of the components could be disastrous.

To evaluate the sources of uncertainty several aspects need to be considered. Bethke (1996) suggests that the following questions be asked when geochemical modelling is undertaken:

1. Is the chemical analysis used accurate (and representative) enough to support the modelling?
2. Does the thermodynamic dataset contain all the species and minerals likely to be important in the study?
3. Are the equilibrium constants for the important reactions in the thermodynamic database sufficiently accurate?
4. Do the kinetic rate constants and laws apply well to the system being studied?
5. Is the assumed nature of equilibrium appropriate?
6. Most importantly, is the conceptual model correct?

In addition several other questions need to be asked to evaluate the confidence of a geochemical model in opencast situations in South Africa:

7. Are the flow- and transport parameters of the system well-defined?
8. Is the mineralogical data representative?
9. Have specific on-site conditions (temperature, Redox conditions, dissolved oxygen etc.) been accurately measured?

Another vital question would be:

10. Is the geochemical modelling code appropriate to the system modelled?

Several of these aspects will be dealt with briefly below. It is emphasised that although these uncertainties are dealt with in this section, they apply to the interpretation and prediction of mine drainage chemistry, using most of the currently used methods. The effect of several of the parameters below has been illustrated before by e.g. Scharer *et al.* (1993).

1. Accurate and complete analyses

The need for accurate and sufficient chemical analyses to adequately describe a system is self-evident. Any uncertainty in the sampling and preservation of analysis of samples used to describe a system will be propagated throughout the rest of the modelling process. A time series of analyses for the system should also be used to ascertain the system's response to variation in seasonal climatic conditions. Samples should also be obtained for all of the most important points to minimise uncertainty in interpretation and further extrapolation with time. Initial and boundary conditions are often unknown and unknowable (Lichtner, 1996) and this can lead to inaccuracies throughout the modelling process.

2. Accurate and complete thermodynamic data

Accurate thermodynamic data for **all** the species/minerals likely to be important in the system under consideration are required. Several of the most commonly used geochemical models have attached thermodynamic databases. Inspection of these databases shows that differences exist between thermodynamic values given for specific minerals/species. While the uncertainties these values can bring are probably minor in comparison to those introduced by other sources, such as field measurements (or more often lack thereof), and the assertion that a model's results are definitive should be evaluated with this in mind.

Several commonly used models (e.g. WATAIL (Scharer *et al.,* 1993), Salmine (James, 1996), etc.) utilise only a subset of the species/minerals to obtain results. Thus any system where species are present that are not included in the dataset will be modelled with decreased confidence by these models. In most cases such models are written with this in mind and can be used fruitfully to illustrate the most important considerations in a system or the effect of a change in conditions.

Other models such as the widely used HYDROGEOBIOCHEM (Yeh *et al.,* 1998) have no associated thermodynamic database, for the sake of versatility and being able to model a range of problems and thus all thermodynamic data and reaction constraints have to be defined by the modeller. This makes models such as these very powerful and able to include all the required parameters customised to the problem at hand, which leads to optimisation of the computing code. Any modeller using such codes needs to have a very good understanding of thermodynamics and the range of reactions possible in the system modelled since each assigned value and reaction constraint has to be justified. Despite this, authors such as Suarez and Simunek (1996) feel that the model, HYDROGEOCHEM (Yeh and Tripathi, 1991, superseded by Yeh *et al.*, 1998) is one of the most important in terms of its potential to handle a wide range of problems.

3. Accurate equilibrium constants

In most systems several of the reactive species are regarded as reacting according to equilibrium considerations. The collection of thermodynamic data is subject to error in experiment, chemical analysis and interpretation of experimental results. Error margins are seldom reported and never seem to appear in data compilations (Bethke, 1996).

Mineral solubilities are often determined at high temperatures where equilibrium is reached more rapidly in many cases. The results are then extrapolated to conditions typically found in mine sites and although care is taken and well-defined thermodynamic laws have been used to minimise errors, this can be a source of uncertainty.

4. Uncertainties in kinetic rate constants and laws.

Using kinetic rate laws to describe a system adds an element of realism to a geochemical model but can be a source of substantial error (Bethke, 1996). Much of the difficulty arises because a measured rate reflects the dominant reaction mechanism in the experiment from which it is obtained and not necessarily that which occurs in the natural system being modelled. Thus **several valid rate laws can describe the reaction of single minerals** (Brady and Walther, 1985). There are often large discrepancies between those physical and chemical properties measured in the field and those deduced from laboratory experiments (Oelkers, 1996). Brantley (1992) reports that, for example, albite weathers up to four orders of magnitude slower in the field than in the laboratory. Some of the discrepancy is attributed to difficulties in determining the reactive mineral surface area, which will be discussed in more detail later on.

Research on geochemical kinetics has revealed a wealth of possible mechanisms and rates by which minerals, organisms and aqueous species may interact (Steefel and MacQuarrie, 1996). Thus, in the best-case situation, even by adopting the best-constrained independent input parameters, one must accept *at least one order of magnitude uncertainties in each parameter*. It follows that the results of reactive transport calculations performed using independently constrained parameters, will also most likely have uncertainties of several orders of magnitude, at best (Oelkers, 1996).

Reactions can either be transport or surface controlled (Lasaga, 1984) depending on the reaction rate's dependence on the speed at which the products are removed from the mineral or the rate at which chemical bonds are formed or broken. Surface controlled reactions are usually represented in a form derived from transition state theory (Lasaga, 1981). According to this theory mineral dissolution results from the creation of an unstable activated complex of higher energy, which subsequently decays. The rate of decay defines the rate of dissolution.

In general this rate law is represented as follows:

$K=Ae^{-Ea/RTk}$

where

A = Arrenhius pre-exponential factor

Ea = Arrenhius activation energy (J/mol)

R= universal gas constant

T= temperature in Kelvin

This is often modified to show pH-dependence (Scharer *et al.*, 2000) or oxygen catalysing effect in sulphide (Scharer *et al.,* 1996). There are some points to be highlighted for the use of these equations; the equation determines that the overall reaction proceeds on a molecular scale as elementary reaction(s). Generally the exact elementary reactions that occur as a mineral dissolves and precipitates are not unequivocally known (Bethke, 1996). The rate law might also not be linear and allowance can be made for this in equations utilising the transition theory approach. Furthermore kinetic expressions are lacking for realistic representation of most chemical processes under field conditions (Suarez and Simunek, 1996).

5. Reactive surface area

One of the most difficult aspects to characterise accurately is the reactive surface area for minerals in the system. Two of the most important factors leading to uncertainties are:

- Surface roughness
- Flow channelling

The surface roughness is the ratio of true reactive surface to the equivalent geometric surface area of a hypothetical smooth surface. Often the true reactive surface is not measured but estimated from other data such as field data, with roughness often estimated from empirical values. The effect of roughness in increasing the true reactive surface is very important, since this needs to be accounted for in geochemical models utilising the reactive surface area in describing rate laws. Several models use particle size equations and distributions to yield the reactive surface area (for example the Pareto approximation utilised by WATAIL (Scharer *et al.*, 1994) and ACIDROCK

(Scharer, 1998)). This type of approach is very useful but the effect of surface roughness may not be fully included, leading to some degree of uncertainty.

The particle-size distribution and calculation of reactive surface area is a very important factor if one considers the extreme heterogeneity found from digging test pits in the spoils at different opencast collieries. This heterogeneity cannot be incorporated into any model and is an uncertainty that can only be minimised by taking sufficient samples so as to obtain a representative distribution for the spoils under consideration.

The channelling of reactive fluid flow is probably a more important consideration in reactive transport modelling. Oelkers (1996) gives an illustration of a cubic metre of sand with a 0.2 mm diameter; a roughness which has a reactive surface of 300 000m^3 while one side of this block of the same material will have a reactive surface area of 2m^3. Thus channelling is a very important factor which leads to uncertainty. This phenomenon will be expanded on in the section which follows.

More uncertainties exist regarding the amount of surface available in the field, since portions of the mineral surface can be shielded from the reacting water. This could occur through coatings as illustrated by Scharer *et al*. (2000) in an experiment on large-sized limestone used as neutralising material. Contact with other grains, adsorbed organic matter and other features may also inhibit a portion of the mineral surface.

In the vadose zone, only a small portion of the mineral may be in contact with water intermittently while where any fracture flow/channelling occurs many mineral surfaces will have little to no influence on the observed drainage chemistry.

6. Flow and transport-related values

For accurate predictions of drainage chemistry, the flow system needs to be adequately described (Hawkins, 1998). The flow paths, rate of transport and variation under conditions found on site are vital components for characterising discharge chemistries over time. The factors will influence which portions of the system are actively involved in determining the observed and long-term hydrochemical evolution, which portions will play no role, the time that each portion of the system has to react with a specific pore volume and several other vital factors. Unsaturated flows in waste rock are heterogeneous and flow channelling is ubiquitous. The results imply that the transport of solutes from oxidised waste rock to its toe drainage is subject to various controlling mechanisms, including geochemical control and successive pore water dilution control (Li, 2000).

The amount of detailed information required on a site as heterogeneous as opencast spoils to accurately describe the system would be impossible to gather and thus attempts to accurately quantify these flows are fraught with uncertainty. Tompson and Jackson (1996) put it as strongly as this: “From the perspective of contaminant hydrology, the impact of geologic heterogeneity is difficult to consider in practice” and “(Therefore) oversimplified conceptualisations of system behaviour are used”. Thus through no fault of modellers or modelling codes which would need to be too complex to be practical if such heterogeneities were incorporated, oversimplifications usually occur. The codes that can accommodate these features have the problem of not being able to be verified. It is somewhat paradoxical that as more and more sophisticated representations of heterogeneous porous media are developed, it becomes increasingly difficult to compare the resulting calculations with experimental or field observations to validate model predictions. This because of the greater burden placed on the detail of observation required to compare with the model calculations (Lichtner, 1996).

Apart from flow-related phenomena and geochemical reactions taking place along the flow path, various other transport-related features need to be considered. The likelihood of sorption, degree of dispersion and diffusion and relative mobilities of different ions need to be taken into account, again yielding values with variable degrees of confidence. The main limitation of geochemical modelling is that a lot of high quality information on both hydrology and geochemistry of a site is often needed to produce useful and reliable results. With poorer quality data and less information generally available, more assumptions with greater uncertainties are required (Brady *et al.*, 2000).

7. On-site measurements.

Although the need for accurate on-site measurements appears to be self-evident when attempting to make predictions of the development of mine drainage chemistry over a century or more, it is often a component which is neglected and more emphasis is placed on the computational effort required to predict the system. Various sections in this report deal with the importance of the mineralogy in determining the rate and sequence of mineral reaction, for accurate long-term prediction very detailed mineralogical assessment of the system providing representative mineral assemblage for each critical area in the system is required. The importance of oxygen for sulphide oxidation is an important consideration and thus some on-site measurement of this parameter should be made. Several modelling codes model the oxygen ingress and distribution and while this provides an indication of the values, verification of this critical parameter through measurement is vital if any confident predictions are to be made. Often simple equations for these oxygen profiles will suffice if verified on site. More complex models are available but their assumptions, boundary conditions and requirements for frequently measured input data and missing processes do not make their predictions any more reliable (Morin and Hutt, 1997). Another difficulty is that there is no agreement in published literature on whether the rate of sulphide oxidation is independent of, linear to, or some power of oxygen level (Morin and Hutt, 1997). The effect of Pco_2 is discussed in more detail in section 5.4.

Henry (Personal Communication, 2000) states that to get accurate field rates to be used in modelling the following parameters (and their distribution across the site) are required *in situ*:

- Concentrations of gases in the reactor (spoils/tailings).

- Moisture content (In order to model the true rate in these mine waste environments, the rate of sub-aerial pyrite oxidation must be determined as a function of relative humidity and partial pressure of oxygen (Jerz and Rimstidt, 2000).
- Temperature distribution.
- Gas fluxes (to prevent non-unique solutions).

As illustration for a single waste pile in Canada, the following apparatus (apart from the usual monitoring wells) were installed to obtain these values:

- 140 gas probes in 14 locations across the site.
- 20 Neutron probes for moisture content.
- 28 gas flux rings.
- Pressure transducer systems.
- 1 weather station.

Without detail such as this, modelling which includes gas transport will at best be an illustration and identification of the most important processes and strongly reliant on the intuitive conceptual model of the modeller, rather than an accurate portrayal of the system's response.

Other variables that are vital are the accurate determination of recharge rates, the delineation of flow paths and travel times in each portion of the modelled system. Where possible measurements of the hydraulic conductivities, porosity, etc. in each portion of the system should be obtained and if detailed modelling required calibration of flow rate in each critical section. The temperature profile is also important since the reaction kinetics are temperature dependent, as is the catalytic effect of the bacteria. These should therefore be accurately measured to limit the inherent uncertainties in the models.

8.1.1.1 LIMITING UNCERTAINTY

The best method to limit the uncertainties outlined above, is to ensure that the data available for each of the points mentioned above are as accurate as possible.

Once the accuracy has been established, the uncertainty can be limited by doing probabilistic and sensitivity analysis to quantify the uncertainties, so that the uncertainty can be included in the assessment of the situation (Boer, 2000).

- **probabilistic assessment -** to quantify the general **level of uncertainty** regarding climatic, mineralogical, kinetic and transport-related inputs .
- **sensitivity analyses -** designed to examine the **influence of** specific selected **parameters** (e.g. infiltration rate, porosity, moisture content, buffering availability).

It is clear that, for reliable predictions to be made by computer simulations, the uncertainties in the input parameters must be thoroughly investigated and given as intervals rather than as single values, thus producing an interval as the result of the simulation. In addition, the selection of conceptual model may be crucial (Ekberg, 1999).

8.2 THE INFLUENCE OF DIFFERENT VARIABLES ON REACTION SEQUENCE

In an attempt to indicate the influence of the different variables that need to be taken into account when modelling reactive systems, a simple system consisting of a single reactive node/cell will be used. Arbitrary values will be used to illustrate the influence of each variable.

The system under consideration will have the following characteristics:

- Largely inert mass ignored in calculations.
- Pyrite being oxidised to generate acidity.
- A small quantity of carbonates present to react.
- Clay minerals as the additional acid-consuming phases.

For the sake of clarity, only the pH-profile against time is considered.

The base case is illustrated below; all further simulations should be considered relative to this reaction sequence. For the simulations an input water quality containing some dissolved quantities of the common macro elements, some alkalinity and a pH of 7.2 is used. The minerals considered are calcite, pyrite and initially illite as the clay mineral under consideration. The system is also considered to be recharged with clean water, so that over the course of the reaction (arbitrarily 500 years) one renewal volume is added.

Reaction rates are based on those given in Stromberg and Banwart (1994) and Lasaga (1984). An assumed surface area of 1000 cm^2 has been used with the reactive surface area for each mineral relative to the molar fraction, in accordance with arguments presented by Lasaga (1984) and others. For the base case simulation an inert mass of 1 kg is assumed; 20 mmol of pyrite, 20 mmol of calcite and 1 mol of illite are the reactants. The Geochemist's Workbench (Bethke, 1996) was for all simulations.

The values used in these simulations are within the range expected at many South African coal mines. These simulations serve as an illustration of what is likely, should the uncertainty for any key parameter be large.

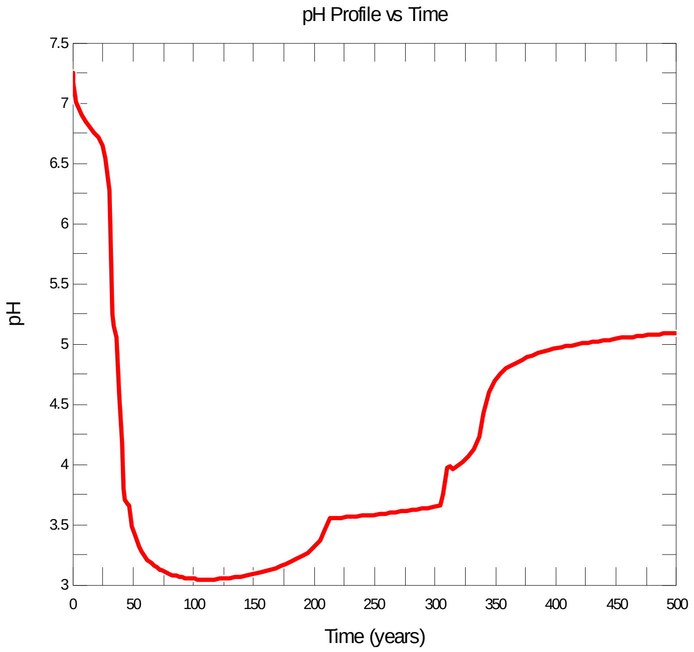


Figure 91. pH-profile vs. time for base case simulation.

The profile above shows the rapid acidification within less than 50 years, followed by a fairly long period of circa pH-3 conditions before the illite can adequately start consuming sufficient acidity to increase the pH again.

8.2.1 REACTIVE SURFACE

The pH-profile obtained from doubling the total reactive surface area is shown in Figure 92. The natural consequence of this is to double the effective reaction rate and consequently the pH-profile shows a similar shape, but it is accelerated so that the acidification and eventual return to higher pH-values occur in a shorter time period.

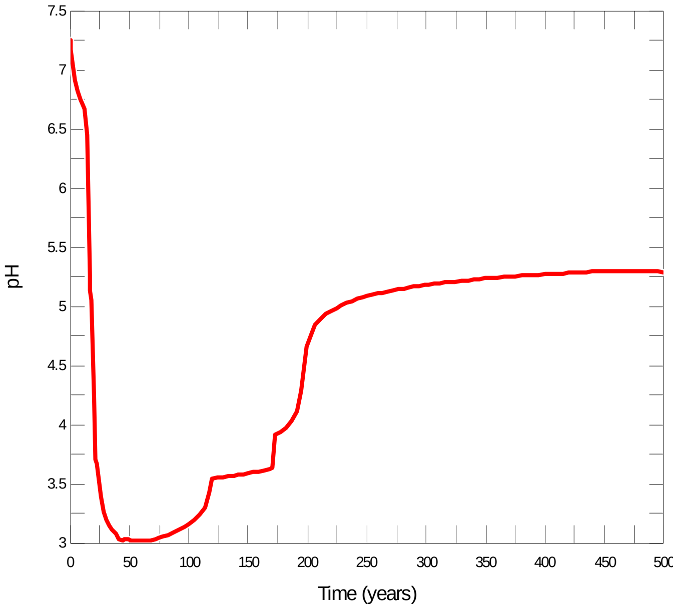


Figure 92. pH-profile vs. time with a doubling of reactive surface area.

8.2.2 MOLAR QUANTITIES

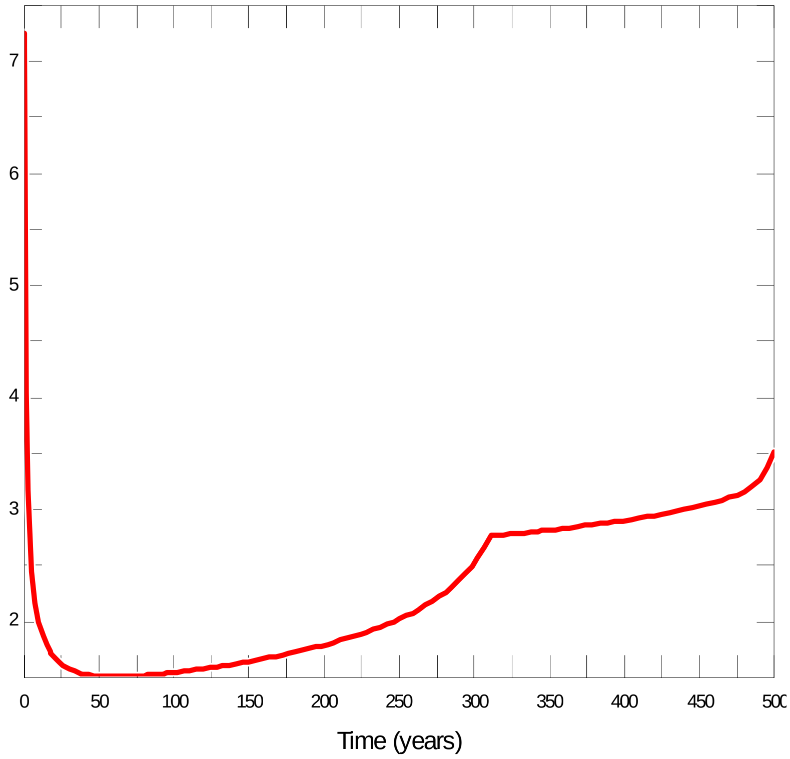


Figure 93. Doubling pyrite quantity (and thus reactive surface).

Doubling the molar amount of pyrite yields a radically different pH-profile, with more rapid acidification, far lower pH-values occurring and much longer highly acidic conditions. It is also clear that in 500 years the pH has not recovered substantially at all. The pH will in time recover but the time required is far longer. A more realistic simulation is shown below (Figure 94) with a 25% increase in pyrite as opposed to the original. This simulation shows the grave risk associated with assuming an incorrect pyrite value throughout an area. The slight increase in pyrite results in a very different profile and far lower pH-values. The determination of molar quantities of all minerals playing a role is therefore evident. The assumptions as far as integrating mineralogical data, often reported in terms of major, minor, dominant, etc. species for use in geochemical models are vital to the eventual output obtained. Incorrect integration/extrapolation of available data can yield variable results, which are vastly different from those in the field.

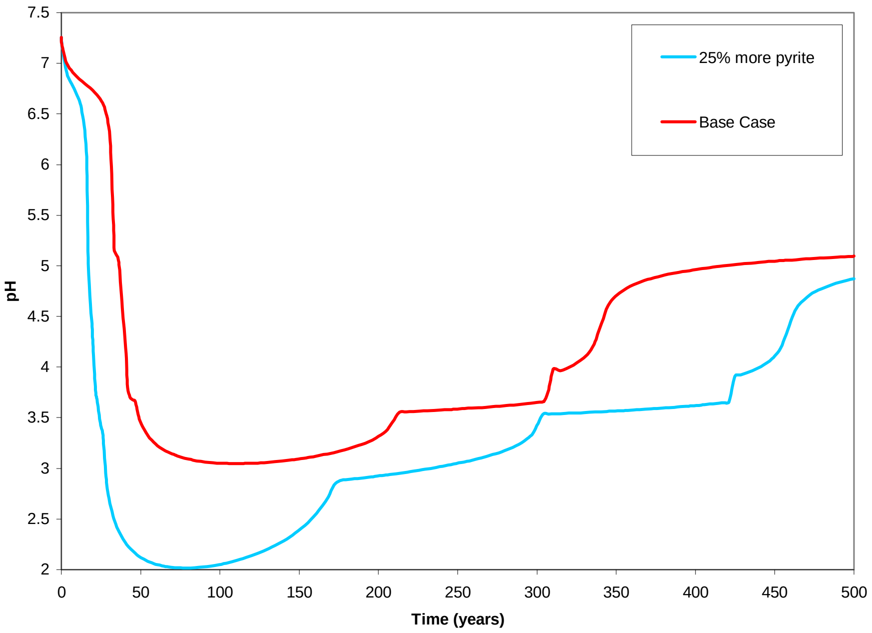


Figure 94. pH-profile with 25% increase in pyrite compared to the base case.

8.2.3 REACTION RATES

The reaction rates used in most geochemical models are based on either laboratory observations or on the assumption that the transition state theory (Lasaga, 1984) is valid. Several authors (Bethke, 1996, etc.) report that there can be several orders of magnitude variation in such reaction rates. This is therefore, despite the best efforts of modellers, often a potential source of uncertainties.

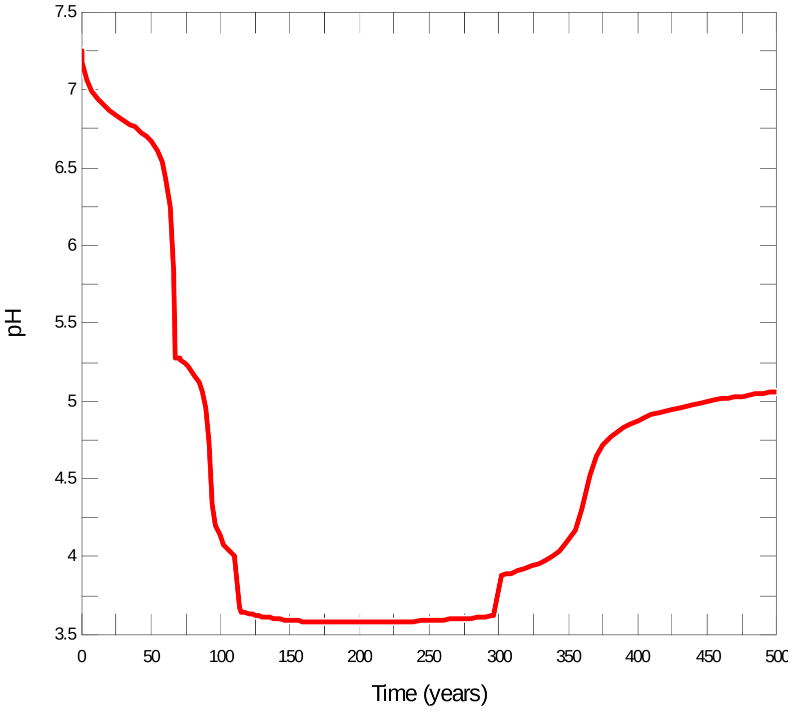


Figure 95. pH-profile with a halving of original pyrite reaction rate.

In the figure above (Figure 95), the dramatic effect of lowering the pyrite rate by half is shown. If one considers that for each mineral in a system the reaction rates can be up to an order of magnitude or more in error when compared to the real-life situation, the implication for long-term predictions are dire.

8.2.4 FLUSHING OF THE SYSTEM

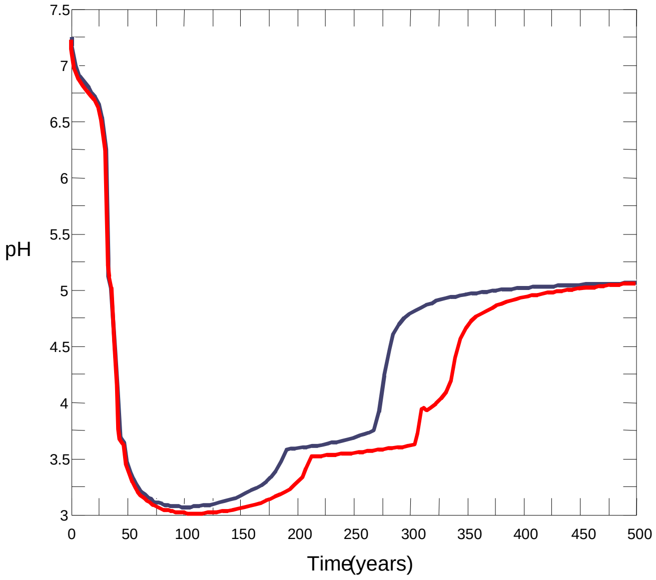


Figure 96. Influence of doubling of flushing rate.

Figure 96 above shows the influence of getting the flow wrong in even the most simple of systems. The flow rate in any system being modelled with reactive transport has at least two major implications, namely the time it takes to flush the system (displace the original fluid out of the system) and the residence time/contact time that the particular water has to interact with the defined mineral assemblage in that portion of the model. The correct determination of the flow rates and flow paths is therefore a vital component in minimising uncertainties in reactive modelling of acid drainage and any model purporting to correctly quantify the drainage chemistry should be able to accurately model the heterogeneous flow obtained in mining environments.

8.2.5 ILLUSTRATION OF KINETIC AND EQUILIBRIUM RESPONSES

The issue of using equilibrium and kinetic approaches to reaction modelling has been discussed previously in this document. The section which follows will illustrate the influence of relative reaction rates on the way a system reacts to the generation of acidity from pyrite oxidation. Use has been made of the software “Geochemist’s Workbench” (Bethke, 1996) for these simulations.

The simulation of the system included the following: input water chemistry typical of rainwater in the Highveld and the following molar percentages

30% Quartz

15% Illite

15% Kaolinite

10% K-feldspar

8% Albite

8% Pyrite

7% Anorthite

2.5% Calcite

2.5% Dolomite

2 % Enstatite

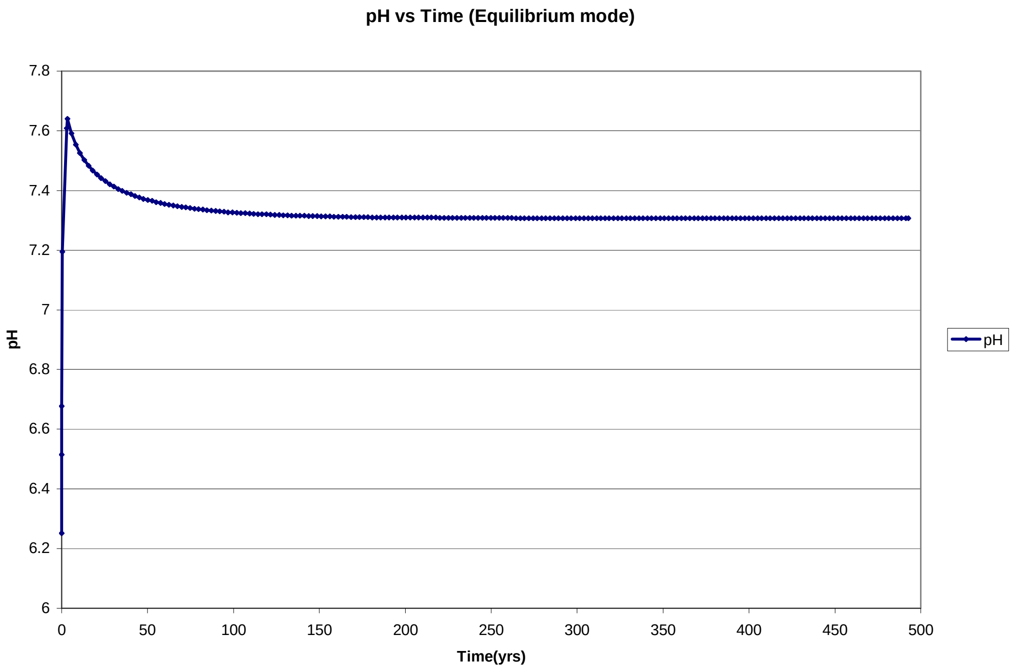


Figure 97. pH-profile in equilibrium reaction.

As can be seen from Figure 97, if the system is assumed to react according to equilibrium considerations, there is a very flat pH-profile with all the minerals reacting to consume the acid generated by the pyrite oxidation (also reacting as an equilibrium reaction in this scenario). Such a situation is clearly not representative of the field situation, thus one has to deduce that that the reactions in the field are kinetically controlled. This is however an oversimplification, since all the minerals are considered to be acid consumers. Using equilibrium considerations and the relative reaction rates (fast, intermediate etc. after Kwong, 1997), one could simulate the field situation more realistically.

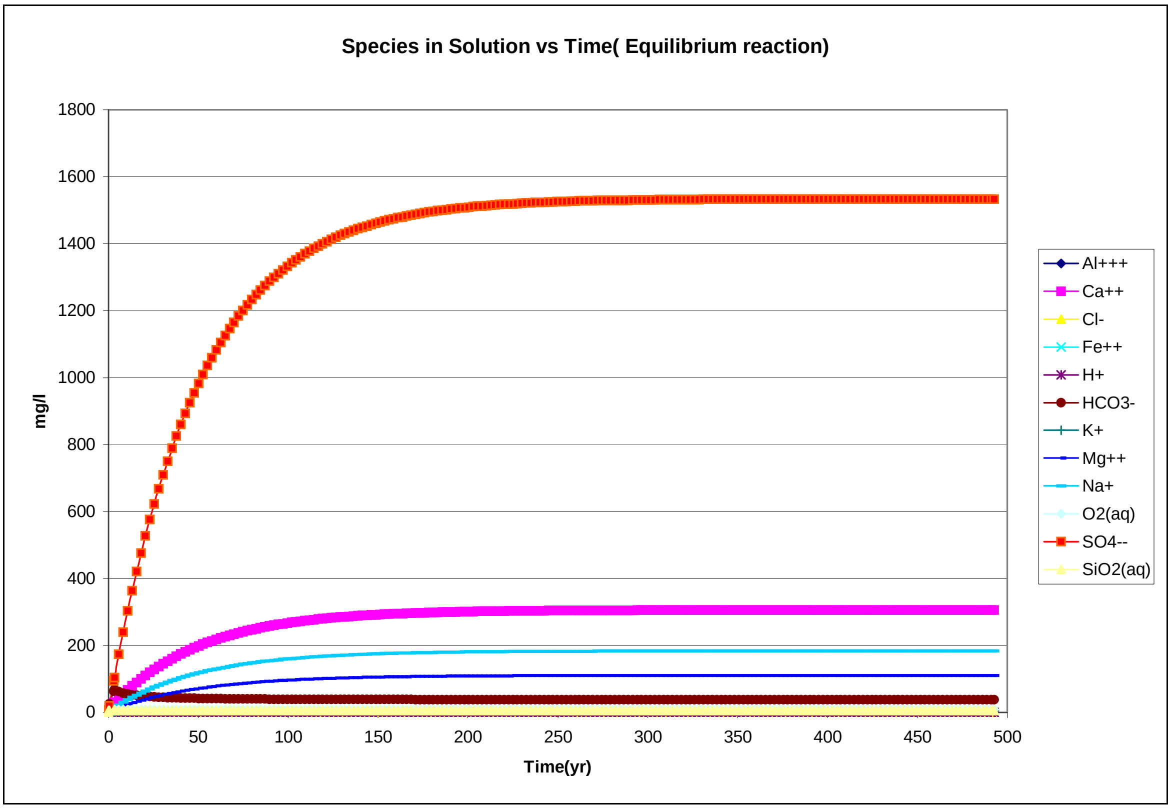


Figure 98.Species distribution over time assuming all minerals reacts to equilibrium rapidly.

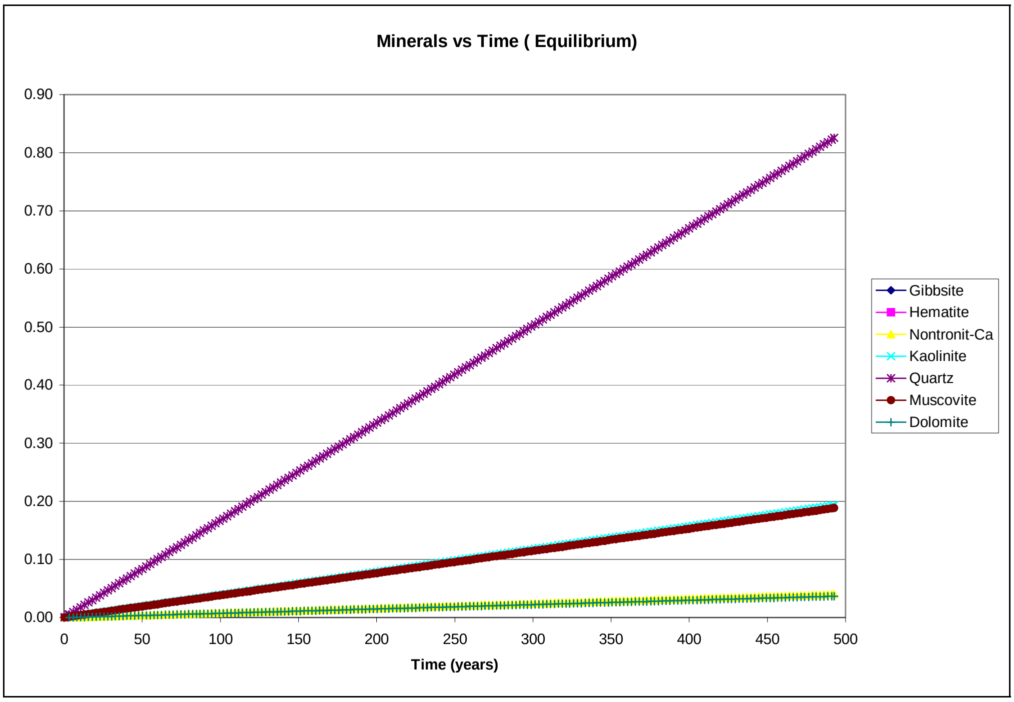


Figure 99. Mineral distribution over time assuming all minerals reacts to equilibrium .

8.2.6 KINETIC CONSIDERATION

Shown below is the system's response should it be assumed that the minerals all react in a kinetic fashion. Rates have been obtained from Stromberg and Banwart (1994), Lasaga (1984) and Scharer *et al.* (2000) (for simplification the influence of Fe^{2+} as catalysing species has not been included in this illustrative discussion). The pH-profile over time (Figure 100) shows the effect of considering the kinetic response of the minerals most clearly. A high proportion of pyrite was included to show the effects over the entire range of pH and the minerals which play a role.

To place the implication of these rates in context, the values from Lasaga (1984) will briefly be discussed. He reported the rates of silica release in weathering reactions at 25 °C and pH of 5 to be the following (Table 23).

Table 23. Weathering rates of some common minerals.

Mineral	**Rate Mol/m^2/s**	**Reference**
Quartz	4.1e-14	Rimstidt& Barnes (1980)
Muscovite	2.56e-13	Lin & Clemency (1981)
Forsterite	1.2e-12	Grandstaff (1980)
K-Feldspar	1.67e-12	Busenberg (1976)
Albite	1.19e-10	Holdren & Berner (1979)
Enstatite	1e-10	Schott *et al* (1981)
Diopside	1.4e-10	Schott *et al* (1981)
Nepheline	2.8e-9	Tole and Lasaga (1983)
Anorthite	5.6e-9	Fleer (1982)

Based on these reaction rates it can now be determined, under these conditions, what the mean lifetime of a 1 mm crystal would be for each mineral.

Table 24. Mean lifetime of a 1mm cube of different minerals based on reaction rates above (Lasaga, 1984), in years.

Mineral	**Lifetime (years)**
Quartz	34 Million
Muscovite	2.7 Million
Forsterite	600 000
K-Feldspar	520 000
Albite	80 000
Enstatite	8 800
Diopside	6 800
Nepheline	211
Anorthite	112

The rates reported by different authors naturally influence the mean lifetimes and introduce a major source of uncertainty. Pyrite reaction rates are often the most problematic, being greatly dependent on the biotic catalysis, temperature variations and O2 (g) availability. These factors have not explicitly been included. The calculations using different pyrite rates implicitly take these variations into account. Stromberg and Banwart (1994) report biotic rates for pyrite of up to 8e-10 mol/m^2/s under optimal conditions.

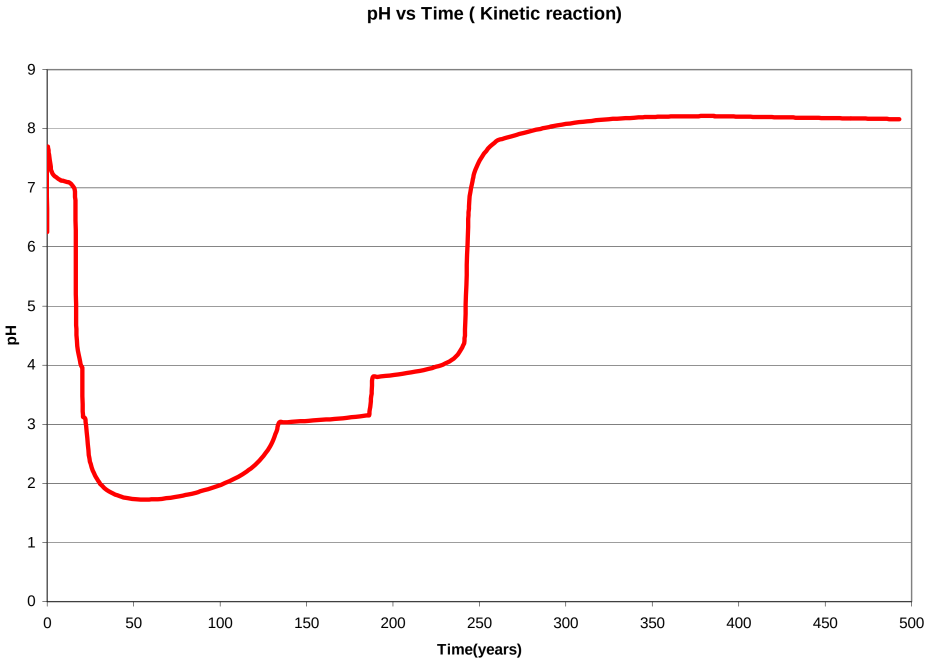


Figure 100. pH-profile for kinetic reaction, under constraints discussed.

One of the most important observations is that the pH drops relatively rapidly once the carbonates have been depleted (shown below in Figure 103). This reiterates the observation made in Section 2.3 that although several minerals have an acid consuming nature, the relative rate at which these minerals can react is most often too slow to effectively buffer the system from further acidification, if optimal oxidation conditions and sufficient pyrite occurs. In real situations the problem is complicated by the fact that the drainage comes into contact with various minerals along the flow path. An evolving sequence of equilibrium conditions can therefore appear incorrectly as kinetic conditions on a large scale, depending on relative flow rates (Morin and Hutt, 1997). Figure 102 shows that once the fast reacting minerals are depleted, the system's pH can begin to increase.

The stepwise increase in pH results from acid consumption from each specific mineral in order of the relative reaction rate. The shape of the curve is a function of the net reaction rates, the specific minerals included for consideration and the relative quantity of each mineral. It is therefore self-evident that the accurate determination of each of these parameters as a minimum is needed for each point in any system that is to be modelled. When the outflow/discharge chemistry from one particular area is used as a time-dependent input to another zone or area, the possibility of cumulative error propagation, should any parameter be wrongly applied, is magnified.

From the curve above, it is clear that in a short time acidity can occur but that over the period of many hundreds of years the system can return to relatively neutral values.

It must be noted that in this model the system has been regarded as open to the atmosphere, with the atmospheric gas composition regarded as fixed fugacity buffer controlling carbon dioxide and oxygen availability in the aqueous phase.

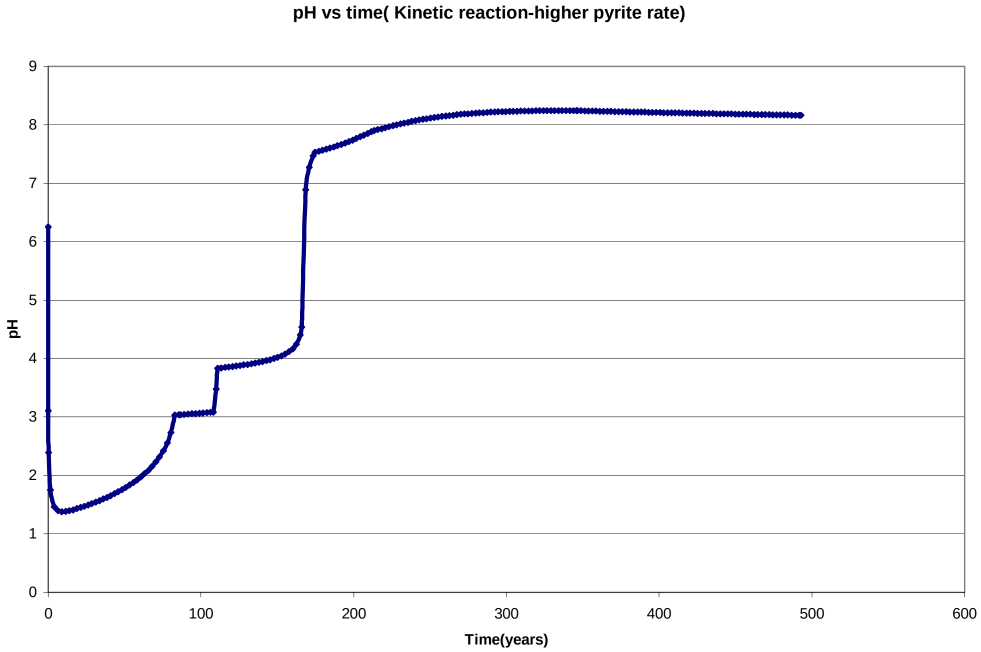


Figure 101. pH-profile at higher pyrite reaction rate.

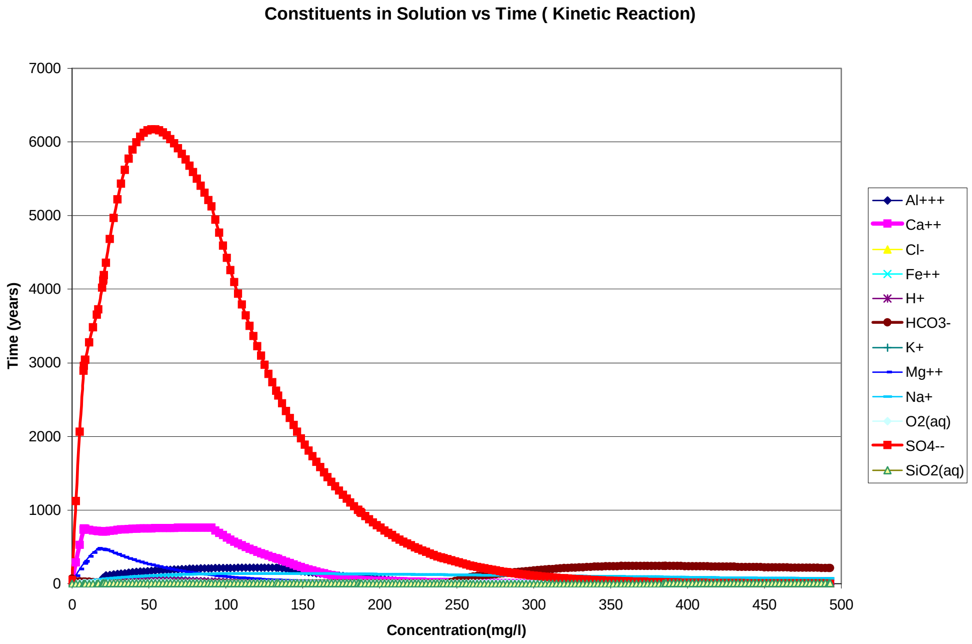


Figure 102. Distribution of different species over time.

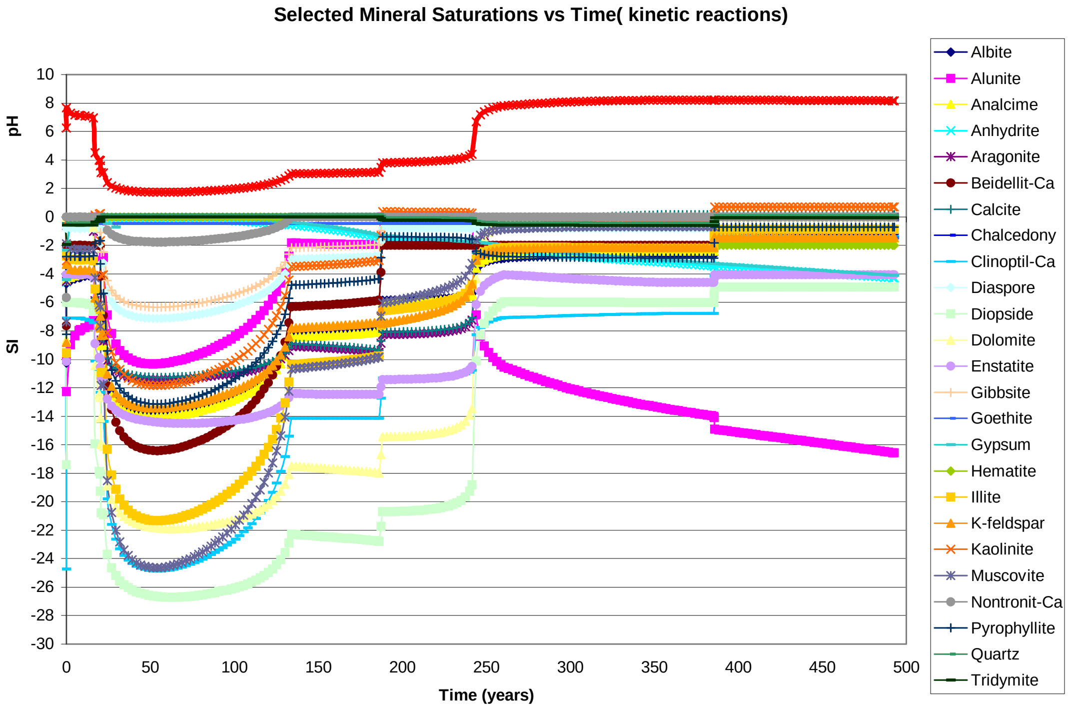


Figure 103. Mineral saturation related to the simulated pH-profile.

The profile above (Figure 101) shows the variation in minerals buffering over time, showing the consumption of different buffering minerals over the course of the process (and at different pH) and also the production and eventual precipitation over secondary minerals. More details of this profile are shown in Appendix 4, which shows detail for the pH-variation over time and the related mineralogical changes, which occur in the system.

It has been suggested that, in South Africa, the term "prediction of acid rock drainage" must be synonymous with computer models; often these are used inappropriately with insufficient detailed input data. No single model is yet available which adequately addresses all of these variables, but computer models for oxygen and water movement, moisture relations and geochemical processes are being developed and are expected to become more useable for in the future (Miller, 1998).

The question of whether to use ABA or computer models is therefore often posed by regulatory authorities and environmental managers in the mining industry. The ABATE strategy suggests that both be used depending on the level of investigation and level of answers required. To illustrate this belief the views of Scharer, of Waterloo University in Canada, one of the leading exponents and developers of acid mine drainage-related geochemical models are given (from Scharer *et al.*, 2000): "We doubt that ABA tests alone are able to predict potential acid formation after 100 years or more. This does not necessarily mean that computer simulations are better predictors, since computer models are at best very poor and simplistic analogies of natural processes. Nevertheless, they are proven to be useful tools for *research purposes* and can be used *in combination with other methods* for predictive purposes as well." Used in this context it is clear that all the methods in the ABATE toolbox are necessary and should be used for long-term predictions.

8.2.6.1 SIMULATING HUMIDITY CELL RESPONSE

The humidity cells discussed in Section 6.3 were modelled to determine whether it would be possible to simulate the cells' response. This modelling indicated the extreme sensitivity that a simple system has, to changes in rate, particle size and contribution of each mineral. In the duration of the humidity cells the fast-reacting species are dominant when they are present in significant quantities, as discussed previously. The uncertainty associated with the exact amount of each mineral, is again noteworthy since this is a determining factor in the evolution of the system.

As illustration the longest-running cells were used. The methodology employed was:

- Use the mineralogical data for the cell (Section 5.4) and assign values to each mineral.
- Use the ABA data to quantify the pyrite and carbonate contribution.
- Use oxygen and CO_2 as fixed fugacity buffers.
- Allow the quantity of water which was drained from the cell over the testing period to "flush" the system.

- Employ rates as described above.
- Use the particle size/reactive surface area arguments from Lasaga (1984) and Stromberg and Banwart (1994) to define a surface area for each mineral.

The Geochemist's Workbench (Bethke, 1996) was used for the simulations.

From preliminary results two modifications were made to the system. Firstly from the equivalent values of calcium and magnesium emanating from the cell, the carbonate phase was assigned to be dolomite, rather than calcite. Secondly, instead of a linear kinetic rate, the catalysing effect of pH on pyrite dissolution as described by Williamson and Rimstidt (1994) and McKibben and Barnes (1986) was included, together with the influence of pH on dolomite dissolution. From these considerations, the following profiles were obtained and compared to measured outflow values (Figure 104 to Figure 108). Once this has been shown to be successful, several of the other cells were dealt with in the same manner. An example is shown for the sandstone cell in Figure 109 to Figure 110.

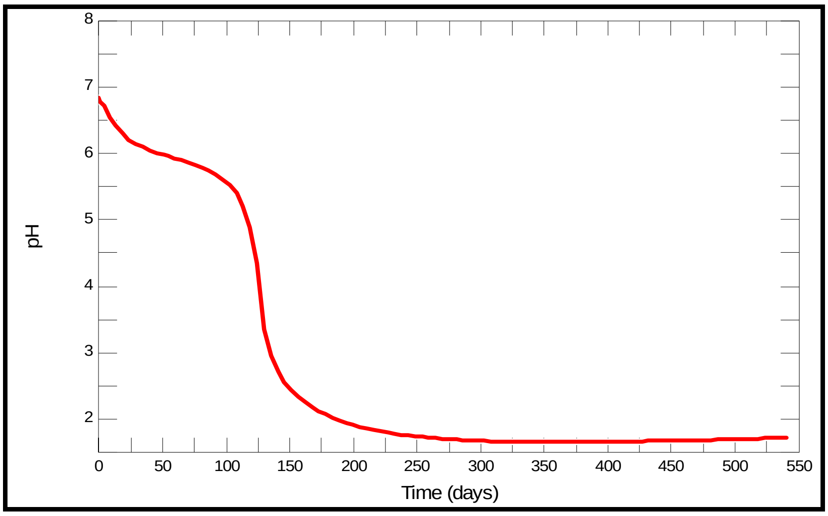


Figure 104. Simulated pH-profile for humidity cell.

