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THE DEVELOPMENT AND EVALUATION OF HYDROGEOCHEMICAL PREDICTION TECHNIQUES FOR SOUTH AFRICAN COALMINES

by

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THESIS

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1 INTRODUCTION

South Africa is the fourth largest producer of coal in the world. In 2001 the total sales value of coal amounted to R26.5 billion (Chamber of Mines, 2002). The 224 million metric tons of coal produced per year directly supports employment for approximately 50 000 employees. Coal occurs in several areas through South Africa, associated with post-glacial conditions of the early Permian period (approximately - 260 Ma) (See Figure 1). Most of the coal formed in the stable tectonic conditions along with sedimentation of sandstones and shales of the Ecca formation of the Karoo Supergroup (Snyman, 1998).