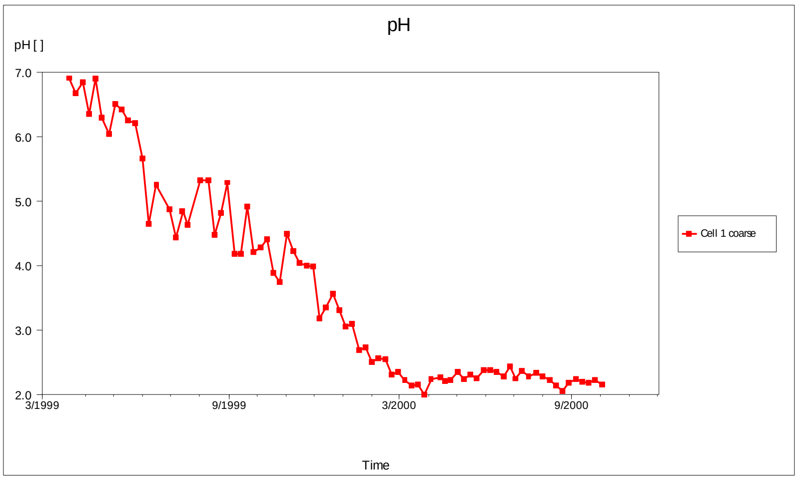


Figure 105. Observed pH-profile from humidity cell.

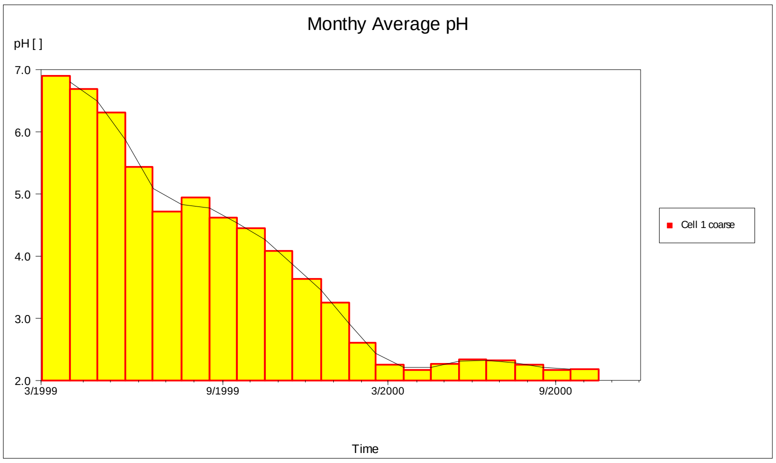


Figure 106. Observed pH expressed as a monthly average, with the two month moving average line shown.

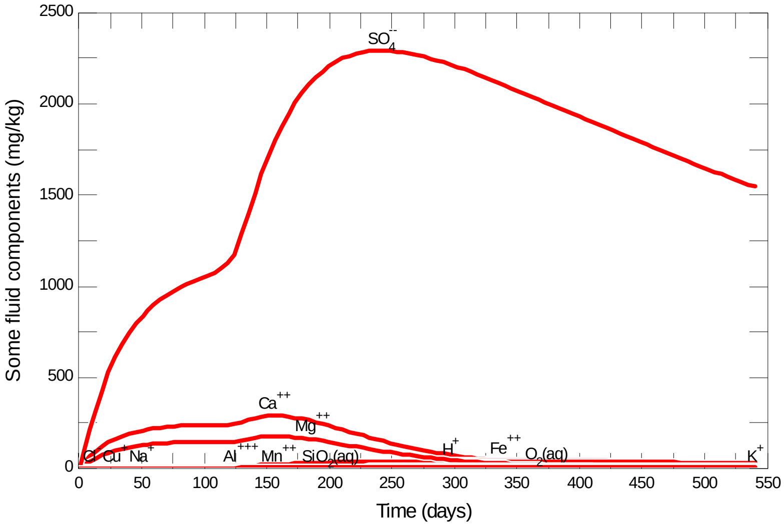


Figure 107. Simulated aqueous components for humidity cell.

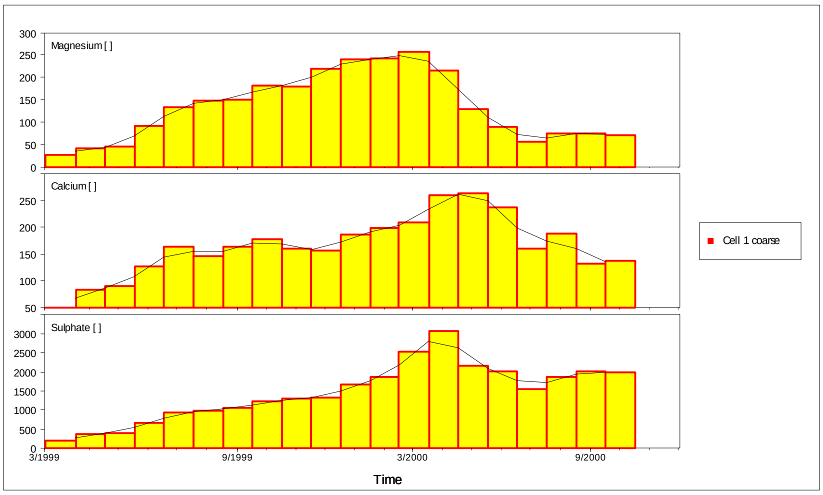


Figure 108. Observed aqueous components expressed as a monthly average, with the two month moving average line shown.

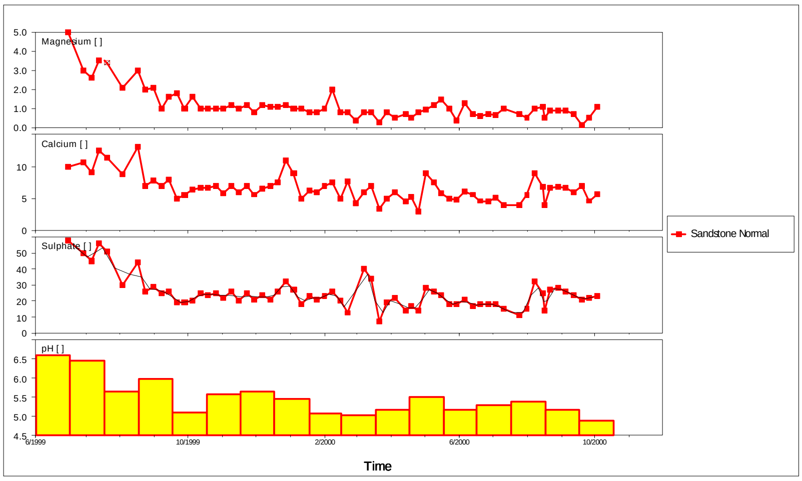


Figure 109. Outflow data from the sandstone cell.

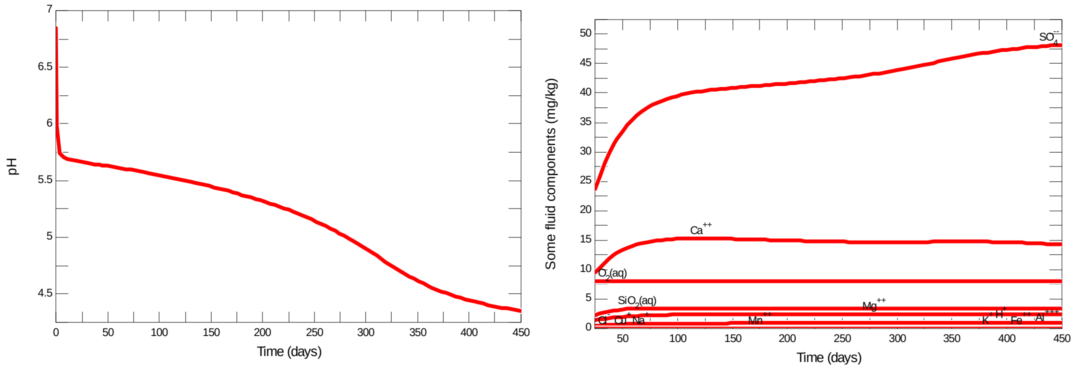


Figure 110. Simulated profiles from the sandstone cell.

From this it would appear that it is possible to simulate the system's response over time, if one has data on the mineralogy, rates, flushing rate and quantity of purite and fast-reacting species. However, it must be pointed out that the solutions shown are not unique; a variation of several parameters (relative amounts of each mineral, surface areas, etc.) can give a similar response. Care must therefore be taken in trying to extrapolate this to the field too readily.

8.2.7 GENERAL MODELLING METHODOLOGY

The following is a generic approach to the steps that need to be taken in geochemical modelling (adapted from Boer, 2000):

- Collect and review site data.
- Identify objectives, including required detail and confidence in model.
- Select, adapt or develop model(s).
- Prepare model inputs and parameter estimates.
- Calibrate model to field data.

- Perform simulations.Interpret the results.
- Identify controlling processes.

  -Compare to concentrations at other sites

  -Compare to estimates obtained using alternate approach
- Start at simplest level that meets objective.

The flow chart below (Figure 111) illustrates the iterative nature of these steps.

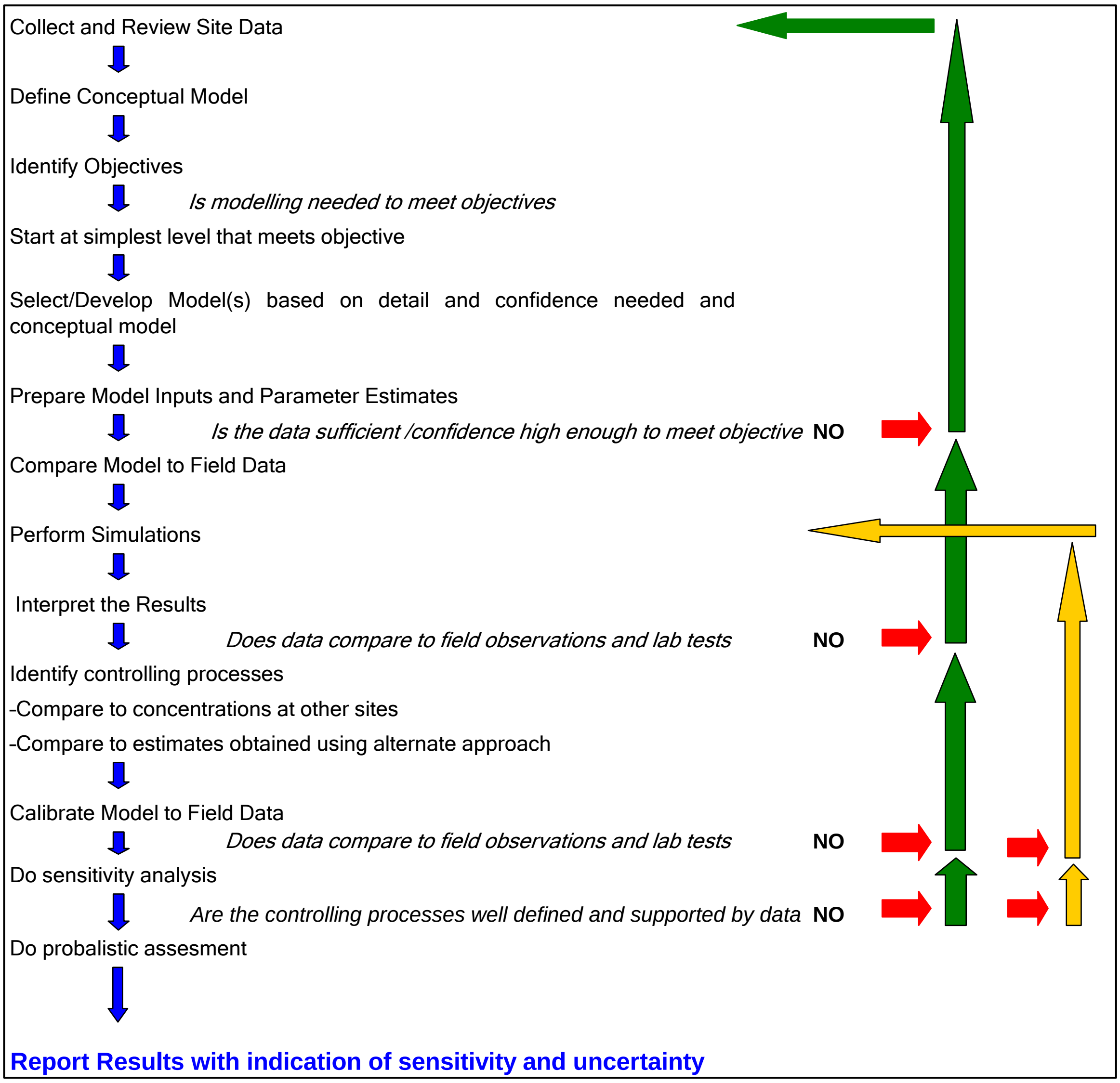


Figure 111. Suggested iterative flow path for geochemical modelling.

8.2.7.1 COMMON MODELLING CODES

There are literally tens of models that can be used fruitfully as part of the modelling subsection of the ABATE process's prediction wheel. The decision as to which code to use should be based primarily on the objective of the modelling, in conjunction with the definition of the appropriate conceptual model. Models which are expected to yield accurate long-term predictions of the drainage chemistry are naturally data-hungry and should be supported by sufficient, accurate and site-specific data.

8.2.7.2 MODEL SELECTION CRITERIA

Criteria for selection of an appropriate fate and transport model (ASTM,1999) include:

- Type of information required from the model (e.g. screening versus detailed evaluation).
- The fate and transport pathway to be modelled.
- Complexity of available models.
- Required input parameters.
- Availability of data on input parameter values.
- Model output requirements.
- Limitations on model use and output.
- The user's and target audience's familiarity and comfort with the model.

Important technical considerations in selection of a model package(s) (ASTM,1999) are:

- The algorithm(s) used to model each fate and transport pathway and the inherent limitations on applicability of each model.
- Degree of documentation, validation and general acceptance of algorithms incorporated in the package.
- Ability to access and modify data fields for input parameters (i.e. are input values "hard-wired" from databases of default values or can individual input parameters be tailored to site-specific conditions?).
- How the model results or output from individual fate and transport models are reported and linked to other model components.
- Familiarity of the user with various risk assessment components (i.e. model packages are not intended to be expert systems for use by those with little or no assessment expertise).

The table below shows some aspects of a subset of the more commonly used tools for South African coal mining applications with some of their key features. For more complete assessments of the different modelling codes the reader is referred to the WRC sponsored Internet Service Centre for Mine Related Water Models (http://www.cosmiclink.co.za/iscp/).

Table 25. Summary of salient features in some commonly used models in South African coal mines.

Model	Class	Type	Availability	Cost	Dimensions (Max)	Min. Data requirements*	Output	Perceived limitations	Source	GUI
ACIDROCK	Engineering	ES, KS,NF	Propreitary	4	3	All	CT	Nodal flow, limited subset of species	SENES	?
Geochemists Workbench	Equilbrium, with kinetic	EA, KS,	Commercial	3	1		CT,I,S	Handles separate nodes completely seperately	Rockware/ Univ Of Illinois	N
HYDROGEOBIOCHEM	Reactive transport	EA,KA,RT3	Free, Commercial	1	3	All	CT,I,S	All datasets, thermodynamics, flow regimes need to be reconfigured for each model, data intensive	US D.O.E/Oak Ridge National Laboratory	N,Y
MINTEQA2	Equilibrium	EA	Free	1	1	Ch	I,S	Only for chemical speciation and Saturation Index determination	US EPA	Y
MINTEQL	Equilibrium	EA	Commercial	3	1	Ch	I,S	Only for chemical speciation and Saturation Index determination	Environmental Research Software	Y
MINTRAN	Reactive transport	RT3	Proprietary	4	3	All	CT	?	Univ of Waterloo	?
MODFLOW	Flow	F	Free, Commercial		3	F.P, R	FT	Only models saturated flow	USGS	N.Y
MT3D	Mass transport	MT	Commercial		3	T	CT	Small set of reactive species	US EPA	Y
PH3D	Reactive transport	RT3	Commercial		3	All	CT	Gas phases currently not user defined	IGS, Univ of Edinburgh	Y
PHREEQC	Equilibrium, with kinetic	EA, KS, RT(1)	Free	1	1	Ch	CT,I,S	Only1-D reactive transport, kinetics need to be defined by user	USGS	Y
ROCKSTAR	Reactive transport	ES, KS,NF	Proprietary	4	3	All	CT	Nodal flow, limited subset of species	SENES	?
Salmine	Engineering	ES, KS,NF	Free	1	1	M,CL,F,P		1-D, very small subset of species,	WRC/Metago	Y
WATTAIL	Engineering	ES, KS,NF	Free	1	psuedo-3	All	CT,I,S	Nodal flow, subset of species	Univ of Waterloo	Y

* Depends on onsite situation and objectives of modelling

Key

Types		**Output**		**Cost**		**Data requirements**	
Equilibrium_ all species	EA	Speciation	S	Free	1	Climatic	CL
Equilibrium_subset of species	ES	Saturation Indices	I	<$200	2	Chemical analyses	Ch
Kinetic_all species	KA	Reaction simulation	R	> $200	3	Mineralogy	M
Kinetic_subset of species	KS	Time-dependent concentrations	CT	Proprietry	4	Gas	G
Flow	F					Saturation	S
Mass Transport	M					Particle size	S
Nodal flow	NF					Flow	F
Continuum Flow	CF					Aquifer parameters	P
Reactive Transport(1, 2 or 3-D	RT (1-3)					Transport parameters	T

8.3 CONCLUSIONS FOR GEOCHEMICAL MODELS

Geochemical models are an important tool in the ABATE process, when used appropriately. This chapter has shown that geochemical modelling:

- Needs **many input parameters**, which have been **accurately determined**. (Section 3.3 and 8.1)
- **Requires the selection of an appropriate model tool, which is vital**. (Section 8.2.7)
- Can provide long-term estimates of changes/trends in AMD quality.
- Is often associated with large uncertainties, wherein **small changes** to any one of the important **input** parameters can **alter the results drastically.** (See section 8.1.11 and 8.2)
- Can be assisted by field and laboratory validation to decrease uncertainty.
- Is regarded as an advanced step in the ABATE process.

There are several model codes available, and the selection of an appropriate code is vital. Results of models should be evaluated against the confidence of the important input parameters, the scale (area, time period and relative weight given to results) and the objectives of the model.

9 COMPARING RESULTS FROM DIFFERENT PERSPECTIVES AND CASE STUDIES

9.1 COMPARISON OF FIELD VALUES TO STATIC ABA and KINETIC TESTS

An important consideration is the integration and comparison between values observed in the field and those obtained in standard ABA testing. In this section several other mine sites will be used for comparison.

9.2 ACID-BASE ACCOUNTING AND LONG-TERM MINE-WATER CHEMISTRY AT OPTIMUM OPENCAST

9.2.1 INTRODUCTION AND SCOPE OF INVESTIGATION

Optimum Colliery is currently mining in four distinct areas. Current mining extends over approximately 4000 ha. Future mining included, this will cover 7 300 ha.

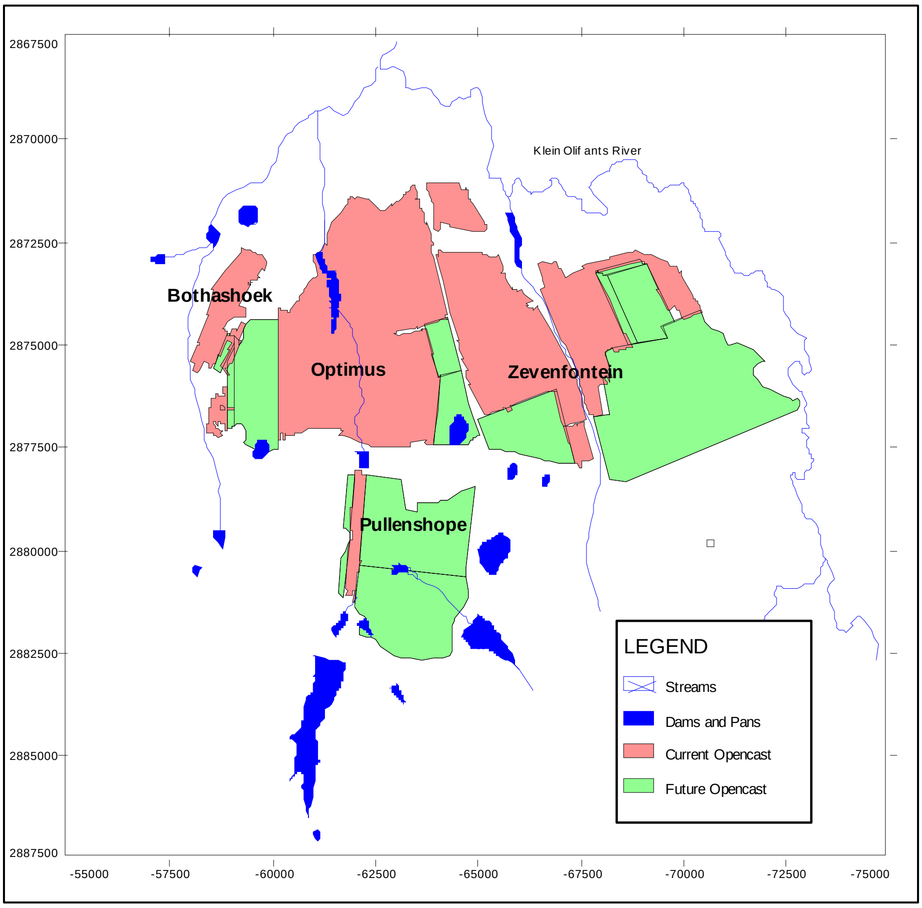


Figure 112. Plan showing current and future Optimum Opencast sections, including surface water features.

To determine the long-term influence of the opencast it was required:

1. To investigate the potential chemical reactions at Optimum Colliery and to predict the future chemical character of the mine water.
2. To investigate the vertical stratification of water and its chemical character within the spoils.
3. To calculate the water and salt balances for the pits.
4. To identify, investigate and select management options that could have positive impacts on water quality and quantity within the Opencast.

Water balances were calculated in a separate investigation by Van Tonder (IGS, 1999). Their conclusions are used as input in this investigation to quantify the nature of the hydrochemical regime.

The current investigation consists of:

- Acid-Base Accounting (ABA) on rock and coal samples.
- Solubility determinations on these samples.
- Establishment of leaching and solubility curves at various pH-levels for rock and coal.
- Selective sampling and analysis of water to supplement ABA and results from previous water analyses.
- Chemical profiling of water within available monitoring boreholes.
- Calculating concentrations of constituents that will be present during and after mining.
- Calculating salt balances for current and post-closure scenarios.
- Identification of management options to minimise water quality deterioration and regional impacts.

9.2.2 ACID-BASE ACCOUNTING (ABA)

9.2.2.1 pH-LEVELS

11 cored boreholes were drilled by Optimum in areas still to be mined (Figure 113). Geological logs of these boreholes are included in Appendix 5. The cores were subdivided into recognisable lithological units, crushed and submitted for ABA to the Institute for Groundwater Studies.

In instances where the base potential exceeds the acid potential, little or no drop in the pH occurs.

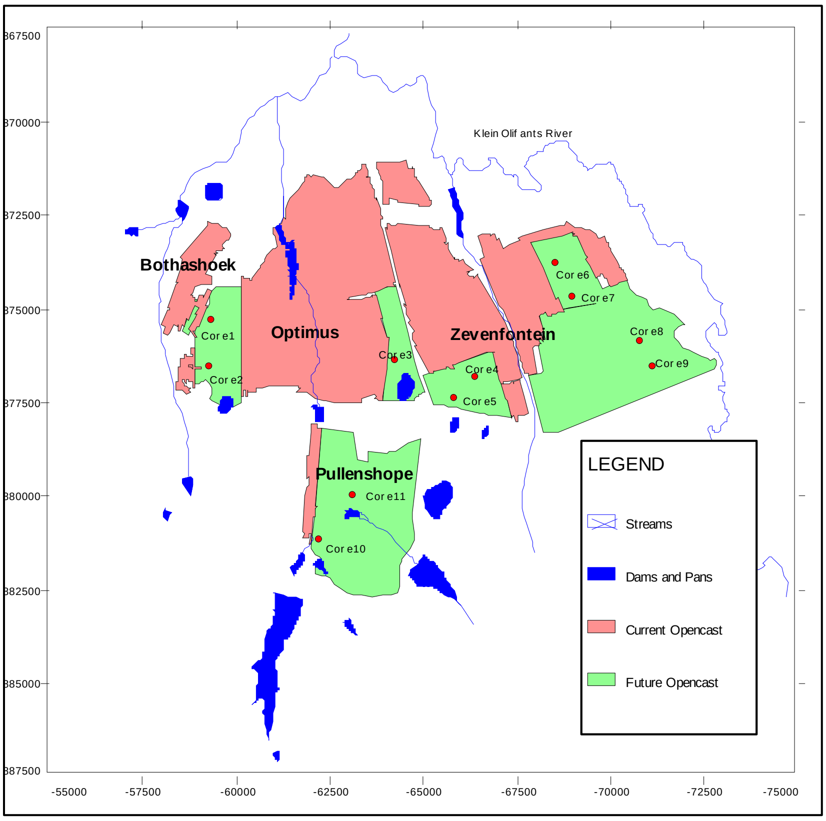


Figure 113. Localities of cored boreholes for acid-base testing.

Figure 114 and Figure 115 respectively demonstrate pH-levels before and after oxidation. On the y-axes, pH-values have been sorted from low to high in both diagrams. The lithologies for each of the samples are indicated on the x-axes. Full information of the ABA results for each sample and different type of test is given in Appendices 5 and 6.

The following is a translation of the codes used in Figure 114 and Figure 115:

SOIL	Soft overburden.
Weathered	Sediments above the first Coal Seam forming part of the unconfined system.
5Seam	No. 5 Coal Seam.
4	Hard sediments between the. No. 4 and No. 5 Coal Seams.
4Seam	No. 4 Coal Seam, both upper and lower seams and interbedded sedimentary layers.
2	Hard sediments between the No. 2 and No. 4 Coal Seams.
2Seam	Seam No. 2 Coal Seam.
1	Hard sediments below the No. 2 Coal Seam.
1Seam	No. 1 Coal Seam.

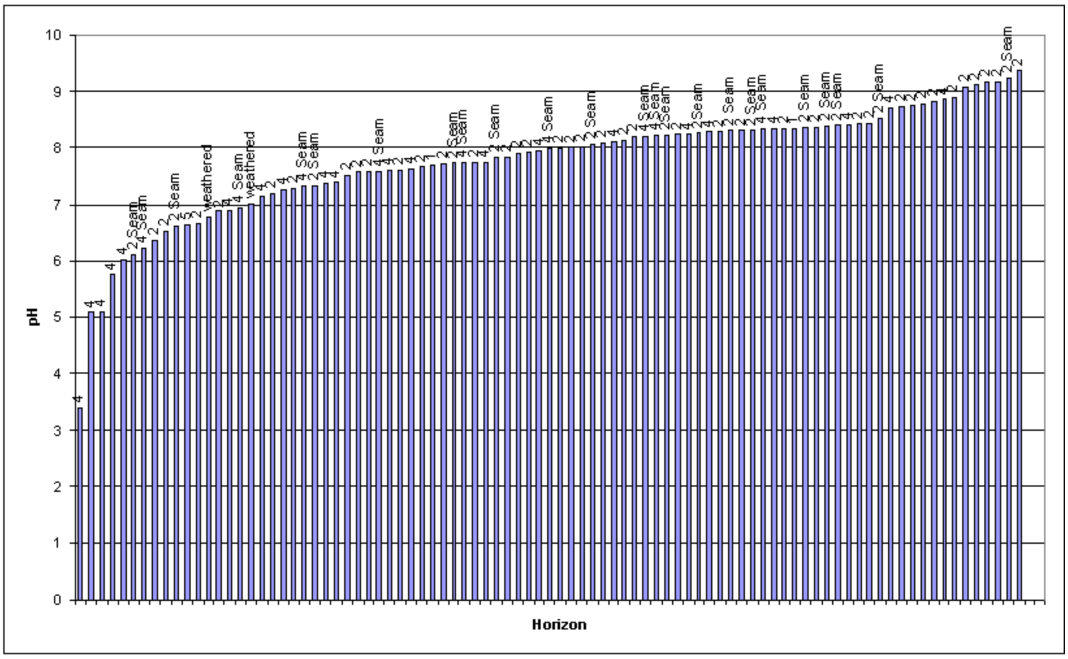


Figure 114. Natural pH vs. horizon.

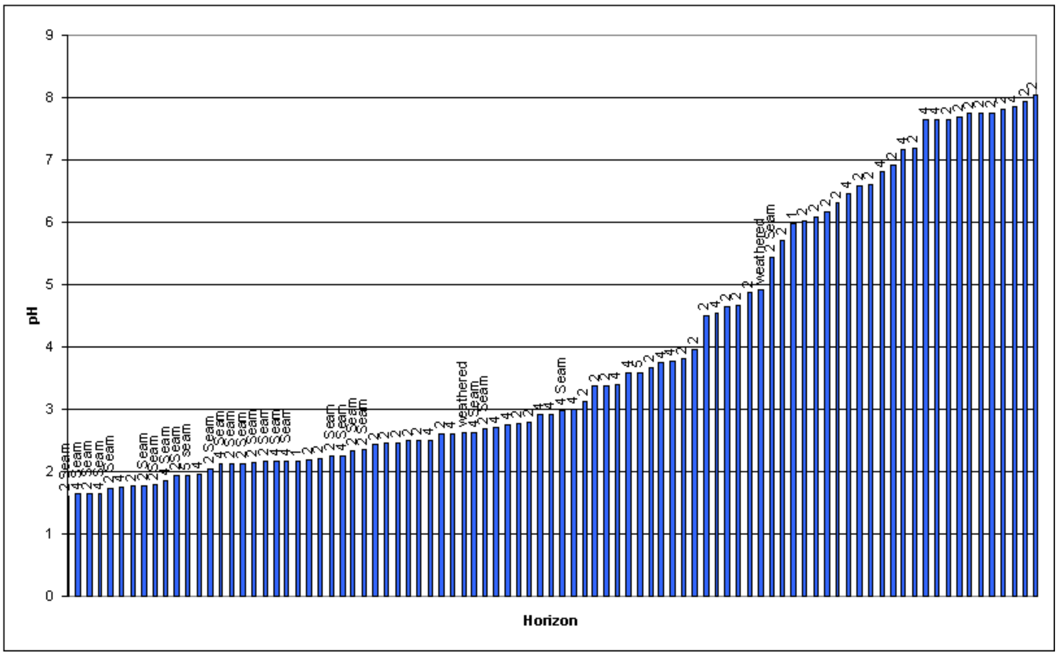


Figure 115. Oxidised pH vs. horizon.

Conclusions from the natural pH-levels (Figure 114) are:

- Over 80 percent of the samples have natural pH-levels at or above 6,2. These samples currently have excess base material available, which prevents immediate acidification during the mining phase.
- In the upper weathered sediments, indications are that the reactive species have largely been leached from the sediments and thus they are near neutral pH-levels (Appendices 5 and 6).
- The samples that are acid are predominantly from the sediments above the No. 4 Seam. If mining of these rocks takes place and the sediments are exposed to air and water, a risk of lateral acid propagation into the rest of the spoil exists. All or most of the base potential has been leached from these horizons over many years of groundwater circulation, preceding mining. As far as acid potential in these rocks is concerned, almost all of this has been preserved due to the near absence of oxygen in the groundwater.
- Many samples have pH-levels above 8,2. This suggests the presence of significant carbonate species. These are released through solution and represent the first line of acid neutralisation. Figure 115 shows that the sediments between the No.'s 2 and 4 Coal Seams often fall in the latter category. The fact that significant carbonate species are present suggests that groundwater flow within this horizon has been low in the past, otherwise the carbonates would have been more extensively leached.

Conclusions from the oxidised pH-levels (Figure 115) are:

- About 65% of samples acidified under oxidising conditions, suggesting excess acid potential over base potential.
- More than 50% of the samples acidified to pH-levels below 3,0. At this low pH-level, many other reactions also come into play. The most important of these is heavy metal release into the water.

9.2.2.2 ACID VERSUS BASE POTENTIAL

Two other tests were performed on the cored samples. These are separate measurements of the acid and base potential contained in each of the samples. In these static tests, the amount of acid that can potentially be produced by each sample and the associated potential each sample has to counteract this generated acidity, are determined separately. It is important to realise that these tests determine the maximum availability of the acid-producing minerals (usually sulphides) and of the neutralising species (at pH-levels above 6,0, usually calcium/magnesium carbonates). The test methods are designed to utilise all the potential inherent in the sample.

In nature, carbonates are more reactive than the sulphides, resulting in base potential leaching by circulating groundwater. This invariably results in an acid problem over the long term, despite an initial excess of neutralising potential. The results from these tests are shown in Figure 116 to Figure 118.

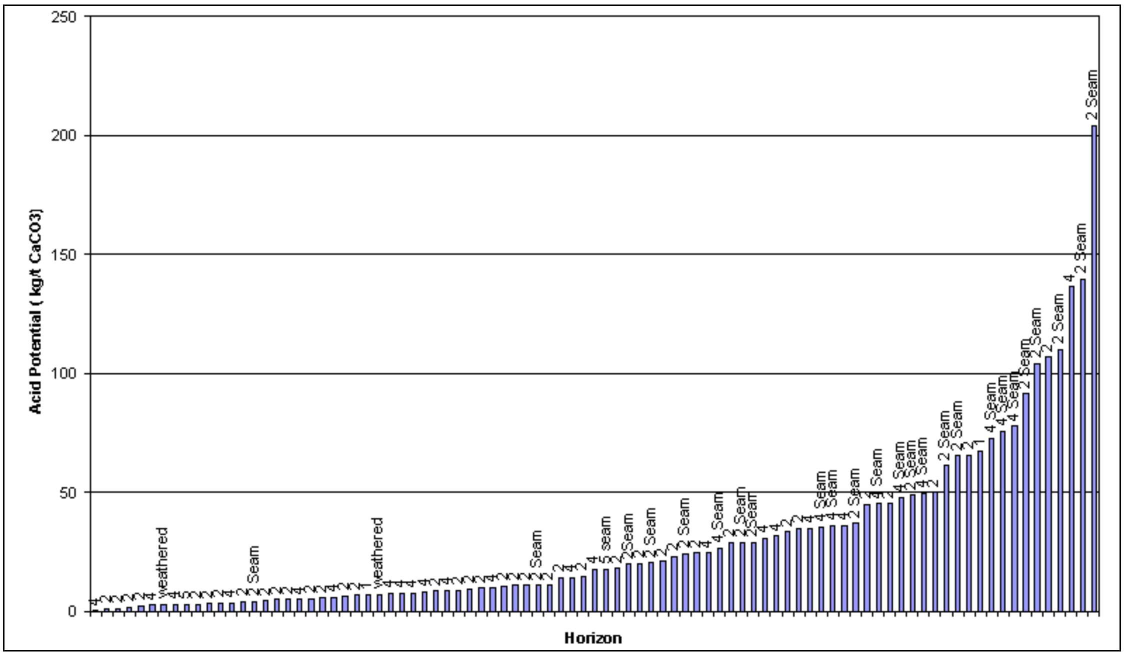


Figure 116. Acid Potential by horizon.

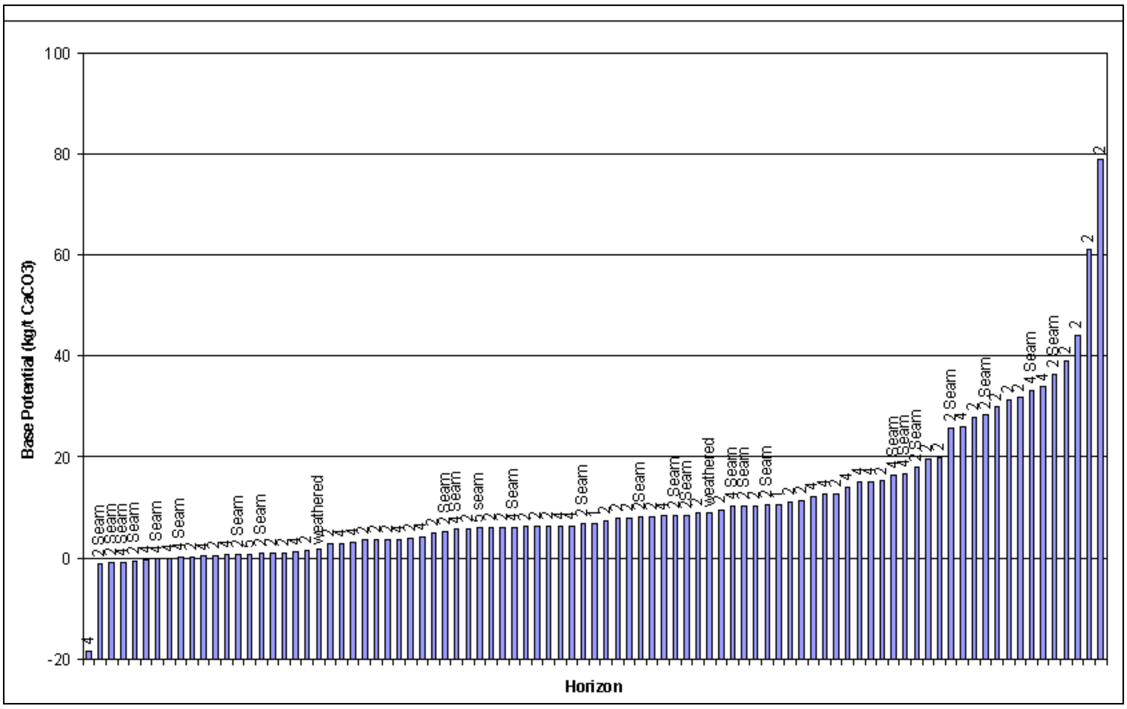


Figure 117. Base Potential by horizon.

The following conclusions are drawn:

- The uppermost, weathered layers have low acid and base potentials. This confirms that the reactive minerals in these layers have been consumed. The layers above the uppermost coal seams can thus be regarded as relatively inert in the Optimum area. This is well illustrated by the graph of Net Neutralising Potential (NNP) against Horizon (Figure 118). The NNP is calculated by subtracting the acid potential from the base potential for each of the samples.
- Down to the No. 4 Seam, the fresh rock often has relatively low base potential and high acid potential. *In situ* pyrite oxidation is much slower than carbonate dissolution. This explains the relatively high acid:base ratios in these sediments.
- Higher base potentials are often associated with rock located between the No. 2 and 4 Seams. This seems to be independent of the rock type, e.g. shale, siltstone or sandstone. The explanation lies in the lack of natural groundwater circulation at depth and thus relatively little carbonate leaching on this horizon.
- The coal seams generally have significantly higher acid than base potentials (Figure 118). Although most of the coal is removed from the pits through mining, about 10% of the coal remains in the pits and will eventually produce acid leachate. Coal discards are also placed into the pits. This introduces an additional acid component.
- In the calculations of acid potential and consequently NNP, a distinction is made between so-called open and closed conditions. Under closed conditions, the base potential is halved due to the production of CO_2. The latter produces carbonic acid (H_2CO_3) upon dissolution in the available water. This acid reacts with the carbonate species in the rock, thus increasing the overall acid potential. Under field conditions, it can be assumed that most of the CO_2 ends up in the water. However, instances would certainly occur where some of the CO_2 is released into the air. A continuum between closed and open systems, which tends towards a closed system, is therefore likely.
- A composite graph, showing the combination of natural and oxidised pH-levels as well as the results from acid and base determinations, has been plotted in Figure 119. In this diagram, natural pH-levels are shown on the y-axis as diamonds and oxidised pH-levels as squares. On the x-axis, the NNP is plotted. Advantages of this plot are:
  - The drop in pH as a result of oxidation for each of the samples can be demonstrated.
  - A check on the accuracy of the analyses can be made. The position of acidification should approximately coincide with the zero NNP value. The conclusion is that the analyses appear to be accurate.
  - The representative spread of values on both axes confirms adequacy in the number of samples analysed.

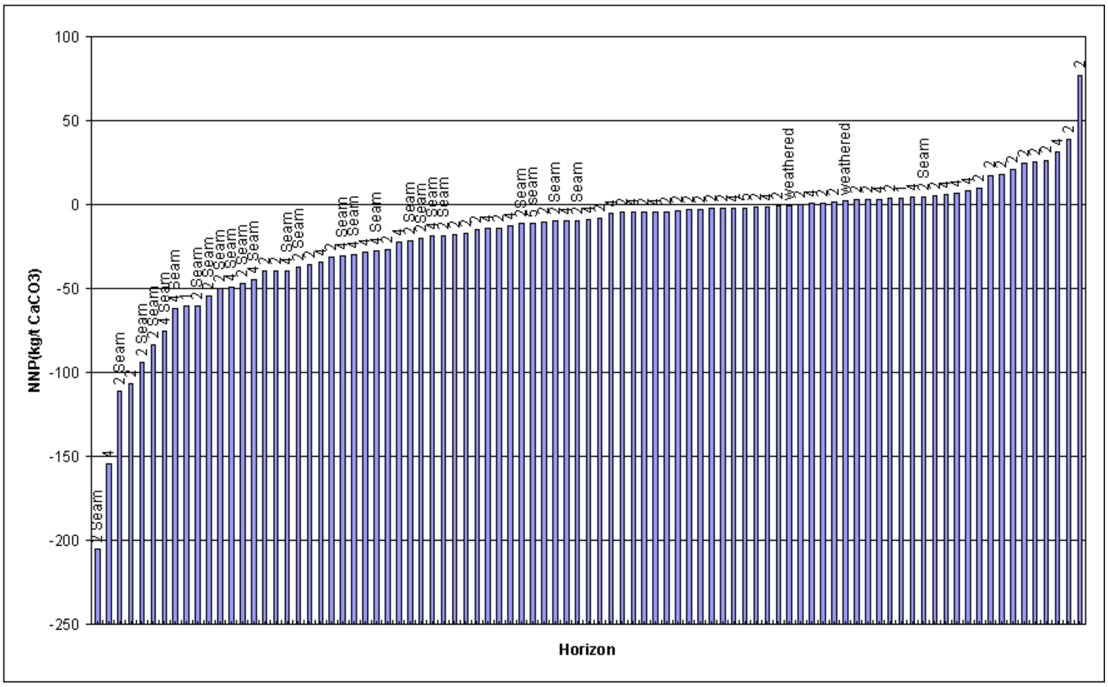


Figure 118. NNP by Horizon .

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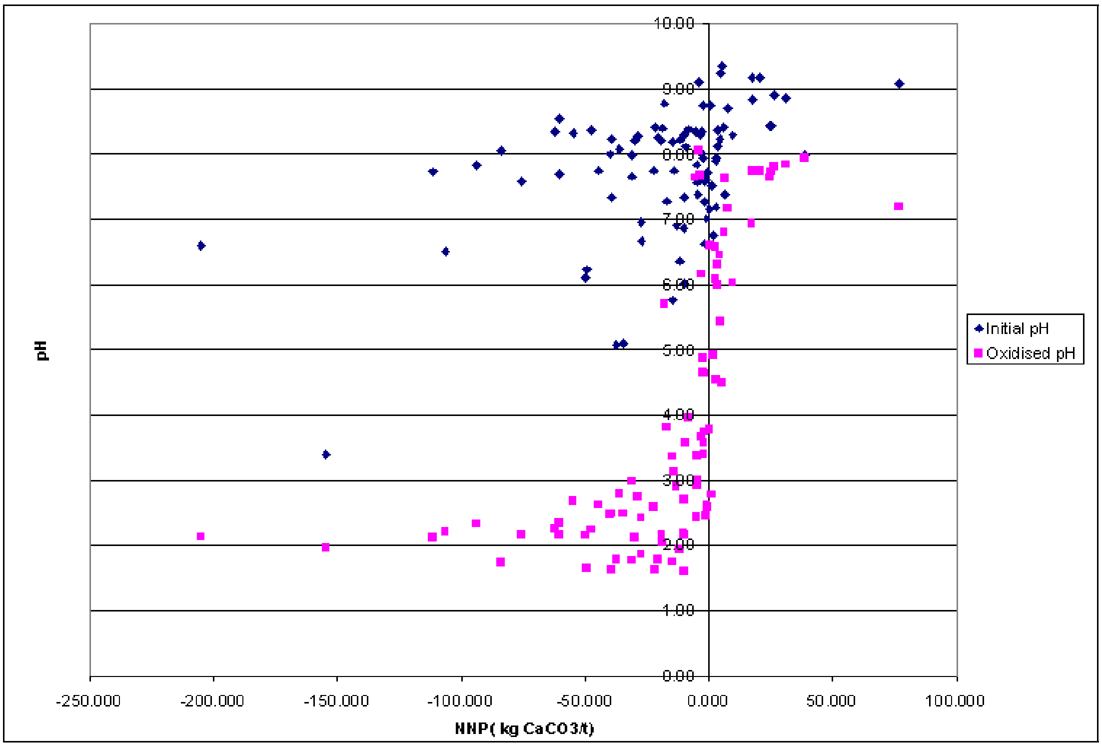


Figure 119. Initial and Oxidised pH vs. Closed NNP.

An additional graph to demonstrate the likelihood of long-term acidification is shown in Figure 120. The Neutralising Potential Ratio (NPR) is calculated from Base Potential/Acid Potential. The graph is divided into different sectors - the red sector with low NPR (0.3 - 1,0% S), is a field where long-term acidity is very probable. The green sector is an area where there should be enough neutralising potential and too little sulphur for significant acidity to occur. Samples in this field will be likely long-term buffers in the system. The grey area on the chart represents samples with a low sulphide content but low neutralising potential. These samples should not theoretically have enough sulphides for long-term acid generation, but can yield acidity in the short term until the sulphides have been depleted.

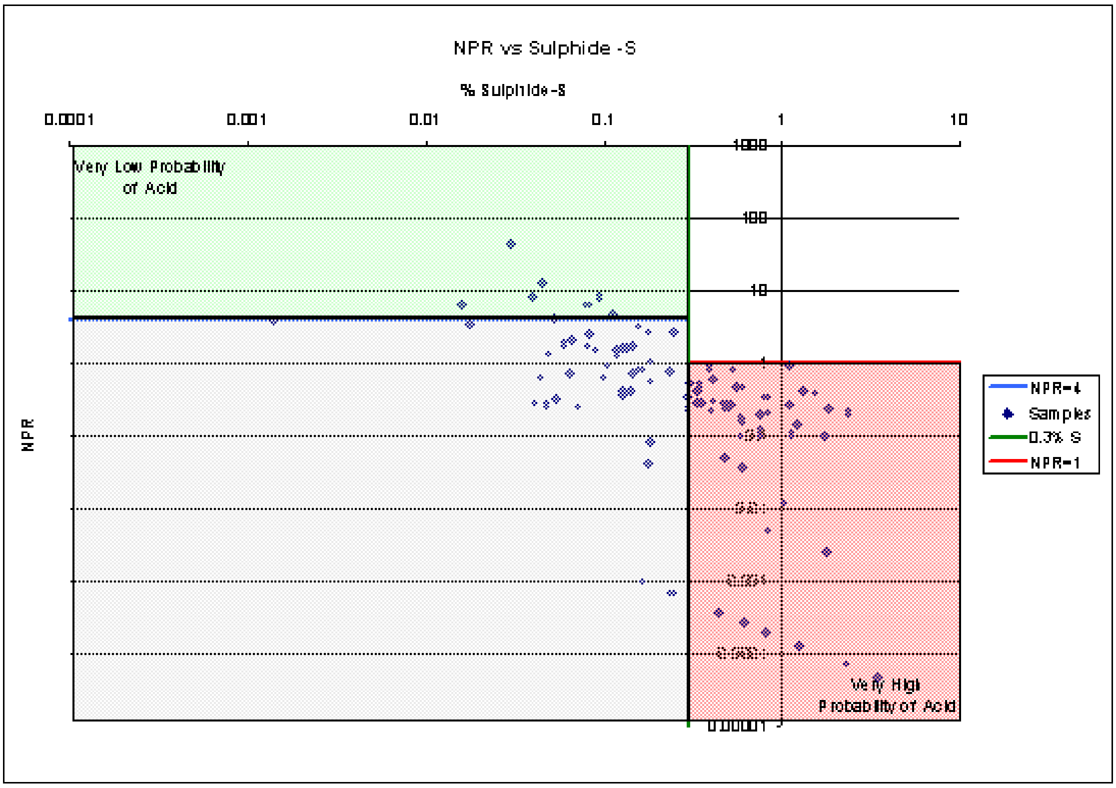


Figure 120. Acid-generating probability of the spoil.

The next step in Acid-Base Accounting is to relate the laboratory measurements to the field situation. Table 26 lists these results. Two columns are provided, indicating the normalised NNP's. The first accounts for all the sediments while in the second, 90% of the coal has been removed. Negative values imply excess acid, expressed as kg/t $CaCO_3$. Under field conditions, limestone is more soluble and will leach from the rock faster than the oxidation rate of pyrite. Field addition of limestone will therefore not be effective in the long run.

Another way of expressing the impact which coal removal as a result of mining will have on the total acid versus base potential on the mine is displayed in Figure 121. In this diagram, successive amounts of coal have been removed, ranging from 0 - 95%. The graphs show the remaining acid, base and NNP for the spoil. As the coal is progressively removed, an overall improvement is achieved, with the NNP increasing from -12,3 to -8,0 kg/t as CaCO3. In the context of the mine, however, removal of the coal will not change the end situation because acidification will still take place.

Table 26. Normalised NNP for different areas with and without coal removed.

Area		**Normalised Sum of NNP (kg/t)**	**Normalised Sum of NNP with 90% coal removed (kg/t)**
Area 1	Core1	-23	-24
Area 1	Core2	-4.5	1.2
Average		**-14**	**-11**
Area 2	Core3	-8.7	-3.6
Average		-8.7	-3.6
Area 3 West	Core4	-33	-38
Area 3 West	Core5	-12	-6.7
Average		**-23**	**-23**
Area 3 East	Core6	-6.5	0.29
Area 3 East	Core7	-9.2	-6.1
Area 3 East	Core8	0.88	0.88
Area 3 East	Core9	-1.0	2.1
Average		**-3.9**	**-0.73**
Area 4	Core10	-6.4	0.34
Area 4	Core11	-7.5	-8.8
Average		**-7.0**	**-4.2**

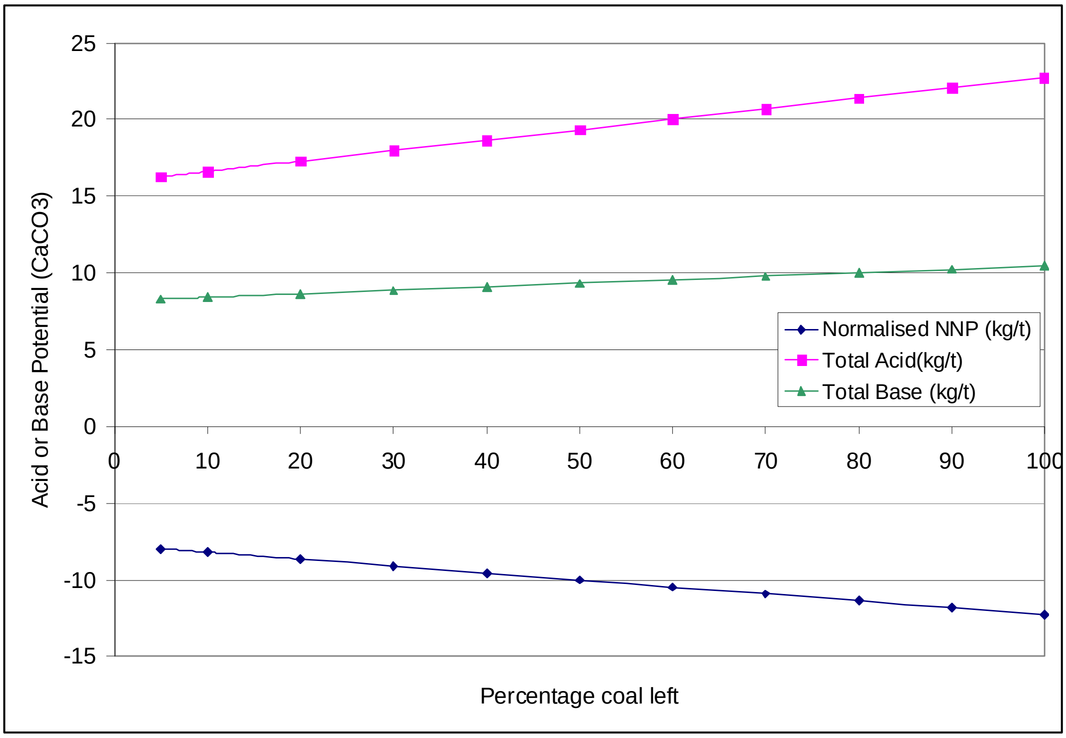


Figure 121. Acid, base and NNP in the spoil as they relate to various percentages of coal extracted.

The probability of spoil acidification can also be calculated. The results are presented in Figure 122.

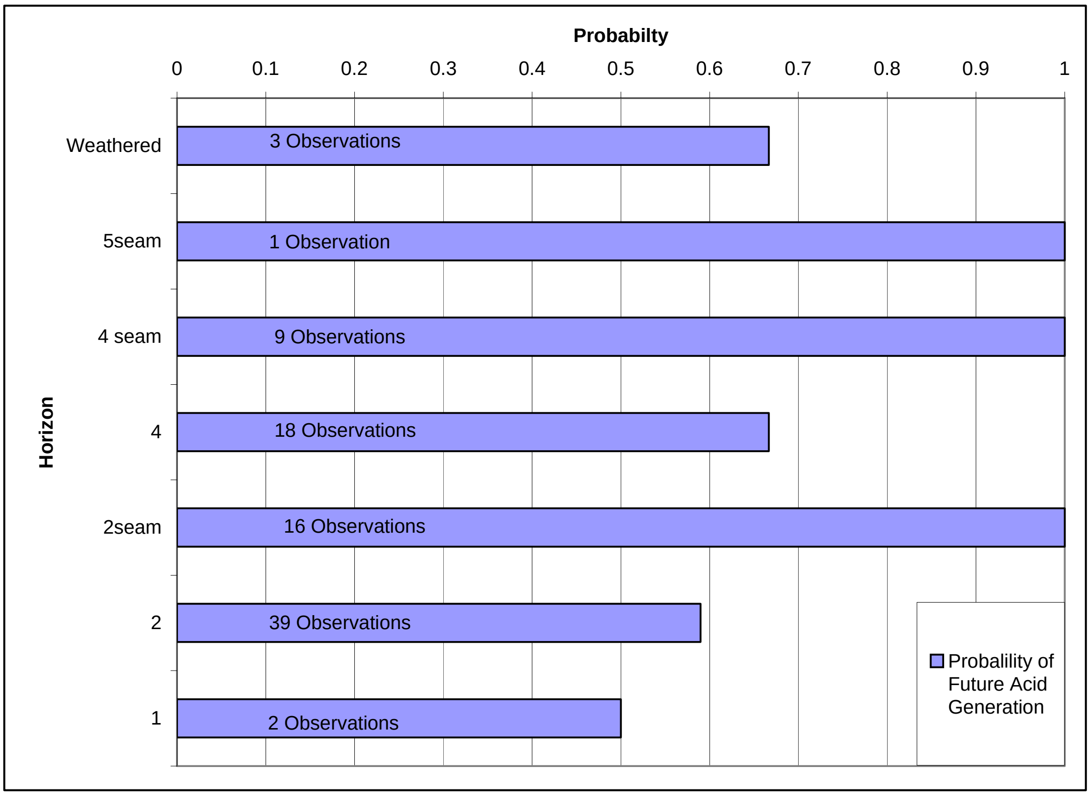


Figure 122. Probability of acidification of the spoil for the various lithologies.

The following conclusions are drawn:

- The coal seams have the highest probabilities of eventual acidification. This is followed by the sediments above the No. 4 Coal Seam and lastly by the sediments between the Nos. 2 and 4 Coal Seams. All probabilities of acidification are above 50%.
- The **acidification will not be over the whole area**; **neither will it be immediate** because the existing base potential will have to be exhausted before the spoil will acidify. **Acidification will therefore be patchy**, extending over larger areas with time as the base potential is locally depleted. Furthermore, **acidification will start in the unsaturated spoi**l, seeping down into the saturated spoil, eventually impacting on the chemistry of the spoil beneath the water table. **Flooding the spoil with water therefore provides no guarantee that it will not acidify.**

9.2.2.3 EXTRAPOLATION TO THE ENTIRE MINED AREA USING THEISSEN POLYGONS

One of the biggest criticisms against ABA is that the results are often difficult to extrapolate to a field scale. The preceding section showed a depth normalisation and weighting method which can be used. This section will explain an extrapolation technique that can be used if lithological samples have been tested across the extent of the mine.

The Theissen polygon technique is used by the Pennsylvanian State authorities to assist in the evaluation of opencast coal mines (Perry, 1998). The Theissen polygon method provides an excellent method for weighting the influence of each drilled borehole on which ABA is done. **When the entire extent of the borehole has been tested, as is recommended in this document, it provides a relatively easy, yet powerful, volumetric calculation to predict what would happen at an opencast mine**.

The subdivision of Optimum using the Theissen polygon method is shown in Figure 123 below.

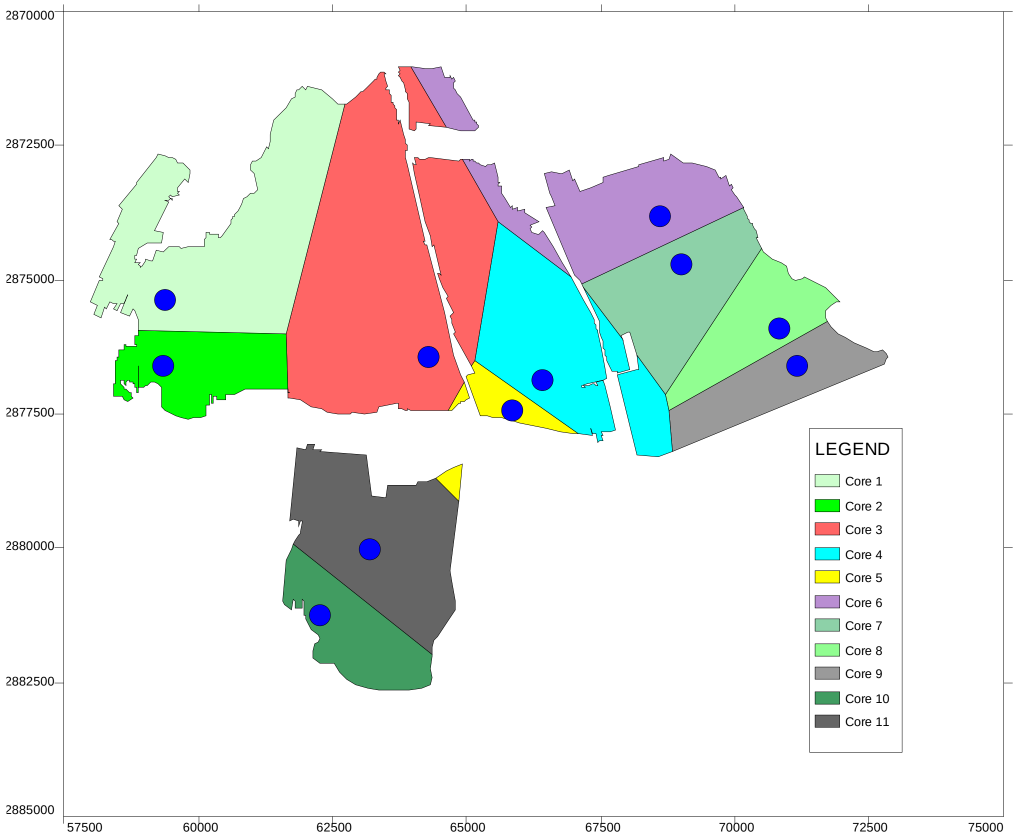


Figure 123. Subdivision of different areas using the Theissen polygon method.

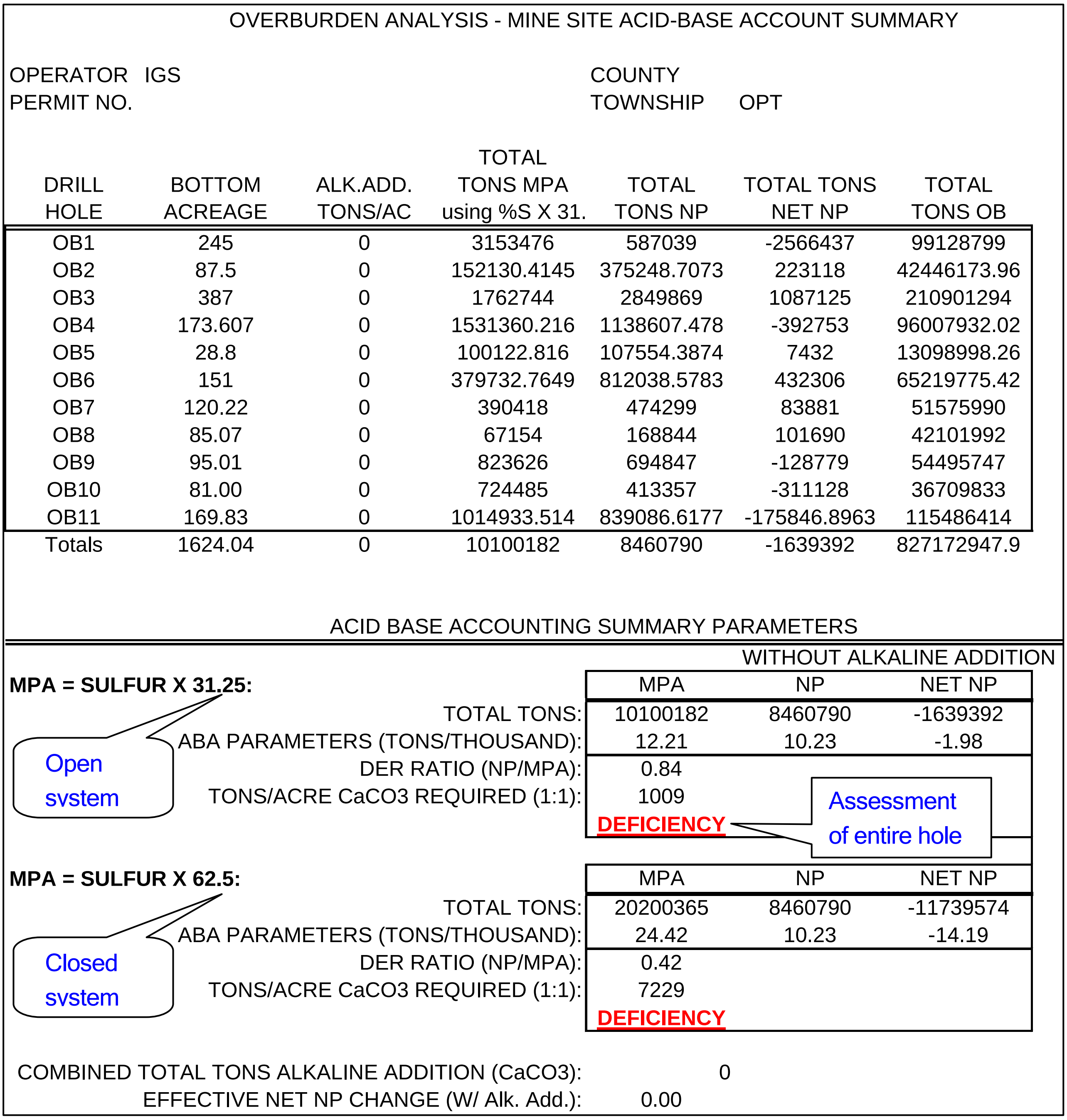
The areas that each borehole "represents" can therefore be calculated and is given in the table below.

Table 27. Area associated with each core borehole.

Core Hole	Acres	Hectares
1	245.2	1068.1
2	87.5	381.1
3	387.1	1686.2
4	173.6	756.2
5	28.8	125.4
6	151.4	659.3
7	120.2	523.7
8	85.1	370.6
9	95.0	413.8
10	84.1	366.3
11	169.2	737.0

Using the methodology set out by Perry (1998) and making use of the spreadsheets provided by the Pennsylvania Department of Environmental Protection, it is possible to calculate the approximate tonnage of overburden that will be spoiled and the associated tonnage of acid production and neutralisation potential. This is shown in Table 28.

Table 28. Combined results for the entire mine using the PDEP spreadsheet methodology.



OVERBURDEN ANALYSIS - MINE SITE ACID-BASE ACCOUNT SUMMARY

OPERATOR IGS
PERMIT NO.

COUNTY
TOWNSHIP OPT

DRILL HOLE	BOTTOM ACREAGE	ALK.ADD. TONS/AC	TOTAL TONS MPA using %S X 31.	TOTAL TONS NP	TOTAL TONS NET NP	TOTAL TONS OB
OB1	245	0	3153476	587039	-2566437	99128799
OB2	87.5	0	152130.4145	375248.7073	223118	42446173.96
OB3	387	0	1762744	2849869	1087125	210901294
OB4	173.607	0	1531360.216	1138607.478	-392753	96007932.02
OB5	28.8	0	100122.816	107554.3874	7432	13098998.26
OB6	151	0	379732.7649	812038.5783	432306	65219775.42
OB7	120.22	0	390418	474299	83881	51575990
OB8	85.07	0	67154	168844	101690	42101992
OB9	95.01	0	823626	694847	-128779	54495747
OB10	81.00	0	724485	413357	-311128	36709833
OB11	169.83	0	1014933.514	839086.6177	-175846.8963	115486414
Totals	1624.04	0	10100182	8460790	-1639392	827172947.9

ACID BASE ACCOUNTING SUMMARY PARAMETERS

WITHOUT ALKALINE ADDITION

MPA = SULFUR X 31.25:

Open system

	MPA	NP	NET NP
TOTAL TONS:	10100182	8460790	-1639392
ABA PARAMETERS (TONS/THOUSAND):	12.21	10.23	-1.98
DER RATIO (NP/MPA):	0.84		
TONS/ACRE CaCO3 REQUIRED (1:1):	1009		
	DEFICIENCY		

Assessment of entire hole

MPA = SULFUR X 62.5:

Closed system

	MPA	NP	NET NP
TOTAL TONS:	20200365	8460790	-11739574
ABA PARAMETERS (TONS/THOUSAND):	24.42	10.23	-14.19
DER RATIO (NP/MPA):	0.42		
TONS/ACRE CaCO3 REQUIRED (1:1):	7229		
	DEFICIENCY		

COMBINED TOTAL TONS ALKALINE ADDITION (CaCO3): 0
EFFECTIVE NET NP CHANGE (W/ Alk. Add.): 0.00

The results above are based on a volumetric calculation, which is done by utilising the thickness of each tested unit, the expected average density for the particular unit and the area that the borehole represents. This allows accurate determination of the overall characteristics of the spoiled overburden, provided the boreholes can be regarded as representative of the area.

Table 29. Example of data input with calculated parameters.

OVERBURDEN ANALYSIS SPREAD SHEET

OPERATOR	IGS	COUNTY	
PERMIT NO.	1	TOWNS OPT	
DRILL HOLE	OB11		

THRESHOLD	AP	NP
VALUES	1	10

		TOP		BOTTOM	
TOTAL DEPTH	238.73	ACREAGE	169.83		169.83

CARBONOLITH	CARB	2580
CLAY	CLAY	3450
COAL	COAL	1800
LIMESTONE	LMSN	3670
OTHER	OTHR	3670
SANDSTONE	SNDS	3670
SHALE	SHLE	3700
SILTSTONE	SLSN	3750
SOIL	SOIL	2000
TILL	TILL	3600

ALK ADD (TONS/AC CaCO3) 0

LATITUDE ________

LONGITUDE ________

COAL SEAMS: ________

STATE PLANE ZONE

FEET (NORTH/SOUTH)

FEET (EAST/WEST)

SURFACE ELEV.(FT.)

MPA, NP -TH = With Thresholds

BOTTOM DEPTH (FT)	THICKNESS FEET	ROCK TYPE	AP	FIZZ RATING	NP	ACREAGE	UNIT WT. TONS/AC-FT	FRACTION SPOILED	TONS MPA -TH	TONS MPA	TONS NP -TH	TONS NP	NET NP TONS -TH	NET NP TONS	TONS OF OB
25.26	25.26	SOIL	0.00	1.1	0.00	169.83	2000	1.00	0.0	0.0	0.0	0.0	0.0	0.0	8581068.3
56.11	30.84	SLSN	3.98	1.10	14.06	169.83	3750	1.00	78203.9	78203.9	276184.7	276184.7	197980.9	197980.9	19641731.1
111.98	55.88	SNDS	3.82	1.10	3.18	169.83	3670	1.00	133196.2	133196.2	0.0	110804.6	-133196.2	-22391.6	34825820.1
116.21	4.23	COAL	3.81	1.10	2.86	169.83	1800	0.10	492.5	492.5	0.0	369.6	-492.5	-122.9	129384.7
125.30	9.09	COAL	17.76	1.10	16.39	169.83	1800	0.10	4934.0	4934.0	4553.3	4553.3	-380.7	-380.7	277826.0
143.97	18.67	SNDS	36.37	1.10	10.31	169.83	3670	1.00	423139.1	423139.1	120015.2	120015.2	-303123.9	-303123.9	11635873.0
174.39	30.41	SLSN	4.32	1.10	6.25	169.83	3750	1.00	83769.5	83769.5	0.0	121073.9	-83769.5	37304.4	19370090.1
203.00	28.61	SNDS	10.39	1.10	5.95	169.83	3670	1.00	185356.7	185356.7	0.0	106064.1	-185356.7	-79292.6	17832128.7
221.43	18.44	COAL	4.64	1.10	29.86	169.83	1800	0.10	2616.4	2616.4	16832.9	16832.9	14216.5	14216.5	563675.9
224.98	3.54	SNDS	45.63	1.10	36.38	169.83	3670	1.00	100775.4	100775.4	80339.0	80339.0	-20436.5	-20436.5	2208566.4
227.34	2.36	COAL	24.36	1.10	-1.10	169.83	1800	0.10	1759.3	1759.3	0.0	-79.7	-1759.3	-1839.0	72214.7
238.73	11.39	COAL	1.98	1.10	8.42	169.83	1800	0.10	690.5	690.5	0.0	2929.0	-690.5	2238.5	348034.8
						TOTAL (TONS):			1014933.5	1014933.5	497925.1	839086.6	-517008.4	-175846.9	115486413.8
						TOTAL (TONS/THOUSAND):			8.79	8.79	4.31	7.27	-4.48	-1.52	

As a comparison to the preceding section, the values for each area were again determined. The results, given below, show a good correlation with the methods used in Section 9.2.2.2. The differences are a result of the PDEP method, using primarily the "open-system" assumption. However in the overall assessment both scenarios are given. Thus for area 2 and area 3 West, the system appears to have a barely sufficient neutralisation capacity for the open system consideration and insufficient neutralisation, should the system more closely approximate a closed system. As discussed previously, spoils probably fall between these two extremes (Krantz and Hodgson, 1995 and others).

Table 30. Evaluation of NNP by area.

	DRILL HOLE	Area No.	BOTTOM ACREAGE	TONS MPA	TOTAL TONS NP	TOTAL TONS NET NP	TOTAL TONS OB
	OB1	1	245.0	3153476.0	587039.2	-2566436.9	99128798.9
	OB2	1	87.5	152130.4	375248.7	223118.3	42446174.0
Area Totals			**332.5**	**3305606.4**	**962287.9**	**-2343318.6**	**141574972.8**
	OB3	2	387.0	1762744.2	2849869.0	1087124.9	210901294.4
			387.0	**1762744.2**	**2849869.0**	**1087124.9**	**210901294.4**
Area Totals							
	OB4	3 East	173.6	1531360.2	1138607.5	-392752.7	96007932.0
	OB5	3 East	28.8	100122.8	107554.4	7431.6	13098998.3
Area Totals			**202.4**	**1631483.0**	**1246161.9**	**-385321.2**	**109106930.3**
	OB6	3 West	151.0	379732.8	812038.6	432305.8	65219775.4
	OB7	3 West	120.2	390417.6	474298.7	83881.1	51575989.6
	OB8	3 West	85.1	67153.5	168844.0	101690.4	42101992.1
	OB9	3 West	95.0	823626.1	694846.7	-128779.4	54495746.7
Area Totals			**451.3**	**1660930.0**	**2150028.0**	**489098.0**	**213393503.9**
	OB10	4	81.0	724485.2	413356.9	-311128.3	36709832.7
	OB11	4	169.8	1014933.5	839086.6	-175846.9	115486413.8
Area Totals			**250.8**	**1739418.7**	**1252443.5**	**-486975.2**	**152196246.5**

Table 31 and Table 32 show the overall assessment for the two areas apparently with excess neutralisation potential. It is clear from these tables that if closed system conditions apply, there is a deficit of neutralising material, which correlates well with the depth normalisation and weighting technique used previously.

ACID BASE ACCOUNTING SUMMARY PARAMETERS Area 2			
	WITHOUT ALKALINE ADDITION		
MPA = SULFUR X 31.25:	MPA	NP	NET NP
TOTAL TONS:	1762744	2849869	1087125
ABA PARAMETERS (TONS/THOUSAND):	8.36	13.51	5.15
DER RATIO (NP/MPA):	1.62		
TONS/ACRE CaCO3 REQUIRED (1:1):	2809	EXCESS	
	-		
MPA = SULFUR X 62.5:	MPA	NP	NET NP
TOTAL TONS:	3525488	2849869	-675619
ABA PARAMETERS (TONS/THOUSAND):	16.72	13.51	-3.20
DER RATIO (NP/MPA):	0.81		
TONS/ACRE CaCO3 REQUIRED (1:1):	1746		
	DEFICIENCY		

Table 31. Area 2 overall evaluation.

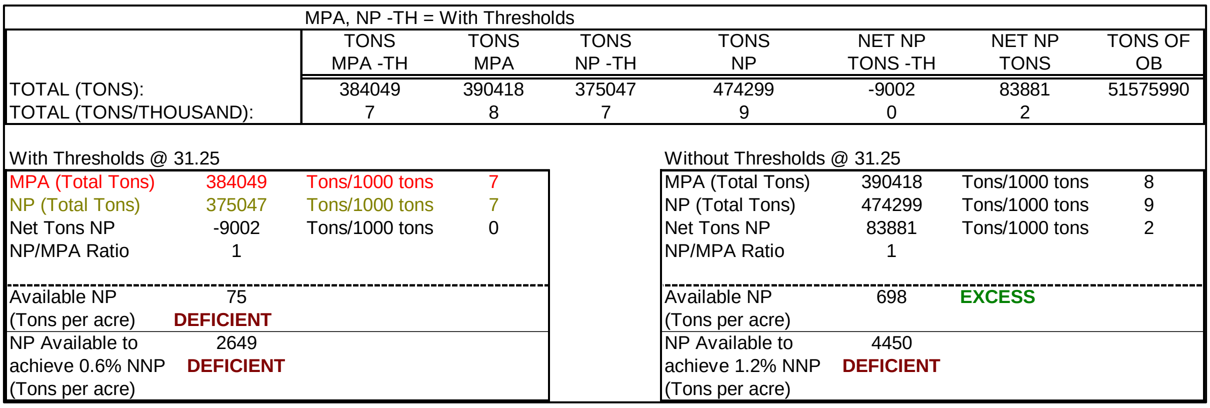
ACID BASE ACCOUNTING SUMMARY PARAMETERS for AREA 3 West			
	WITHOUT ALKALINE ADDITION		
MPA = SULFUR X 31.25:	MPA	NP	NET NP
TOTAL TONS:	1660930	2150028	489098
ABA PARAMETERS (TONS/THOUSAND):	7.78	10.08	2.29
DER RATIO (NP/MPA):	1.29		
TONS/ACRE CaCO3 REQUIRED (1:1):	1084	EXCESS	
	-		
MPA = SULFUR X 62.5:	MPA	NP	NET NP
TOTAL TONS:	3321860	2150028	-1171832
ABA PARAMETERS (TONS/THOUSAND):	15.57	10.08	-5.49
DER RATIO (NP/MPA):	0.65		
TONS/ACRE CaCO3 REQUIRED (1:1):	2597		
	DEFICIENCY		

Table 32. Area 3 West overall evaluation.

9.2.2.3.1 THRESHOLD VALUES

The concept of threshold values is an important one to consider for ABA interpretation. Threshold values for AP and NP are values defined through experience in a particular area and cognisance of ABA concepts and limitations, below which the value is disregarded in an assessment. As an illustration, in Pennsylvania the threshold values are set at 30 kg/t $CaCO_3$ for NP and 0.5% S(16.25 kg.t $CaCO_3$ AP). Summary data computed with "threshold" values include only NP and percent sulphur values that exceed 30 ppt $CaCO_3$ and 0.5 percent respectively. Samples that do not meet these criteria are assigned a value of zero and in essence are treated as chemically inert (Perry, 1998).

Use of these thresholds then disregards these very low values so that only the layers actively acidifying or neutralising are considered. Shown below is an illustration of this concept for Core Borehole 7. Thresholds were set at a conservative 5 kg/ton $CaCO_3$ for AP and 10 kg/ton $CaCO_3$ NP (compare the 16 to 30 ratio used by the PDEP). Using the conventional methods as described in the rest of this subsection (indicated as without thresholds in the figure below) we can see that for the area of influence for this borehole the net volumetric balance under open system conditions shows an excess of 698 ton of NP per acre. However, when the thresholds are considered, it can be seen that there is a deficit of 75 tons per acre, which changes the assessment.



MPA, NP -TH = With Thresholds

	TONS MPA -TH	TONS MPA	TONS NP -TH	TONS NP	NET NP TONS -TH	NET NP TONS	TONS OF OB
TOTAL (TONS):	384049	390418	375047	474299	-9002	83881	51575990
TOTAL (TONS/THOUSAND):	7	8	7	9	0	2	

With Thresholds @ 31.25

MPA (Total Tons)	384049	Tons/1000 tons	7
NP (Total Tons)	375047	Tons/1000 tons	7
Net Tons NP	-9002	Tons/1000 tons	0
NP/MPA Ratio	1		
Available NP (Tons per acre)	75 **DEFICIENT**		
NP Available to achieve 0.6% NNP (Tons per acre)	2649 **DEFICIENT**		

Without Thresholds @ 31.25

MPA (Total Tons)	390418	Tons/1000 tons	8
NP (Total Tons)	474299	Tons/1000 tons	9
Net Tons NP	83881	Tons/1000 tons	2
NP/MPA Ratio	1		
Available NP (Tons per acre)	698	**EXCESS**	
NP Available to achieve 1.2% NNP (Tons per acre)	4450 **DEFICIENT**		

Figure 124. Illustration of the use of thresholds.

9.2.2.4 LEACHING CHARACTERISTICS OF ROCK AND COAL

The core samples that were used for Acid-Base Accounting have also been used for leaching tests. The leachate from the oxidation process is used to determine the chemistry after oxidation. The result is saturation chemistries in instances where an abundance of constituents are available; otherwise the total availability of the constituents is reflected. This information is valuable in determining the long-term mine water chemistry.

Comprehensive chemical analyses are done during leaching tests to compensate for the unknown mineralogy of the spoil. Results are shown in Figure 125 to Figure 128. The discussion of these results is as follows:

- These diagrams serve to determine the likely concentration for each of the constituents at any pH under stagnant conditions. This is valuable in predicting medium- and long-term mine water concentrations. Constituents to be analysed for during future monitoring can also be determined from these presentations.
- Almost all constituents analysed for increase with a drop in the pH. The rate of increase varies, depending on the constituent's solubility and availability. Iron, for instance, increases over almost five orders of

magnitude during a drop in pH from 8 to 2.

- Many other heavy metals exhibit solubility ranges of three orders of magnitude. In acid environments, these should all be analysed for.
- Sodium, potassium and molybdenum are present in quantities below their solubility limits, thus showing no rise in concentration with a decline in the pH.
- Barium concentrations show only a scatter in their concentrations with a drop in pH. In the presence of high sulphate concentrations, barium combines with sulphate and precipitates as barite, which has very low solubility.
- Iron and sulphate exhibit an associated rise indicating that pyrite is the most common sulphide mineral present.
- Calcium and magnesium concentrations increase with a drop in pH until they are depleted from the rock and coal through reaction with the acid. Thereafter, their increase with respect to a drop in the pH is significantly reduced.
- Only two constituents analysed for did not register at the lower detection limit for the analytical instrument (an ICP-AES, axial view with ultrasonic nebuliser). These are Hg and Sb. They are therefore regarded as absent for current purposes.

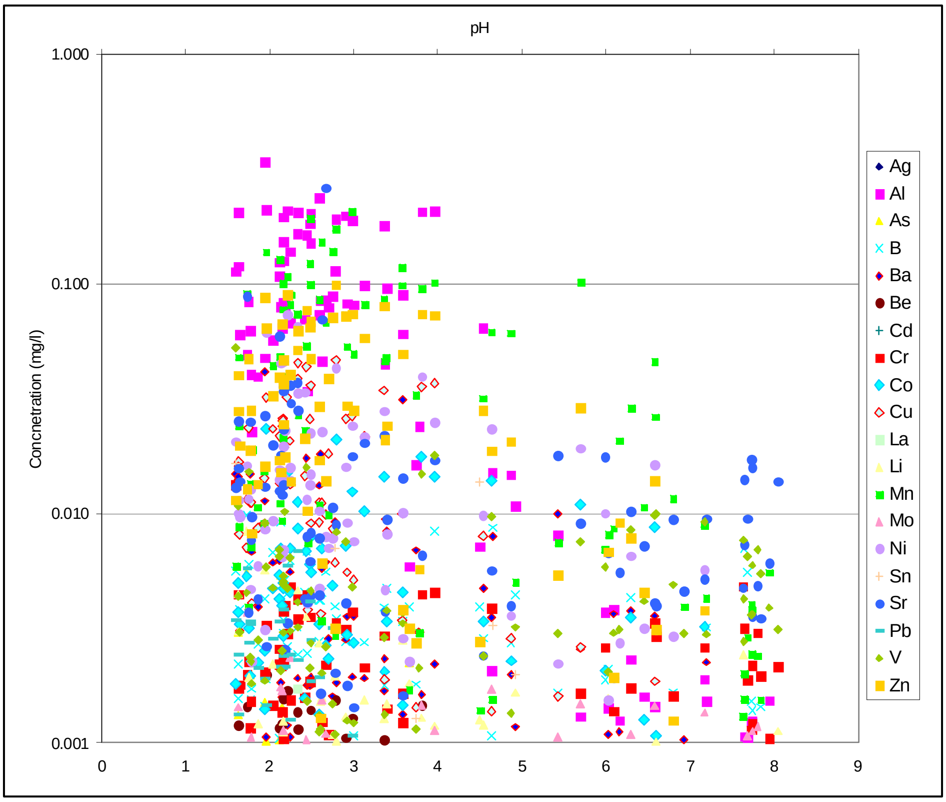


Figure 125. Concentration of macro-elements after oxidation, showing the likely composition of leachate, depending on pH.

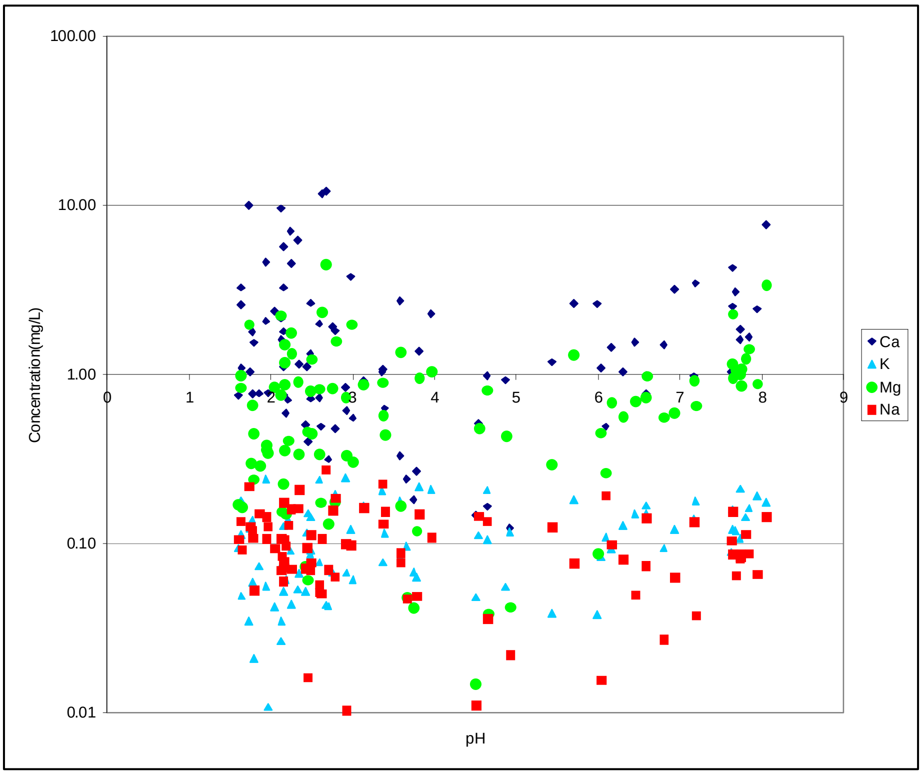


Figure 126. Concentration of micro-elements after oxidation, showing the likely composition of leachate, depending on pH.

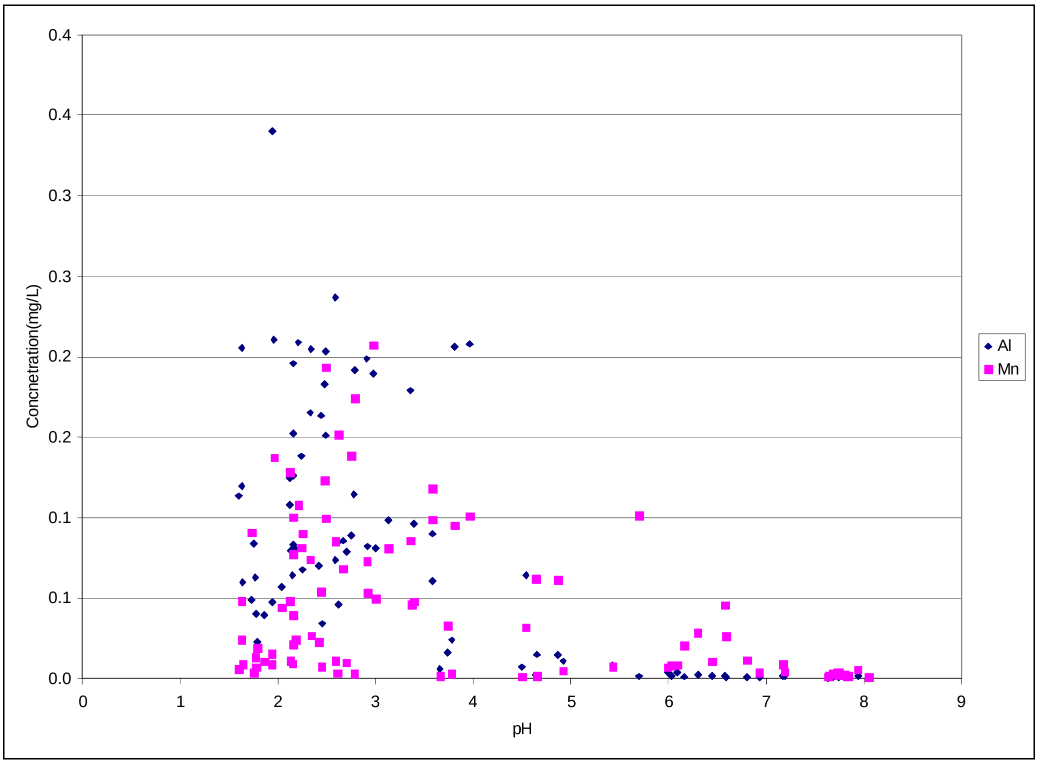


Figure 127. Concentration of Al and Mn after oxidation, showing the likely composition of leachate, depending on pH.

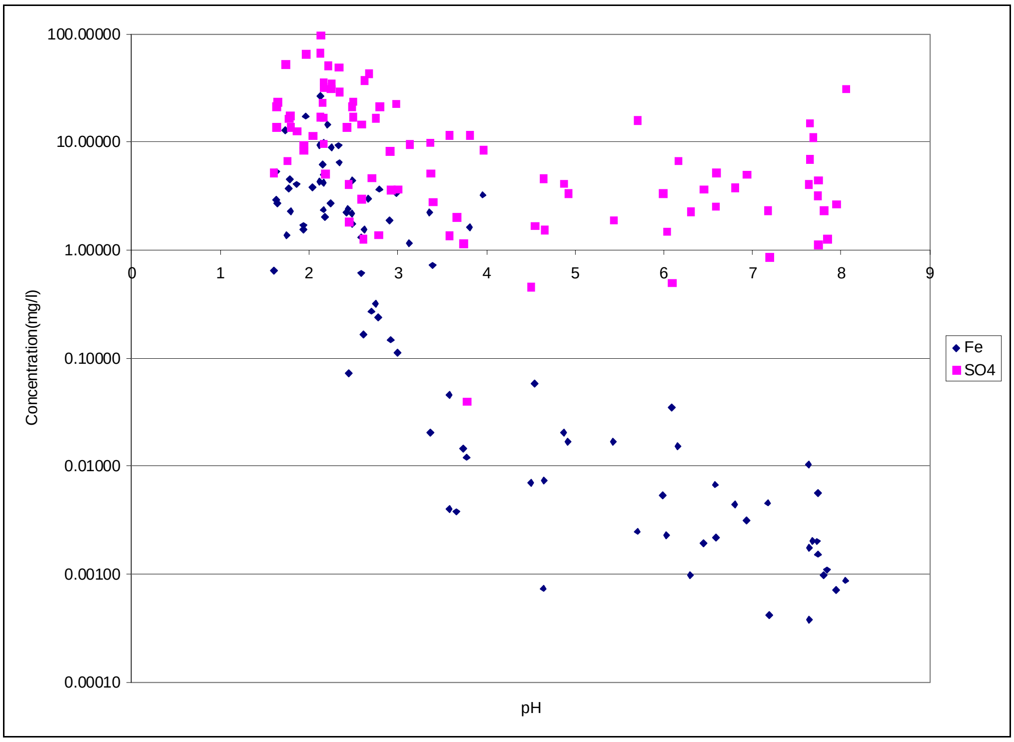


Figure 128. Concentration of Fe and SO_4 after oxidation, showing the likely composition of leachate, depending on pH.

9.2.3 CURRENT MINE WATER QUALITY

9.2.3.1 WATER QUALITY THROUGH SAMPLING

Water sampling positions for this investigation are shown in Figure 129. The analytical results are presented in Appendix 2. Samples P1 – P11 are surface water samples. This sampling was to supplement and test the validity of information from Acid-Base Accounting.

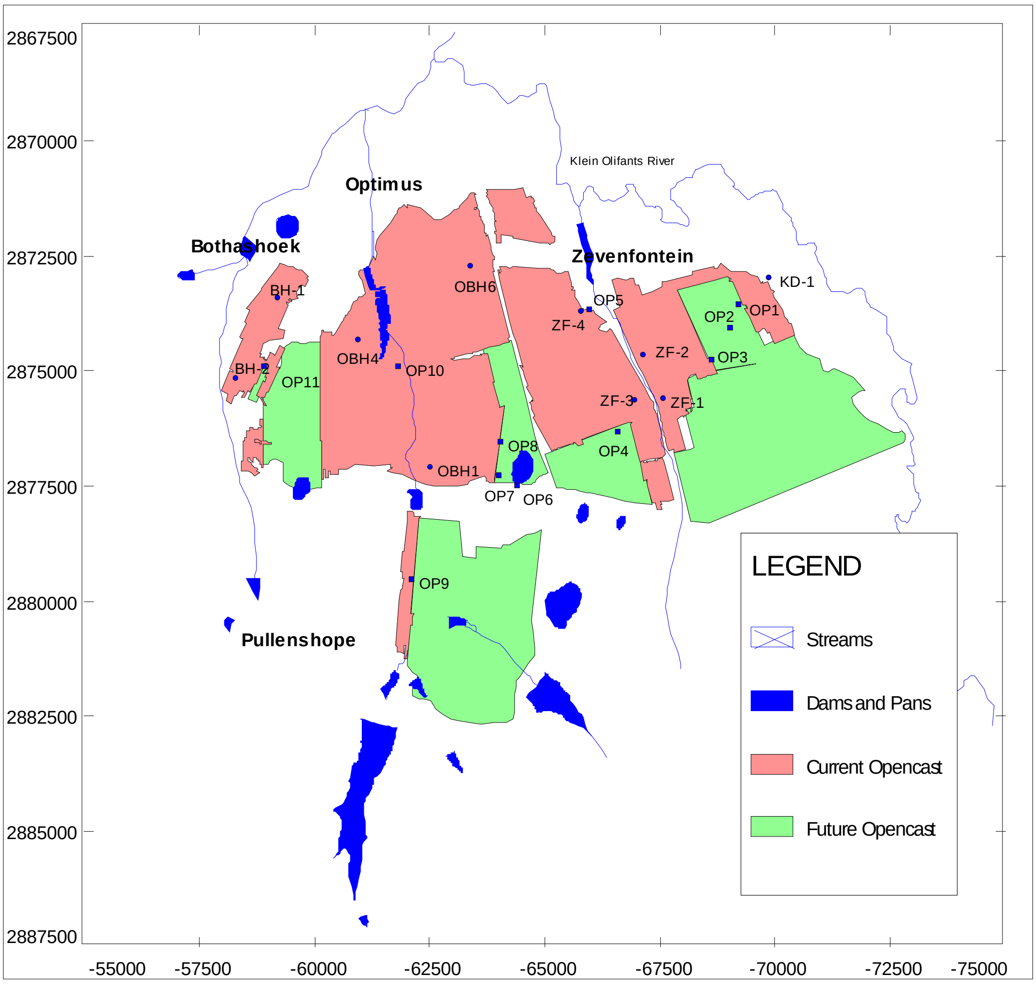


Figure 129. Localities of water samples for chemical analyses.

The following conclusions are drawn from chemical analyses of the water samples:

- Only one borehole and one surface water sample are acid. This reiterates the findings from the ABA samples, that currently the base potential exceeds the acid that has been generated.
- The major cations in the borehole samples are calcium and magnesium with either

predominant bicarbonate or sulphate anions. The former is typical of ambient water in the Karoo sediments, whilst the sulphate dominant waters show the influence of mining.

- Due to the neutral pH-values at most of the sites, the associated metals are very low. The acidic samples are the exception as is evident from the high iron and other metal values. The fact that especially iron levels are high would suggest that pyrite is the predominant form of the sulphide minerals that can undergo oxidation.
- Water from Area 1 and 4 generally has higher alkalinity than that from the rest of the mine. It appears as if calcium and magnesium carbonate currently buffer the mine from acidification.
- In boreholes ZF-1 and ZF-4 the high sulphate values and the slightly acidified pH-values suggest that oxidation is active. The lower bicarbonate values and higher sodium suggest that the carbonate species, which act as the most available buffer, have reacted and are largely depleted. Area 3 thus seems to be in the process of acidifying in places.
- The water quality in borehole KD-1 is good. This borehole is possibly drilled into unmined sediments. Its composition is not unusual for the lower Ecca sediments. Unfortunately the geological logs for all these boreholes are not available. This makes interpretation of results more tentative than should be the case.

To further characterise the observations from these results, use was made of the equilibrium program, PHREEQC (Parkhurst and Appelo, 1999), to speciate the different waters. The current samples from BH1, ZF2 and KD1 were used to speciate waters from the different areas.

- This speciation shows that the waters are generally undersaturated with respect to most species. In Area 1 and KRD (Eastern Area 3) waters, the iron and aluminium species show oversaturation.
- The Area 1 spoil water is oversaturated with respect to calcite and dolomite, confirming the high buffering capability of this area. Based on Acid-Base Accounting for Area 1, this saturation is not likely to be present over the whole of this area. Core 1, for instance, has significantly less base potential than Core 2, demonstrating the degree of areal variability.
- The acidic Area 3 sample is oversaturated with most of the iron oxide/hydroxide species, but severely undersaturated with respect to all sulphide and sulphate minerals. The implication is that sulphate values in these waters can increase significantly if there is enough pyrite to be oxidised.
- The low salinity in KD1 allows all the species to be undersaturated. The fact that this water is sodium chloride dominated and the high solubility of halite as mineral allows this continued undersaturation.

9.2.4 *IN SITU* DETERMINATION OF GROUNDWATER QUALITY

In situ measurement of water qualities was done at nine localities in the Optimum area. Parameters that have been measured are pH, EC, Redox, dissolved oxygen, temperature and depth. These *in situ* measurements have the following advantages above laboratory analyses:

- They measure true values as they are in the field.
- Errors in the sampling of water, such as mixing of waters from different horizons in the boreholes, do not occur.
- Numerous measurements can be done within a relatively short period.

The results are presented in Appendix 5.

Conclusions from these logs are as follows:

- The water temperature ranges from 18 – 24 °C. The lower of these values is regarded to be normal for groundwater in the Optimum area. Oxidation of pyrite elevates the water temperature and thus the slightly higher temperatures in some instances, such as at boreholes OBH1 and OBH6. A maximum bacterial oxidation rate for pyrite is at 30 °C.
- Specific conductance (EC at 25 °C) is a measure of the salinity in the water. Generally, the specific conductance of water in the boreholes increases with depth. The better water at the top is ascribed to recharge from rain. The spoil water is more stagnant towards the bottom, approaching equilibrium conditions. Borehole BH-1 is the only exception, with no stratification. This anomaly is explained by dynamic circulation of spoil water here, thereby introducing mixing. Water at Area 1 generally has the lowest conductance (145 – 170 mS/m), followed by Area 2 (260 – 500 mS/m) and finally Area 3 (520 – 600 mS/m). Borehole KD-1 shows contamination right at the bottom.
- Under normal circumstances, oxygen can reach a maximum concentration of 8 mg/L in water. As rain infiltrates into the ground, the dissolved oxygen reacts as part of oxidation/reduction processes, thus it is depleted. The degree of oxygen depletion in groundwater is a measure of the influx rate and mineral reactivity. In Optimum spoil water; oxygen has been almost totally depleted. This suggests restricted recharge and/or high availability of reactive material. The latter is probably the case.
- The pH of spoil water is one of the most informative parameters, on condition that it is evaluated in the right context. Several buffer levels exist, at which minerals that occur naturally buffer the water against acidification. Typical buffering levels are that of sodium carbonate species (pH 9,5 – 6,5); calcium/magnesium carbonate (pH 8,0 – 6,5); iron carbonate (pH 5,5); clay minerals (pH 5,0 – 4,5); Fe^{3+} - Fe^{2+} (pH 3,1) and the silicate minerals (pH 2,5 – 2,0). In these terms, most

of the spoil waters have pH-levels suggesting calcium/magnesium buffering. A slight tendency towards buffering by sodium carbonate species is present in some of the holes, such as at specific elevations in BH-2, ZF-4 and OBH-1. Borehole KD-1 shows unpolluted water at the top with a pH well above 7,0. Despite these variations, the important issue is that sufficient base potential still regionally exists in the spoil to keep the pH of the spoil water at approximately 6,5 for a significant period of time. Acid spots will develop where this base potential is depleted locally.

- The Redox potential is a measure of the oxidising and reducing conditions in the water. Positive values suggest oxidising conditions, whereas negative values indicate reducing conditions. The conclusion is that spoil waters at Area 1 and Area 3 are mildly oxidising and those of the Area 2 pit are reducing. It should be realised that the spoil water represents the composite result of water leaching downwards through the spoil. Above the water table in the pits, oxidising conditions are likely to exist. Once the leachate through the unsaturated zone reaches the water table, it impacts on the water chemistry below, where it is dominated by the local mineralogy of the spoil. It is therefore possible for two systems, i.e. oxidising and reducing, to co-exist above one another. The rate of reaction and leaching from the unsaturated zone into the water below will be one of the main controlling factors in determining the potential of the water in the pit.

In conclusion, hydrochemical profiling is an essential tool without which the behaviour of the spoil water in opencast mines cannot be studied. In addition to this, follow-up investigations of the unsaturated zone should be an ongoing periodic task by trenching into the spoil.

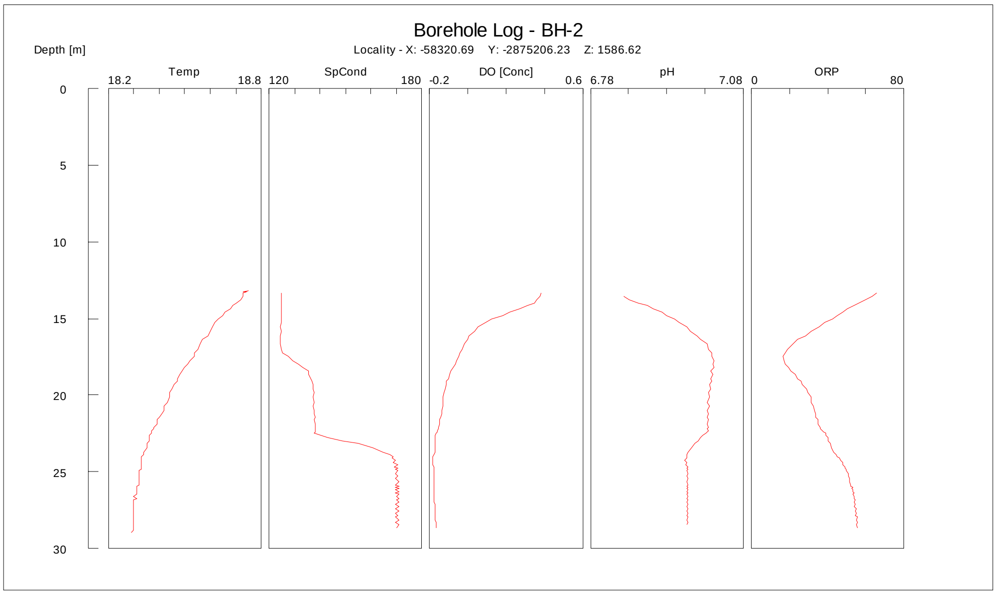


Figure 130. An example of the hydrochemical logs of spoil water at Optimum.

9.2.5 INSPECTION PITS INTO THE SPOIL

15 inspection pits were dug in the spoil at Optimum Colliery. Eight of these were dug in the western part of the Area 2 spoil and seven on the eastern side of the Area 3 spoil (Figure 131).

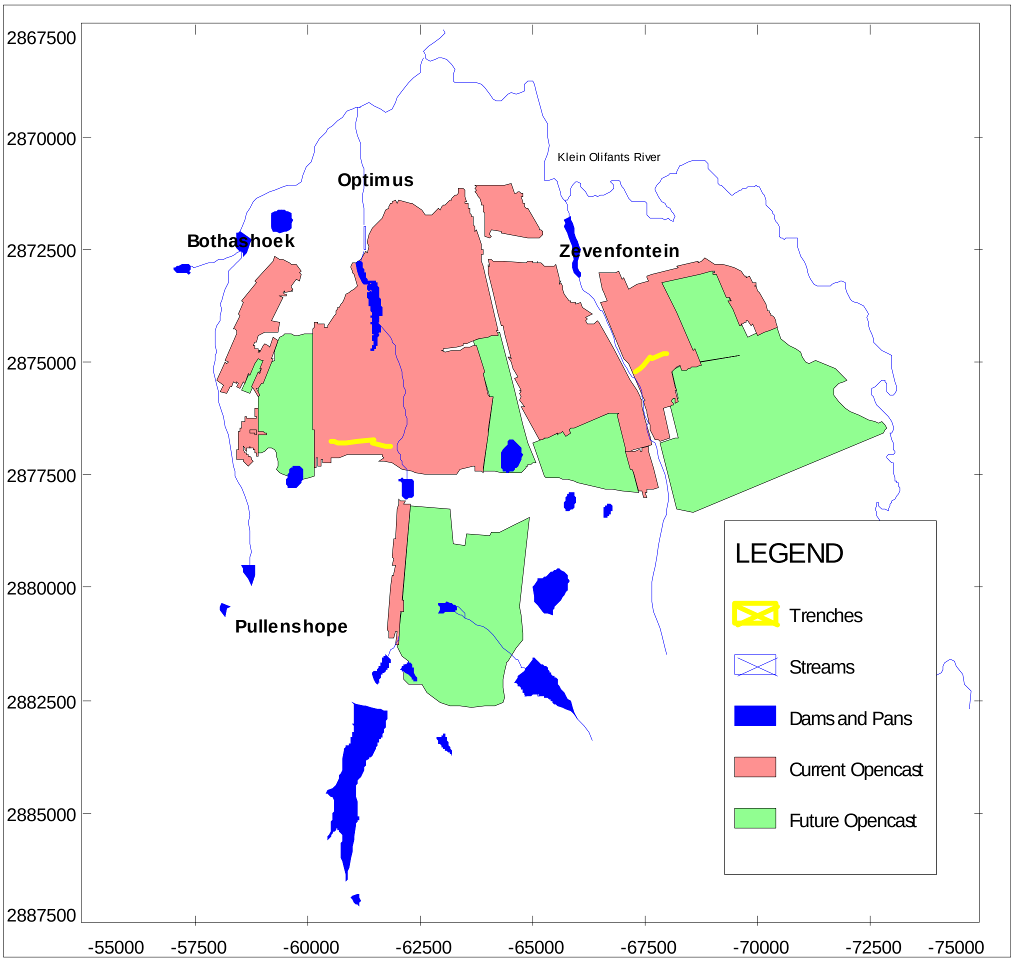


Figure 131. Localities of inspection pits at Area 2 and Area 3.

An excavator was used to dig the inspection pits to depths in excess of three metres. The aim was to evaluate the condition of the spoils at different localities at first hand and correlate this information with the hydrochemical logs from below the water table in the pits. The results from these test pits are dealt with in Section 7.3, relating to field methods in the ABATE strategy.

9.2.6 WATER AND SALT BALANCES FOR OPTIMUM

This section relies on, amongst other things, a report by Van Tonder *et al.* (1999) in which, as part of a modelling exercise, water balances for each section at Optimum Colliery have been calculated. Their results are tabled below.

Table 33. Expected post rehabilitation decant volumes [m^3/day].

PIT	AREA [HA]	MINIMUM VOL. [M^3/DAY]	AVERAGE VOL. [M^3/DAY]	MAXIMUM VOL. [M^3/DAY]
Area 2	2790	10490	11810	13540
Area 3 North	110	430	490	560
Area 3 West	1140	4270	4810	5510
Area 3 East	1940	7290	8210	9400
Area 4	1120	4220	4760	5450

Stage curves for three of the pits, up to their decanting levels, are shown in Figure 132 to 134. Surface contours and floor contours are shown in Figure 135 and Figure 136, respectively. The degree to which the floor of the pits will be flooded is shown in Figure 137. Overburden thickness is shown in Figure 138.

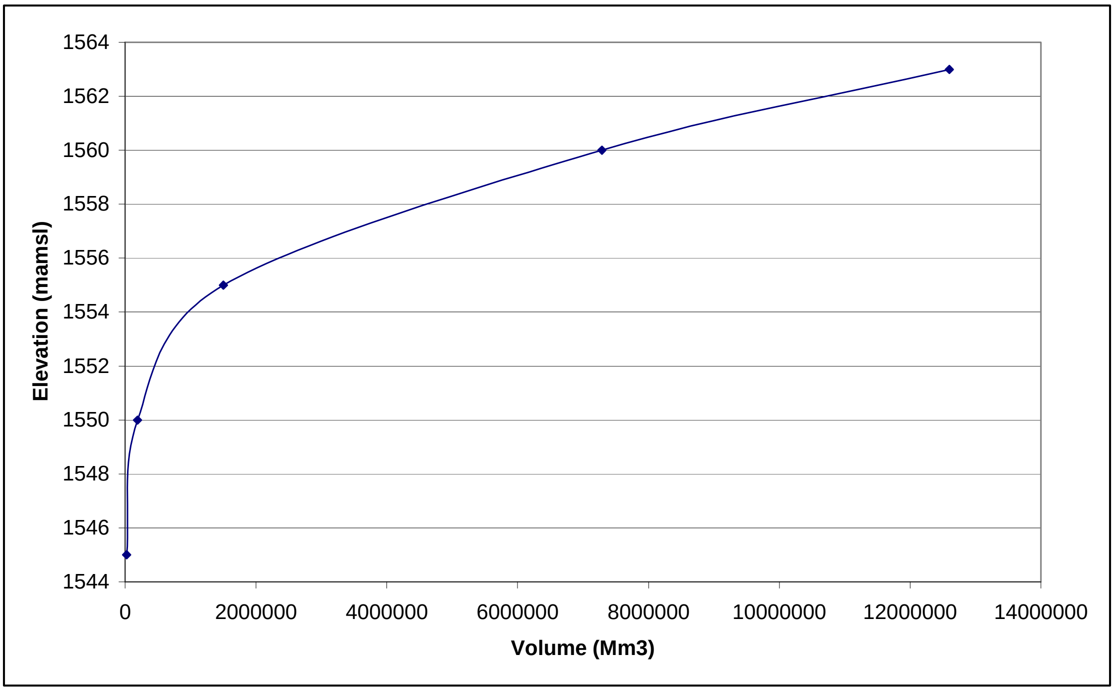


Figure 132. Stage curve for Area 2 pit, up to its decanting level.

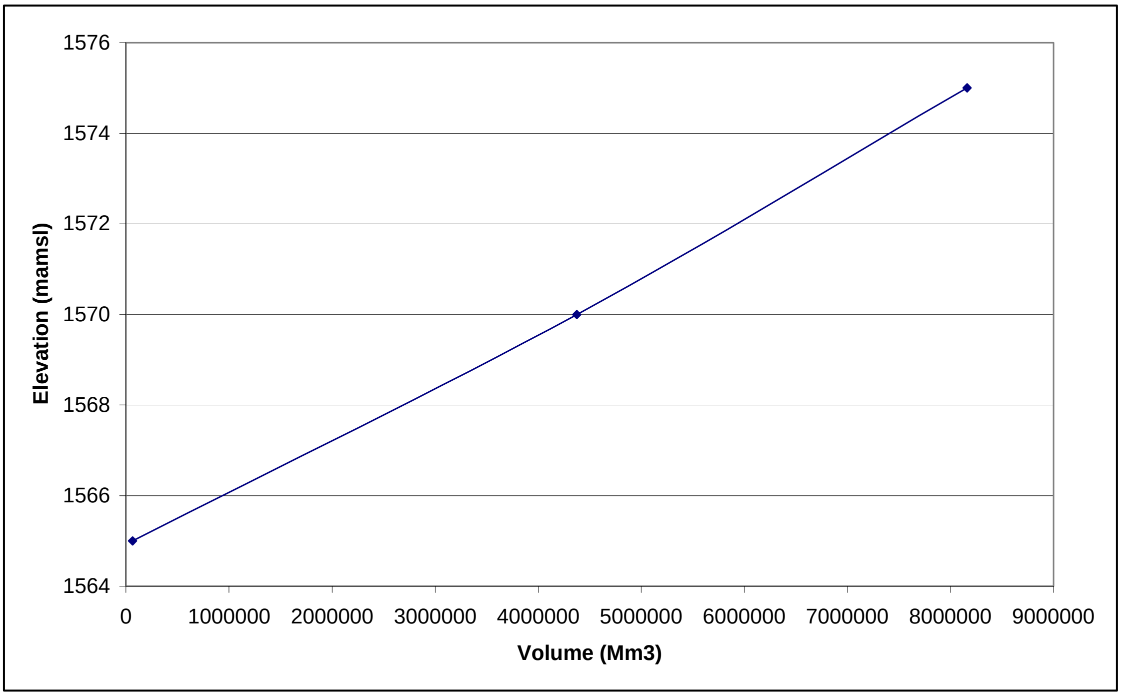


Figure 133. Stage curve for Area 3 pit, up to its decanting level.

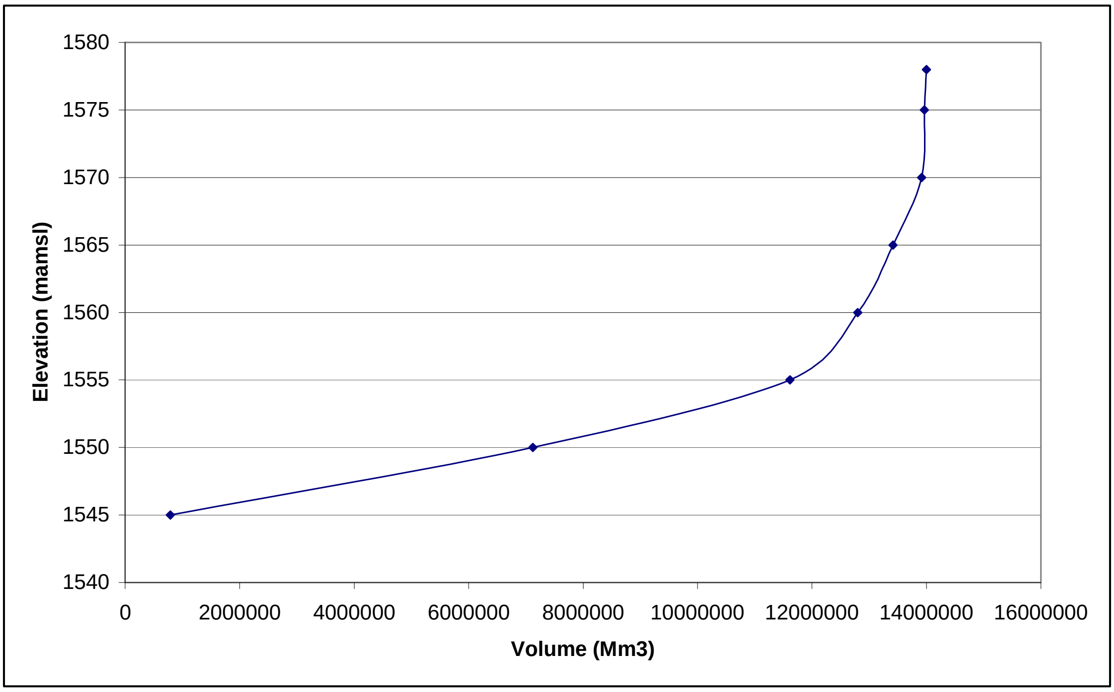


Figure 134. Stage curve for Area 4 pit, up to its decanting level.

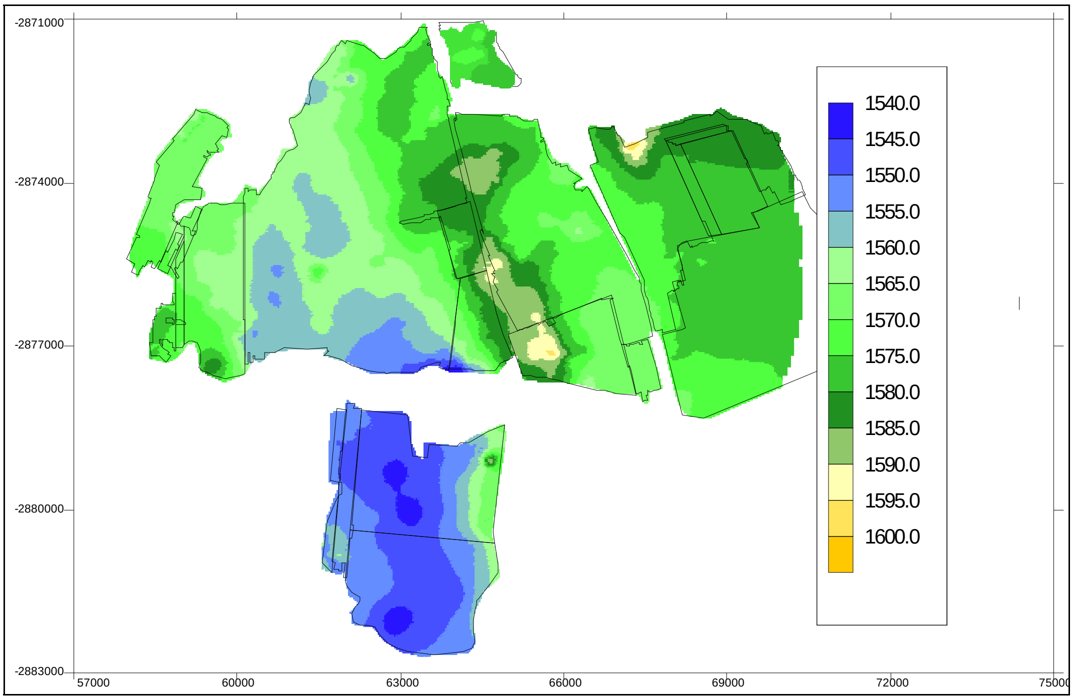


Figure 135. Coal floor contours (mamsl) in the pit areas.

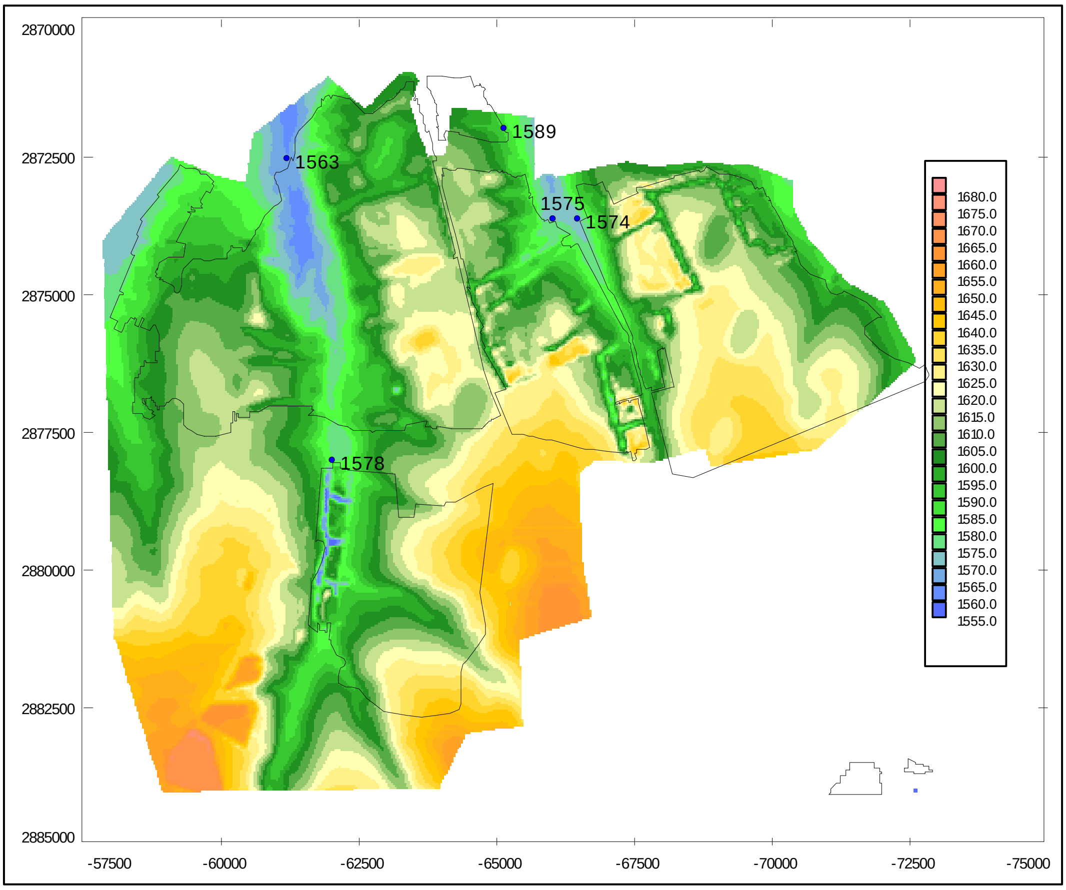


Figure 136. Current surface contours (mamsl).

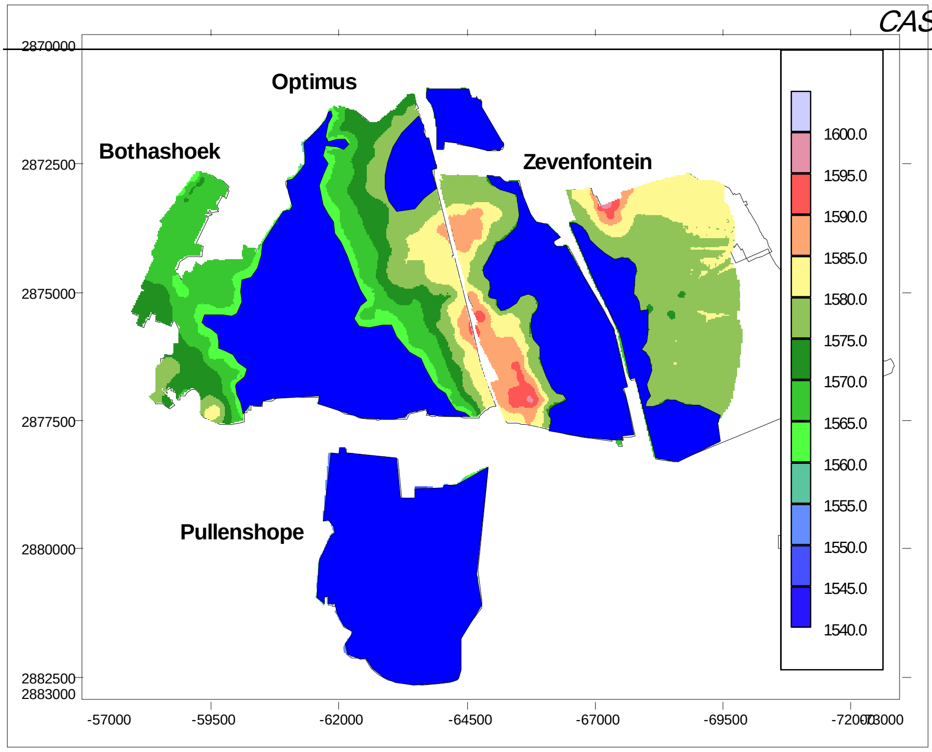


Figure 137. Coal floor contours (mamsl) and future water accumulations in the pits at their various decanting levels.

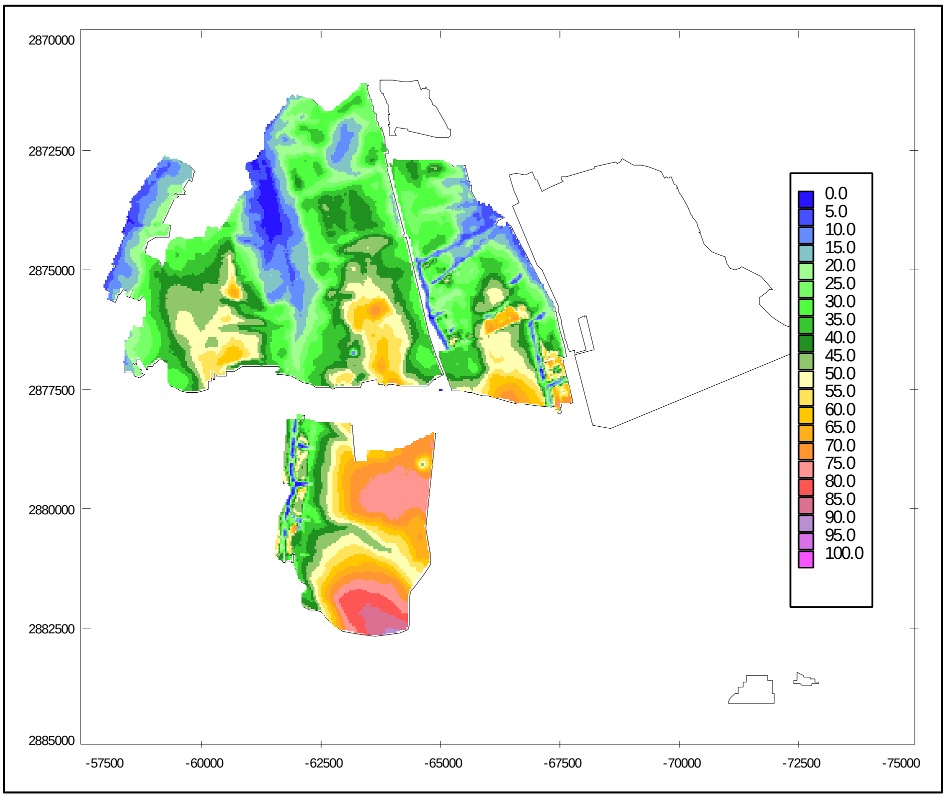


Figure 138. Spoil thickness contours (m) in mined areas and overburden thickness in future area to be mined (m).

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Conclusions from this information are as follows:

- Floor gradients and decanting levels are such that only small portions of the pit floors will eventually be flooded. This generally constitutes less than 10% of the spoil, except for the Area 4 Pit, where 16% of the spoil will be flooded.
- The volumes of influx are such that the decanting levels will be reached within less than 10 years after pit closure. In the case of the Area 2 Pit, water has been decanting for many years.
- The expected long-term salinity of the pit waters can be calculated from the current reaction rate, which generates 7 kg/ha/d SO_4. This yields a long-term average concentration of sulphate in the pit water of 1700 mg/L. In this respect, it should be remembered that Van Tonder (IGS) calculated the potential long-term influx into the pits based on a calibration for the Area 2 Pit. Any deviance of the recharge rate for the other pits will impact on the eventual water quality. Higher concentrations are for instance expected at Area 3 because the stream water does not enter into this pit, as is the case at Area 2.

9.2.7 REACTION SEQUENCE AND FUTURE CHEMISTRIES

Based on all previous information, the interpolated sequence of chemical changes during and after mining at Optimum Colliery is as follows:

- Pyrite oxidation commenced when mining commenced. At first, this oxidation is primarily of a chemical nature. The pH of the mine water is initially in the range of 7,5 – 8,5, until available alkalinity within the spoil and water has been leached or depleted locally. Depletion occurs within a few years after mining commences. The salinity of the spoil water will rise during this period and eventual salt concentrations will depend on the residence time of the water in the pit. The ratio of sulphate versus total other salts is in the order of 1:1.
- Gradually, the pH of the water drops to about 6,5. At this level, calcium/magnesium carbonate buffers the mine water against immediate further acidification. Typical water chemistries for this phase are listed in Table 34, for low, average and high residence regimes. Low residence regimes are typically found where water is drained from the pit by pumpage, for instance. High residence regimes are in low-lying areas, where water accumulates. Several such low-lying areas exist. These can be identified from the floor contours and current water accumulations.
- Saturation conditions exist under stagnant situations. In reality, true stagnant water never exists in opencast pits. A through flow of water is always present, no matter how little. It is commonly found in the so-called stagnant areas at Optimum Colliery that the upper portion of stagnant water improves in quality during summer, when

recharge from rainfall is high. After the winter, this water has mixed due to the dispersion through slow regional flow within the pit. The high residence chemistry in Table 34 refers to a recharge component of 14% of the annual rainfall. At recharge levels below this figure, the pit water will become saturated in sulphate and gypsum will precipitate, as long as the pH remains at 6,5.

- Laboratory tests have shown that the calcium/magnesium carbonate content of the spoil varies greatly across the mine. A few areas exist where these two minerals have been leached from the rock. Here, acidification proceeds without intermediate buffering. Acid pockets have thus started to appear in the spoil. General and regional acidification will not occur for many years, because the remainder calcium/magnesium carbonate neutralising potential will first have to be depleted.
- After the calcium/magnesium carbonate has been exhausted, the pH will drop (Table 35). Calcium and magnesium levels in the pit water will also drop and sulphate levels will rise. Sulphate levels of 4 500 mg/L or higher are not uncommon at this stage, because of accelerated pyrite oxidation at low pH-levels. Heavy metals will dissolve in the water. Constituents of concern are aluminium, manganese and iron, followed by many others, such as arsenic, cadmium, cobalt, copper, lead, nickel and zinc (see Figures 12 – 15).

Table 34. Predicted mine water chemistries for various scenarios during and after mining.

Parameter	Low residence regimes, alkaline	Average alkaline pit water	High residence, regimes, alkaline	High residence pH 3,0	High residence pH 2,3
pH	6.5	6.5	6.5	3.5	2.5
EC mS/m	200	340	480	600	800
Ca mg/L	200	380	500	150	100
Mg mg/L	125	225	310	85	60
Na mg/L	30	38	45	45	45
K mg/L	7	10	12	12	12
Malk mg/L	60	60	60	0	0
Cl mg/L	25	32	40	40	40
SO4 mg/L	1000	1825	2500	3500	4500
F mg/L	1	1.3	1.6	1.6	1.6
Al mg/L	0	0	0	10	30
Mn mg/L	1	1.5	2	4	8
Fe mg/L	0.5	1	2	200	500

9.2.8 CONCLUSIONS

The following conclusions are drawn from this investigation:

Opencast mining at Optimum Colliery has been ongoing for more than 20 years. In this time about half of the Opencast areas have been mined.

The fact that acid production through pyrite oxidation has been ongoing has been known for many years. To date, this acid has mostly been neutralised by the natural base potential of the spoil. Only isolated areas of spoil acidification exist.

Acid-Base Accounting has shown that significant base potential is present in the spoil.

This base potential is sufficient to buffer spoil water from acidification for many years. Over the long term, the base potential is, however, insufficient in about two thirds of the cases investigated (89 samples).

Through trenching into the upper 3 m of the spoil, the conclusion is that all spoil, no matter whether it was disposed of a few years ago or more than 20 years ago, is in the process of chemical alteration through oxidation. The pH of the spoil has dropped from the initial 7,5 - 8,5 to 6,0 - 7,0. In isolated instances, pH-values as low as 3,2 have been recorded. Acidification is currently patchy, starting in areas of low natural base potential. Several such areas currently exist at Optimum Colliery. From these areas, the acidity spreads vertically into the spoil below, thus impacting even on spoil below the water table in the pits.

Spoil at the pH-range of 6,0 - 7,0 is buffered by calcium/magnesium carbonate in the spoil. The pH will remain at this level until this buffering effect is depleted. Leaching and mineralogical tests have shown that the next level of buffering will be at 3,1 through the conversion of Fe^{3+} to Fe^{2+}. Thereafter the pH will drop to 2,0 - 2,5 where buffering will be through silicates in the spoil. It is noteworthy that siderite which buffers at a pH of 5,5 and the clay minerals (at 4,5) are considered to have negligible potential to buffer the spoil against acidification at Optimum.

At these low pH-levels (<5,0) heavy metals will be mobilised from the spoil. Solubility curves for most heavy metals have been determined and are included in this report. Heavy metal can be removed from the acid water through lime addition. At a pH of 7,0, only manganese will remain in significant quantities. To remove the latter, sufficient lime to raise the pH above 9,5 will have to be added. At this high pH, many complementary reactions will occur, such as precipitation of magnesium hydroxide, calcium sulphate and calcium carbonate. It is not usually economical to lime the mine water to this extent for the sole purpose of precipitating the minerals.

It is considered inevitable that the spoil water at Optimum Colliery will eventually acidify to the extent that acid water will be the dominant type. The time span over which this will happen cannot be predicted cost-effectively, due to the complex and heterogeneous nature of the spoil. Hundreds of observation points, scattered over the whole of the mined area, are required to evaluate the system on a statistically representative basis. It is not worth the money to narrow down on the time scale for acidification. Acidification has already commenced. Through careful observation of the complete spoil water chemistry and not just the pH, trends should be recognised. This will provide invaluable information on the time scale for regional acidification.

In terms of the expected future salt load, a sulphate generation rate of 50 t/d SO_4 for a mine of 7 300 ha is suggested in this report. This will result in an average SO_4 concentration of 1700 mg/L. In areas of lesser water through flow, such as the Area 3 pit for instance, the sulphate concentration is expected to rise to saturation levels. At a pH of 6,5 and a calcium value of 250 - 380, the sulphate concentration here will be in the range of 1825 - 3300 mg/L. At pH-levels below 3,0, sulphate levels well in excess of 4000 mg/L could be expected.

The overall conclusion is that eventual acidification of the spoil water at Optimum Colliery is unavoidable. The scale of mining is simply too large and mining has progressed too far to make a meaningful and permanent change at this late stage. The mine should provide for neutralisation of the mine water in their closure plan. Controlled flood release of treated water or irrigation is still the preferred option to dispose of this water. The final solution in terms of water management at Optimum Opencast will, without any doubt, lie in a combination of actions based on well-established and proven technologies.

9.3 ARTHUR TAYLOR COLLIERY

The rehabilitated spoils area at Tavistock's Arthur Taylor Colliery were investigated using different approaches. The spoils have been fully rehabilitated by standard soil management, slope control and water management. The rehabilitation of the section is discussed in detail by Surmon (1996).

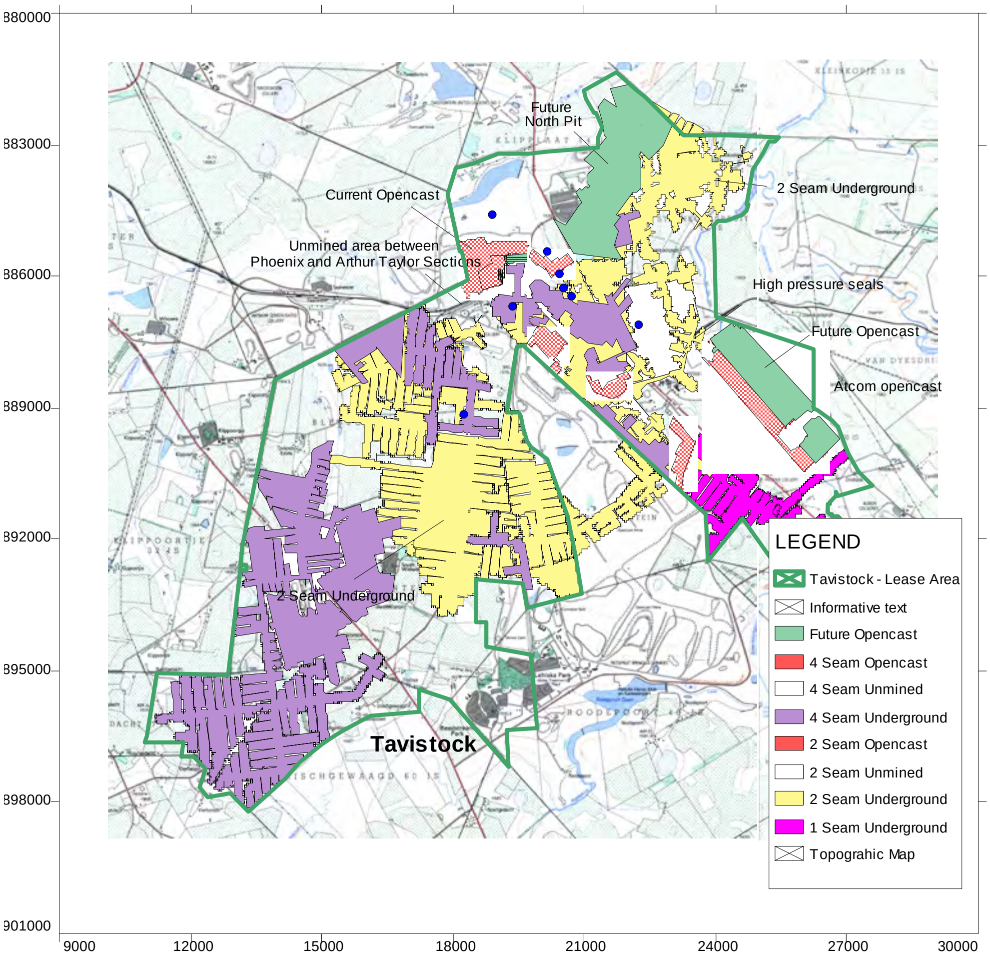


Figure 139. Locality plan for Arthur Taylor Colliery.

Acid-Base Accounting has been done on several samples from Tavistock Colliery. In the tables below, the ABA results from samples collected at the various sections and from the discards at ATC are given. These results show a clear potential for acidification to occur.

Table. 35. Initial pH and solubilised elements.

Water soluble constituents in kg/t						
Sample numbers	**Initial pH**	**Al**	**B**	**Ba**	**Ca**	**Cd**
ATC-1 Drewboy discard	8.74	0.00064	0.02560	0.00263	0.24000	0.00000
ATC-2 Cyclone discard	8.63	0.00093	0.02210	0.00149	0.22000	0.00000
ATC1-2-4 Seam	8.32	0.00000	0.00860	0.00380	0.38000	0.00000
ATC2-2-4seam	8.57	0.00110	0.00820	0.00330	0.43000	0.00000
	Cr	**Co**	**Cu**	**Fe**	**K**	**Mg**
ATC-1 Drewboy discard	0.00000	0.00000	0.00003	0.00033	0.02500	0.05800
ATC-2 Cyclone discard	0.00000	0.00000	0.00003	0.00036	0.02800	0.05400
ATC1-2-4 Seam	0.00000	0.00000	0.00020	0.00000	0.03000	0.09000
ATC2-2-4seam	0.00000	0.00000	0.00010	0.00010	0.02700	0.06400
	Mn	**Na**	**Ni**	**Sr**	**Zn**	**SO4**
ATC-1 Drewboy discard	0.00020	0.01690	0.00008	0.00620	0.00045	0.51000
ATC-2 Cyclone discard	0.00032	0.01850	0.00000	0.00310	0.00014	0.49000
ATC1-2-4 Seam	0.00040	0.08000	0.00020	0.00670	0.00210	0.50000
ATC2-2-4seam	0.00050	0.07000	0.00020	0.00500	0.00120	0.62000

Table. 36. Oxidised pH and solubilised elements.

Constituents released during complete oxidation in kg/t						
Samples	**Final pH**	**Al**	**B**	**Ba**	**Ca**	**Cd**
ATC-1 Drewboy discard	3.43	0.0745	0.0000	0.0000	6.1400	0.0001
ATC-2 Cyclone discard	2.07	0.1131	0.0000	0.0000	4.9500	0.0002
ATC1-2-4 Seam	3.28	0.0460	0.0134	0.0000	7.7800	0.0000
ATC2-2-4seam	3.29	0.4690	0.0128	0.0000	7.6700	0.0000
	Cr	**Co**	**Cu**	**Fe**	**K**	**Mg**
ATC-1 Drewboy discard	0.0013	0.0060	0.0119	3.5197	0.0400	3.2420
ATC-2 Cyclone discard	0.0009	0.0041	0.0150	13.1996	0.1120	4.1260
ATC1-2-4 Seam	0.0012	0.0019	0.0085	4.9499	0.0000	2.9100
ATC2-2-4seam	0.0009	0.0018	0.0103	5.1699	0.0000	2.0360
	Mn	**Na**	**Ni**	**Sr**	**Zn**	**SO4**
ATC-1 Drewboy discard	0.119	0.083	0.015	0.048	0.015	25.490
ATC-2 Cyclone discard	0.125	0.062	0.011	0.035	0.015	54.210
ATC1-2-4 Seam	0.056	0.000	0.007	0.034	0.009	21.760
ATC2-2-4seam	0.065	0.000	0.004	0.032	0.012	23.680

Table. 37. ABA calculations for tested samples.

Acid/base calculations							
Samples	**Initial pH**	**Final pH**	**Acid (Open)**	**Acid (Closed)**	**Base**	**NNP (Open)**	**NNP (Closed)**
ATC-1 Drewboy discard	8.74	3.43	24.5	48.9	65.9	41.5	17.0
ATC-2 Cyclone discard	8.63	2.07	52.0	104.1	46.4	-5.6	-57.6
ATC1-2-4 Seam	8.32	3.28	20.9	41.8	38.3	17.4	-3.5
ATC2-2-4seam	8.57	3.29	22.7	45.5	37.7	15.0	-7.8

As far as the opencast sections are concerned, acid-base and leaching tests have been performed on two complete cores. These results are given below. Borehole AB1 is closest to the area where test pits (see next section) were dug in the spoils.

Table 38. Acid/base accounting on core samples from two boreholes at Tavistock Colliery.

Hole No.	Top m	Bottom m	Lithology	Initial pH	Final pH	Acid (Open) kg/t	Acid (Closed) kg/t	Base kg/t	NNP (Open) kg/t	NNP (Closed) kg/t
AB1	0.00	9.00	SOIL	8.07	5.60	2.27	4.53	3.14	0.88	-1.39
AB1	9.00	12.65	SNDS	7.67	6.57	0.43	0.86	1.48	1.05	0.62
AB1	12.65	16.31	SNDS	7.36	3.50	8.72	17.44	9.57	0.85	-7.88
AB1	16.31	19.70	SNDS	7.05	3.87	9.77	19.54	15.85	6.08	-3.70
AB1	19.70	24.18	SHLE	7.17	7.02	6.33	12.66	10.89	4.56	-1.77
AB1	24.18	25.33	4 Seam U	8.42	2.30	36.20	72.41	10.72	-25.48	-61.68
AB1	25.33	26.70	SNDS	7.62	2.29	16.48	32.96	0.72	-15.76	-32.24
AB1	26.70	30.50	4 Seam	4.65	2.20	30.15	60.29	1.87	-28.27	-58.42
AB1	30.50	33.00	SNDS	6.70	2.79	3.43	6.86	-0.07	-3.50	-6.93
AB1	33.00	33.36	3 Seam	6.27	2.14	26.81	53.62	-0.63	-27.44	-54.25
AB1	33.36	36.05	SNDS	9.32	8.15	10.07	20.15	82.89	72.82	62.75
AB1	36.05	37.21	SHLE	8.39	4.00	5.36	10.73	9.12	3.75	-1.61
AB1	37.21	41.79	SLSN	9.13	7.58	5.10	10.21	16.58	11.48	6.37
AB1	41.79	45.10	SHLE	8.43	3.41	5.99	11.98	5.14	-0.85	-6.84
AB1	45.10	46.76	2 Seam	8.08	2.33	61.99	123.99	30.70	-31.30	-93.29
AB1	46.76	50.32	2 Seam	8.51	2.12	10.70	21.40	11.76	1.06	-9.64
AB1	50.32	51.41	DWKA	8.47	2.72	5.22	10.44	1.09	-4.13	-9.35
AB2	0.00	9.72	SNDS	8.92	9.07	0.84	1.69	192.69	191.84	191.00
AB2	9.72	12.57	SNDS	9.28	5.61	0.54	1.08	3.76	3.22	2.68
AB2	12.57	20.55	SNDS	9.65	6.56	0.54	1.08	11.82	11.28	10.74
AB2	20.55	23.64	SNDS	9.37	6.56	1.08	2.15	6.71	5.64	4.56
AB2	23.64	24.83	5 Seam	8.36	2.10	64.93	129.85	12.62	-52.30	-117.23
AB2	24.83	29.04	SHLE	5.17	3.00	35.34	70.68	6.47	-28.87	-64.21
AB2	29.04	35.45	SNDS	8.20	3.47	40.52	81.04	33.63	-6.88	-47.40
AB2	35.45	39.57	SNDS	8.44	5.23	8.27	16.54	8.26	-0.01	-8.29
AB2	39.57	43.68	SHLE	7.91	7.02	9.15	18.29	13.27	4.13	-5.02
AB2	43.68	50.29	SHLE	7.90	7.50	7.04	14.08	14.70	7.66	0.63
AB2	50.29	52.22	4 Seam U	8.19	2.11	41.62	83.25	31.02	-10.60	-52.22
AB2	52.22	52.58	SHLE	8.73	5.47	1.80	3.61	7.85	6.05	4.24
AB2	52.58	55.25	4 Seam	8.18	2.42	40.29	80.59	42.22	1.93	-38.36
AB2	55.25	58.17	SHLE	8.57	2.51	3.76	7.53	2.05	-1.72	-5.48
AB2	58.17	58.67	3 Seam	8.00	2.58	1.73	3.46	0.91	-0.82	-2.55
AB2	58.67	61.74	SNDS	8.23	7.07	3.21	6.42	8.58	5.37	2.16
AB2	61.74	62.50	SHLE	7.93	4.18	2.43	4.85	5.71	3.28	0.85
AB2	62.50	67.96	SHLE	8.13	7.46	3.20	6.40	14.80	11.60	8.40
AB2	67.96	71.30	SHLE	7.99	5.01	2.24	4.47	11.79	9.55	7.32
AB2	71.30	74.54	2 Seam	8.61	7.22	6.47	12.94	51.28	44.81	38.34
AB2	74.54	78.05	2 Seam	8.24	6.06	32.88	65.75	55.81	22.93	-9.94
AB2	78.05	80.00	DWKA	8.81	2.58	16.01	32.02	9.99	-6.02	-22.03

Table. 39. Solubilised elements from on core samples from two boreholes at Tavistock Colliery.

Hole No.	Top	Bottom	Lithology	Ag	Al	As	B	Ba	Be	Ca	Cd	Cr	Co	Cu	Fe	Hg	K
	m	m		kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t
AB1	0.00	9.00	SOIL	0.0221	0.0029	0.0000	0.0145	0.0037	0.0000	0.5978	0.0000	0.0003	0.0028	0.0002	0.0050	0.0000	0.1120
AB1	9.00	12.65	SNDS	0.0028	0.0097	0.0000	0.0095	0.0022	0.0000	0.1393	0.0000	0.0003	0.0004	0.0001	0.0141	0.0000	0.0550
AB1	12.65	16.31	SNDS	0.0230	0.1390	0.0000	0.0071	0.0003	0.0005	1.1055	0.0003	0.0016	0.0094	0.0170	0.6496	0.0000	0.1870
AB1	16.31	19.70	SNDS	0.0137	0.2039	0.0000	0.0071	0.0003	0.0005	1.8289	0.0003	0.0024	0.0077	0.0262	1.0037	0.0000	0.1576
AB1	19.70	24.18	SHLE	0.0015	0.0006	0.0000	0.0033	0.0000	0.0000	1.3105	0.0000	0.0015	0.0005	0.0001	0.0032	0.0000	0.1364
AB1	24.18	25.33	4 Seam U	0.0000	0.1262	0.0000	0.0282	0.0006	0.0005	4.3490	0.0002	0.0030	0.0043	0.0179	11.7600	0.0000	0.1180
AB1	25.33	26.70	SNDS	0.0017	0.1760	0.0000	0.0067	0.0000	0.0002	0.6800	0.0001	0.0006	0.0034	0.0102	3.1880	0.0000	0.0908
AB1	26.70	30.50	4 Seam	0.0000	0.1393	0.0000	0.0182	0.0044	0.0003	2.0942	0.0002	0.0010	0.0043	0.0143	6.7723	0.0000	0.0354
AB1	30.50	33.00	SNDS	0.0039	0.1333	0.0000	0.0013	0.0024	0.0002	0.4736	0.0002	0.0009	0.0088	0.0065	0.8639	0.0000	0.1054
AB1	33.00	33.36	3 Seam	0.0005	0.0713	0.0011	0.0149	0.0009	0.0010	0.7035	0.0004	0.0041	0.0408	0.0252	6.8822	0.0000	0.0611
AB1	33.36	36.05	SNDS	0.0000	0.0009	0.0000	0.0000	0.0010	0.0000	3.4067	0.0000	0.0009	0.0001	0.0003	0.0108	0.0000	0.1163
AB1	36.05	37.21	SHLE	0.0079	0.2691	0.0000	0.0058	0.0075	0.0012	1.2021	0.0006	0.0063	0.0262	0.0451	4.1180	0.0000	0.2485
AB1	37.21	41.79	SLSN	0.0002	0.0007	0.0000	0.0000	0.0004	0.0000	1.1336	0.0000	0.0014	0.0003	0.0000	0.0033	0.0000	0.1692
AB1	41.79	45.10	SHLE	0.0027	0.2225	0.0000	0.0048	0.0084	0.0012	1.1562	0.0008	0.0051	0.0232	0.0507	4.8325	0.0000	0.2316
AB1	45.10	46.76	2 Seam	0.0000	0.0891	0.0000	0.0131	0.0010	0.0001	9.7950	0.0002	0.0004	0.0022	0.0097	9.5099	0.0000	0.0000
AB1	46.76	50.32	2 Seam	0.0000	0.0562	0.0000	0.0000	0.0077	0.0001	3.0498	0.0002	0.0005	0.0010	0.0000	2.8000	0.0000	0.0073
AB1	50.32	51.41	DWKA	0.0004	0.2547	0.0000	0.0000	0.0007	0.0003	0.4660	0.0002	0.0008	0.0028	0.0251	0.4620	0.0000	0.0860
AB2	0.00	9.72	SNDS	0.0000	0.0031	0.0000	0.0026	0.0009	0.0003	2.4433	0.0000	0.0007	0.0000	0.0007	0.0046	0.0000	0.0870
AB2	9.72	12.57	SNDS	0.0000	0.0045	0.0000	0.0025	0.0006	0.0000	0.7839	0.0000	0.0004	0.0000	0.0005	0.0016	0.0000	0.0992
AB2	12.57	20.55	SNDS	0.0000	0.0019	0.0000	0.0016	0.0000	0.0000	1.5594	0.0000	0.0007	0.0000	0.0002	0.0003	0.0000	0.2544
AB2	20.55	23.64	SNDS	0.0000	0.0043	0.0000	0.0014	0.0000	0.0000	0.8663	0.0000	0.0009	0.0005	0.0004	0.0011	0.0000	0.2335
AB2	23.64	24.83	5 Seam	0.0000	0.1712	0.0000	0.0052	0.0019	0.0000	7.8324	0.0000	0.0009	0.0027	0.0083	15.7515	0.0000	0.1086
AB2	24.83	29.04	SHLE	0.0000	0.2629	0.0000	0.0046	0.0010	0.0001	4.3830	0.0000	0.0021	0.0099	0.0116	0.9320	0.0000	0.0358
AB2	29.04	35.45	SNDS	0.0000	0.1957	0.0000	0.0015	0.0024	0.0002	11.9319	0.0000	0.0012	0.0046	0.0021	0.0263	0.0000	0.2000
AB2	35.45	39.57	SNDS	0.0000	0.1137	0.0000	0.0011	0.0013	0.0000	1.4260	0.0000	0.0013	0.0064	0.0056	0.0051	0.0000	0.2324
AB2	39.57	43.68	SHLE	0.0000	0.0018	0.0000	0.0017	0.0025	0.0000	1.5797	0.0000	0.0027	0.0014	0.0010	0.0007	0.0000	0.1943
AB2	43.68	50.29	SHLE	0.0000	0.0011	0.0000	0.0031	0.0020	0.0000	1.7341	0.0000	0.0048	0.0000	0.0002	0.0003	0.0000	0.1319
AB2	50.29	52.22	4 Seam U	0.0000	0.1415	0.0026	0.0045	0.0126	0.0000	14.2330	0.0000	0.0027	0.0022	0.0176	11.7509	0.0000	0.0970
AB2	52.22	52.58	SHLE	0.0000	0.0212	0.0000	0.0041	0.0102	0.0000	1.0484	0.0000	0.0012	0.0015	0.0031	0.0208	0.0000	0.0801
AB2	52.58	55.25	4 Seam	0.0000	0.0563	0.0005	0.0048	0.0124	0.0000	14.2663	0.0000	0.0018	0.0016	0.0140	9.1845	0.0000	0.0311
AB2	55.25	58.17	SHLE	0.0000	0.1984	0.0000	0.0027	0.0218	0.0000	1.2009	0.0000	0.0016	0.0030	0.0085	1.1834	0.0000	0.0950
AB2	58.17	58.67	3 Seam	0.0000	0.2860	0.0005	0.0020	0.0293	0.0000	0.5114	0.0000	0.0018	0.0044	0.0099	0.4353	0.0000	0.1183
AB2	58.67	61.74	SNDS	0.0000	0.0029	0.0000	0.0022	0.0022	0.0000	0.6920	0.0000	0.0043	0.0029	0.0012	0.0029	0.0000	0.1661
AB2	61.74	62.50	SHLE	0.0000	0.3434	0.0000	0.0035	0.0180	0.0000	0.8444	0.0000	0.0050	0.0073	0.0413	3.8995	0.0000	0.2082
AB2	62.50	67.96	SHLE	0.0000	0.0029	0.0000	0.0011	0.0032	0.0000	1.0141	0.0000	0.0015	0.0011	0.0003	0.0085	0.0000	0.1705
AB2	67.96	71.30	SHLE	0.0000	0.3332	0.0000	0.0019	0.0035	0.0000	0.7349	0.0000	0.0047	0.0139	0.0385	0.1346	0.0000	0.1831
AB2	71.30	74.54	2 Seam	0.0000	0.0024	0.0000	0.0011	0.0022	0.0000	2.8929	0.0000	0.0005	0.0000	0.0006	0.0020	0.0000	0.0428
AB2	74.54	78.05	2 Seam	0.0000	0.0016	0.0000	0.0010	0.0048	0.0000	10.4080	0.0000	0.0000	0.0001	0.0007	0.0010	0.0000	0.0491
AB2	78.05	80.00	DWKA	0.0000	0.3185	0.0000	0.0003	0.0031	0.0000	4.6701	0.0000	0.0009	0.0041	0.0079	1.0122	0.0000	0.0983

Table. 40. Solubilised elements from on core samples from two boreholes at Tavistock Colliery.

Hole No.	Top	Bottom	Lithology	La	Li	Mg	Mn	Mo	Na	Ni	Sb	Se	Sn	Sr	Pb	V	Zn	SO4
	m	m		kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t
AB1	0.00	9.00	SOIL	0.0000	0.0006	0.2410	0.2324	0.0002	0.0860	0.0030	0.0000	0.0000	0.0000	0.0022	0.0000	0.0027	0.0175	2.3607
AB1	9.00	12.65	SNDS	0.0000	0.0003	0.0654	0.0435	0.0001	0.0691	0.0006	0.0000	0.0000	0.0000	0.0002	0.0000	0.0020	0.0006	0.4493
AB1	12.65	16.31	SNDS	0.0001	0.0008	1.2969	0.2022	0.0008	0.0923	0.0174	0.0000	0.0002	0.0000	0.0041	0.0000	0.0065	0.0479	9.0841
AB1	16.31	19.70	SNDS	0.0001	0.0007	1.5448	0.1386	0.0007	0.1042	0.0173	0.0000	0.0004	0.0000	0.0081	0.0000	0.0084	0.0473	10.1796
AB1	19.70	24.18	SHLE	0.0000	0.0005	1.1227	0.0092	0.0004	0.0901	0.0033	0.0000	0.0004	0.0000	0.0054	0.0000	0.0019	0.0006	6.5934
AB1	24.18	25.33	4 Seam U	0.0004	0.0000	1.1320	0.0500	0.0005	0.1446	0.0162	0.0000	0.0012	0.0000	0.0226	0.0021	0.0047	0.0179	37.7116
AB1	25.33	26.70	SNDS	0.0001	0.0003	0.2834	0.0885	0.0002	0.0834	0.0124	0.0000	0.0001	0.0000	0.0026	0.0008	0.0010	0.0338	17.1649
AB1	26.70	30.50	4 Seam	0.0001	0.0002	0.1606	0.0082	0.0005	0.1504	0.0095	0.0000	0.0013	0.0000	0.0205	0.0000	0.0023	0.0191	31.4011
AB1	30.50	33.00	SNDS	0.0000	0.0003	0.2072	0.0476	0.0004	0.0918	0.0114	0.0000	0.0002	0.0000	0.0047	0.0008	0.0020	0.0465	3.5714
AB1	33.00	33.36	3 Seam	0.0002	0.0000	0.1743	0.0097	0.0009	0.1503	0.0450	0.0000	0.0010	0.0000	0.0086	0.0055	0.0127	0.0602	27.9258
AB1	33.36	36.05	SNDS	0.0000	0.0000	1.2053	0.0007	0.0006	0.0723	0.0004	0.0000	0.0004	0.0000	0.0097	0.0000	0.0039	0.0009	10.4934
AB1	36.05	37.21	SHLE	0.0000	0.0000	0.9944	0.1166	0.0017	0.1834	0.0321	0.0000	0.0008	0.0000	0.0120	0.0000	0.0164	0.0785	5.5883
AB1	37.21	41.79	SLSN	0.0000	0.0000	0.9222	0.0017	0.0006	0.1169	0.0008	0.0000	0.0004	0.0000	0.0092	0.0000	0.0018	0.0007	5.3162
AB1	41.79	45.10	SHLE	0.0000	0.0000	0.8153	0.0849	0.0019	0.2027	0.0323	0.0000	0.0013	0.0000	0.0146	0.0000	0.0134	0.0871	6.2419
AB1	45.10	46.76	2 Seam	0.0001	0.0000	3.0271	0.0838	0.0001	0.1768	0.0045	0.0000	0.0005	0.0000	0.0694	0.0000	0.0010	0.0096	64.5772
AB1	46.76	50.32	2 Seam	0.0000	0.0000	0.9712	0.0485	0.0002	0.0857	0.0051	0.0000	0.0006	0.0000	0.0223	0.0000	0.0013	0.0081	11.1468
AB1	50.32	51.41	DWKA	0.0001	0.0000	0.2471	0.0204	0.0005	0.0958	0.0030	0.0000	0.0001	0.0000	0.0074	0.0031	0.0022	0.0212	5.4367
AB2	0.00	9.72	SNDS	0.0000	0.0000	0.1239	0.0044	0.0002	0.2077	0.0008	0.0000	0.0007	0.0000	0.0028	0.0000	0.0016	0.0005	0.8800
AB2	9.72	12.57	SNDS	0.0000	0.0000	0.0462	0.0028	0.0000	0.1081	0.0008	0.0000	0.0002	0.0000	0.0008	0.0000	0.0000	0.0005	0.5600
AB2	12.57	20.55	SNDS	0.0000	0.0001	0.3994	0.0049	0.0005	0.1707	0.0007	0.0000	0.0001	0.0000	0.0037	0.0000	0.0014	0.0005	0.5600
AB2	20.55	23.64	SNDS	0.0000	0.0002	0.3185	0.0072	0.0008	0.2045	0.0014	0.0000	0.0002	0.0000	0.0035	0.0000	0.0022	0.0018	1.1200
AB2	23.64	24.83	5 Seam	0.0000	0.0000	0.7617	0.0339	0.0011	0.3099	0.0045	0.0000	0.0005	0.0005	0.0290	0.0120	0.0018	0.0093	67.6311
AB2	24.83	29.04	SHLE	0.0000	0.0007	4.9030	0.5878	0.0000	0.3876	0.0230	0.0000	0.0003	0.0000	0.0651	0.0000	0.0044	0.0395	36.8100
AB2	29.04	35.45	SNDS	0.0000	0.0002	3.0031	0.2316	0.0007	0.1744	0.0085	0.0000	0.0001	0.0000	0.0322	0.0000	0.0061	0.0390	42.2057
AB2	35.45	39.57	SNDS	0.0000	0.0004	1.4731	0.1241	0.0008	0.2449	0.0152	0.0000	0.0002	0.0000	0.0172	0.0000	0.0052	0.0325	8.6164
AB2	39.57	43.68	SHLE	0.0000	0.0000	1.7548	0.0248	0.0008	0.2344	0.0069	0.0000	0.0005	0.0000	0.0201	0.0000	0.0048	0.0024	9.5275
AB2	43.68	50.29	SHLE	0.0000	0.0001	1.8914	0.0015	0.0003	0.2471	0.0012	0.0000	0.0003	0.0000	0.0164	0.0000	0.0035	0.0005	7.3316
AB2	50.29	52.22	4 Seam U	0.0000	0.0000	2.9910	0.0503	0.0009	0.3267	0.0067	0.0000	0.0014	0.0000	0.0794	0.0092	0.0045	0.0095	43.3574
AB2	52.22	52.58	SHLE	0.0000	0.0013	0.4102	0.0034	0.0003	0.1226	0.0026	0.0000	0.0006	0.0000	0.0105	0.0000	0.0028	0.0013	1.8800
AB2	52.58	55.25	4 Seam	0.0000	0.0008	4.4797	0.0505	0.0004	0.2138	0.0078	0.0000	0.0006	0.0000	0.0936	0.0065	0.0028	0.0067	41.9724
AB2	55.25	58.17	SHLE	0.0000	0.0003	0.4123	0.0112	0.0006	0.2445	0.0089	0.0000	0.0002	0.0000	0.0151	0.0016	0.0040	0.0572	3.9200
AB2	58.17	58.67	3 Seam	0.0000	0.0005	0.1709	0.0057	0.0006	0.2132	0.0073	0.0000	0.0002	0.0000	0.0113	0.0010	0.0032	0.0440	1.8000
AB2	58.67	61.74	SNDS	0.0000	0.0000	1.2043	0.0146	0.0010	0.2496	0.0076	0.0000	0.0006	0.0000	0.0116	0.0000	0.0082	0.0063	3.3436
AB2	61.74	62.50	SHLE	0.0000	0.0002	0.9658	0.0762	0.0004	0.2749	0.0124	0.0000	0.0007	0.0000	0.0219	0.0036	0.0140	0.0720	2.5276
AB2	62.50	67.96	SHLE	0.0000	0.0000	0.8874	0.0026	0.0010	0.2733	0.0012	0.0000	0.0003	0.0000	0.0166	0.0000	0.0042	0.0020	3.3312
AB2	67.96	71.30	SHLE	0.0000	0.0012	1.1316	0.0503	0.0023	0.3123	0.0274	0.0000	0.0011	0.0000	0.0171	0.0000	0.0115	0.0697	2.3307
AB2	71.30	74.54	2 Seam	0.0000	0.0000	1.6914	0.0018	0.0002	0.2264	0.0012	0.0000	0.0003	0.0000	0.0143	0.0000	0.0010	0.0006	6.7384
AB2	74.54	78.05	2 Seam	0.0000	0.0000	3.9357	0.0096	0.0004	0.2395	0.0015	0.0000	0.0005	0.0000	0.0458	0.0000	0.0010	0.0008	34.2463
AB2	78.05	80.00	DWKA	0.0000	0.0004	0.8210	0.0714	0.0006	0.2447	0.0454	0.0000	0.0002	0.0000	0.0262	0.0019	0.0020	0.0244	16.6793

The results of the Acid-Base Accounting from these two samples are indicated in a more presentable manner in the two figures which follow. Using this type of diagram, the most problematic layers are easily identified. It is evident from these two diagrams that most of the lithological layers have a tendency to acidify. This then should be reflected in the spoil chemistry discussed in the section which follows.

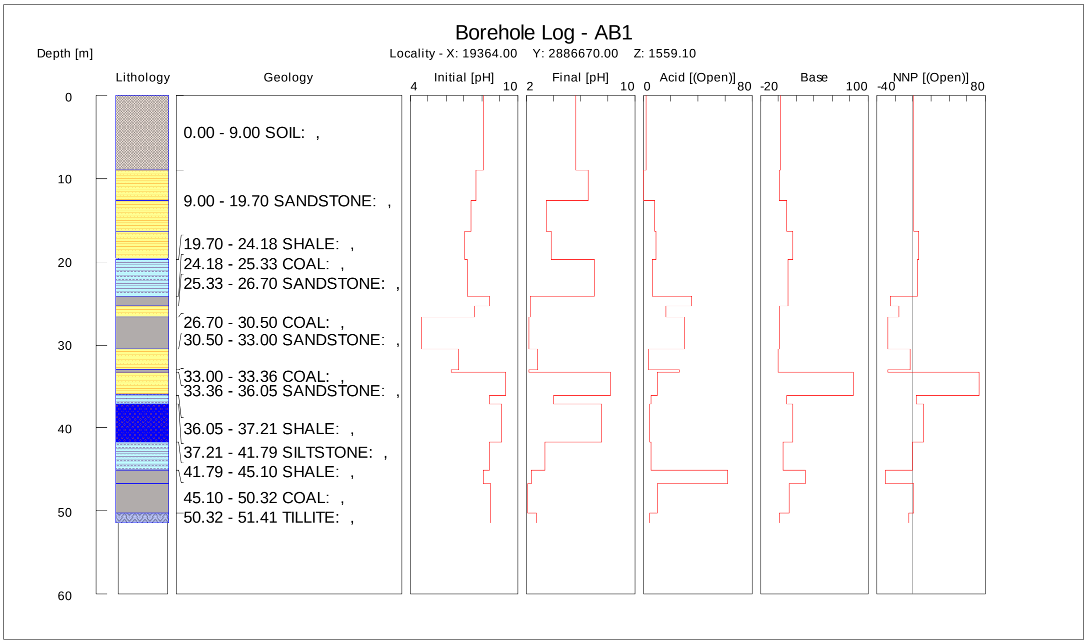


Figure 140. Acid-Base Accounting results with depth and compared to lithology for AB1.

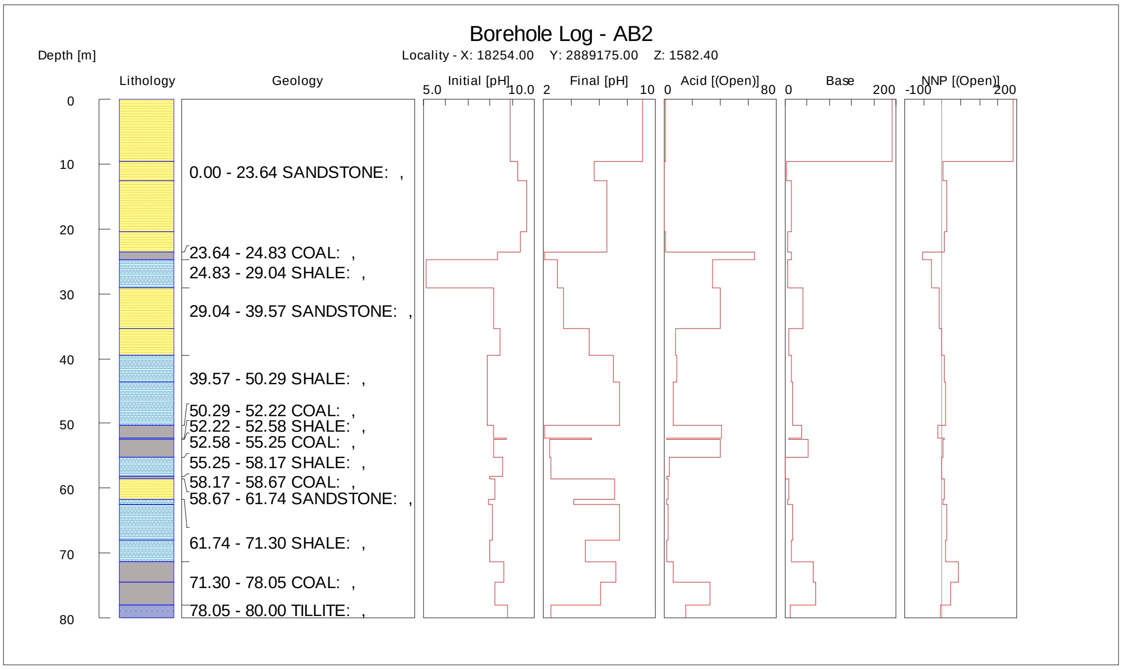


Figure 141. Acid-Base Accounting results with depth and compared to lithology for AB2.

Conclusions from this information are as follows:

- A clear tendency exists towards acidification of the spoil. Of the 38 samples tested, only 12 did not acidify during complete oxidation.

- Acidification of the spoil is a progressive process. The outsides of rocks oxidise first. It is not uncommon to find pH-levels between 3,5 - 6,0 on the outside of a rock, in spoil above the water table. The inside of the rock would still be at an alkaline pH, because it does not partake in the oxidation process, due to a lack of oxygen.

9.3.1 TEST PITS IN REHABILITATED SPOILS

Several trenches were dug in the rehabilitated spoils at ATC. These provided valuable information in terms of the heterogeneity of rehabilitate spoils material. The aim of the test pits was to investigate the *in situ* conditions in spoils in the upper three metres.

Several of the test pits dug by the excavator were completely filled with topsoil and previously disturbed soil horizons. It could thus not provide any meaningful information regarding the spoil reactions. Three test pits at different locations in this area where sufficient spoils were found in the upper portion will be discussed.

As with the spoils discussed previously, the heterogeneity across the site and as far as material at any point in the system is concerned, can again be highlighted. The spoils in this area consists of very large boulders with a random gradation down to extremely fine material. As such it is only really possible to test the *in situ* pH-conditions in the finer material, which volumetrically constitutes a maximum of approximately 75% of the material down to about 20% in certain portions of the exposed wall.

The first two pits showed little sign of acidification with pH-values in the pits at around 5.7 and ranging from 6.15 to 5.95 in pit 2. Deionised water was used in all of the determination, thus anything above 5.65 (pure water pH in equilibrium with atmospheric carbon dioxide will have a pH of 5.69) can be considered non-acidic.

In the third test pit, there were definite signs of acidity, particularly in the lower portion of the pit. Visually the pit exhibited similar characteristics as the previous pits, with the exception of some signs of secondary mineralisation around the edges of several rocks. Low *in situ* pH-values in the lower portion ranging from 4.5 to 3.5 were encountered, although this was very localised and varied considerably over distances of less than half a metre.

9.3.2 STATIC TESTING OF SHALE FROM TEST PIT 3

To further investigate the reasons behind the acidic *in situ* pH-values found in Test Pit 3, one of the larger shale boulders removed from the pit was selected (at random from the several boulders removed) for further testing.

9.3.2.1 SAMPLE TREATMENT

Since the emphasis of the testing was to ascertain the cause of the acidity, it was decided to remove any secondary products from the boulder before crushing. This was achieved through vigorous scrubbing with a new plastic bristle brush with deionised water. This process was repeated three times after air-drying the boulder after each successive wash, until the initial contact with water after drying yielded no visible fine material in solution or suspension.

The boulder was then crushed to 4mm, quartered and half recrushed to 0.75μm. This sample was tested according to the recommended ABA procedures outlined in this document.

9.3.2.2 RESULTS FROM STATIC TESTING

The ABA testing on this sample was considered crucial to the understanding and elucidation of the observed spoil paste pH. The results of the testing are given in the table below.

Table 41. ABA results from boulder obtained from test pit in spoils.

Water soluble constituents in kg/t										
Sample	**Initial pH**	**Ag**	**Al**	**As**	**B**	**Ba**	**Be**	**Ca**	**Cd**	**Cr**
Shale	7.61	0.0000	0.0030	0.0000	0.0070	0.0006	0.0000	0.2558	0.0000	0.0000
	Co	**Cu**	**Fe**	**Hg**	**K**	**La**	**Li**	**Mg**	**Mn**	**Mo**
	0.0000	0.0001	0.0026	0.0000	0.0535	0.0000	0.0000	0.0914	0.0005	0.0001
	Na	**Ni**	**Sb**	**Se**	**Sn**	**Sr**	**Pb**	**V**	**Zn**	**SO4**
	0.0000	0.0002	0.0000	0.0002	0.0000	0.0012	0.0001	0.0001	0.0005	0.3953
Constituents released during complete oxidation in kg/t										
Sample	**Final pH**	**Ag**	**Al**	**As**	**B**	**Ba**	**Be**	**Ca**	**Cd**	**Cr**
Shale	2.10	0.0001	0.6191	0.0000	0.0208	0.0000	0.0007	7.2234	0.0005	0.0047
	Co	**Cu**	**Fe**	**Hg**	**K**	**La**	**Li**	**Mg**	**Mn**	**Mo**
	0.0085	0.0230	23.9730	0.0000	0.0743	0.0021	0.0010	4.4209	0.2444	0.0001
	Na	**Ni**	**Sb**	**Se**	**Sn**	**Sr**	**Pb**	**V**	**Zn**	**SO4**
	0.0805	0.0372	0.0000	0.0005	0.0000	0.0135	0.0038	0.0074	0.1170	126.6866
	Acid/base calculations (kg/t CaCO3 where applicable)									
Sample	**Initial pH**	**Final pH**	**Acid**	**Acid**	**Base**	**NNP**	**NNP**			
			Open	**Closed**		**Open**	**Closed**			
Shale	7.61	2.10	132	264	24	-108	-240			

The first point worth highlighting is the initial pH of the pulverised shale boulder. The pH-value of 7.61 indicates that currently the basic ions exceed the acidic ions and that prior to any oxidation the rock would be non-acidic. This is important for several reasons. It firstly shows that the washing and removal of the secondary products on the surface of the rock have been removed and that these are not contributing to any acidity which may be present. The initial near neutral to alkaline pH also suggests that the measured pH in the field was not indicative of fresh fine material with a similar source as this boulder. The oxidised pH is thus of special interest.

The most important observation is that the ABA predicts that this particular shale boulder has insufficient neutralising potential to prevent acidification from occurring, should oxidation occur. Furthermore the NAG or Final pH as discussed previously, is also very low as would be expected from an NNP of less than 100 and an NPR of more than 5. This would imply that if this boulder was allowed to be oxidised fully in nature, it would produce acidic drainage.

This therefore tied in excellently with the observed paste pH-values (as low as pH of

3.5) obtained for this test pit in the field. The fines in the field are therefore in all likelihood of similar matter to the tested boulder and conditions have been provided wherein the shale could oxidise.

The conclusion from this is therefore that the **static ABA testing would have predicted the acidification and thus can be regarded as a reliable tool in this instance**. It is clear from these examples that spoil acidification is a complex process.

9.3.3 KINETIC TESTING

Having shown that the static ABA proved to be very effective in predicting the acidic conditions, the remainder of the crushed and pulverised boulder was used for kinetic testing. The procedures and apparatus used are discussed in Section 6.3, along with most of the results.

This section will focus on the verification of the static test and the comparison to the field values.

Duplicate cells of the pulverised and coarser material were tested; the excellent correlation is discussed in Section 6.3. Only one of the cells will therefore be used as an illustration here.

Figure 142 shows the pH-profile from this humidity cell over time.

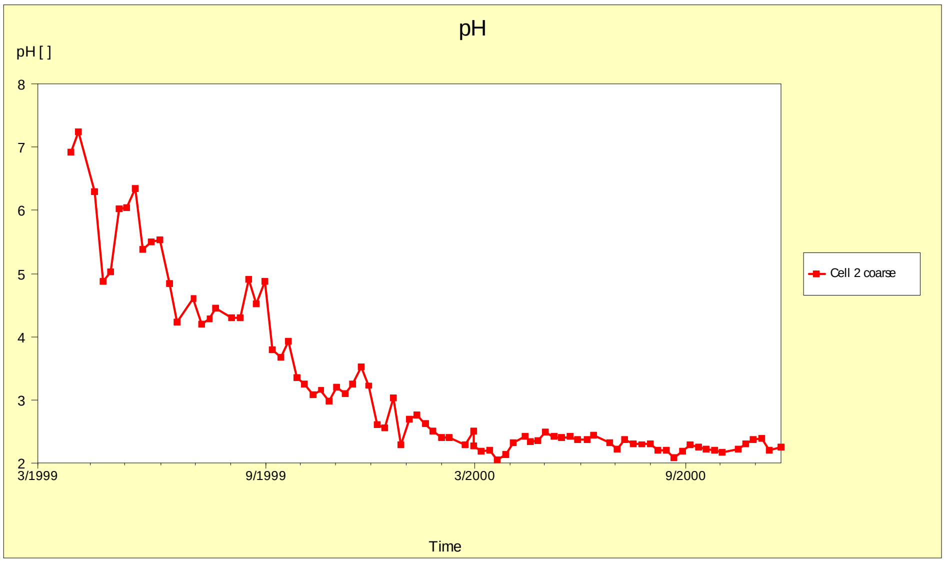


Figure 142. pH-profile from crushed spoil shale boulder in humidity cell test.

The figure shows how a pH of above 5 was maintained initially for the first 10 weeks but a drop to around pH 4 followed this quickly. This buffer level was maintained and then followed by a drop to around pH 3 and then a steady decline to a pH of around 2.

Comparison to the NAG or oxidised pH from the ABA shows that the cell did in fact reach the pH predicted. The figure below (Figure 143) shows the NAG pH to observed pH ratio and the pH-profile showing how the lowest value corresponds very well to a ratio of 1 (exact match).

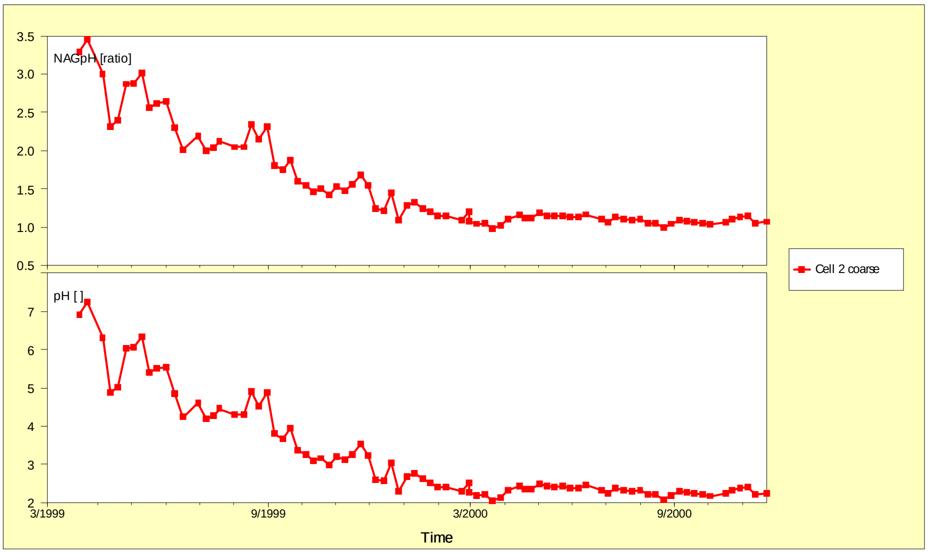


Figure 143. Comparison between the observed cell pH and the predicted oxidised pH from ABA.

Of interest too, is the correlation between the predicted neutralising potential and the pH-profile. The figure below shows clearly how the neutralising potential depletion coincides with the observation of the oxidised pH and that any neutralisation which occurs once this point is reached is not reflected in the ABA. However, by this stage the system is already acidic and the remaining buffering cannot be included as neutralisation potential.

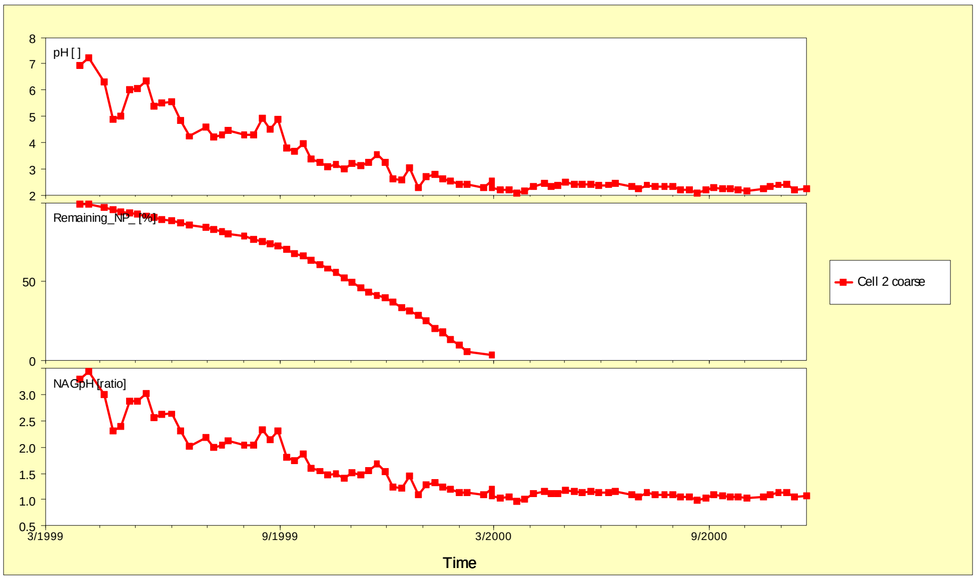


Figure 144. Comparison between theoretical remaining neutralising potential and observed pH.

The humidity cell results, ABA and field observations are therefore in excellent

agreement as all point to the same conclusion for this case.

9.3.3.1 ALTERNATIVE "KINETIC" TEST

In reports in South Africa, there has been some discussion and an occasional reference to the reactions on the surface and within boulders. The fact that acidity occurs in spoils in the presence of boulders expected to have latent neutralising potential has been raised during discussions with various parties. In order to investigate this, a modified test was undertaken.

Another shale boulder from Test Pit 3 was selected for testing. The testing conditions can best be described as pseudo-kinetic as it was a long-term modified NAG test which was performed on the boulder. The methodology was basically as follows:

- Add 10% H_2O_2 to the boulder, exposing as much of the surface to the oxidation agent as possible. This included periodically turning the boulder over to alternate the sides partially submerged in the hydrogen peroxide.
- Allow the oxidant to evaporate.
- Repeat daily.
- Add 250 mL of water once weekly and collect the leachate.
- Analyse and measure pH.

The aim of this testing was to determine what type of response successive oxidation and removal (successively "peeling" away the skin of the boulder) would result in. Two possible scenarios are possible; progressive acidification or a repeated drop in pH followed by buffering from the newly exposed inner material.

Figure 145. Top view of boulder before test.

Figure 146. Side on view of boulder before test.

In the figures (Figure 145 and Figure 146) above some idea of the boulder used can be obtained. The boulder was photographed from several angles as a record of its natural appearance.

Shown below is the boulder after the initial treatment with hydrogen peroxide. Some reaction was observed but initially this appeared to be minimal.

Figure 147. Boulder being treated with hydrogen peroxide at start of test.

The pH-profile for this test is shown below (Figure 148). It shows a fairly rapid acidification and no evidence of any cyclic buffering followed by acidification. This would seem to indicate that the acidification in this particular boulder is irreversible once acidification has begun.

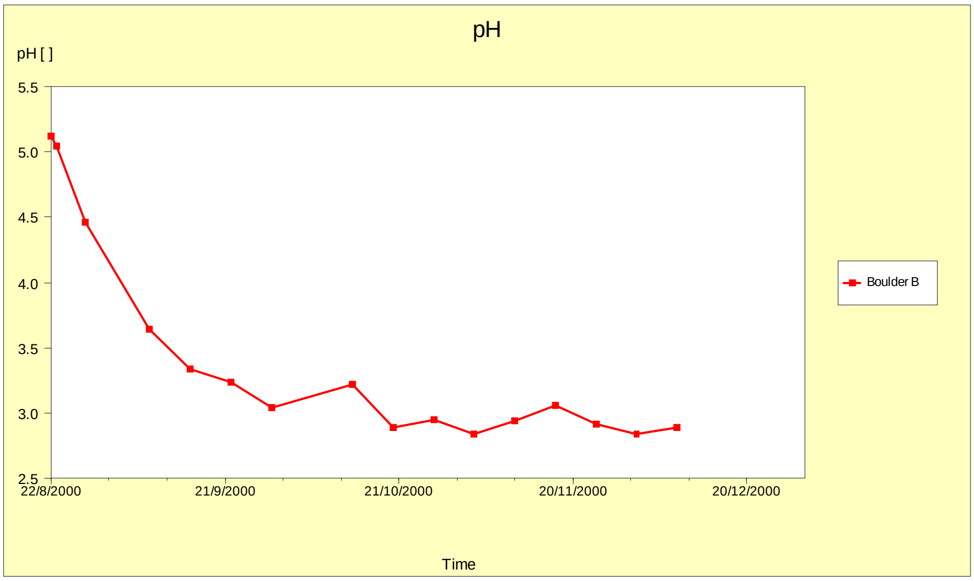


Figure 148. pH-profile of hydrogen peroxide test on shale boulder.

Apart from this continuous decline in pH, the most noticeable facet was the disintegration of the rock. The micro-fissures, which were just perceptible at the commencement of the test, all developed into major areas of weakness and over time the entire structure of the rock disintegrated (see Figure 149 to Figure 151).

This allowed a far bigger reactive surface area to develop, which, together with the increased solubilisation as pH-levels declined, was reflected in the increase in salinity.

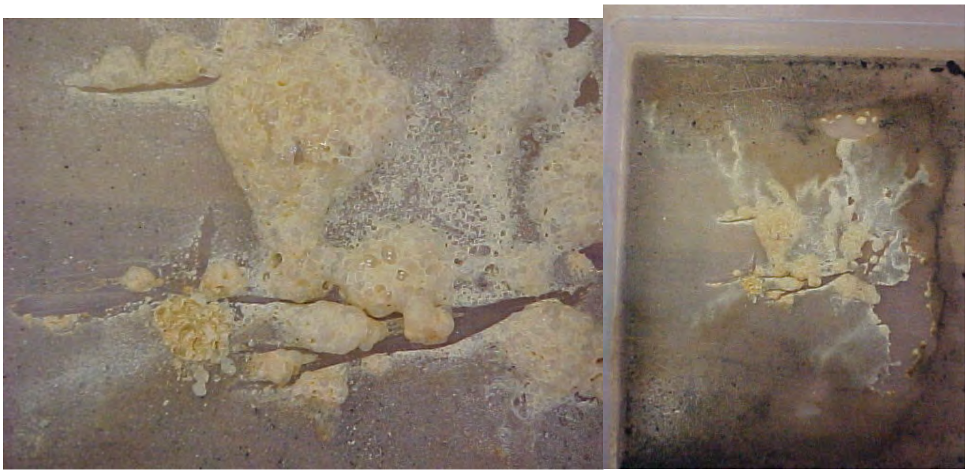


Figure 149. Top view of boulder after third cycle, with a close-up on the left.

Figure 150. Side view with a close-up showing development of cracks.

Figure 151. Late time photographs illustrating significant breakdown of structure.

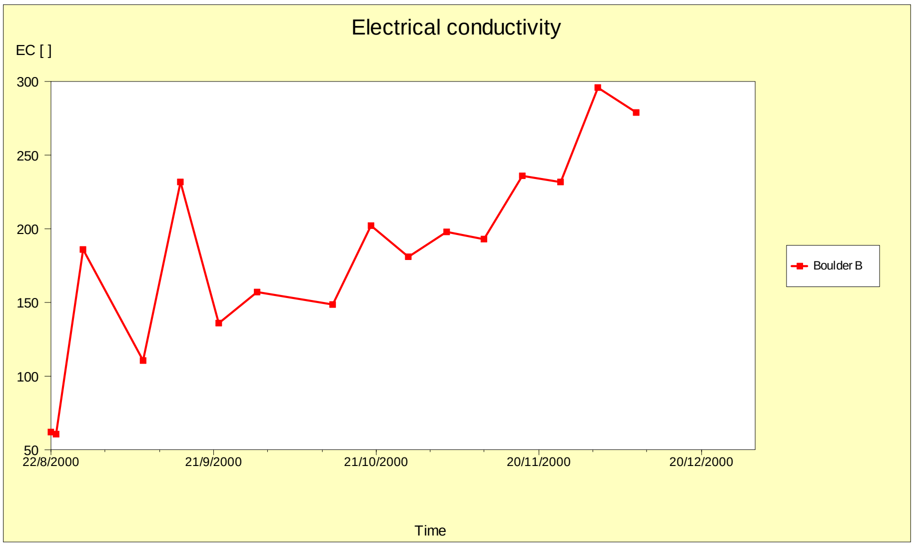


Figure 152. Increase in salinity over time due to increased surface area and acidification.

This evidence appears to support the notion of outer reactive surface, leading to rapid acidification, with the material within the boulder not able to provide the required buffering to prevent this from occurring.

9.4 KRIEL

Kriel Colliery has been investigated at various times to determine whether a potential for AMD exists. The findings of these investigations are outlined below.

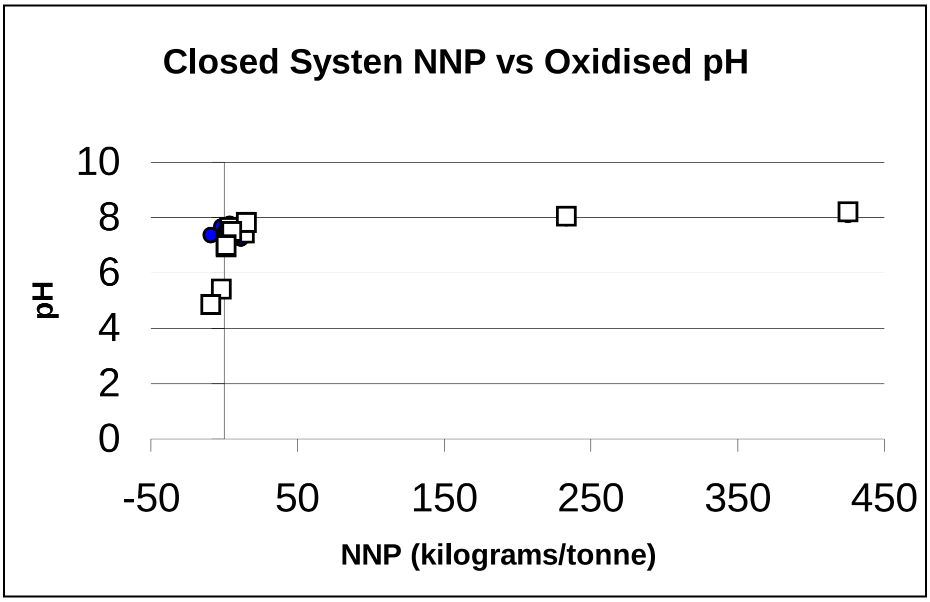


Figure 153. Closed system NNP versus initial pH (dots) and oxidation pH (open squares).

From Figure 153 above, it can be seen that for this particular investigation the probability of acidification of the spoils is very low, based on the ABA results. There appears to be an abundance of neutralising potential to counteract the relatively low acid potentials. The table below lists the most important parameters from this assessment.

Table 42. Statistics for the graph above.

Statistics	**NNP open**	**NNP close**	**Initial pH**	**Final pH**
Mean	**29.2**	**27.1**	**7.58**	**7.12**
Median	**2.2**	**2.1**	**7.61**	**7.47**
Std. Dev.	**66.6**	**67.7**	**0.34**	**1.01**
Minimum	**-4.5**	**-13.9**	**7.07**	**4.87**
Maximum	**212.7**	**212.6**	**8.09**	**8.21**

Table 43. Statistics on soluble elements within the spoil samples.

Statistics	Al mg/g	B mg/g	Ba mg/g	Ca mg/g	Cd mg/g	Co mg/g	Cu mg/g	Fe mg/g
Mean	0.00010	0.00027	0.00043	0.16673	0.00000	0.00000	0.00039	0.00024
Median	0.00000	0.00000	0.00024	0.16266	0.00000	0.00000	0.00040	0.00000
Std. Dev.	0.00036	0.00093	0.00043	0.10873	0.00000	0.00000	0.00013	0.00055
Minimum	0.00000	0.00000	0.00000	0.00547	0.00000	0.00000	0.00015	0.00000
Maximum	0.00125	0.00321	0.00149	0.31827	0.00000	0.00000	0.00058	0.00148
Count	12	12	12	12	12	12	12	12
Statistics	K mg/g	Mg mg/g	Mn mg/g	Na mg/g	Ni mg/g	Sr mg/g	Zn mg/g	S mg/g
Mean	0.07349	0.04416	0.00016	0.06847	0.00050	0.00168	0.00007	0.14204
Median	0.06093	0.02873	0.00005	0.05328	0.00047	0.00093	0.00000	0.02766
Std. Dev.	0.03770	0.03937	0.00029	0.04549	0.00022	0.00182	0.00012	0.16644
Minimum	0.03696	0.00194	0.00000	0.03760	0.00000	0.00003	0.00000	0.00000
Maximum	0.14712	0.11829	0.00100	0.20574	0.00082	0.00626	0.00034	0.46764
Count	12	12	12	12	12	12	12	12

Statistics on elements released during complete oxidation of spoil samples, NNP and pH change.

Statistics	Al mg/g	B mg/g	Ba mg/g	Ca mg/g	Cd mg/g	Co mg/g	Cu mg/g	Fe mg/g
Mean	0.07675	0.00000	0.00163	0.50233	0.00006	0.00075	0.00043	0.14536
Median	0.01780	0.00000	0.00044	0.33650	0.00000	0.00018	0.00000	0.02097
Std. Dev.	0.12059	0.00000	0.00216	0.51309	0.00012	0.00139	0.00079	0.30742
Minimum	0.00130	0.00000	0.00003	0.02627	0.00000	0.00000	0.00000	0.00250
Maximum	0.36834	0.00000	0.00612	1.47314	0.00031	0.00394	0.00207	1.00852
Count	12	12	12	12	12	12	12	12
Statistics	K mg/g	Mg mg/g	Mn mg/g	Na mg/g	Ni mg/g	Sr mg/g	Zn mg/g	S mg/g
Mean	0.07971	0.23469	0.01826	0.06527	0.00159	0.00556	0.00425	0.66634
Median	0.05510	0.1014	0.00158	0.04044	0.00000	0.00160	0.00056	0.04062
Std. Dev.	0.08159	0.38648	0.03374	0.04893	0.00406	0.01108	0.00924	1.25799
Minimum	0.00570	0	0.00000	0.02532	0.00000	0.00008	0.00000	0.00232
Maximum	0.27449	1.27828	0.11497	0.17378	0.01355	0.03936	0.03083	3.59782
Count	12	12	12	12	12	12	12	12

A subsequent investigation at the Colliery yielded the following data (Table 44):

Table 44. Statistics from further ABA at mine.

	Initial pH	Final pH	Acid (Open)	Acid (Closed)	Base	NNP (Open)	NNP (Closed)
SOIL	7.38	6.91	0.029	0.058	2.518	2.489	2.461
SOIL SN	7.53	5.46	0.154	0.307	0.986	0.833	0.679
SNDS MS Y	8.33	6.13	0.067	0.134	0.811	0.744	0.677
SNDS/SHLE INTB WT	7.24	6.57	0.077	0.154	3.402	3.325	3.249
SNDS/SHLE INTB +	8.04	5.93	0.403	0.806	9.046	8.643	8.240
5 SEAM	8.52	2.2	24.173	48.346	9.453	-14.720	-38.893
SNDS/SHLE INTB	8.29	6.42	3.072	6.144	6.372	3.300	0.228
SAND	7.84	5.14	0.374	0.749	0.678	0.304	-0.070
SHLE	6.72	3.17	0.250	0.499	-0.981	-1.231	-1.481
SNDS	7.82	4.74	0.854	1.709	1.100	0.246	-0.608
SNDS/SHLE/SLSN	7.86	4.33	3.859	7.718	12.131	8.271	4.412
SNDS MS W	8.84	8.88	0.317	0.634	70.786	70.469	70.152
SNDS/SHLE INTB -	8.42	8.77	0.336	0.672	33.012	32.676	32.340
SNDS/SHLE INTB	8.46	8.27	0.307	0.614	21.627	21.320	21.012
SNDS/SHLE INTB +	8.15	3.46	22.973	45.946	21.948	-1.025	-23.997
4 SEAM	8.89	6.67	18.355	36.710	46.936	28.581	10.226
SNDS/SHLE INTB	7.88	4.11	3.120	6.240	0.871	-2.249	-5.369

This again shows that apart from the 5 seam data, most of which would be removed and not occur in the spoils, the risk of AMD is fairly low. Several of the samples appear to be comparatively inert with low acid and neutralising potentials. A further set of ABA data is available for the same mine (although the area is slightly to the north), which is useful for comparison. The following figure shows these results.

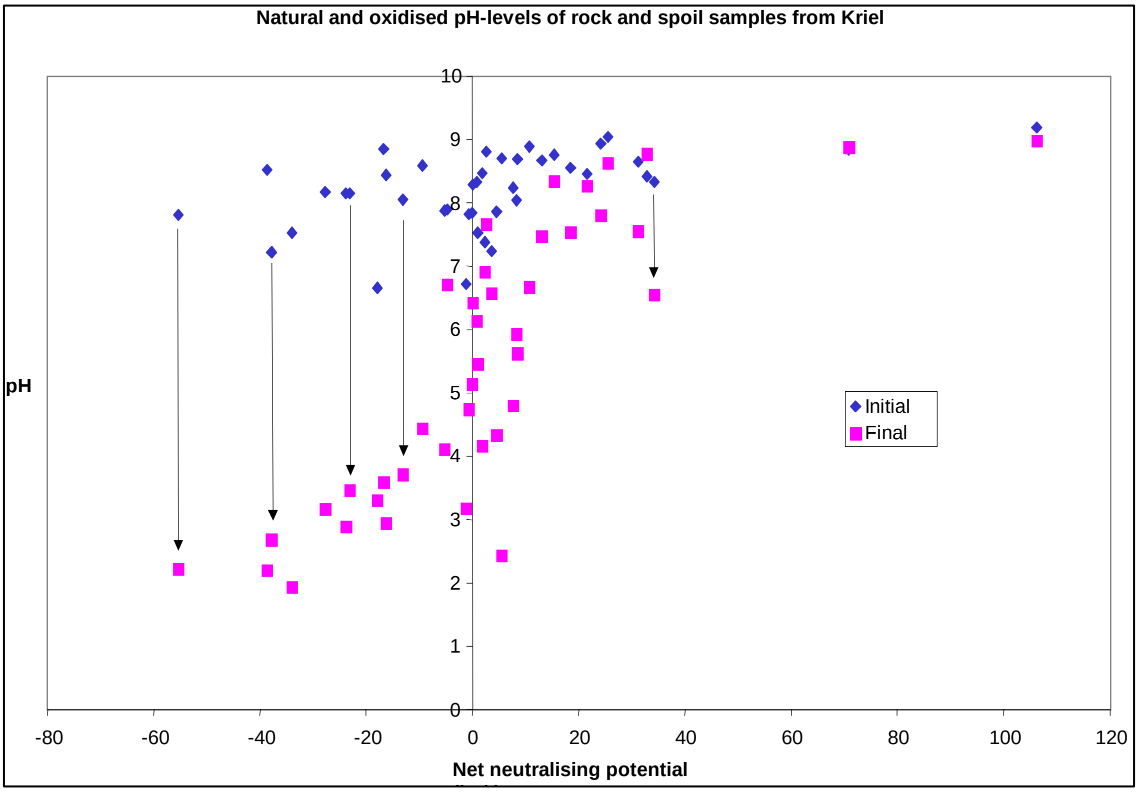


Figure 154. NNP and Initial and Oxidised pH-values.

From the above data it would appear that several of the samples have a potential to yield acidic drainage if oxidised. This is, however, not the entire picture. Shown in the figures which follow is the normalised values of the NNP-values. This technique allows the relative contribution of each layer to be taken into account and more clearly shows the layers that are problematic.

The final calculation and presentation interrelates the boreholes to each other and to the field situation.

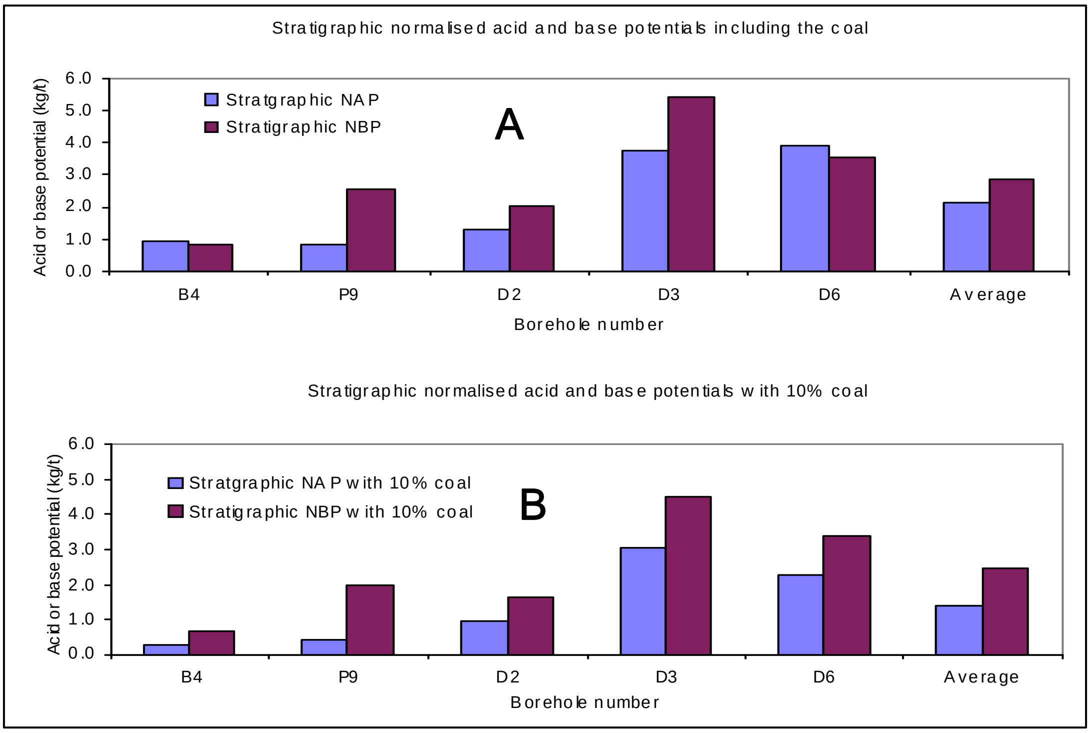


Figure 155. Stratigraphic normalised acid/base potentials for the area.

In these two bar plots, the following should be noted:

The normalised acid and base potentials for the total thickness of sediments at each of the boreholes are shown in the upper half (labelled A) of Figure 155. On the right-hand side, an average value for these holes has been indicated.

In the lower half (labelled B) of Figure 155, 90% of the coal has been extracted. A noticeable decrease in the acid potential and an increase in the base potential can be observed.

From the above data sets it can be concluded that although the potential for acidification does exists, the probability of acidification is low and it can be expected that in the short term the spoils should remain alkaline. The next step would thus be to find *in situ* values for the spoils.

9.4.1 TEST PITS IN THE SPOILS

Seven Test Pits were dug in the spoils in regions ranging from very recently deposited and rehabilitated soils to older established rehabilitation areas.

The positions of the dug test pits are shown on the figure below.

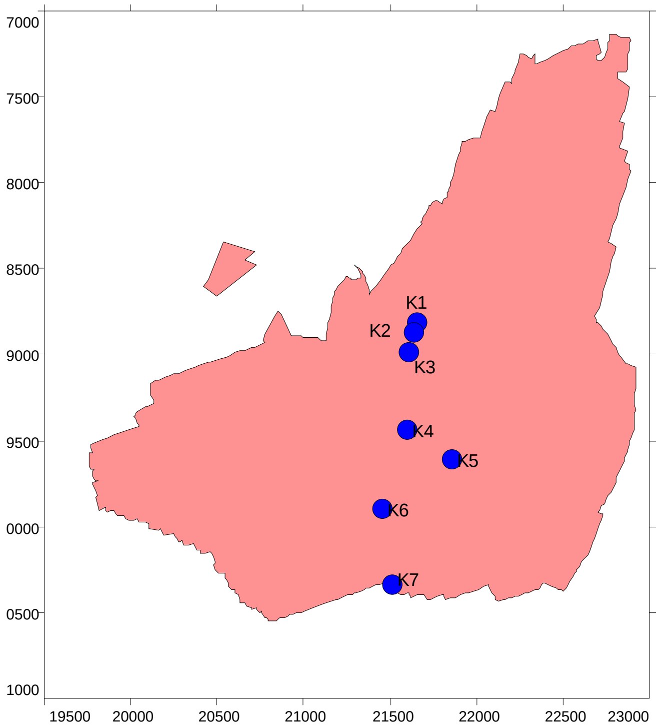


Figure 156. Position of dug trenches.

The *in situ* paste pH measured and the relative age of the spoils showed no relationship. The spoil pH appears to be very homogenous across the spoils and independent of spoil age. Since the spoils have all been handled using a similar methodology, any differences could only be due to mineralogical variation in the spoils. A good comparison is in the Optimum case study in section 9.5.1 and 7.3.

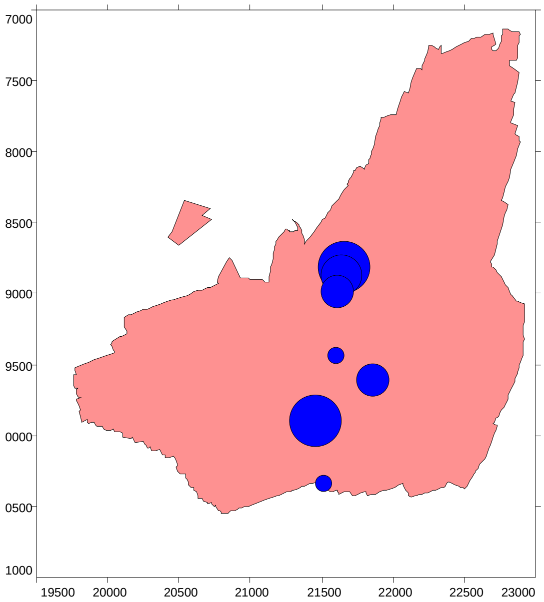


Figure 157. Relative ages of spoils(Old: Large dot; Young : Small dot).

Shown below are the measured paste pH-values:

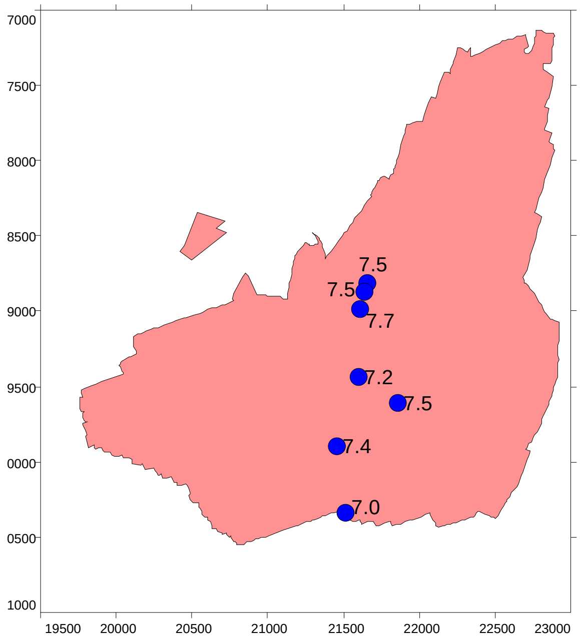


Figure 158. The measured paste pH-values.

The variation in the paste pH as indicated above is too small to be regarded as meaningful and thus it can be assumed that the system is reacting in a very similar way across the rehabilitated area. This contrasts sharply with what was found at the other two sites where *in situ* test pits were dug.

9.4.2 ON-SITE WATER QUALITY DATA

From the on-site water quality data detailed below it is clear that the current pH-values in the nearest monitoring points reflect fairly stable, neutral water. **The results from the various ABA investigations and the *in situ* test pit measurements therefore agree and the ABA can be regarded as a useful tool for the prediction of leachate quality at this mine.**

Table 45. Water Quality Monitoring Data Summary

	pH	EC	M.Alk	Ca	Mg	Na	K	SO4	Cl	F	Fe	Mn	Al
		mS/m	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
2629ACCB18T													
Average	6.93	44.8	137.3	26.3	13.5	43.9	5.9	79.3	20.1	0.25	0.309	0.401	0.236
Minimum	5.9	23	22	10.8	5.6	13.8	0.1	3	8	0	0.01	0.01	0.01
Maximum	8.72	117.4	338	68.9	24.1	190	37.4	243	197	2.1	3.3	3.3	2.54
2629ACCB18B													
Average	6.90	39.6	140.7	22.4	11.5	42.1	5.7	57.7	14.2	0.32	0.357	0.242	0.023
Minimum	5.8	29	28	11.7	3.8	15.9	0.4	14	6	0.01	0.01	0.01	0
Maximum	8.87	74.8	346	38	19	119	10.4	157	47	2.1	3.4	2.7	0.1

The figure below shows the small variation over time, probably as a result of sampling inconsistencies rather than real changes in the chemistry. There does, however, seem to be some loss of alkalinity and a pH drop to circa neutral conditions.

Figure 159. Variation in pH and EC over the last decade.

9.5 REPORTED SOUTH AFRICAN EXAMPLES

There are several researchers and consulting companies within South Africa working on acid rock drainage problems. Unfortunately, the results of these investigations are seldom published in a format which can be used for publications such as these. Furthermore the **methods used are often not standardised methods or have been applied inconsistently.** The reports are also often confidential in nature and the clients (mines) are understandably reluctant to allow potential problems to become public knowledge. Despite this, there are a few instances where the results and applications of ABA have been shown. Some of these will be given very briefly below.

9.5.1 CASE 1

An excellent illustration of the power of ABA is given in a DWA&F report (2000). The report forms part of the DWA&F's Water Quality Management Series and deals with the Blesbok Spruit Catchment's mines.

All the mines in this area have long ceased mining and the area is experiencing severe environmental problems, including acid mine drainage (DWA&F, 2000).

Current water qualities at the mines are very poor, with pH-values in most cases below DWA&F compliance and several values below a pH of 3.0. Sulphate values of above 3500 mg/L are present with most of the values approaching 2000 mg/L. The upper values appear to be controlled by secondary mineral deposition. An example of this is

BSG-B18 with a pH of 3.80 and a sulphate value of 3742 mg/L. Associated with this is a calcium value of 671 mg/L and magnesium at 592 mg/L. The saturation index for gypsum is calculated to be 0.08, suggesting equilibrium chemistry controls. Iron values are also very high, associated with the low pH-values; leading to the conclusion that pyrite oxidation is the probable cause of the acidity.

As part of the investigation, several boreholes were drilled and 15 samples selected and submitted for static ABA testing. It is assumed that the samples were representative of a cross-section of the lithologies in the area.

The ABA results showed that the tested lithologies had a great potential for acid generation. The acid potentials are generally low with negligible neutralisation potential in the tested samples. In the coal samples the sulphide contents are somewhat higher, but also associated with no neutralisation potential. This means that any acid generated will not be neutralised by the system and progressive acidification should occur.

The ABA results predict that the system would eventually become acidic. The field values show the occurrence of this extreme acidity. **The current field situation is therefore an undoubted verification of the validity of ABA techniques in coal mining in South Africa.**

9.5.2 CASE 2

Scharer *et al.*, 2000 report on a case study in South Africa, where geochemical modelling was done to predict long-term quality and management options. The Acid-Base Accounting test work in this case study indicated that the coarse discard dump is potentially acid-generating. Using geochemical modelling, the overall seepage from the dump is predicted to change from neutral drainage quality (pH 7-8) to AMD quality (pH 4 to 5) within 10 years and to become strongly acid-generating (pH<3) within 100 years. This is thus an excellent example of prediction methods being integrated to obtain maximum use from available data. In this case, ABA and geochemical modelling point to very similar results. Unfortunately, the authors did not give any field values from this dump as comparison to verify the ABA or geochemical modelling.

9.5.3 OTHER CASES

In studies completed at coal mining sites in South Africa by Hodgson and Grobbelaar (1998), Hodgson (1997 & 1998) and Krantz and Hodgson (1993), static tests were used. Johnstone and Hinz (2000) report the use of ABA and leachpads to characterise material and for handling purposes. Their overall conclusion is that it is an excellent method for characterising waste from mines.

9.5.4 EXPERIENCES ELSEWHERE

Despite all the in-built deficiencies in ABA discussed previously, it remains one of the most widely used tools for the prediction of eventual acid conditions at mines. Of the several reported methods a couple are mentioned below for illustration puposes.

Manalta Coal Ltd. applied for a Project Approval Certificate for the Telkwa Coal Project in BC, in 1997. It is the basis for the first major stage of the Environmental Assessment Process for new mine developments proposed for BC. On this site, 1109 static (ABA) tests, 28 laboratory kinetic tests and 6 site kinetic tests were completed for prediction studies. It is a surface coal mine with coal washing facilities, tailings disposal area, clean coal haul road, access road and rail load-out facility. Over a 25-year period, the mine is expected to produce approximately 25 million clean tons of coal primarily for the export market (Telkwa Coal Project Application, 1997).

In Canada, acid-generating wastes are 1900 (tailings) and 750 (waste rock) million tons (Feasby, 1997). Coal is potentially acid-generating based on an average total sulphur concentration of 1.5% and neutralisation potential of 21 kg CaCO3/t. The presence of neutralisation potential indicates that acid generation would be delayed (Telkwa, 1997).

Mehling and Sharman (2000) report on the use of ABA at the Quinette Coal Mine in north-eastern Quebec. There are low sulphur levels and these are distributed disproportionately to specific horizons.

The methodology used consisted of the following:

- ABA/metal analysis of samples representing exposed lithologies and mine products,
- Property wide sampling of accessible seepage,
- Review of monthly monitoring data.

By application of a set of criteria, which evaluates each parameter similar to those discussed earlier in the report, (paste pH, NP, AP, NNP and NPR) the Potentially Acid Generating (PAG) horizons were identified. Plotting of the data to determine a lower limit for sulphur to generate acidity and comparison to obtained results showed that the 0.3 % S value was in this case consistent with the on-site findings and that lowering this criteria did not significantly alter the identification of PAG materials.

The conclusions drawn in this paper include the following:

The application of detailed ABA analyses and comparison of individual samples to (standard) Appalachian criteria for PAG sites has proved reasonably successful in identifying strata or geologic units that produced acidic seeps.

Despite the high metal contents from the identified seeps, overall mine site drainage is excellent, consistent with the predominance of acid-consuming material at the site (obtained from ABA) and the small volume and areal exposure of identified PAG materials.

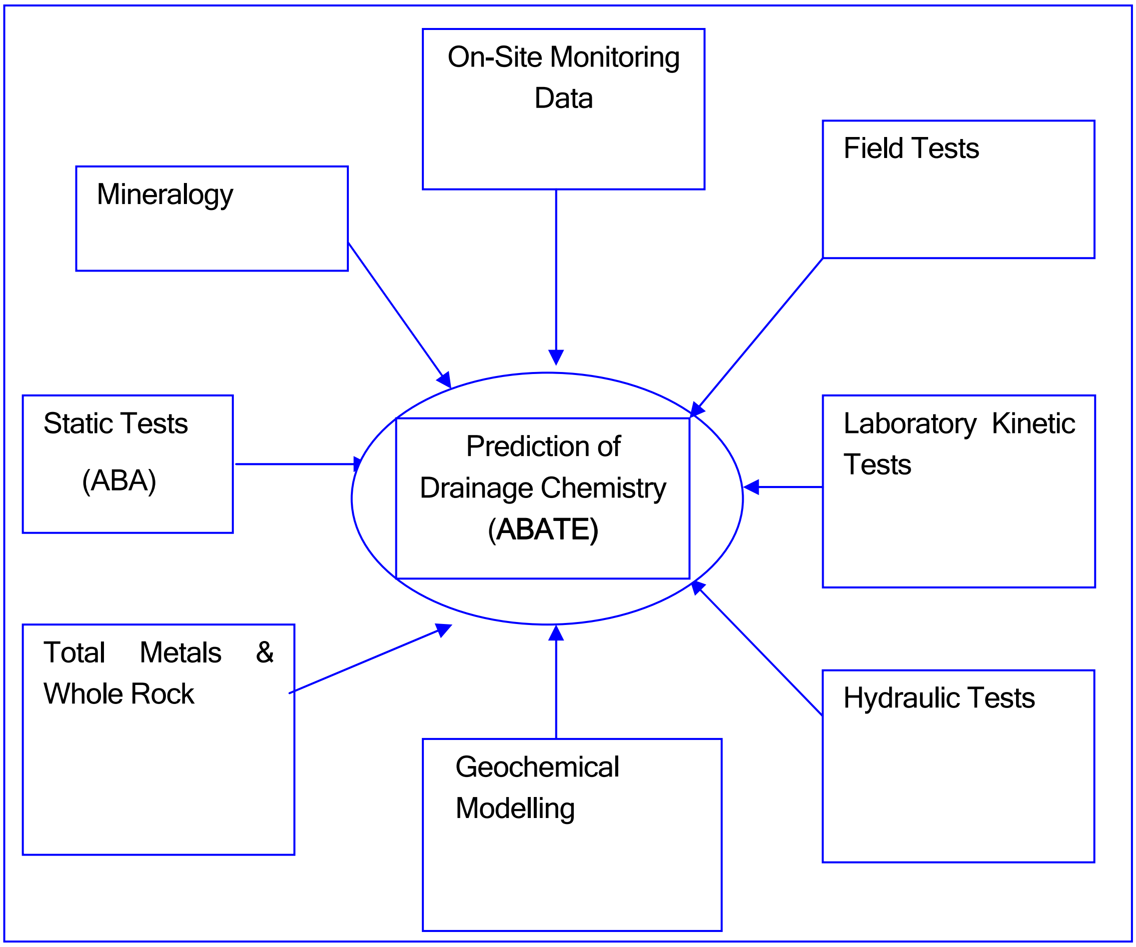
This case study therefore again shows the usefulness of ABA in predicting and identifying potential acidity at a coal mine site.

10 CONCLUSIONS

This report outlines the findings and research delineated for this project.

The aims of the project (investigating ABA at opencast collieries, adapting ABA to South African conditions, creating a database from this project) have been fulfilled and from this the recommended methods have been established with supporting data to substantiate their selection.

It is recommended that to predict the response of opencast spoils, all the components of the so-called prediction wheel be used.



It is recommended that the methods be applied in an iterative and logical manner. A suggested flow path to follow would be as shown in Figure 160:

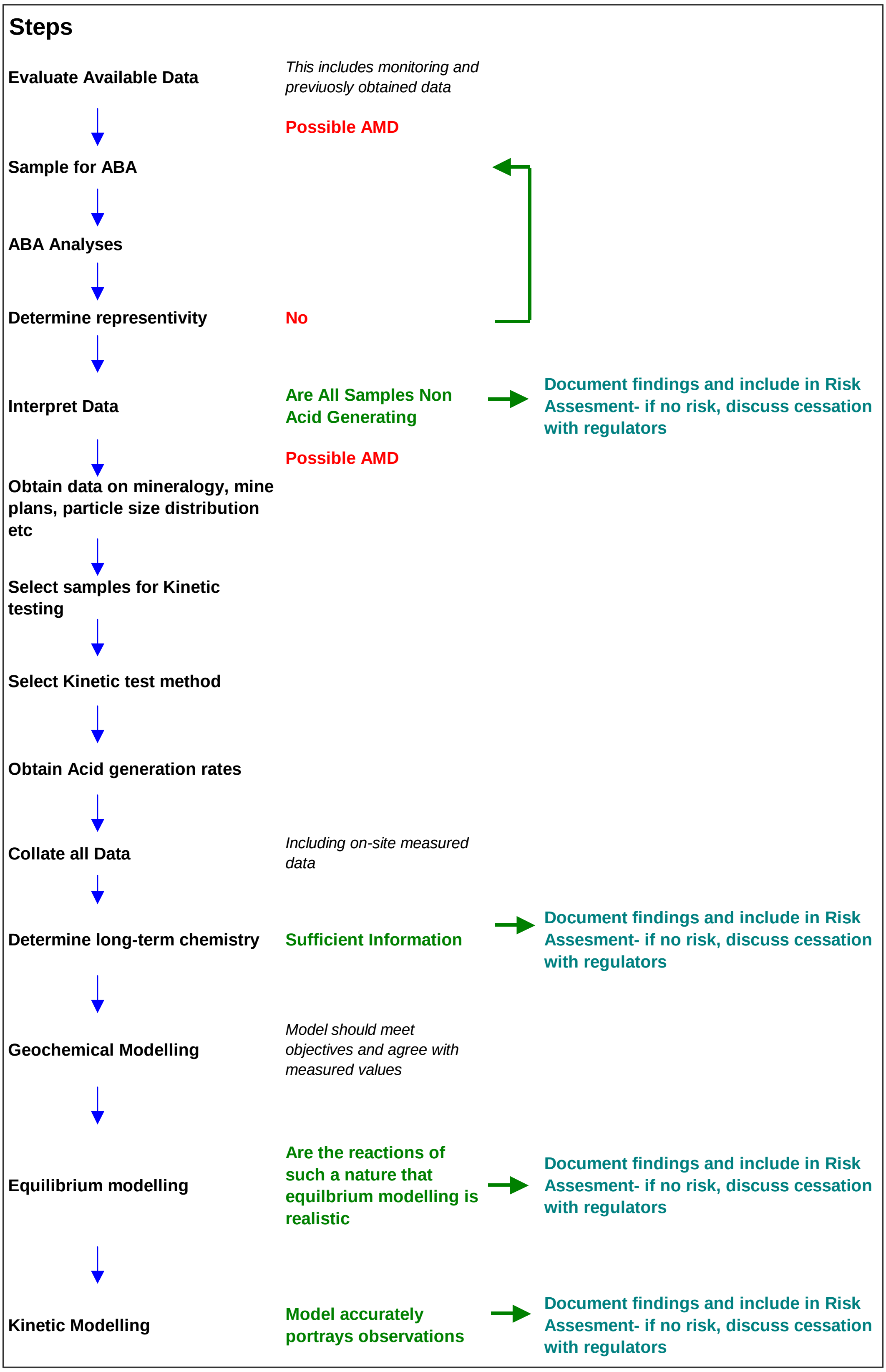


Figure 160. Suggested flow path for opencast spoil chemistry prediction.

The methods below are therefore selected for use in the ABATE strategy.

10.1 FIELD METHODS

Detailed fieldwork, that should include the following, is suggested:

- Water sampling and ongoing monitoring.
- Representative sampling of spoil material, preferably through boreholes so that volumetric and depth determinations can be made.
- *In situ* profiling of water.
- Test pits in established spoils to determine areal and age variation.

The usefulness of field methods is that they:

- are the most reliable measurements.
- represent the best Kinetic reactor there is (As Morin and Hutt,1997 state " Undoubtedly the most valuable and representative kinetic test that can be operated at a minesite is the full-scale operation of minesite components).
- determine current situation.
- provide understanding of controls on chemistry.
- allow comparison to ABA.
- serve as an early warning system.
- provide information to make decisions on appropriate control measures.

10.2 STATIC TESTS

Several static methods have been extensively tested to determine differences and select methods to be used.

The following methods are recommended:

- Paste/Initial pH and determination of solution products
- Acid potential using hydrogen peroxide oxidation, analysis of oxidation products
- Neutralising potential using sulphuric acid adaptation of the Sobek method

From this project the following can be concluded:

- Acid-Base Accounting is an excellent first-order tool to determine whether mine waste has the potential to form acidic drainage.
- The methods developed as part of this project are in agreement with methods used internationally.
- Modifications that have been made and suggested are all scientifically justifiable.

- Well-established criteria exist for the classification of individual samples as potentially acid-generating or neutralising.
- When samples are obtained at specific locations, with depth, the use of depth normalisation and volumetric calculations provide an established methodology of evaluating ABA results for an entire spoil area.
- Initial pH-methods in the laboratory yield similar results. A standard ratio of 1 g sample:10 g water is suggested, since it compares well to traditional paste pH-values, yet provides sufficient supernatant for analysis of naturally available leachable elements.
- Where material is to be used for neutralisation, acid leachable metals should be determined, since these levels may be extremely high if acidification was to occur.
- The hydrogen peroxide acid potential method and the Total S determined, using a Leco analyser, should provide similar assessment of acid potential.
- The hydrogen peroxide method, however, provides additional information such as an indication of oxidised pH and the levels of different potential contaminants, which can be released. Furthermore uncertainties regarding the contribution of different types of sulphur are eliminated, since only reactive sulphur is measured.

10.3 KINETIC TESTS

From the 24 kinetic tests in this project the following comments are pertinent:

- The humidity cell procedure used in this project was repeatable. Cells run with duplicate samples yielded results which were very similar.
- Good correlation was found between standard humidity test methodologies and more simplified methods. Three sets of duplicate tests illustrated that cheaper and less labour-intensive test protocols could yield similar results.
- The humidity cell results correlated very well with the static ABA done prior to testing.
- Humidity cells can provide reaction rates for different species. Reaction rates for all the cells tested could be obtained.
- Increasing the humidity causes an increase in the reaction rate, in agreement with international research.
- The rates of flushing were sufficiently high to prevent secondary mineral precipitation.
- Humidity cells may not provide an indication of acidity for samples that are uncertain, according to the static test results.
- Standardised tests should be used wherever possible, to build up a database of

rates for South African coalfields.

- Where the influence of any particular aspect, e.g. the effect of a cover, is to be proved using a kinetic test, a standard test should be done as a base case for comparison.
- The degree and rate of NP depletion can be determined from these cells.
- The theoretical depletion of NP correlated very well with the pH-development in the cells that acidified.
- A modified NAG/kinetic test showed that under highly oxidising conditions acidification of large boulders will occur due to reactions at the surface of the boulders. This acidification implies that the neutralising potential of the rock may be overestimated by any static NP determination.
- The Ca+Mg/SO_4 ratio appears to be an excellent early indicator of imminent acidification.
- Humidity cells should be able to provide “threshold” values for acid and neutralising potentials. This will greatly enhance the usefulness and likely success of the prediction of acidity.
- The usefulness of these cells for direct translation to field rates is, as yet, unclear from this research and that done worldwide.
- The variability observed in most spoils as far as mineral, rock/fine size and distribution and depth of soil cover makes the determination of sufficient kinetic tests for spoils an unfeasible task.
- The suggested ASTM test period of 20 weeks is shown by the research done in this project to be insufficient. This makes standardisation of the procedure extremely difficult.

Detailed methodologies for the operation of humidity cells and the interpretation thereof are in the accompanying document detailing the methods.

10.4 MODELLING

- Several input parameters which have been accurately determined are needed.
- Selection of appropriate model tool is vital.
- Provides long-term (+100 years) estimates of changes/trends in AMD quality.
- Enables a comparison between different options.
- Provides the basis for comparing the risk and costs associated with each option.

- It is often associated with large uncertainties.
- Field and laboratory validation can decrease uncertainty.
- Regarded as an advanced step in the ABATE process.
- Illustrations using simplified simulations showed how relatively minor variations (relative to the uncertainty of most of the data used in the models) can yield significantly different results.
- Despite limitations modelling is considered to be a very useful tool in prediction.

10.5 CASE STUDIES

Three case studies showed the application of ABA to a field scale.

- All of these studies showed a good correlation to static ABA and observations in the field.
- Spoils are extremely heterogeneous. Great variation in particle size, moisture content and the type of material was observed in test pits dug in the spoil.
- The depth of soil cover has no apparent impact on the spoil water chemistry. Oxygen and moisture penetrate into the system, regardless of the thickness of soil cover.
- Temperatures in the dug pits can be very low at surface. A rapid increase in the spoil temperature with depth is present in most pits and at 3m temperatures above 20°C have been recorded. In several of the dug pits, elevated temperatures ranging from 25-50°C have been recorded.
- There are localised areas of acidification, which are due to specific optimal microclimates; it seems that mineralogical composition plays a more important role than the age of spoils.
- The Optimum case study showed how several of the components in the ABATE process could be used to determine the likely quality emanating from the mine.
- The ATC comparisons illustrated an excellent correlation with ABA from core boreholes, *in situ* determinations, subsequent ABA and kinetic testing.
- Case study 3 used an example of a mine (Kriel) classified previously as an unlikely acid producer. *In situ* determinations in spoils of various ages showed that in the upper two to three metres the spoil was pH neutral to slightly alkaline. Long-term monitoring data from the borehole nearest the test pits, spanning more than a decade, showed that the water quality in the

area was currently neutral to slightly alkaline.

- Three reported case studies from South African coal mines illustrated the use and value of ABA as a tool in the assessment of coal mine water chemistry.
- The most significant of these illustrates how ABA from an area where mining has long ceased and which experiences considerable problems with AMD, consistently predicts that acidification is likely.

10.6 FURTHER RESEARCH

From the findings and experiences in this project, the following suggested future research is needed:

1. Determination of threshold values for ABA parameters in South African coal mines, i.e. the lower limits of ABA parameters to be regarded as meaningful in assessing a mine site and the bounds of uncertainty for ABA parameters.
2. Integration of all ABA and drainage (monitoring) in the coalfields to find regional trends and correlation to assist in the early identification and management of AMD in South Africa.
3. Extensive testing and validation of model codes used in AMD prediction.
4. Development of an affordable and user-friendly reactive transport model that can be used in South African coal mines

10.7 FINAL REMARK

As a final remark, Price (1998) should be kept in mind:

"Although our understanding of Acid Rock Drainage is far from complete, the available prediction and mitigation tools combined with a well informed, cautious approach should allow mines with a potential for AMD to meet receiving environment objectives and minimise the liability and risk."

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APPENDIX 1

Detailed methodologies for several ABA methods

STATIC METHODOLOGIES

1 STATIC NET ACID GENERATION (NAG) PROCEDURE

1.1 Sample Preparation

Drill core and bulk rock samples should be crushed to nominal 4 mm and a sub sample pulverised to approximately 200 Mesh (<75 µm). Tailing and process residue samples can be tested 'as received'.

1.2 Reagents

Reagent 1: H_20_2 - BDH 'Analar' Analytical Reagent 30% w/v (100 V), or equivalent, diluted 1:1 with deionised H_20 to 15% (Refer to Note 1).
Reagent 2: NaOH -0.50 M Standardised Solution.

Reagent 3: NaOH - 0.10 M Standardised Solution.

1.3 Method

1.Add 250 ml of Reagent 1(15 % H_2O_2) to 2.5 g of pulverised sample in a 500 ml wide mouth conical flask, or equivalent. Cover with a watch glass, and place in a fume-hood or well ventilated area (refer to note 2). The H_2O_2 should be at room temperature before commencing test.

2.Allow sample to react until ‘boiling’ or effervescing ceases. Heat sample on hot plate and gently boil until effervescence stops or for a minimum of 2 hours. Do not allow sample to boil dry - add deionised water if necessary.

3.Allow solution to cool to room temperature then record final pH (NAG pH).

4.Rinse the sample that has adhered to the sides of the flask down into the solution with deionised water. Add deionised water to give a final volume of 250 ml.

5.Titrate solution to pH 4.5 while stirring with the appropriate NaOH concentration based on final NAG solution pH as follows:

NAG solution pH	Reagent	NaOH Concentration
>2	2	0.10 M
<2	3	0.50 M

1.4 Calculation

Net Acid Generation (NAG) = 49 x V x M/W, where:

NAG = net acid generation (kg H_2SO_4/tonne), V = volume of base NaOH titrated (ml), M = molarity of base NaOH (moles/l), W = weight of sample reacted (g)

NOTE: If NAG value exceeds 25 kg H_2SO_4 per tonne, repeat using a 1.00 g samples.

1.5 Notes and Precautions

1.1. The pH of the H_2O_2 used in the NAG test should be checked to ensure it is between pH 4 and 7. If the pH is less than 4 then add dilute NaOH (use a solution made up by adding 1 g NaOH to 100 ml deionised H_2O) until the pH is greater than 4 (aim for a pH between 4 and 6). The pH is adjusted to greater than pH 4 to ensure that the phosphoric acid, used to stabilise H_2O_2 in some brands, is neutralised. The pH of the 15 % H_2O_2 should always be checked to ensure that any stabilising acid is neutralised, otherwise, false positive results may be obtained.

1.2. The NAG reaction can be vigorous and sample solutions can 'boil' at temperatures of up to 120^{o}C. Great care must be taken to place samples in a well ventilated area or fume cupboard.

1.3. Caution should be taken in the interpretation of NAG test results for coal reject samples and other materials which may contain a high content of organic material (such as potential acid sulphate soils, dredge sediments and other lake or marine sediments). All organic material must be completely oxidised otherwise acid NAG results can occur which are unrelated to sulphides. Several aliquots of H_2O_2 reagent may be added to the sample to breakdown any organic acidity.

1.4. Samples with positive NAPP value, high sulphur content and high ANC must be carefully evaluated (Miller *et al.*, 1997)

2 BC RESEARCH CONFIRMATION TEST

2.1 Equipment

1.250 ml Erlenmeyer flasks, preferably with a baffled base to facilitate oxygen mass transfer during agitation. 2.Temperature controlled gyratory or reciprocating shaker/incubator equipped with clamps for Erlenmeyer flasks (provision for CO_2 enrichment of the air is desirable). 3.pH meter equipped with a combination pH electrode. 4.Pipette, 5 ml

2.2 Reagents

1.Sulphuric acid, 6N or 12N.

2.Distilled or deionised water.

3.Reagent grade nutrient salts, typically $(NH_4)_2SO_4$, KCl, K_2HPO_4, $MgSO_4.7H_2O$, and $Ca(NO_3)_2$.

4.Bacterial culture containing *T. ferrooxidans* [Cultures should be selected based on their known ability to be able to oxidise ores, waste rock or tailings of similar mineralogy to the test sample.].

2.3 Procedure

1.Crush and pulverise the sample to pass a 400 mesh (Tyler) screen.
2.Prepare bacterial cultures for use as inoculate using standard laboratory techniques. The cultures should have been previously grown on and adapted to ore or waste rock containing pyrite with a sulphur content at least as high as the test sample. Whole pulp inoculate are preferred to cells recovered from solution only. If solids free inoculate, containing very low soluble metal concentrations are required, these should be prepared by differential centrifugation techniques.
3.In duplicate, weigh out 15-30 g (low weight for high sulphur contents) of sample into an Erlenmeyer flask with 70 ml of a nutrient medium containing (typically) 3 g/l $(NH_4)_2SO_4$, 0.1 g/l KCl, 0.5 g/l K_2HPO_4, 0.5 g/l $MgSO_4.7H_2O$, and 0.01 g/l $Ca(NO_3)_2$.
4.Place flask on shaker and periodically add sulphuric acid (6 or 12 N) as required to bring pH to a stable value between pH 2.5 and 2.8. Do not proceed until pH is stable.
5.Inoculate flasks with 5 ml of an active *T. ferrooxidans* culture. Record weight of flask, cap flask with a cotton or foam plug, and place on shaker at 35^oC.
6.Monitor flask regularly for pH. Before each measurement, add distilled water to bring flask to original weight to allow for evaporation. In some cases, the sampling of flasks for a soluble species (e.g. Fe, Cu. Zn) might assist in determining progress of the oxidation process.
7.When oxidative activity has ceased, as evidenced by a stable pH (or metal concentration), add half the weight of sample originally used and continue shaking for 24 hours.
8.Record the pH and if above 3.5, terminate the test. If not, again add half the weight of sample and agitate for up to an additional 72 hours and record the final pH.

Typically, about 3 to 4 weeks following inoculation, are required to complete this test.

3 THE MODIFIED ACID BASE ACCOUNTING PROCEDURE FOR NP

3.1 Procedure

1.Add a few drops of 25% HCl to 1 to 2g of pulverised sample (80% minus 200 mesh) on a watch glass or piece of aluminium foil. Observe the degree of reaction and assign a fizz rating as "none, slight, moderate, or strong fizz".

2.Weigh approximately 2.00g of pulverised sample into a 250ml conical flask and add approximately 90ml of distilled water.

3.At the beginning of the test (time = 0), add a volume of certified or standardised 1.0N HCl according to the fizz rating as follows:

Fizz Rating	Volume of 1.0 N HCl (ml)	
	At time = 0 hour	At time = 2 hour
None	1.0	1.0
Slight	2.0	1.0
Moderate	2.0	2.0

4.Place the flask on a shaking apparatus such a reciprocating shaker, maintained at room temperature. After approximately 2 hours, add the second acid quantity as indicated in the above table.

5.After approximately 22 hours, check the pH of the pulp. If it is greater than 2.5, add a measured volume of 1.0N HCl to bring the pH into the range 2.0 to 2.5. If the pH is less than 2.0, too much acid was added in steps 2 and 3. In this case, repeat the test adding a reduced volume of HCl.

6.After 24 hours, terminate the test and add distilled water to the flask to bring volume to approximately 125ml. Measure and record the pH, making sure it is in the required range of 2.0 to 2.5.

7.Titrate the contents of the flask to a pH of 8.3 (this being the usual endpoint for acidity titrations, corresponding to the stoichiometric equivalence point for carbonate/bicarbonate in natural waters in which carbonic acid it the most dominant weak acid, using standardised 0.5N or 0.1N NaOH.

8.Calculate the NP of the sample as follows:

$$\text{Modified NP (kg CaCO}_3\text{/t)} = \frac{[(\text{N x vol(ml) of HCl}) - (\text{N x vol(ml) NaOH}) \text{ x } 50]}{[\text{weight of sample(g)}]}$$

4 BC RESEARCH INITIAL TEST

4.1 Assay

The neutralisation potential of a sample is determined by titrating a slurry of finely ground sample with 1.0 N sulphuric acid to a stable end-point of 3.5 using an automatic pH titrator. This choice of end pint is based on the assumption that it represents the limit above which iron and sulphide-oxidising bacteria are not active. Therefore, if the theoretical acid production is not sufficient to lower the pH to below pH 3.5, then bacterial oxidation of the material will not occur and AMD formation is unlikely. This acid consumption, in units of kg H_2SO_4 per tonne of material is calculated as follows:

$$\text{Acid Consumption} = \frac{\text{ml } 1.0 \text{ N } H_2SO_4 \times 0.049 \times 1000}{\text{Sample mass (gram)}}$$

This value can be converted to units of kg $CaCO_3$/tonne for comparison with the results of acid-base accounting tests. Typically, the test takes at least 24 hours to complete. Although the test is more time consuming than acid base accounting, the test is considered to provide a good estimation of the practical NP since excess acid is not employed as in the acid-base accounting methods. In addition, the use of sulphuric acid provides a better simulation of field conditions than hydrochloric acid. AP values based on sulphide-sulphur analysis is advisable (Bruynesteyn, 1984, Cuncan and Bruynesteyn, 1979, and Lawrence and Day, 1997).

5 LAPAKKO

5.1 Sample Preparation

Grind or pulverise sample so that 70% passes a 325 mesh (<44 µm).

5.2 Titration Test

Prepare a stirred mixture of 10g sample in 100ml distilled water.

Using an automatic titrator titrate with 1.0 N sulphuric acid until a pH of 6.0 is reached. The test is complete when less than 0.1ml acid is added over a 4hour period. The amount of acid added can then be used to calculate the NP as follows:

$$\text{NP (kg } CaCO_3\text{/tonne)} = \frac{\text{Acid volume (ml) x Normality Acid x 50}}{\text{Sample weight (g)}}$$

The test can be very time consuming, due to the slow rate of acid addition necessary to prevent over-addition. The acid strength should also be low (<0.05N) for the same reason. (Lapakko, 1994) pH 6 was selected since it is a commonly applied water quality standard. Therefore, the neutralisation potential available above this pH represents the amount of acid that a mine waste could neutralize while maintaining drainage pH in a range that meets water quality standards.

It should be noted that this method is intended to give the NP present, rather than the NP available for reaction in the field. Consequently, the value determined for waste rock will exceed that which is practically available in the field. This is the natural consequence of not running the test on field size particles, which would consider the mode of occurrence of neutralising minerals. It's just a bit difficult to squeeze some of that field-sized material into these beakers. Nonetheless, for future testing Lapakko (1994) would consider using a larger particle size for waste rock. In their lab they have made the additional modification of using 2g rather than 10g in the test.

For some solids, this procedure can be quite slow (Lawrence and Wang, 1996). This is particularly the case for elevated carbonate contents and cases where the carbonate occurs with magnesium or magnesium and iron mixtures. The method is time consuming and not recommended for routine assessments (MEND, 1996).

6 PEROXIDE SIDERITE CORRECTION FOR SOBEK METHOD

The method, as developed by a Pennsylvania-West Virginia Overburden Task Force (Leavitt *et al.,* 1995), is as follows (for triplicate samples and a blank):

1. Place 2g sample in each of three beakers with a fourth beaker having no sample.
2. Add an amount and strength of HCl to each beaker based on the sample fizz rating, and adjust volume to 100ml.
3. Add boiling chips to beakers and cover with watch glass.
4. Boil gently for 5 minutes and allow to cool.
5. Gravity filter beakers contents using Whatman No. 40 (0.45 µm) filter.
6. Add 5ml of 30% H_2O_2 to the filtrate.
7. Boil for a further 5min (boiling chips and watch glasses), then cool.
8. Hand titrate, as per Sobek Method, with standard NaOH to achieve and hold an endpoint pH of 7.0 for 30 sec (Skousen *et al.,* 1997)

APPENDIX 2

Specialist Workshop on ABATE Project Participants and Comments Arising

Workshop on acid-base accounting project procedures held at the Water Research Commission on 15 March 2000

Present on invitation:

NAME	**ORGANISATION**	**E-MAIL ADDRESS**
Blanchè Postma	DWA&F	TCF@dwaf.pwv.gov.za
Meiring du Plessis	WRC	Meiring@wrc.org.za
Louis de Wet	Waterlab	Waterlab@iafica.co,za
Jaco vd Berg	Jasper Muller Associates	Jaco@jma-cc.co.za
Andrew Johnstone	Groundwater Consulting Services	Gcs@icon.co.za
John Cowan	SRK	Jcowan@srk.co.za
Alistair James	Metago	Arjames@mweb.co.za
Adel Meyer	Metago	Adele@metago.co.za
Nico Bezuidenhout	Wates, Mering and Barnard	Nocibez@wmb.co.za

Comments received for consideration:

1. The acronym ABATE is agreed upon to describe the test procedures that will be used in South Africa.
2. To determine the sample size, we normalise the data set and apply test statistics valid for normal distributions. The suggestion was made that a beta distribution should be considered.
3. Confidence limits for predictions must by high, 90% for instance, for system that will remain alkaline. For system that will become acid, a low confidence limit such as 60% should be sufficient. Thereafter it becomes an engineering problem to design for and manage the problem.
4. In testing the validity of the sample size, units clearly different from the other should be removed from the statistical analysis; otherwise distorted statistical results may be obtained.
5. Where selective spoil handling is done by a mine, this spoil should be tested separately for its chemistry and sample size.
6. Geophysical borehole logging should be considered as an indirect method that could assist in recognizing different horizons and thus in the reconciliation of laboratory analyses with the field situation.

7. Reactive sulphur measurement procedure should be considered in the determination of the acid generating potential of a sample.

8. The term neutralisation potential is considered to be synonymous to that of base potential.

9. The workshop recommends that a ratio of 1:10 for the measurement of natural pH should be standardised upon for the reason that the fluid may be separated afterwards and analysed chemically. In the field, a 1:1 paste pH is recommended.

10. For base potential titration, a final pH of 7,0 is recommended.

11. It is recommended that 0,06 sulphuric acid should be used in base potential titrations because of the greater stability of sulphuric acid and its greater reactivity with dolomitic lime.

12. For acid potential determination, the H_2O_2 method with no stabilising agent is recommended because it provide a final pH and a leachate that may be analysed.

13. A Leco analyzer provides stable results in the range between 0,1 – 11%. Louis de Wet (Waterlab) will provide material of which the sulphur content has been determined on a Leco analyzer for H_2O_2 determination by the IGS.

14. Consideration should be given for modified limits to the NAG test. The weathered horizon that naturally has a pH of 5,0 but no sulphur should not be considered in the NAG test.

15. A comparison should be made between the EPA shake flask tests versus the stir tests suggested by the IGS.

16. Humidity cells cannot really be standardised because of the scale differences between lab and field situations.

17. Humidity cells cannot successfully simulate the differences between spoils and tailings because of the barometric lung effect.

18. Methodologies finally recommended should be as close as possible to existing overseas methodologies for the sake of comparing data and also since many international companies operate in South Africa and abroad.

19. All methodologies finally recommended should be considered as tools and not as standards.

20. Mines should not be committed to an extensive all-inclusive set of test procedures if sufficient results are forthcoming from a subset of the prescribed test procedures.

21. Special mention must be made of the relevant of mineralogy in ABATE.

22. William Pulles acts at a co-ordinator for the compilation of the best practice guideline for the DWA&F. The WRC document should be the scientific document that should serve as the basis for the compilation of the ABATE section in these guidelines.

23. A well-balanced approach should be striven towards, not losing sight of practicalities.

24. Guidelines should be provided as to the conditions under which ABATE should be used.

25. Standardised procedures for cross laboratory testing should be provided, if this is feasible.

A form(s) for laboratory analysis and data reporting should be provided. The WISH format could be considered for these purposes.

APPENDIX 3

Laboratory determination and PHREEQC comparison of Buffering levels for different minerals

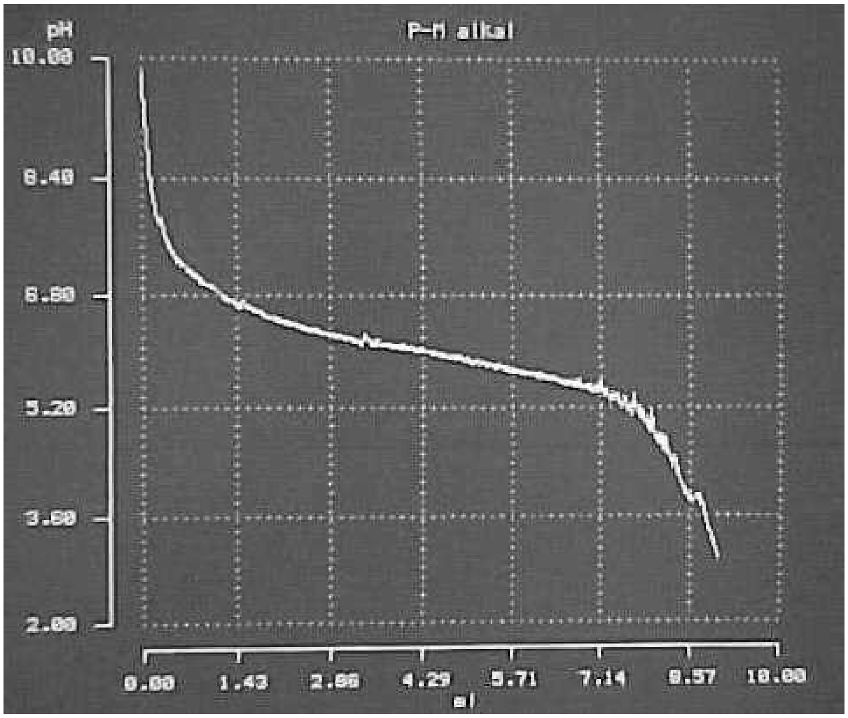


Figure 1. Calcite buffering of H_2SO_4 using an automatic titrator (screenshot)

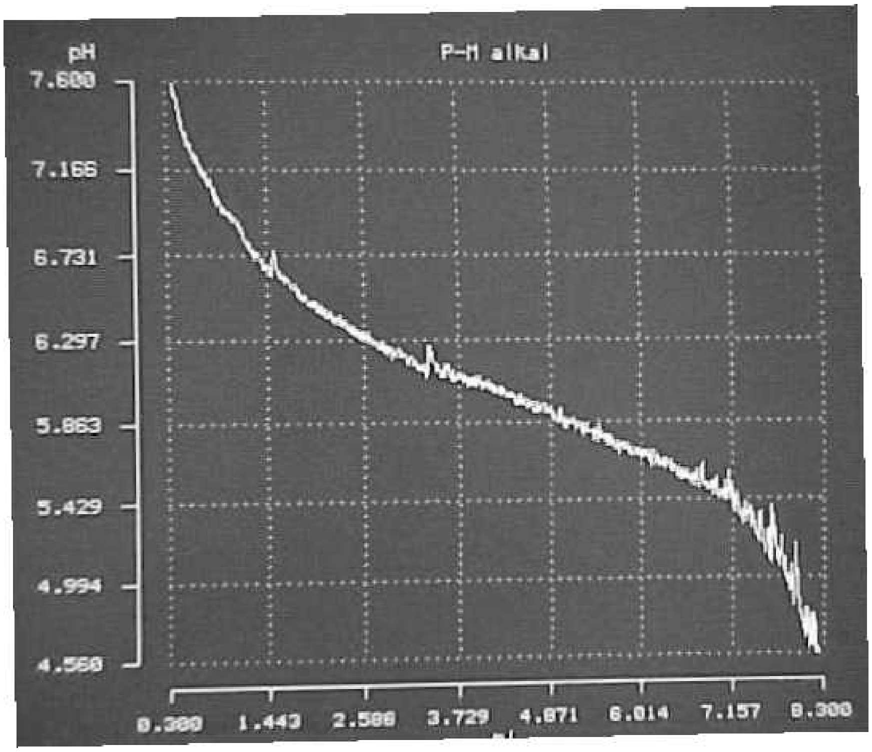


Figure 2. Calcite buffering of H_2SO_4 using an automatic titrator (screenshot). Close-up.

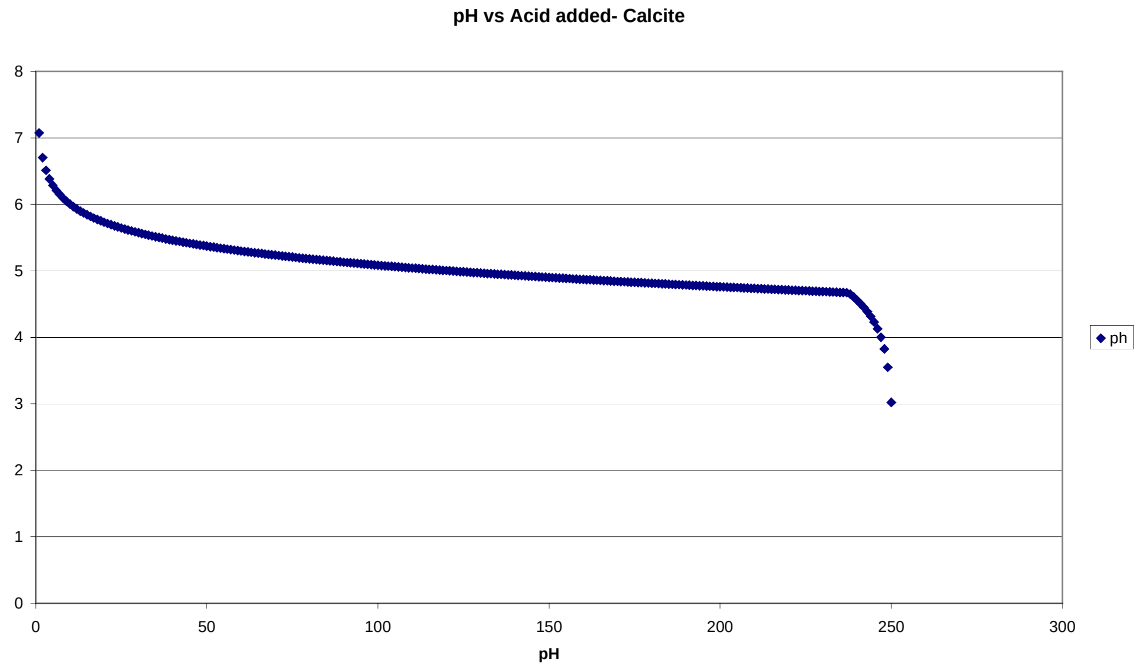


Figure 3. Calcite buffering of H_2SO_4 as determined by PHREEQC.

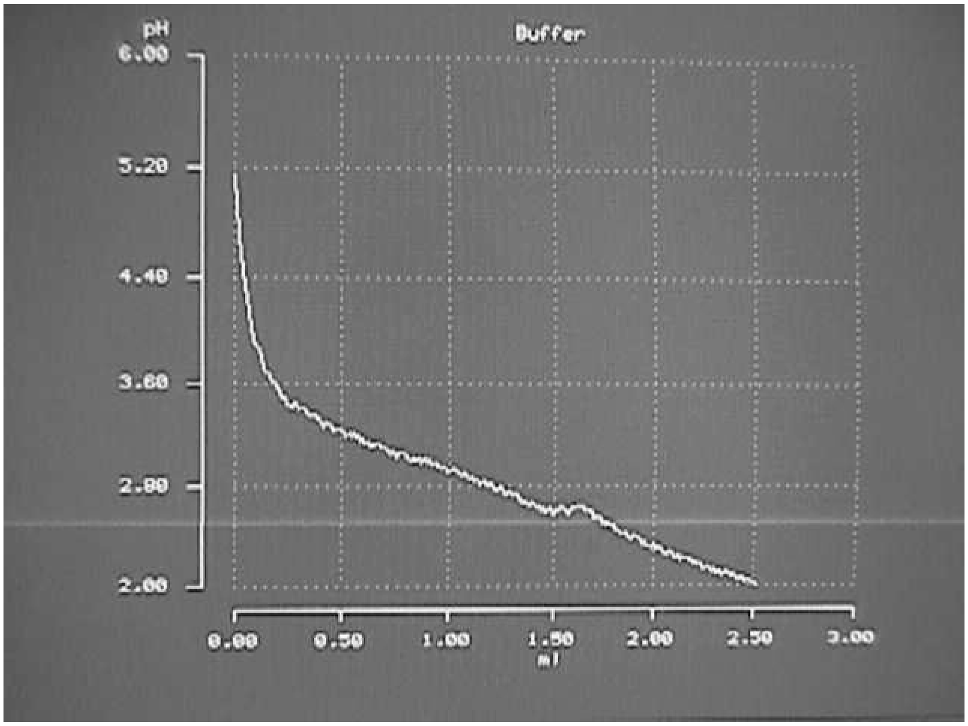


Figure 4. Kaolinite buffering of H_2SO_4 using an automatic titrator (screenshot).

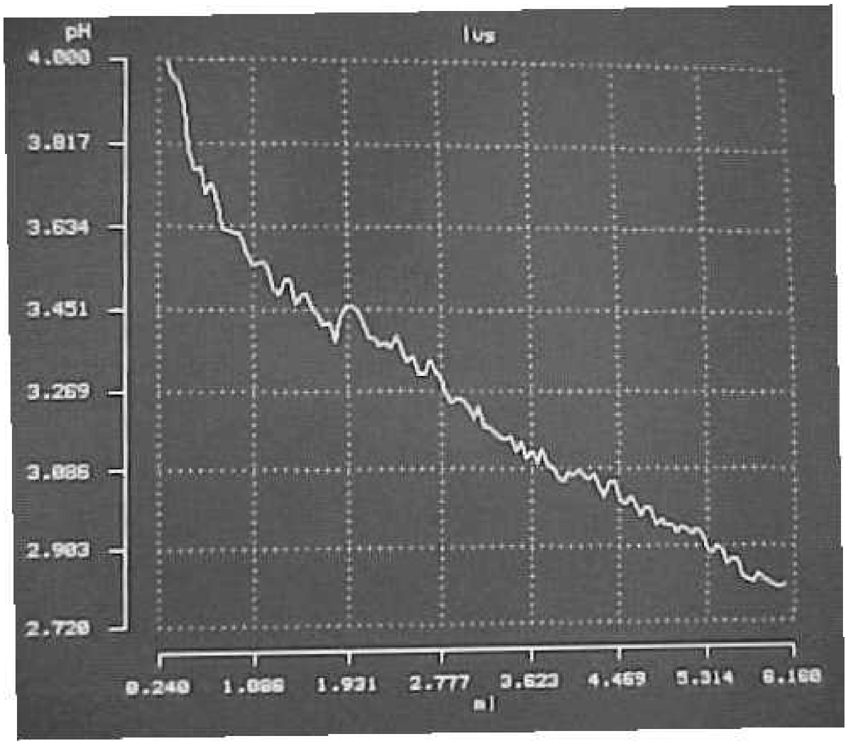


Figure 5. Kaolinite buffering of H_2SO_4 using an automatic titrator (screenshot). Close-up.

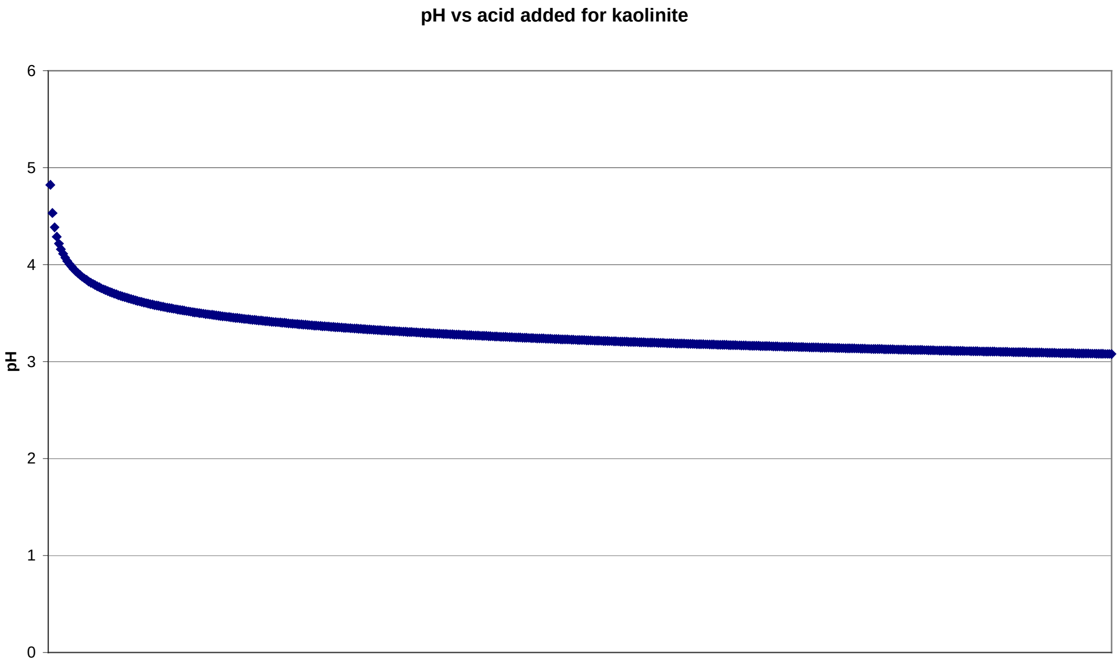


Figure 6. Kaolinite buffering of H_2SO_4 as determined by PHREEQC.

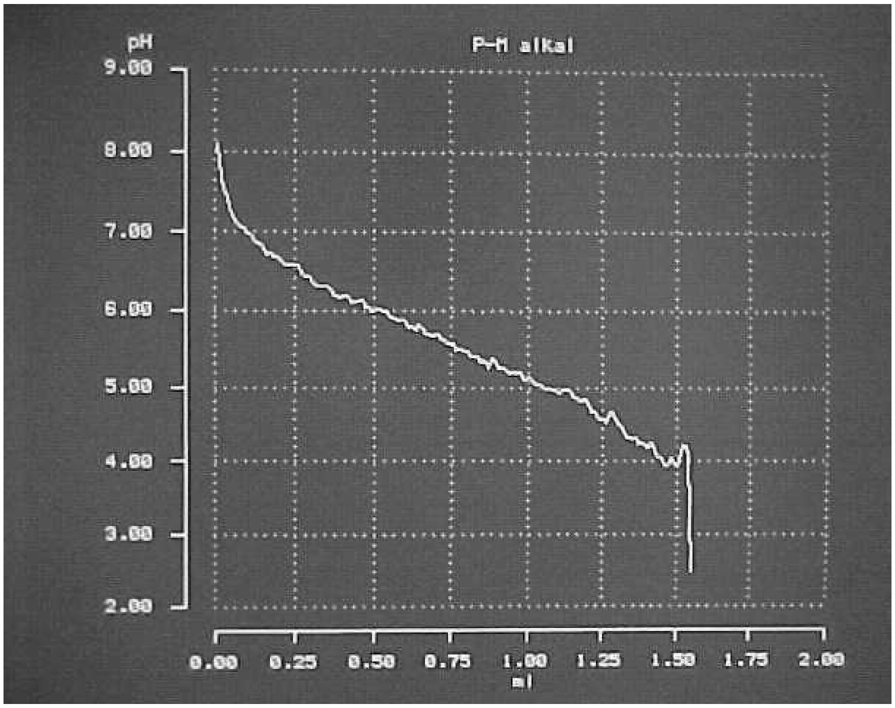


Figure 7. Siderite buffering of H_2SO_4 using an automatic titrator (screenshot).

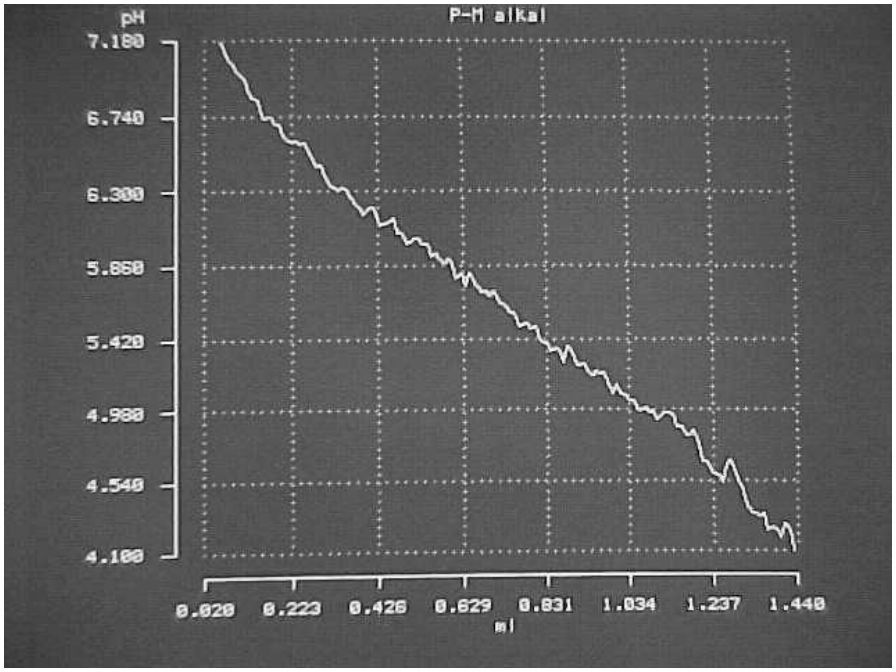


Figure 8. Siderite buffering of H_2SO_4 using an automatic titrator (screenshot). Close-up.

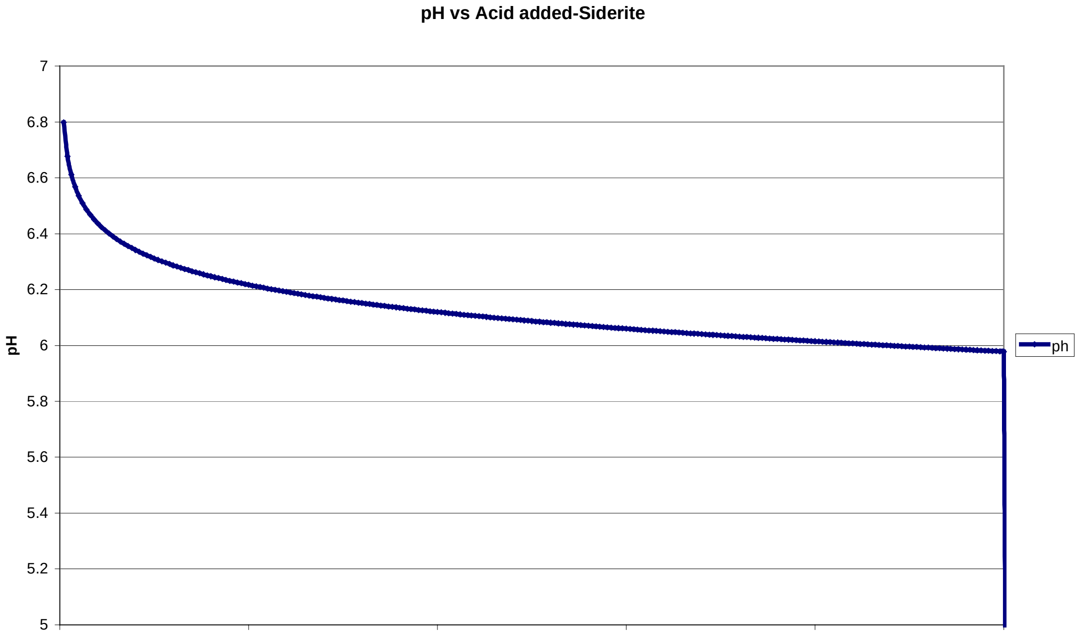


Figure 9. Siderite buffering of H_2SO_4 as determined by PHREEQC.

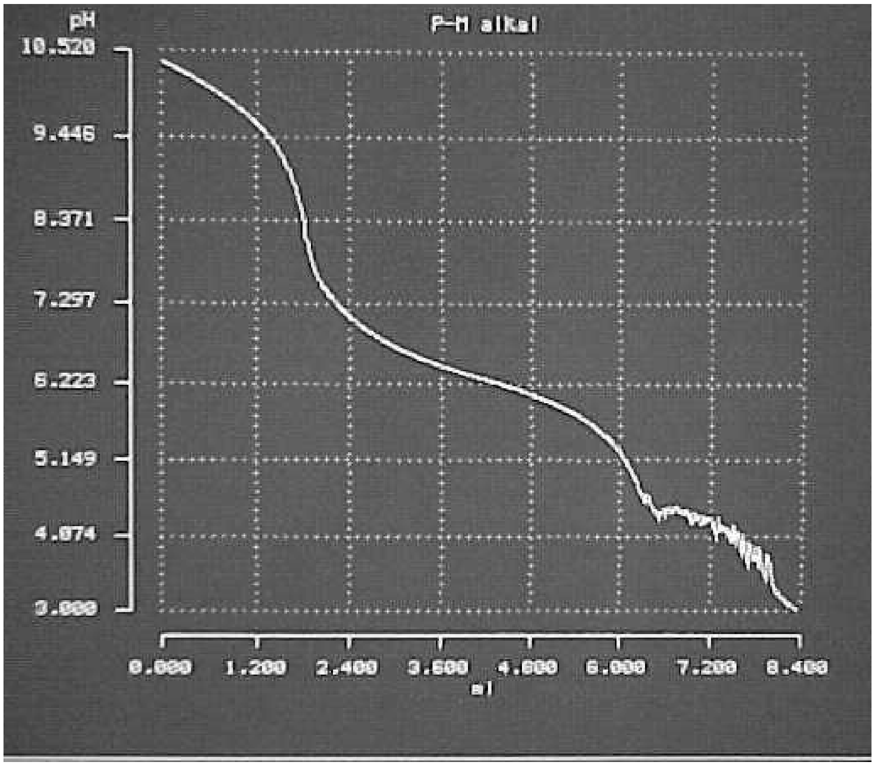


Figure 10. Calcite, $NaHCO_3$ and Kaolinite buffering of H_2SO_4 using an automatic titrator (screenshot). Close-up.

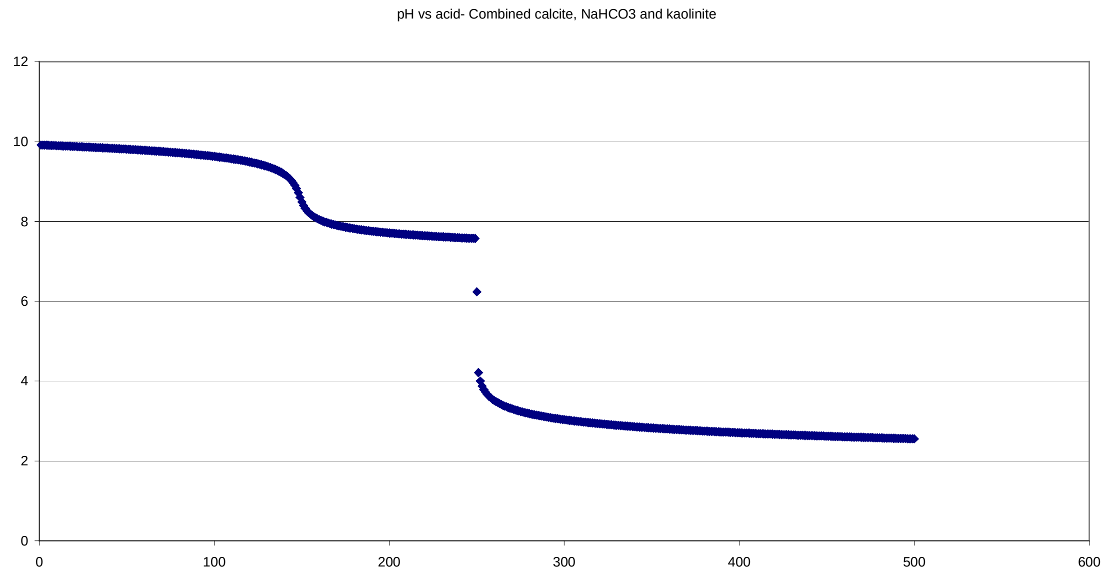


Figure 11. Calcite, $NaHCO_3$ and Kaolinite buffering of H_2SO_4 as determined by PHREEQC.

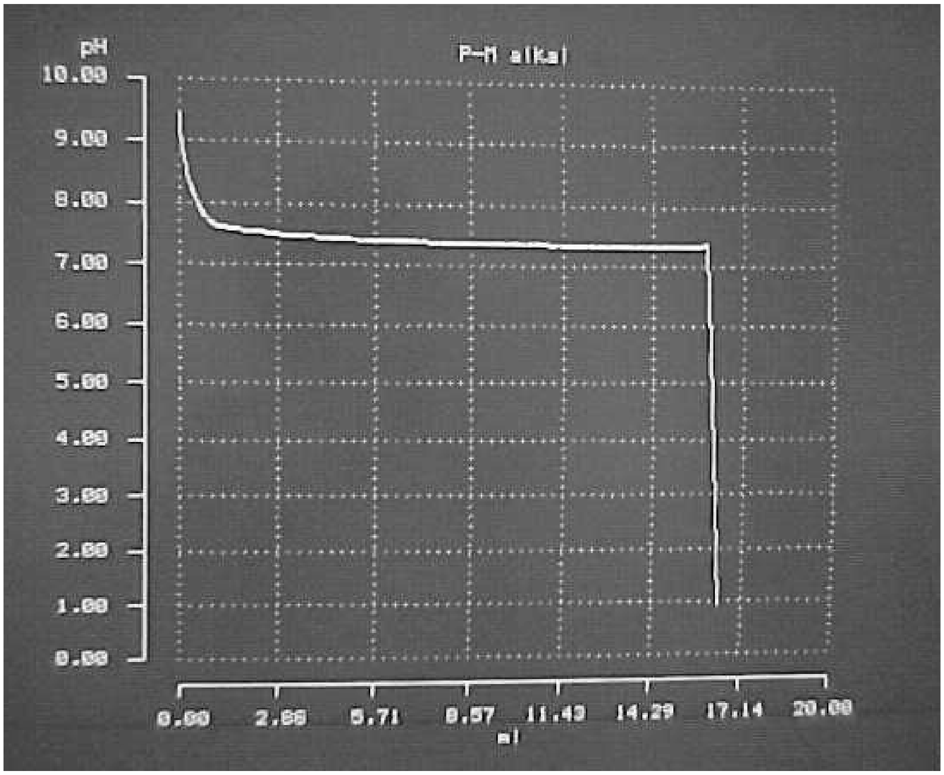


Figure 12. Dolomite buffering of H_2SO_4 using an automatic titrator (screenshot). Close-up.

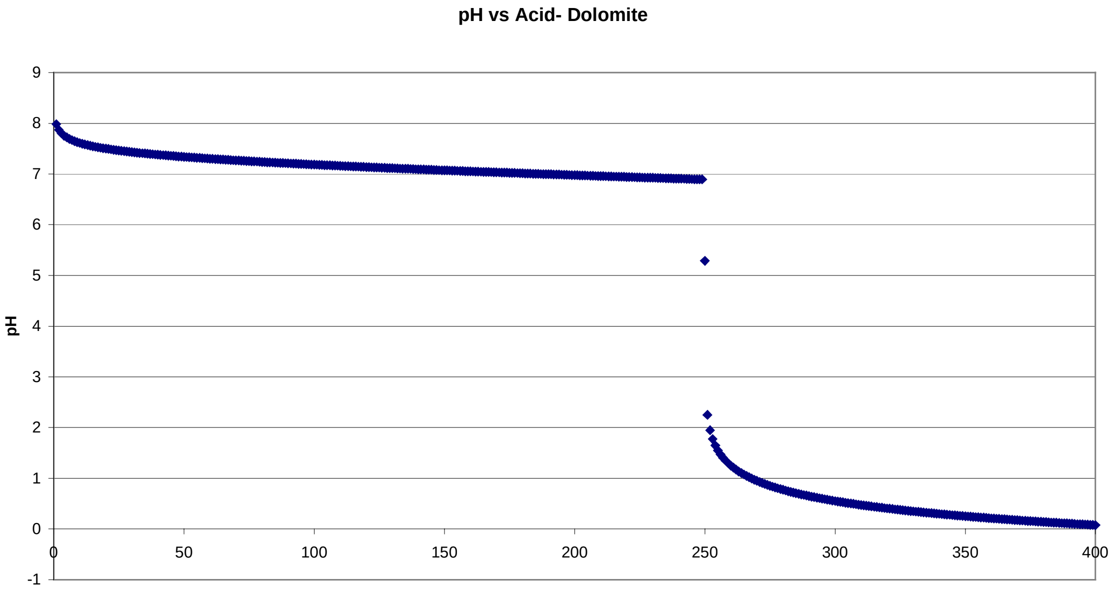
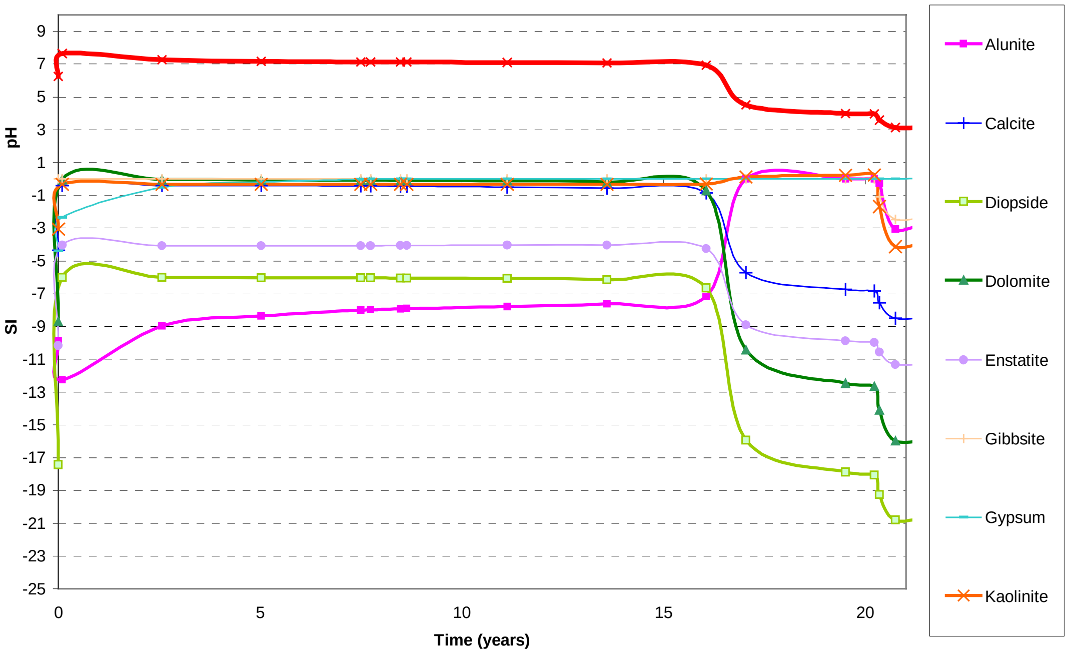


Figure 13 Dolomite buffering of H_2SO_4 as determined by PHREEQC.

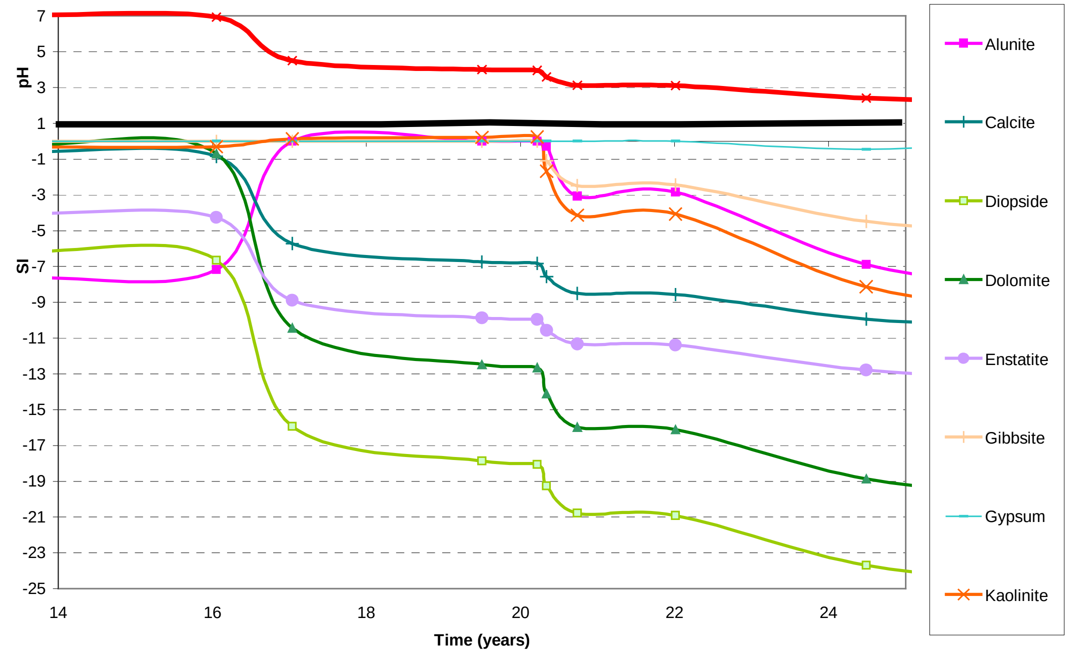
APPENDIX 4

Detail of minerals due to change in pH over time, based on geochemical modelling

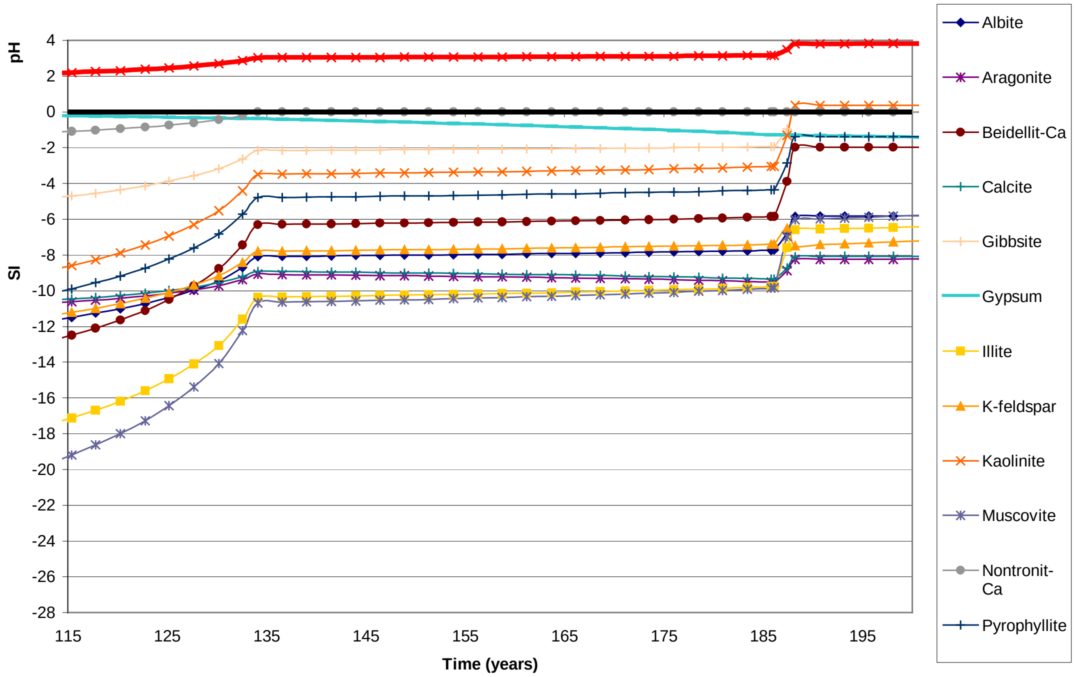
Selected Mineral Saturations vs Time(kinetic reactions)



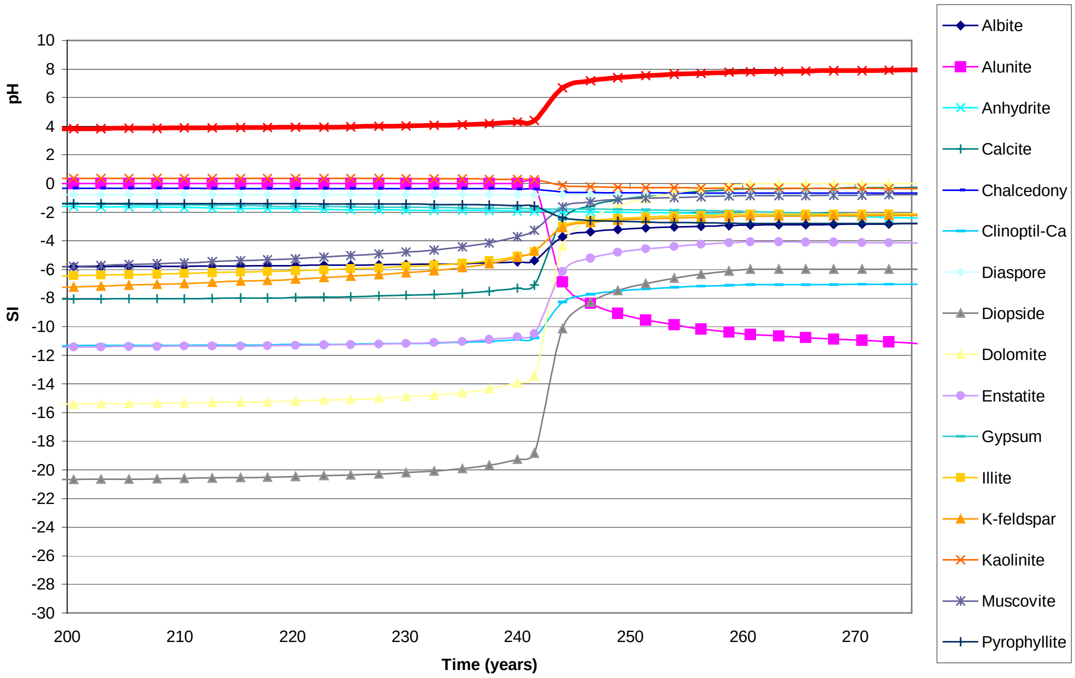
Selected Mineral Saturations vs Time(kinetic reactions)



Selected Mineral Saturations vs Time(kinetic reactions)

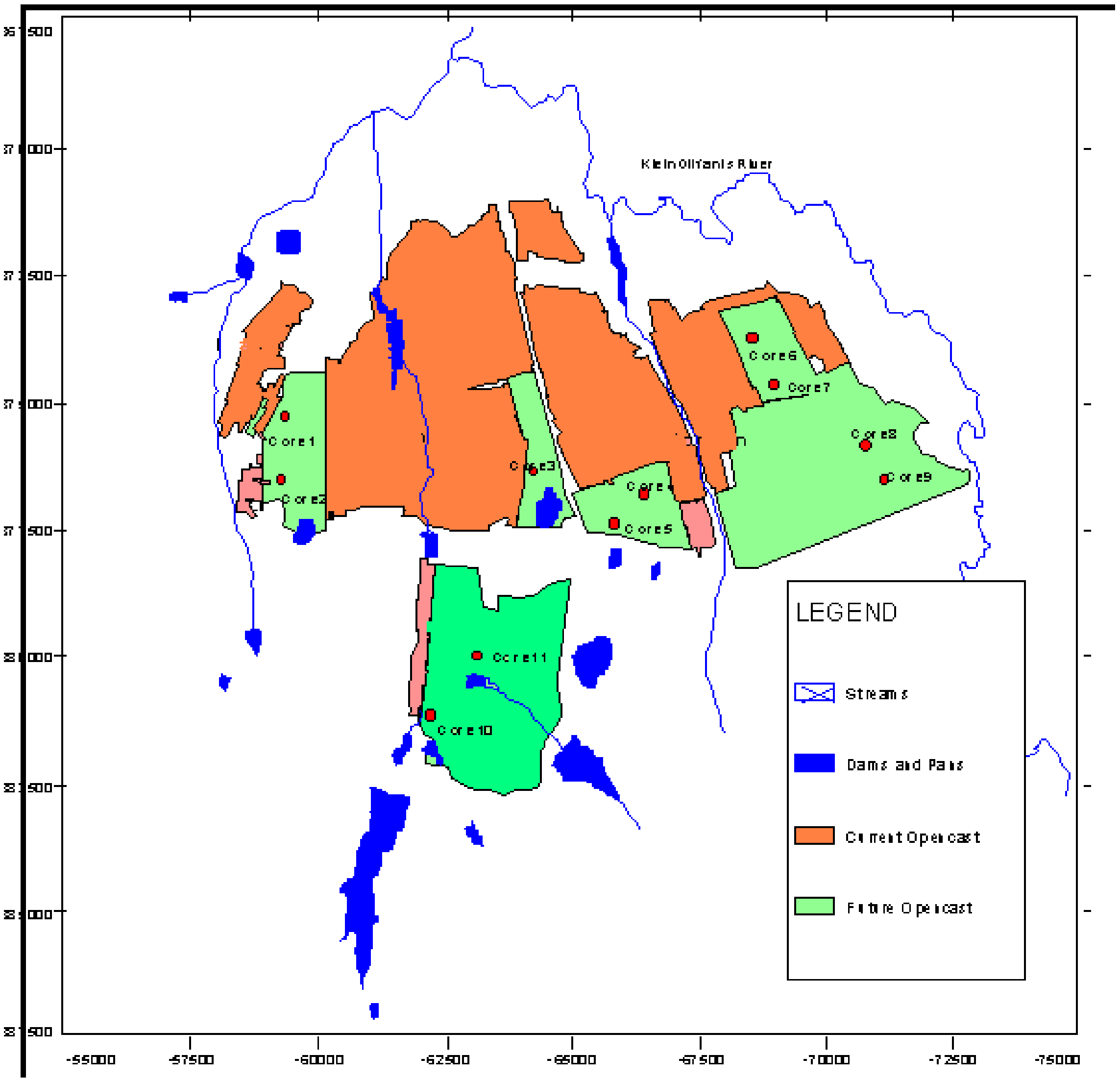


Selected Mineral Saturations vs Time(kinetic reactions)



APPENDIX 5

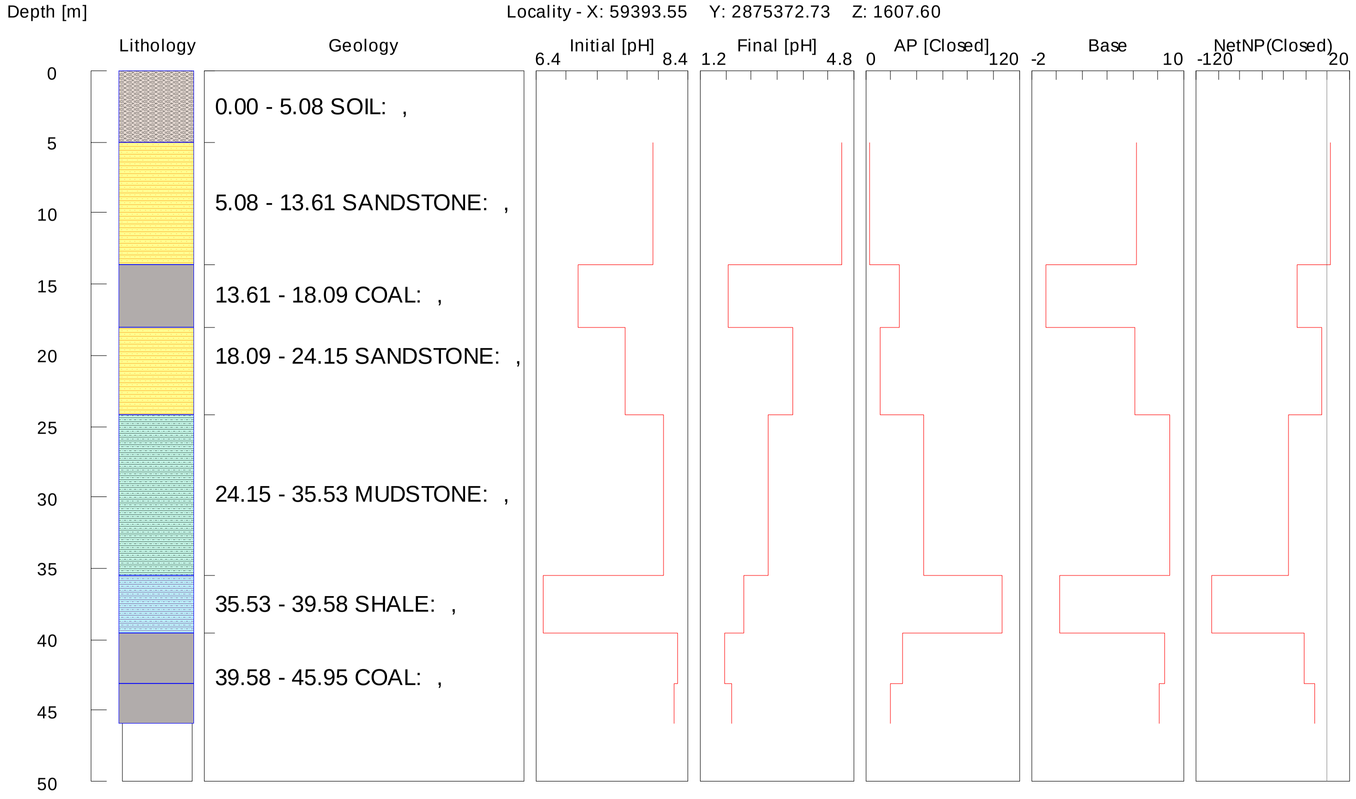
Borehole logs and graphs of acid-base accounting



Localities of cored boreholes

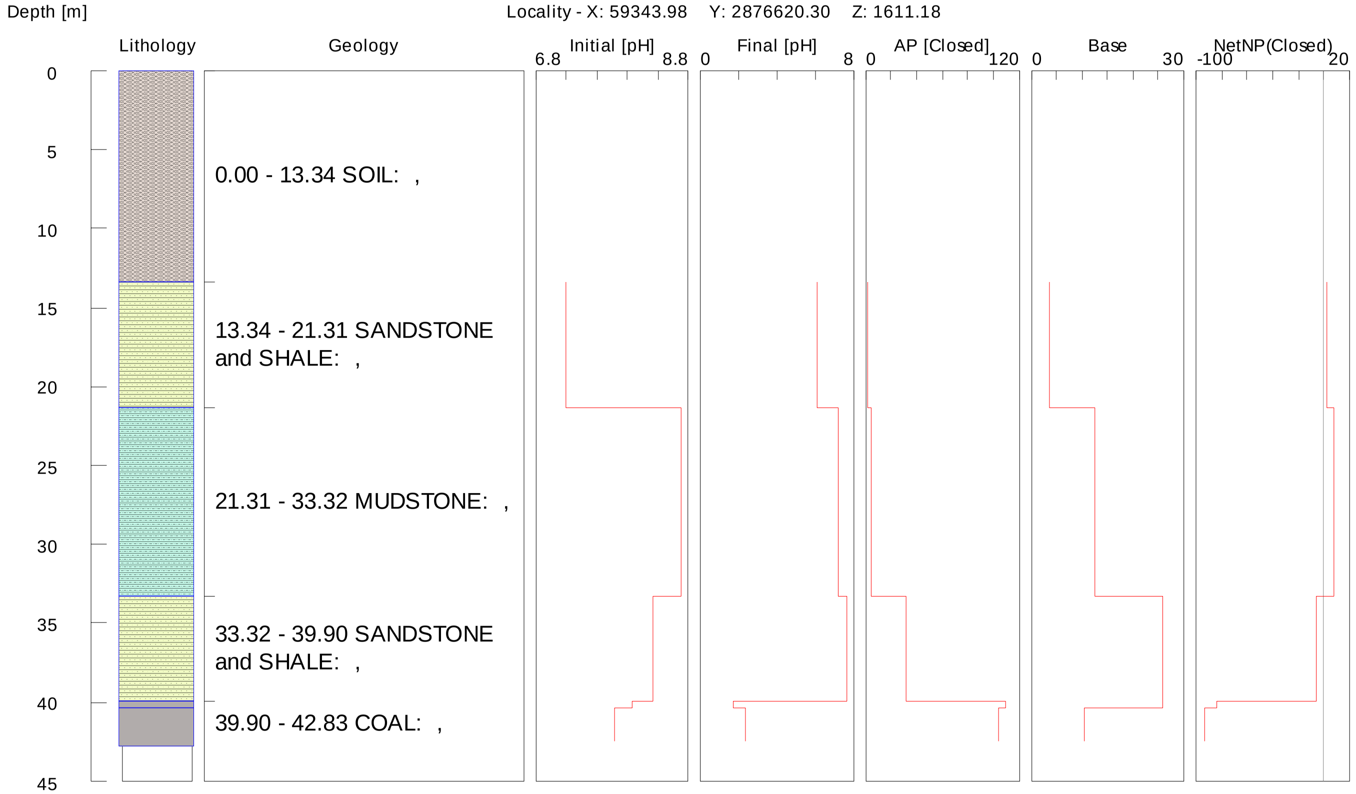
Borehole Log - Core1

Locality - X: 59393.55   Y: 2875372.73   Z: 1607.60



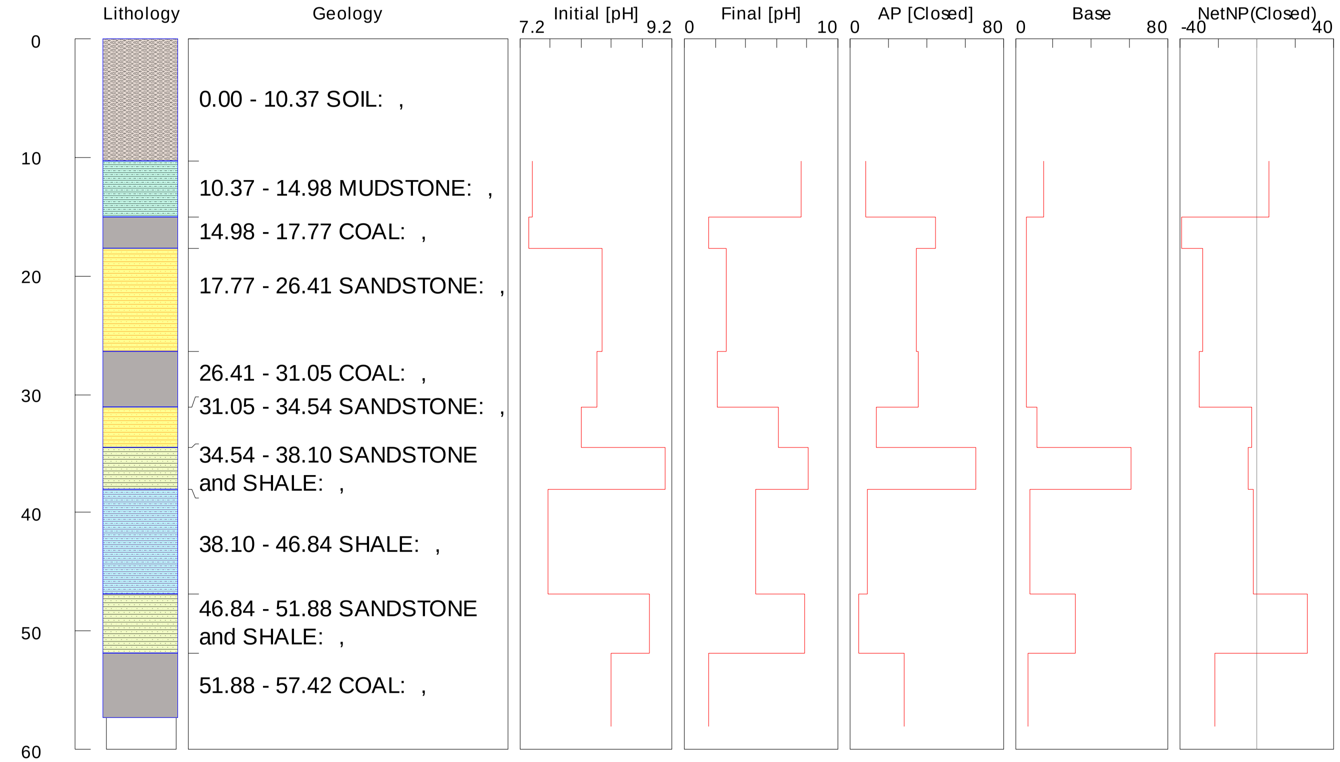
Borehole Log - Core2

Locality - X: 59343.98 Y: 2876620.30 Z: 1611.18



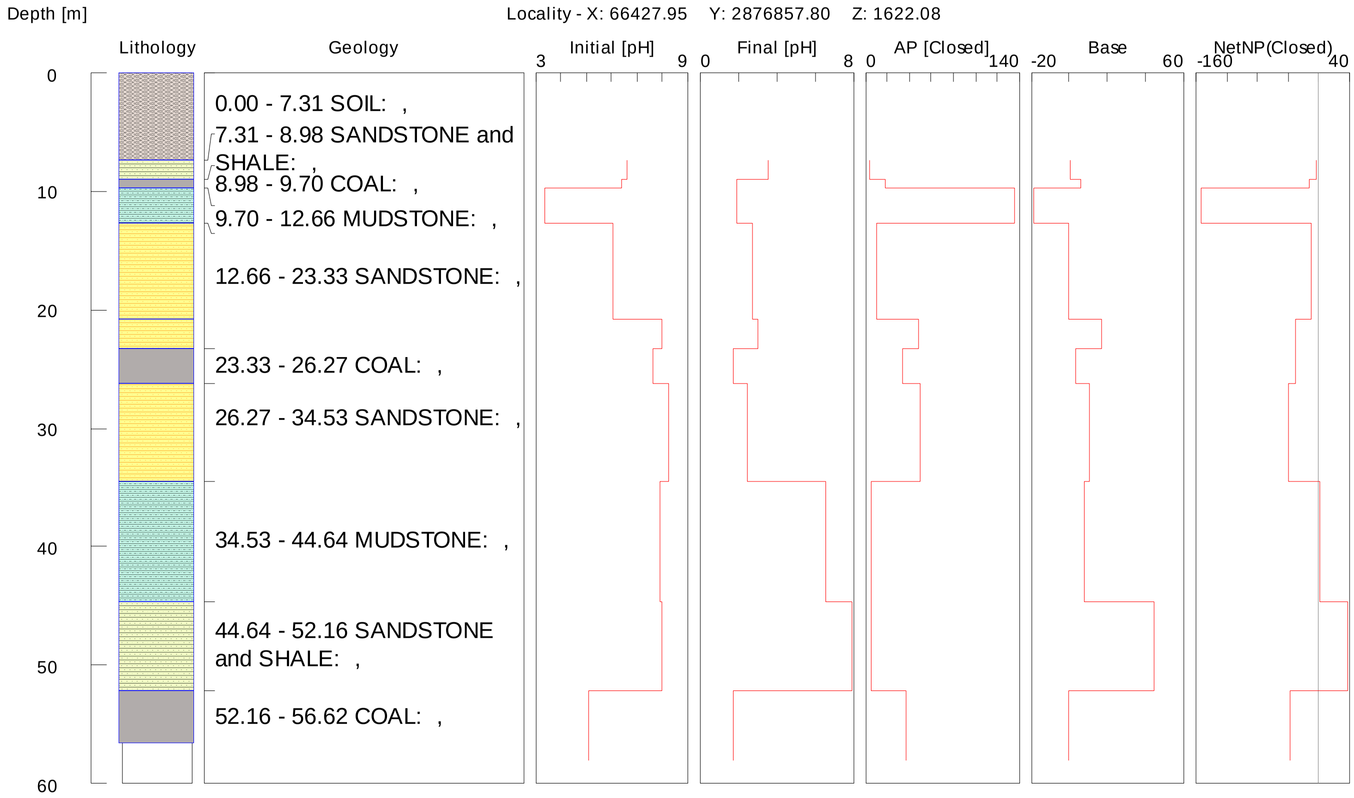
Borehole Log - Core3

Locality - X: 64298.00   Y: 2876450.41   Z: 1625.07



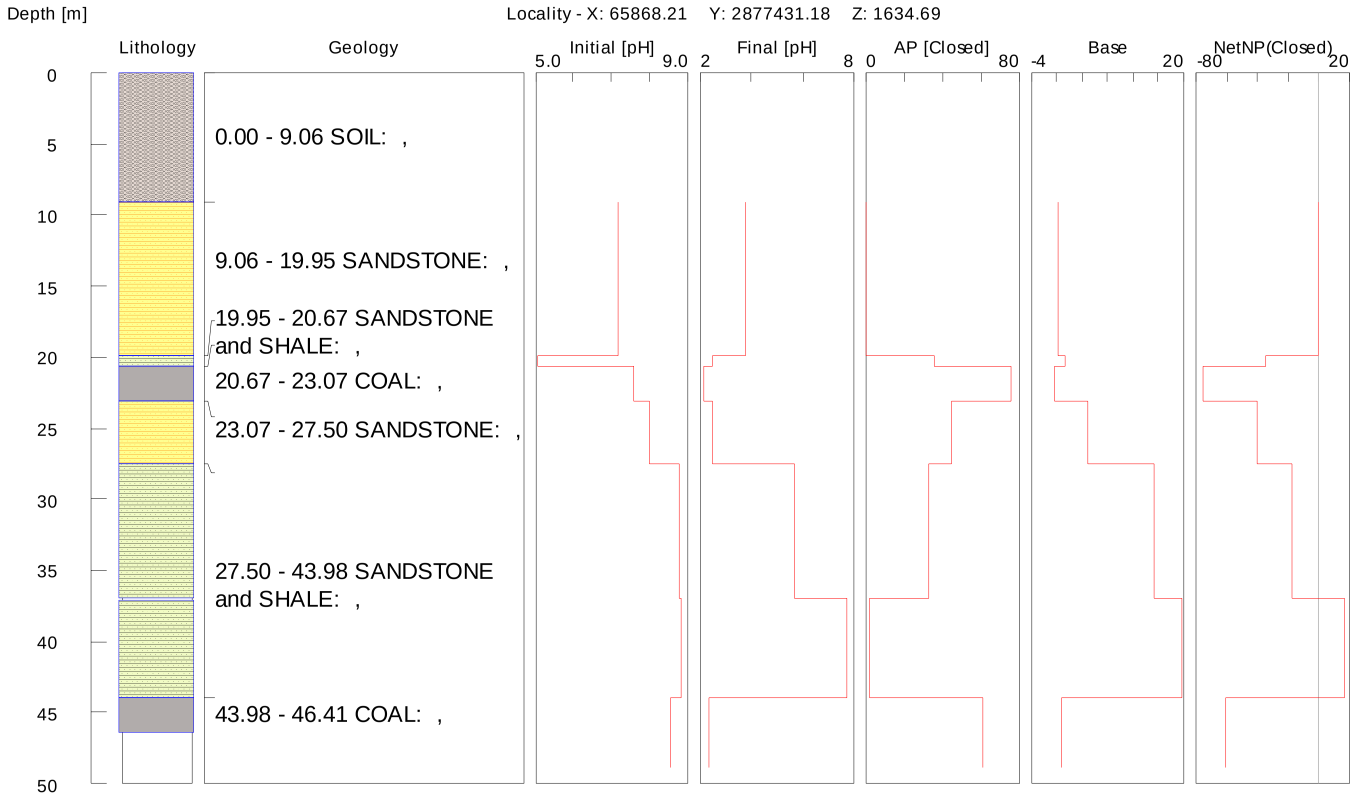
Borehole Log - Core4

Locality - X: 66427.95 Y: 2876857.80 Z: 1622.08



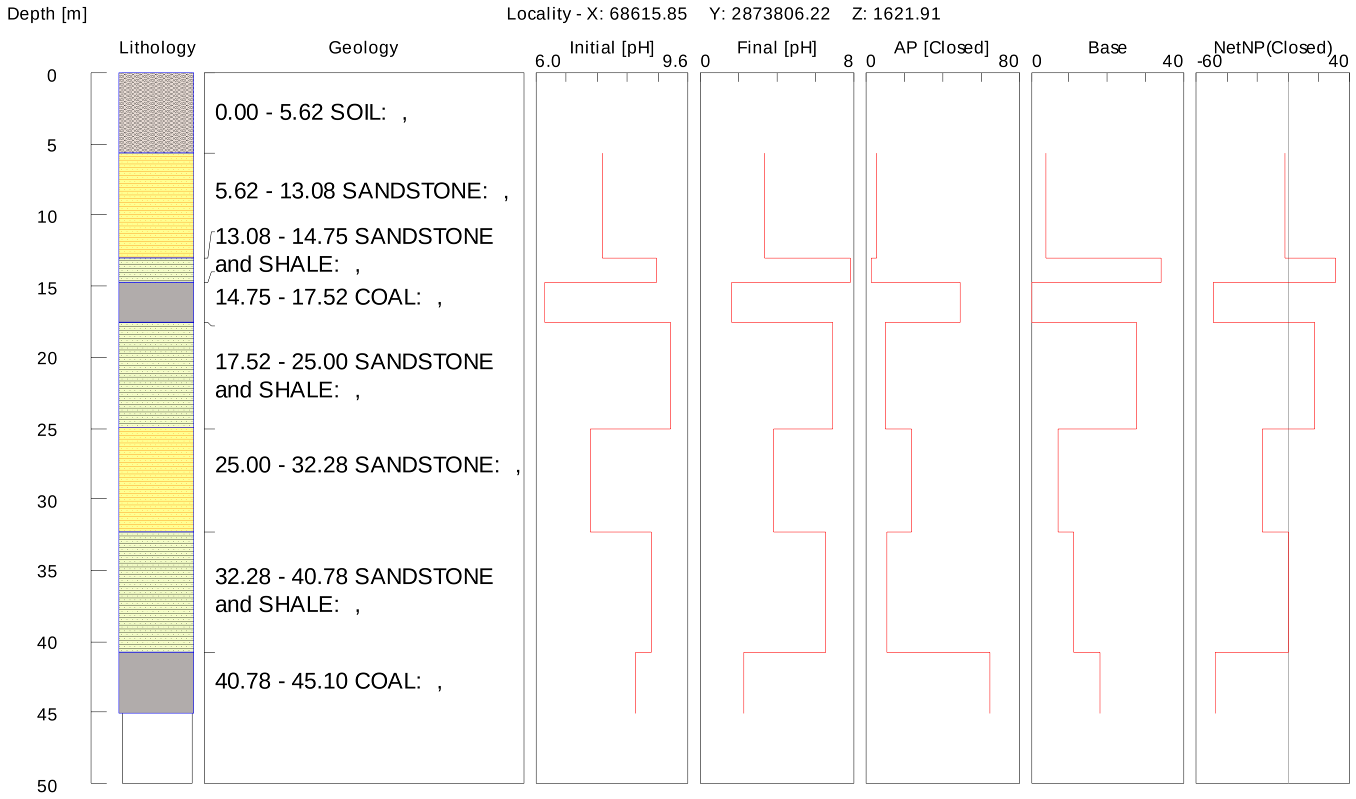
Borehole Log - Core5

Locality - X: 65868.21 Y: 2877431.18 Z: 1634.69



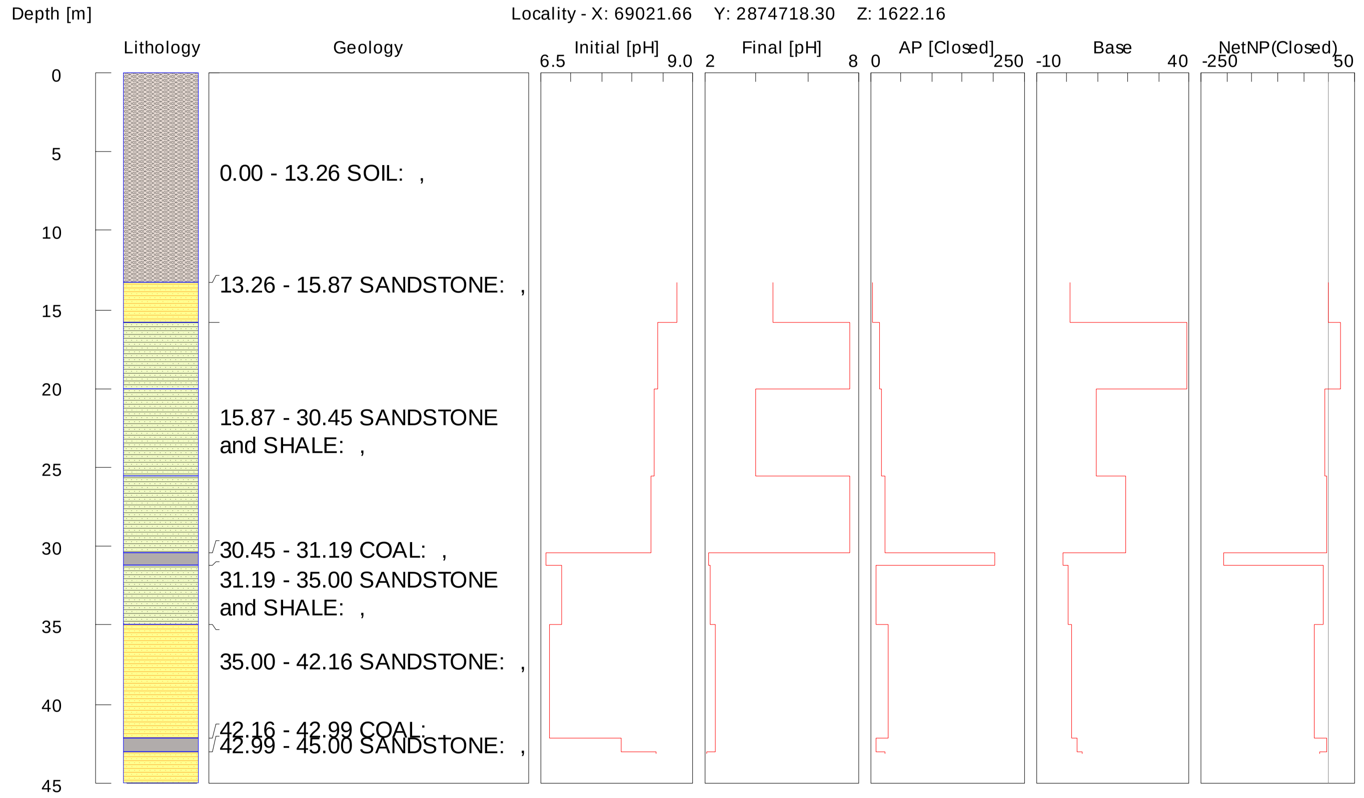
Borehole Log - Core6

Locality - X: 68615.85 Y: 2873806.22 Z: 1621.91



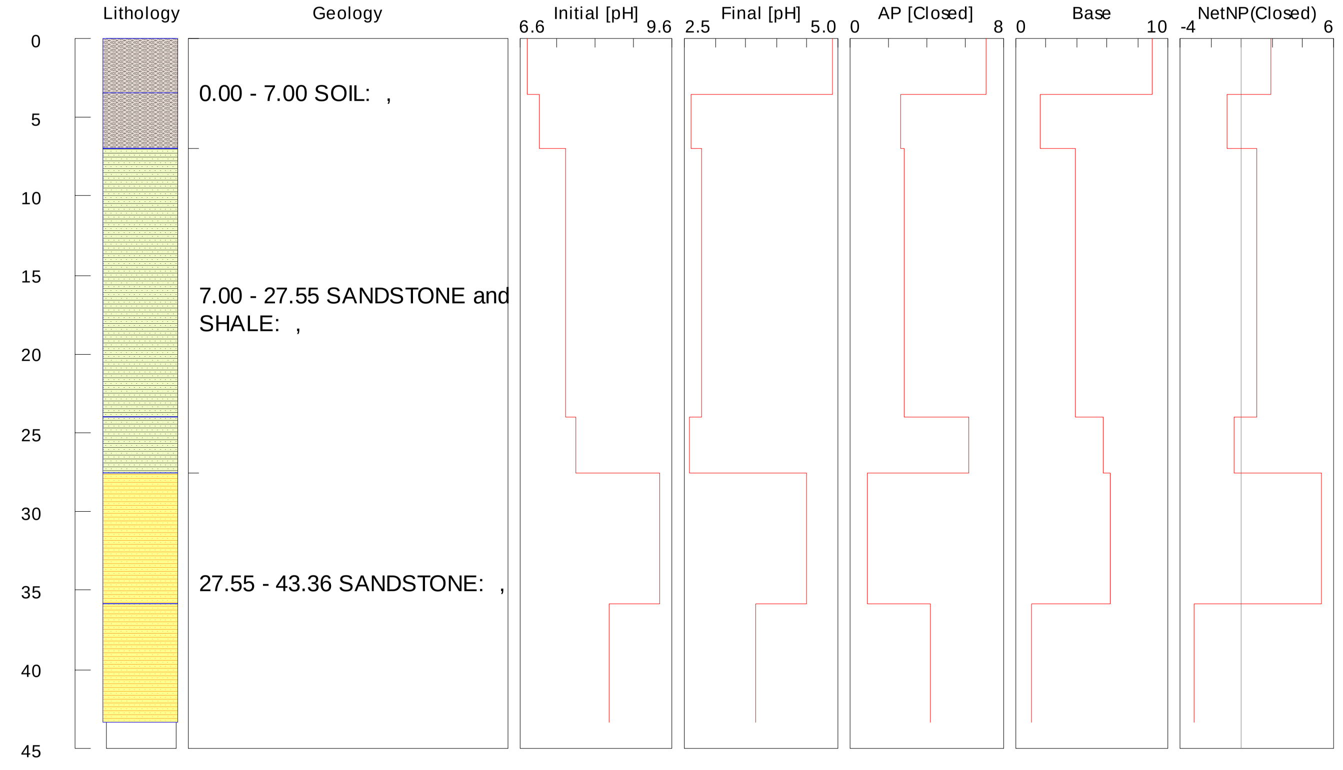
Borehole Log - Core7

Locality - X: 69021.66 Y: 2874718.30 Z: 1622.16



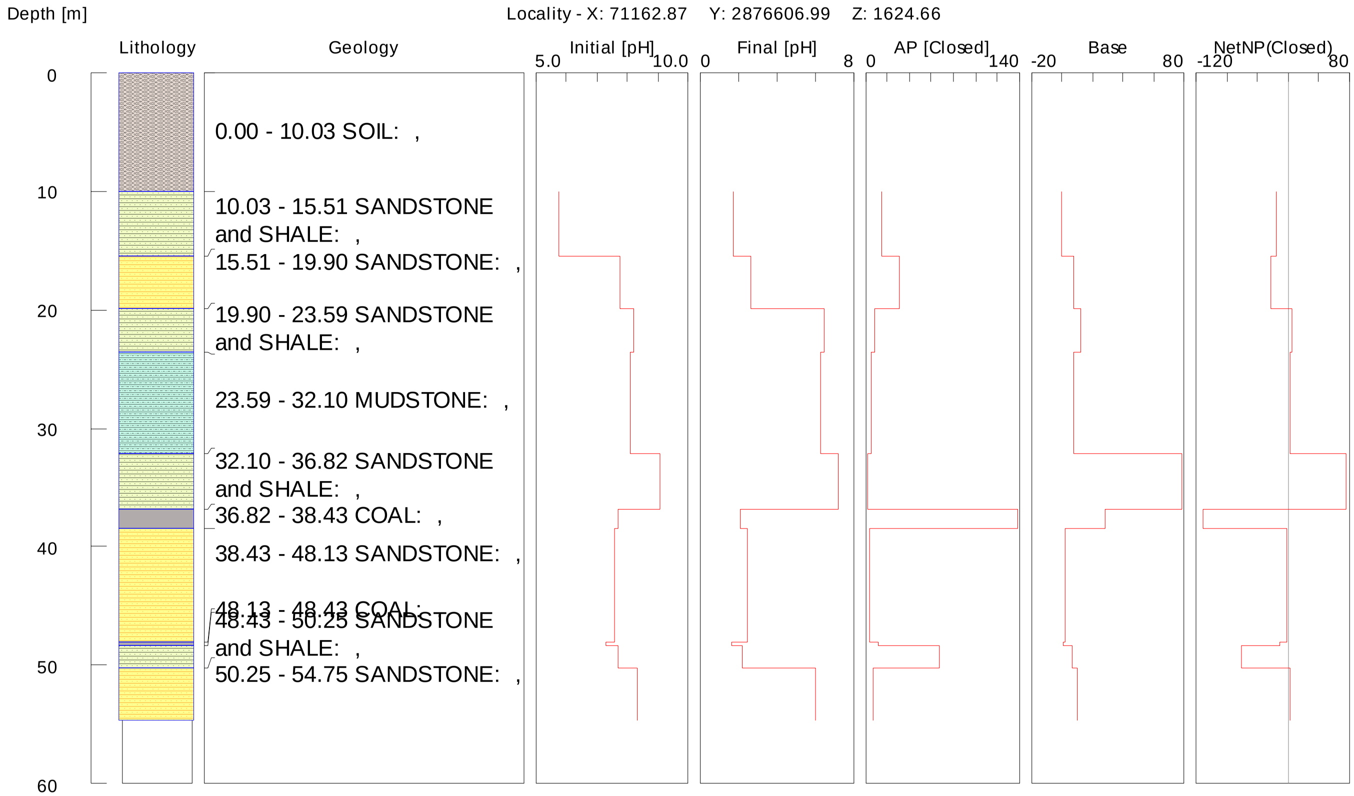
Borehole Log - Core8

Locality - X: 70822.99   Y: 2875901.99   Z: 1612.18



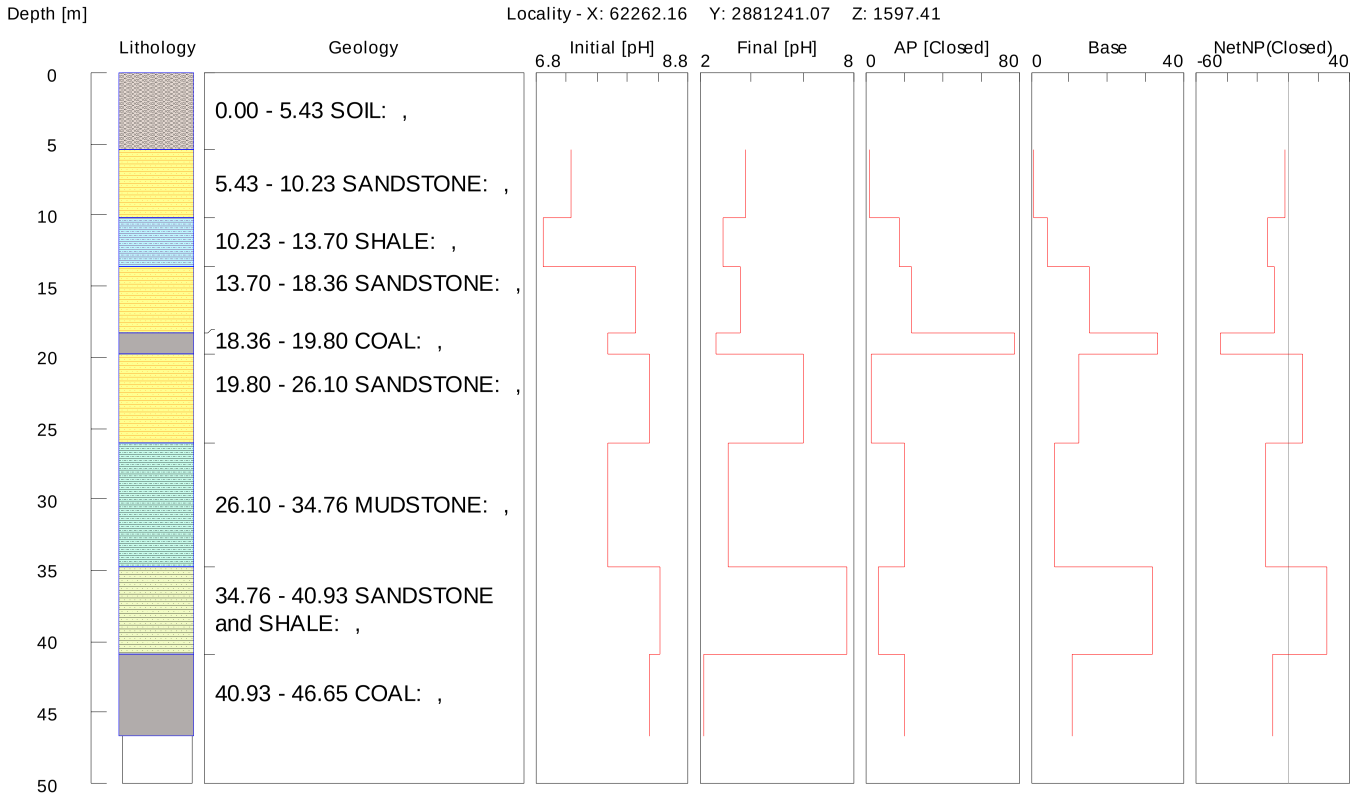
Borehole Log - Core9

Locality - X: 71162.87 Y: 2876606.99 Z: 1624.66



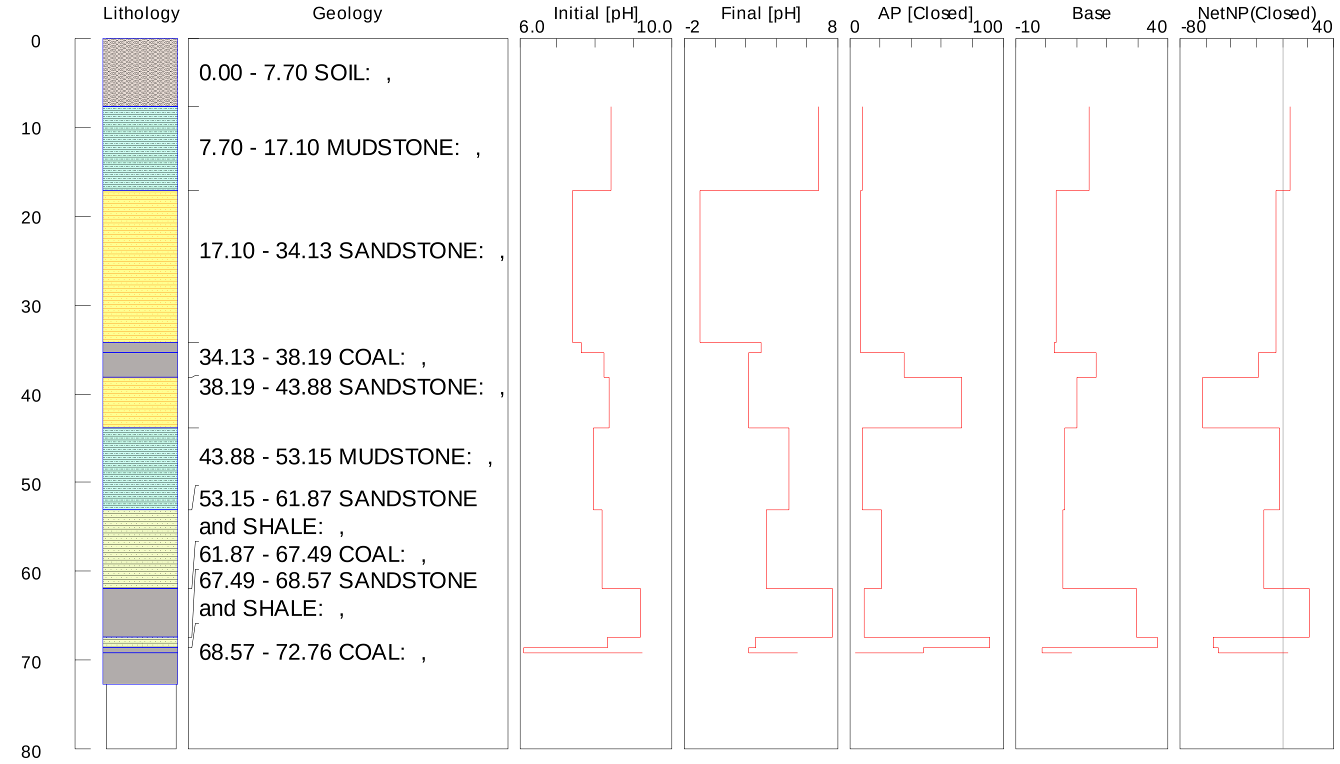
Borehole Log - Core10

Locality - X: 62262.16 Y: 2881241.07 Z: 1597.41



Borehole Log - Core11

Locality - X: 63201.12   Y: 2880024.37   Z: 1614.01



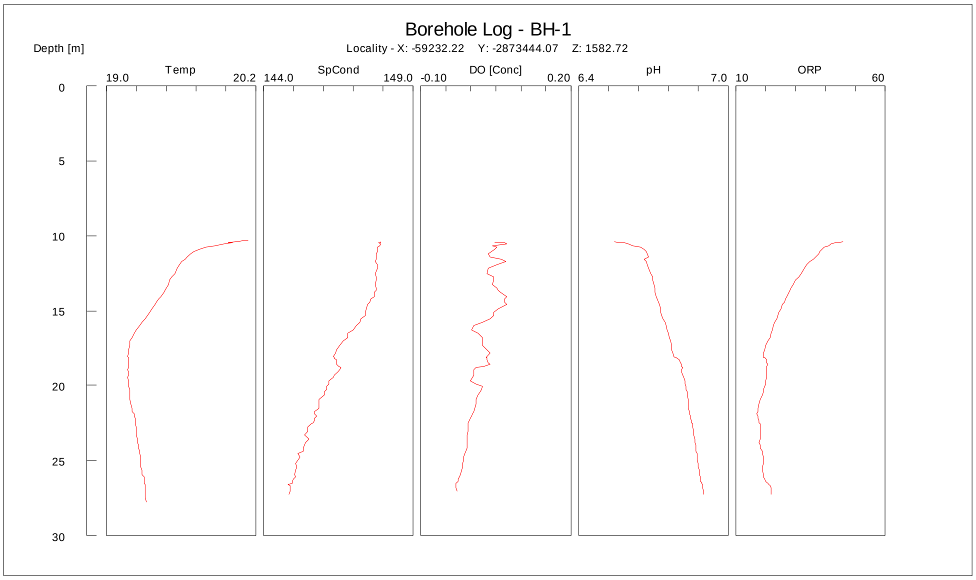


Figure a Hydrochemical logs of spoil water.

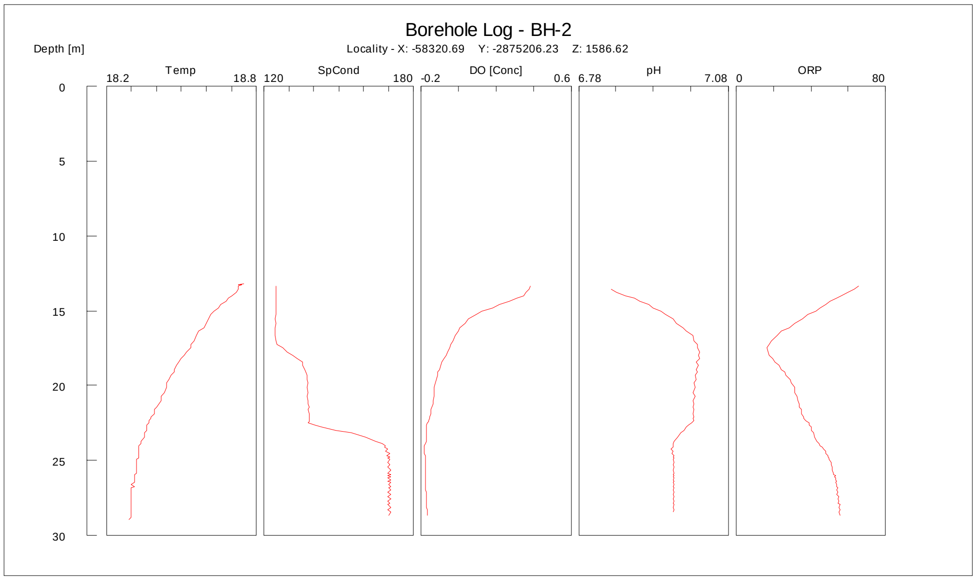


Figure b. Hydrochemical logs of spoil water.

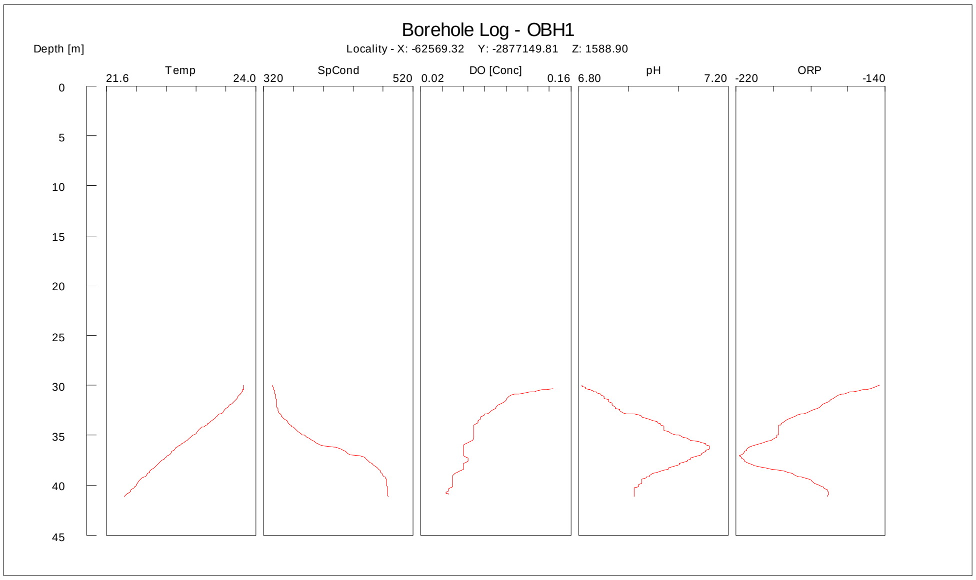


Figure c. Hydrochemical logs of spoil water.

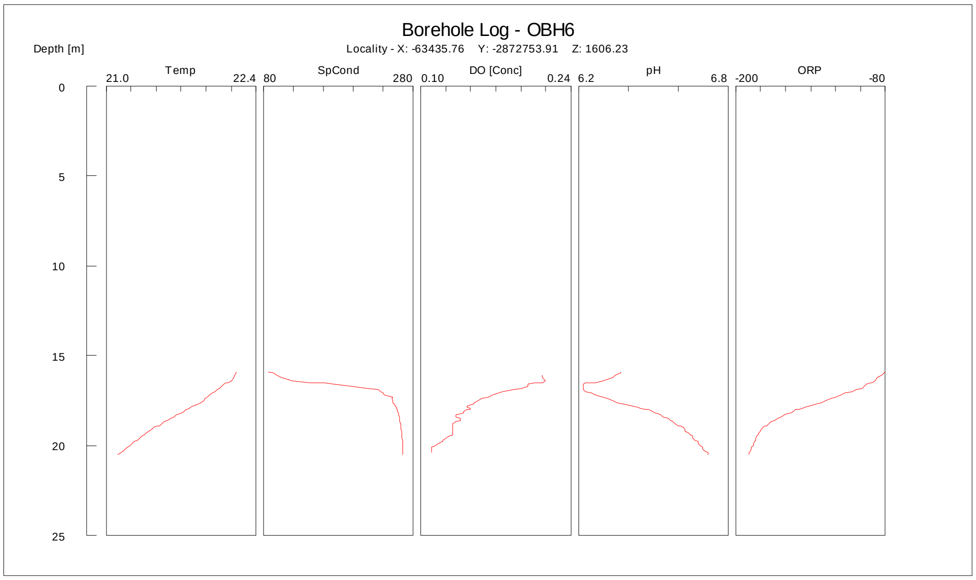


Figure d.Hydrochemical logs of spoil water.

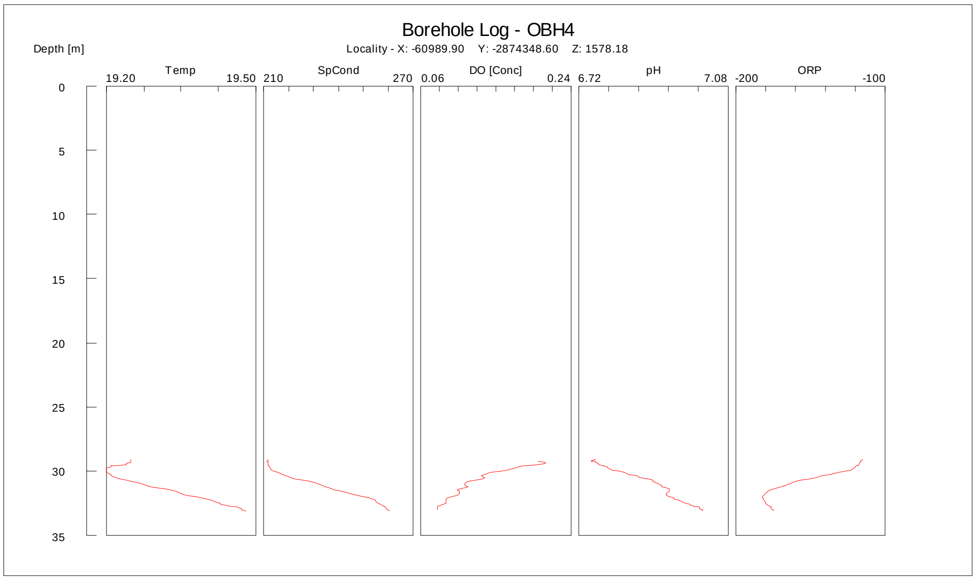


Figure e. Hydrochemical logs of spoil water

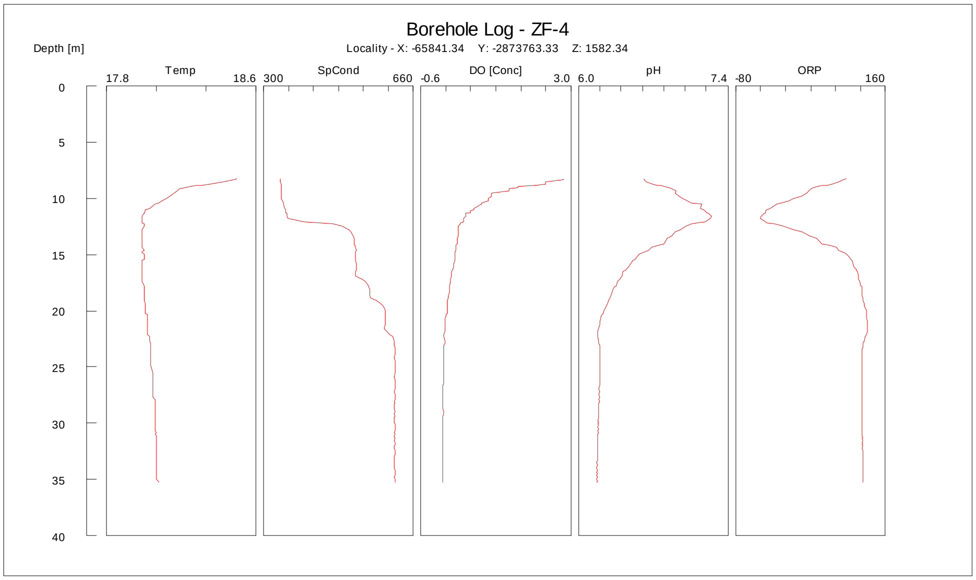


Figure f.Hydrochemical logs of spoil water.

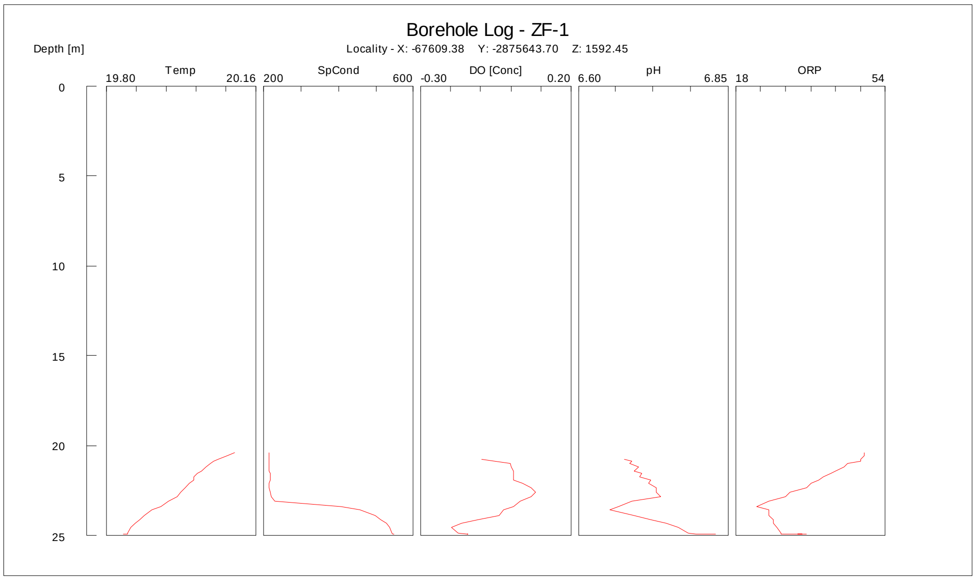


Figure g. Hydrochemical logs of spoil water.

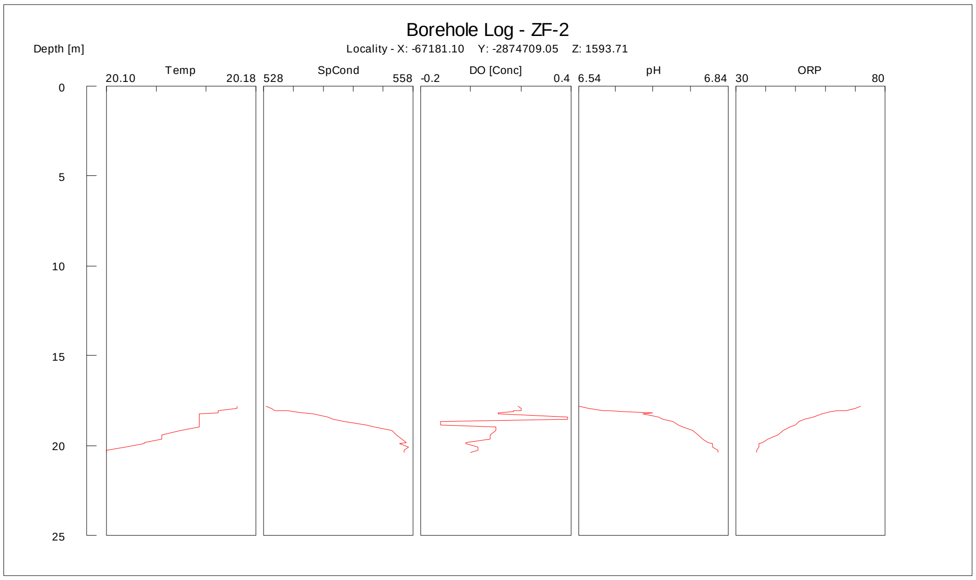


Figure h. Hydrochemical logs of spoil water.

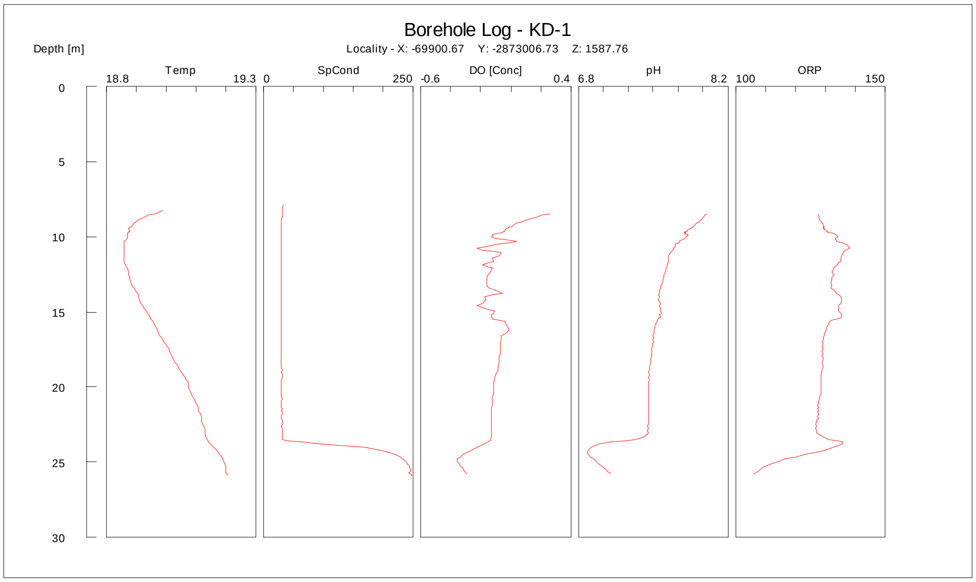


Figure i. Hydrochemical logs of spoil water.

Site	Site Name	Paste/Initial pH	Final pH	Interpretation
Optimum	BG10-1	7.27	3.74	Medium Risk Acid Generation
Optimum	BG10-2	6.9	2.91	Higher Risk Acid Generation
Optimum	BG10-3	8.11	3.58	Medium Risk Acid Generation
Optimum	BG10-4	7.75	2.62	Higher Risk Acid Generation
Optimum	BG10-5	8.29	6.03	Lower Acid Risk
Optimum	BG10-6	7.75	3.13	Higher Risk Acid Generation
Optimum	BG10-7	8.44	7.73	Lower Acid Risk
Optimum	BG10-8	8.3	2.16	Higher Risk Acid Generation

Site	Site Name	Paste/Initial pH	Final pH	Interpretation
Optimum	BG11-1	8.42	6.8	Lower Acid Risk
Optimum	BG11-2a	7.39	3	Higher Risk Acid Generation
Optimum	BG11-2b	7.62	2.92	Higher Risk Acid Generation
Optimum	BG11-3	8.2	2.16	Higher Risk Acid Generation
Optimum	BG11-4	8.35	2.25	Higher Risk Acid Generation
Optimum	BG11-5	7.93	4.87	Medium Risk Acid Generation
Optimum	BG11-6	8.19	3.36	Higher Risk Acid Generation
Optimum	BG11-7	9.17	7.74	Lower Acid Risk
Optimum	BG11-8	8.32	2.67	Higher Risk Acid Generation
Optimum	BG11-9	6.11	2.15	Higher Risk Acid Generation
Optimum	BG11-10	9.24	5.43	Medium Risk Acid Generation

Site	Site Name	Paste/Initial pH	Final pH	Interpretation
Optimum	BG1-1	7.95	4.54	Medium Risk Acid Generation
Optimum	BG1-2	6.95	1.86	Higher Risk Acid Generation
Optimum	BG1-3	7.57	3.37	Higher Risk Acid Generation
Optimum	BG1-4	8.08	2.79	Higher Risk Acid Generation
Optimum	BG1-5	6.51	2.21	Higher Risk Acid Generation
Optimum	BG1-6	8.26	1.79	Higher Risk Acid Generation
Optimum	BG1-7	8.22	1.94	Higher Risk Acid Generation

Site	Site Name	Paste/Initial pH	Final pH	Interpretation
Optimum	BG4-1	6.63	3.58	Medium Risk Acid Generation
Optimum	BG4-10	5.08	1.78	Higher Risk Acid Generation
Optimum	BG4-2	6.36	1.94	Higher Risk Acid Generation
Optimum	BG4-3	3.4	1.96	Higher Risk Acid Generation
Optimum	BG4-4	6.02	2.7	Higher Risk Acid Generation
Optimum	BG4-5	7.99	2.98	Higher Risk Acid Generation
Optimum	BG4-6	7.66	1.77	Higher Risk Acid Generation
Optimum	BG4-7	8.23	2.49	Higher Risk Acid Generation
Optimum	BG4-8	7.89	6.58	Lower Acid Risk
Optimum	BG4-9	7.99	7.94	Lower Acid Risk
Site	**Site Name**	**Paste/Initial pH**	**Final pH**	**Interpretation**
Optimum	BG5-1	7.15	3.78	Medium Risk Acid Generation
Optimum	BG5-2	5.09	2.49	Higher Risk Acid Generation
Optimum	BG5-3	7.59	2.16	Higher Risk Acid Generation
Optimum	BG5-4	8	2.48	Higher Risk Acid Generation
Optimum	BG5-5	8.78	5.7	Lower Acid Risk
Optimum	BG5-6	8.83	7.74	Lower Acid Risk
Optimum	BG5-7	8.54	2.34	Higher Risk Acid Generation
Site	**Site Name**	**Paste/Initial pH**	**Final pH**	**Interpretation**
Optimum	BG6-1	7.6	3.39	Higher Risk Acid Generation
Optimum	BG6-2	8.86	7.84	Lower Acid Risk
Optimum	BG6-3	6.23	1.64	Higher Risk Acid Generation
Optimum	BG6-4	9.17	6.93	Lower Acid Risk
Optimum	BG6-5	7.28	3.81	Medium Risk Acid Generation
Optimum	BG6-6	8.74	6.59	Lower Acid Risk
Optimum	BG6-7	8.37	2.24	Higher Risk Acid Generation

Site	Site Name	Paste/Initial pH	Final pH	Interpretation
Optimum	BG6-1	7.6	3.39	Higher Risk Acid Generation
Optimum	BG6-2	8.86	7.84	Lower Acid Risk
Optimum	BG6-3	6.23	1.64	Higher Risk Acid Generation
Optimum	BG6-4	9.17	6.93	Lower Acid Risk
Optimum	BG6-5	7.28	3.81	Medium Risk Acid Generation
Optimum	BG6-6	8.74	6.59	Lower Acid Risk
Optimum	BG6-7	8.37	2.24	Higher Risk Acid Generation

Site	Site Name	Paste/Initial pH	Final pH	Interpretation
Optimum	BG7-1	8.75	4.65	Medium Risk Acid Generation
Optimum	BG7-2	8.43	7.64	Lower Acid Risk
Optimum	BG7-3	8.38	3.96	Medium Risk Acid Generation
Optimum	BG7-4	8.3	7.68	Lower Acid Risk
Optimum	BG7-5	6.6	2.13	Higher Risk Acid Generation
Optimum	BG7-6	6.87	2.18	Higher Risk Acid Generation
Optimum	BG7-7	6.66	2.42	Higher Risk Acid Generation
Optimum	BG7-8	7.84	2.44	Higher Risk Acid Generation
Optimum	BG7-9	8.4	2.04	Higher Risk Acid Generation

Site	Site Name	Paste/Initial pH	Final pH	Interpretation
Optimum	BG8-1	6.76	4.92	Medium Risk Acid Generation
Optimum	BG8-2	7.01	2.61	Higher Risk Acid Generation
Optimum	BG8-3	7.52	2.78	Higher Risk Acid Generation
Optimum	BG8-4	7.72	2.59	Higher Risk Acid Generation
Optimum	BG8-5	9.36	4.5	Medium Risk Acid Generation
Optimum	BG8-6	8.35	3.66	Medium Risk Acid Generation

Site	Site Name	Paste/Initial pH	Final pH	Interpretation
Optimum	BG9-1	5.76	1.75	Higher Risk Acid Generation
Optimum	BG9-2	7.75	2.59	Higher Risk Acid Generation
Optimum	BG9-3	8.24	6.45	Lower Acid Risk
Optimum	BG9-4	8.12	6.3	Lower Acid Risk
Optimum	BG9-5	9.08	7.19	Lower Acid Risk
Optimum	BG9-6	7.73	2.12	Higher Risk Acid Generation
Optimum	BG9-7	7.61	2.45	Higher Risk Acid Generation
Optimum	BG9-8	7.34	1.6	Higher Risk Acid Generation

Site Name	Acid Potential (Open)	Acid Potential (Closed)	Base Potential	NNP(Open)	NNP (Closed)	Interpretation
BG10-1	1.208265988	2.416531975	0.702	-0.506265988	-1.714531975	Verify with other tests
BG10-2	8.725048208	17.45009642	4.2936	-4.431448208	-13.15649642	Verify with other tests
BG10-3	12.21933825	24.4386765	15.09168	2.87234175	-9.3469965	Verify with other tests
BG10-4	38.88752242	77.77504483	33.0852	-5.802322417	-44.68984483	Potential Acid Generator
BG10-5	1.559217475	3.11843495	12.67368	11.11446253	9.55524505	Verify with other tests
BG10-6	10.0727555	20.145511	5.94792	-4.1248355	-14.197591	Verify with other tests
BG10-7	3.35532445	6.7106489	31.72056	28.36523555	25.0099111	Excess Neutralising Minerlas
BG10-8	10.17718329	20.35436658	10.55424	0.377056708	-9.800126583	Verify with other tests
Site Name	**Acid Potential (Open)**	**Acid Potential (Closed)**	**Base Potential**	**NNP(Open)**	**NNP (Closed)**	**Interpretation**
BG11-1	3.981515438	7.963030875	14.06112	10.07960456	6.098089125	Verify with other tests
BG11-2a	3.824639025	7.64927805	3.18168	-0.642959025	-4.46759805	Verify with other tests
BG11-2b	3.806177421	7.612354842	2.85624	-0.949937421	-4.756114842	Verify with other tests
BG11-3	17.75940792	35.51881583	16.38912	-1.370287917	-19.12969583	Verify with other tests
BG11-4	36.36505033	72.73010067	10.31424	-26.05081033	-62.41586067	Potential Acid Generator
BG11-5	4.324681375	8.64936275	6.25056	1.925878625	-2.39880275	Verify with other tests
BG11-6	10.39453588	20.78907175	5.94792	-4.446615875	-14.84115175	Verify with other tests
BG11-7	4.641694125	9.28338825	29.86272	25.22102588	20.57933175	Probably Excess Neutralising Minerlas
BG11-8	45.62934958	91.25869917	36.37608	-9.253269583	-54.88261917	Potential Acid Generator
BG11-9	24.36208075	48.7241615	-1.10328	-25.46536075	-49.8274415	Potential Acid Generator
BG11-10	1.984131217	3.968262433	8.41584	6.431708783	4.447577567	Verify with other tests
Site Name	**Acid Potential (Open)**	**Acid Potential (Closed)**	**Base Potential**	**NNP(Open)**	**NNP (Closed)**	**Interpretation**
BG1-1	1.758881363	3.517762725	6.27336	4.514478638	2.755597275	Verify with other tests
BG1-2	13.29525431	26.59050863	-0.80496	-14.10021431	-27.39546863	Potential Acid Generator
BG1-3	5.373960333	10.74792067	6.192	0.818039667	-4.555920667	Verify with other tests
BG1-4	22.54681229	45.09362458	8.96256	-13.58425229	-36.13106458	Potential Acid Generator
BG1-5	53.36776104	106.7355221	0.27984	-53.08792104	-106.4556821	Potential Acid Generator
BG1-6	14.44153365	28.88306729	8.4312	-6.010333646	-20.45186729	Potential Acid Generator
BG1-7	9.897009938	19.79401988	8.11752	-1.779489938	-11.67649988	Verify with other tests

Site Name	**Acid Potential (Open)**	**Acid Potential (Closed)**	**Base Potential**	**NNP(Open)**	**NNP (Closed)**	**Interpretation**
BG2-1	0.52416336	1.048326721	3.64272	3.11855664	2.594393279	Verify with other tests
BG2-2	2.447353846	4.894707692	12.62376	10.17640615	7.729052308	Verify with other tests
BG2-3	15.74798783	31.49597567	25.91688	10.16889217	-5.579095667	Verify with other tests
BG2-4	54.93893797	109.8778759	25.8312	-29.10773797	-84.04667594	Potential Acid Generator
BG2-5	52.05225646	104.1045129	10.31424	-41.73801646	-93.79027292	Potential Acid Generator
Site Name	**Acid Potential (Open)**	**Acid Potential (Closed)**	**Base Potential**	**NNP(Open)**	**NNP (Closed)**	**Interpretation**
BG3-1	4.294724354	8.589448708	14.9832	10.68847565	6.393751292	Verify with other tests
BG3-2	22.514848	45.029696	5.6496	-16.865248	-39.380096	Potential Acid Generator
BG3-3	17.48880304	34.97760608	6.33192	-11.15688304	-28.64568608	Potential Acid Generator
BG3-4	17.98486694	35.96973388	6.11064	-11.87422694	-29.85909388	Potential Acid Generator
BG3-5	7.018436708	14.03687342	11.02368	4.005243292	-3.013193417	Verify with other tests
BG3-6	32.70314563	65.40629125	61.10928	28.40613438	-4.29701125	Verify with other tests
BG3-7	4.840756729	9.681513458	7.82352	2.982763271	-1.857993458	Verify with other tests
BG3-8	2.438240652	4.876481304	31.2096	28.77135935	26.3331187	Probably Excess Neutralising Minerlas
BG3-9	14.375	28.75	6.84288	-7.53212	-21.90712	Potential Acid Generator
Site Name	**Acid Potential (Open)**	**Acid Potential (Closed)**	**Base Potential**	**NNP(Open)**	**NNP (Closed)**	**Interpretation**
BG4-1	1.421387892	2.842775783	0.79056	-0.630827892	-2.052215783	Verify with other tests
BG4-10	18.39581812	36.79163624	-0.53376	-18.92957812	-37.32539624	Potential Acid Generator
BG4-2	8.75	17.5	5.89368	-2.85632	-11.60632	Verify with other tests
BG4-3	68.14061906	136.2812381	-18.40584	-86.54645906	-154.6870781	Potential Acid Generator
BG4-4	4.900964104	9.801928208	-0.08448	-4.985444104	-9.886408208	Verify with other tests
BG4-5	23.86125175	47.7225035	16.77744	-7.08381175	-30.9450635	Potential Acid Generator
BG4-6	17.375	34.75	3.52248	-13.85252	-31.22752	Potential Acid Generator
BG4-7	24.91956988	49.83913975	10.35	-14.56956988	-39.48913975	Potential Acid Generator
BG4-8	2.653043315	5.306086629	7.95912	5.306076685	2.653033371	Verify with other tests
BG4-9	2.784075296	5.568150592	44.12304	41.3389647	38.55488941	Probably Excess Neutralising Minerlas

Site Name	Acid Potential (Open)	Acid Potential (Closed)	Base Potential	NNP(Open)	NNP (Closed)	Interpretation
BG5-1	0.041666667	0.083333333	0.33408	0.292413333	0.250746667	Verify with other tests
BG5-2	17.9918606	35.98372121	1.33752	-16.6543406	-34.64620121	Potential Acid Generator
BG5-3	37.7752221	75.55044421	-0.20832	-37.9835421	-75.75876421	Potential Acid Generator
BG5-4	22.49632335	44.99264671	4.94448	-17.55184335	-40.04816671	Potential Acid Generator
BG5-5	16.6071496	33.21429921	15.22728	-1.379869604	-17.98701921	Verify with other tests
BG5-6	1.171882638	2.343765275	19.76064	18.58875736	17.41687473	Verify with other tests
BG5-7	30.53298146	61.06596292	0.74088	-29.79210146	-60.32508292	Potential Acid Generator

Site Name	Acid Potential (Open)	Acid Potential (Closed)	Base Potential	NNP(Open)	NNP (Closed)	Interpretation
BG6-1	2.920465773	5.840931546	3.7512	0.830734227	-2.089731546	Verify with other tests
BG6-2	1.340366648	2.680733296	33.84024	32.49987335	31.1595067	Probably Excess Neutralising Minerlas
BG6-3	24.75214927	49.50429854	0.25272	-24.49942927	-49.25157854	Potential Acid Generator
BG6-4	5.246322077	10.49264415	27.8424	22.59607792	17.34975585	Verify with other tests
BG6-5	12.19374263	24.38748525	7.28112	-4.912622625	-17.10636525	Verify with other tests
BG6-6	5.429569354	10.85913871	11.322	5.892430646	0.462861292	Verify with other tests
BG6-7	32.64995908	65.29991817	17.86896	-14.78099908	-47.43095817	Potential Acid Generator

Site Name	Acid Potential (Open)	Acid Potential (Closed)	Base Potential	NNP(Open)	NNP (Closed)	Interpretation
BG7-1	1.619353352	3.238706703	1.0392	-0.580153352	-2.199506703	Verify with other tests
BG7-2	7.339380021	14.67876004	39.15144	31.81205998	24.47267996	Probably Excess Neutralising Minerlas
BG7-3	8.911532521	17.82306504	9.53208	0.620547479	-8.290985042	Verify with other tests
BG7-4	11.56565375	23.1313075	19.5936	8.02794625	-3.5377075	Verify with other tests
BG7-5	102.0736544	204.1473088	-0.9948	-103.0684544	-205.1421088	Potential Acid Generator
BG7-6	5.351389869	10.70277974	0.44256	-4.908829869	-10.26021974	Verify with other tests
BG7-7	14.36536285	28.73072571	1.47312	-12.89224285	-27.25760571	Potential Acid Generator
BG7-8	4.252058246	8.504116492	3.53424	-0.717818246	-4.969876492	Verify with other tests
BG7-9	12.00435556	24.00871113	5.32416	-6.680195563	-18.68455113	Verify with other tests

Site Name	Acid Potential (Open)	Acid Potential (Closed)	Base Potential	NNP(Open)	NNP (Closed)	Interpretation
BG8-1	3.543127643	7.086255285	9.01248	5.469352357	1.926224715	Verify with other tests
BG8-2	1.322127108	2.644254217	1.66728	0.345152892	-0.976974217	Verify with other tests
BG8-3	1.450380883	2.900761767	3.8868	2.436419117	0.986038233	Verify with other tests
BG8-4	3.131033367	6.262066733	5.78952	2.658486633	-0.472546733	Verify with other tests
BG8-5	0.477171125	0.95434225	6.20064	5.723468875	5.24629775	Verify with other tests
BG8-6	2.107777696	4.215555392	1.06632	-1.041457696	-3.149235392	Verify with other tests

Site Name	Acid Potential (Open)	Acid Potential (Closed)	Base Potential	NNP(Open)	NNP (Closed)	Interpretation
BG9-1	7.0682185	14.136437	-0.37104	-7.4392585	-14.507477	Verify with other tests
BG9-2	15.31544742	30.63089483	8.30736	-7.008087417	-22.32353483	Potential Acid Generator
BG9-3	3.845831817	7.691663633	12.07704	8.231208183	4.385376367	Verify with other tests
BG9-4	2.399607221	4.799214442	8.18952	5.789912779	3.390305558	Verify with other tests
BG9-5	0.902191296	1.804382592	78.81816	77.9159687	77.01377741	Probably Excess Neutralising Minerlas
BG9-6	69.84072542	139.6814508	28.272	-41.56872542	-111.4094508	Potential Acid Generator
BG9-7	1.927742846	3.855485692	2.78352	0.855777154	-1.071965692	Verify with other tests
BG9-8	5.428665531	10.85733106	0.9036	-4.525065531	-9.953731062	Verify with other tests
BG9-9	33.74625983	67.49251967	6.92424	-26.82201983	-60.56827967	Potential Acid Generator
BG9-10	3.505166817	7.010333633	10.64832	7.143153183	3.637986367	Verify with other tests

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Neutralising Potential Ratio(NP/AP) for Closed System	Interpretation Open System	Interpretation Closed System
BG10-1	0.580997899	0.290498949	Likely Acid Generator	Likely Acid Generator
BG10-2	0.492100433	0.246050216	Likely Acid Generator	Likely Acid Generator
BG10-3	1.235065246	0.617532623	Acid under certain conditions	Likely Acid Generator
BG10-4	0.850792181	0.42539609	Likely Acid Generator	Likely Acid Generator
BG10-5	8.128231118	4.064115559	No Acid Potential	No Acid Potential
BG10-6	0.590495818	0.295247909	Likely Acid Generator	Likely Acid Generator
BG10-7	9.453798127	4.726899063	No Acid Potential	No Acid Potential
BG10-8	1.037049221	0.51852461	Acid under certain conditions	Likely Acid Generator

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Neutralising Potential Ratio(NP/AP) for Closed System	Interpretation Open System	Interpretation Closed System
BG11-1	3.53160002	1.76580001	Acid under certain conditions	Acid under certain conditions
BG11-2a	0.831890272	0.415945136	Likely Acid Generator	Likely Acid Generator
BG11-2b	0.750422191	0.375211096	Likely Acid Generator	Likely Acid Generator
BG11-3	0.922841577	0.461420788	Likely Acid Generator	Likely Acid Generator
BG11-4	0.283630571	0.141815286	Likely Acid Generator	Likely Acid Generator
BG11-5	1.445322663	0.722661331	Acid under certain conditions	Likely Acid Generator
BG11-6	0.572216025	0.286108012	Likely Acid Generator	Likely Acid Generator
BG11-7	6.433582049	3.216791025	No Acid Potential	Acid under certain conditions
BG11-8	0.797207945	0.398603972	Likely Acid Generator	Likely Acid Generator
BG11-9	0.000410474	0.000205237	Likely Acid Generator	Likely Acid Generator
BG11-10	4.241574312	2.120787156	No Acid Potential	Acid under certain conditions

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Neutralising Potential Ratio(NP/AP) for Closed System	Interpretation Open System	Interpretation Closed System
BG1-1	3.566676033	1.783338016	Acid under certain conditions	Acid under certain conditions
BG1-2	0.000752148	0.000376074	Likely Acid Generator	Likely Acid Generator
BG1-3	1.15222287	0.576111435	Acid under certain conditions	Likely Acid Generator
BG1-4	0.397508964	0.198754482	Likely Acid Generator	Likely Acid Generator
BG1-5	0.005243615	0.002621808	Likely Acid Generator	Likely Acid Generator
BG1-6	0.58381611	0.291908055	Likely Acid Generator	Likely Acid Generator
BG1-7	0.820199237	0.410099619	Likely Acid Generator	Likely Acid Generator

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Neutralising Potential Ratio(NP/AP) for Closed System	Interpretation Open System	Interpretation Closed System
BG2-1	6.949589145	3.474794573	No Acid Potential	Acid under certain conditions
BG2-2	5.158126203	2.579063101	No Acid Potential	Acid under certain conditions
BG2-3	1.645726443	0.822863221	Acid under certain conditions	Likely Acid Generator
BG2-4	0.470180185	0.235090092	Likely Acid Generator	Likely Acid Generator
BG2-5	0.19815164	0.09907582	Likely Acid Generator	Likely Acid Generator

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Neutralising Potential Ratio(NP/AP) for Closed System	Interpretation Open System	Interpretation Closed System
BG3-1	3.488745438	1.744372719	Acid under certain conditions	Acid under certain conditions
BG3-2	0.250927743	0.125463872	Likely Acid Generator	Likely Acid Generator
BG3-3	0.362055653	0.181027826	Likely Acid Generator	Likely Acid Generator
BG3-4	0.33976565	0.169882825	Likely Acid Generator	Likely Acid Generator
BG3-5	1.570674562	0.785337281	Acid under certain conditions	Likely Acid Generator
BG3-6	1.868605568	0.934302784	Acid under certain conditions	Likely Acid Generator
BG3-7	1.616177064	0.808088532	Acid under certain conditions	Likely Acid Generator
BG3-8	12.80004907	6.400024537	No Acid Potential	No Acid Potential
BG3-9	0.476026435	0.238013217	Likely Acid Generator	Likely Acid Generator

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Neutralising Potential Ratio(NP/AP) for Closed System	Interpretation Open System	Interpretation Closed System
BG4-1	0.556188782	0.278094391	Likely Acid Generator	Likely Acid Generator
BG4-10	0.000543602	0.000271801	Likely Acid Generator	Likely Acid Generator
BG4-2	0.673563429	0.336781714	Likely Acid Generator	Likely Acid Generator
BG4-3	0.000146755	7.33777E-05	Likely Acid Generator	Likely Acid Generator
BG4-4	0.002040415	0.001020207	Likely Acid Generator	Likely Acid Generator
BG4-5	0.703124889	0.351562445	Likely Acid Generator	Likely Acid Generator
BG4-6	0.202732662	0.101366331	Likely Acid Generator	Likely Acid Generator
BG4-7	0.415336222	0.207668111	Likely Acid Generator	Likely Acid Generator
BG4-8	2.999996252	1.499998126	Acid under certain conditions	Acid under certain conditions
BG4-9	15.84836447	7.924182235	No Acid Potential	No Acid Potential

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Neutralising Potential Ratio(NP/AP) for Closed System	Interpretation Open System	Interpretation Closed System
BG5-1	8.01792	4.00896	No Acid Potential	No Acid Potential
BG5-2	0.074340282	0.037170141	Likely Acid Generator	Likely Acid Generator
BG5-3	0.000264724	0.000132362	Likely Acid Generator	Likely Acid Generator
BG5-4	0.219790582	0.109895291	Likely Acid Generator	Likely Acid Generator
BG5-5	0.916911111	0.458455556	Likely Acid Generator	Likely Acid Generator
BG5-6	16.8623029	8.431151451	No Acid Potential	No Acid Potential
BG5-7	0.024264908	0.012132454	Likely Acid Generator	Likely Acid Generator

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Neutralising Potential Ratio(NP/AP) for Closed System	Interpretation Open System	Interpretation Closed System
BG6-1	1.28445265	0.642226325	Acid under certain conditions	Likely Acid Generator
BG6-2	25.24700242	12.62350121	No Acid Potential	No Acid Potential
BG6-3	0.010210022	0.005105011	Likely Acid Generator	Likely Acid Generator
BG6-4	5.307032163	2.653516081	No Acid Potential	Acid under certain conditions
BG6-5	0.597119377	0.298559689	Likely Acid Generator	Likely Acid Generator
BG6-6	2.085248251	1.042624126	Acid under certain conditions	Acid under certain conditions
BG6-7	0.547288894	0.273644447	Likely Acid Generator	Likely Acid Generator

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Neutralising Potential Ratio(NP/AP) for Closed System	Interpretation Open System	Interpretation Closed System
BG7-1	0.641737641	0.320868821	Likely Acid Generator	Likely Acid Generator
BG7-2	5.334434229	2.667217114	No Acid Potential	Acid under certain conditions
BG7-3	1.069634205	0.534817102	Acid under certain conditions	Likely Acid Generator
BG7-4	1.694119539	0.84705977	Acid under certain conditions	Likely Acid Generator
BG7-5	9.79685E-05	4.89842E-05	Likely Acid Generator	Likely Acid Generator
BG7-6	0.082700011	0.041350005	Likely Acid Generator	Likely Acid Generator
BG7-7	0.102546661	0.051273331	Likely Acid Generator	Likely Acid Generator
BG7-8	0.831183346	0.415591673	Likely Acid Generator	Likely Acid Generator
BG7-9	0.443519019	0.221759509	Likely Acid Generator	Likely Acid Generator

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Neutralising Potential Ratio(NP/AP) for Closed System	Interpretation Open System	Interpretation Closed System
BG8-1	2.543650952	1.271825476	Acid under certain conditions	Acid under certain conditions
BG8-2	1.261058781	0.630529391	Acid under certain conditions	Likely Acid Generator
BG8-3	2.679847787	1.339923893	Acid under certain conditions	Acid under certain conditions
BG8-4	1.84907643	0.924538215	Acid under certain conditions	Likely Acid Generator
BG8-5	12.99458344	6.497291721	No Acid Potential	No Acid Potential
BG8-6	0.505897753	0.252948876	Likely Acid Generator	Likely Acid Generator

Site Name	**Neutralising Potential Ratio(NP/AP) for Open System**	**Neutralising Potential Ratio(NP/AP) for Closed System**	**Interpretation Open System**	**Interpretation Closed System**
BG9-1	0.001414784	0.000707392	Likely Acid Generator	Likely Acid Generator
BG9-2	0.542417063	0.271208531	Likely Acid Generator	Likely Acid Generator
BG9-3	3.140293329	1.570146665	Acid under certain conditions	Acid under certain conditions
BG9-4	3.412858542	1.706429271	Acid under certain conditions	Acid under certain conditions
BG9-5	87.36302419	43.68151209	No Acid Potential	No Acid Potential
BG9-6	0.404806792	0.202403396	Likely Acid Generator	Likely Acid Generator
BG9-7	1.443927029	0.721963514	Acid under certain conditions	Likely Acid Generator
BG9-8	0.166449746	0.083224873	Likely Acid Generator	Likely Acid Generator
BG9-9	0.205185405	0.102592703	Likely Acid Generator	Likely Acid Generator
BG9-10	3.037892505	1.518946252	Acid under certain conditions	Acid under certain conditions

APPENDIX 6

Detailed interpretation of acid-base accounting results for Optimum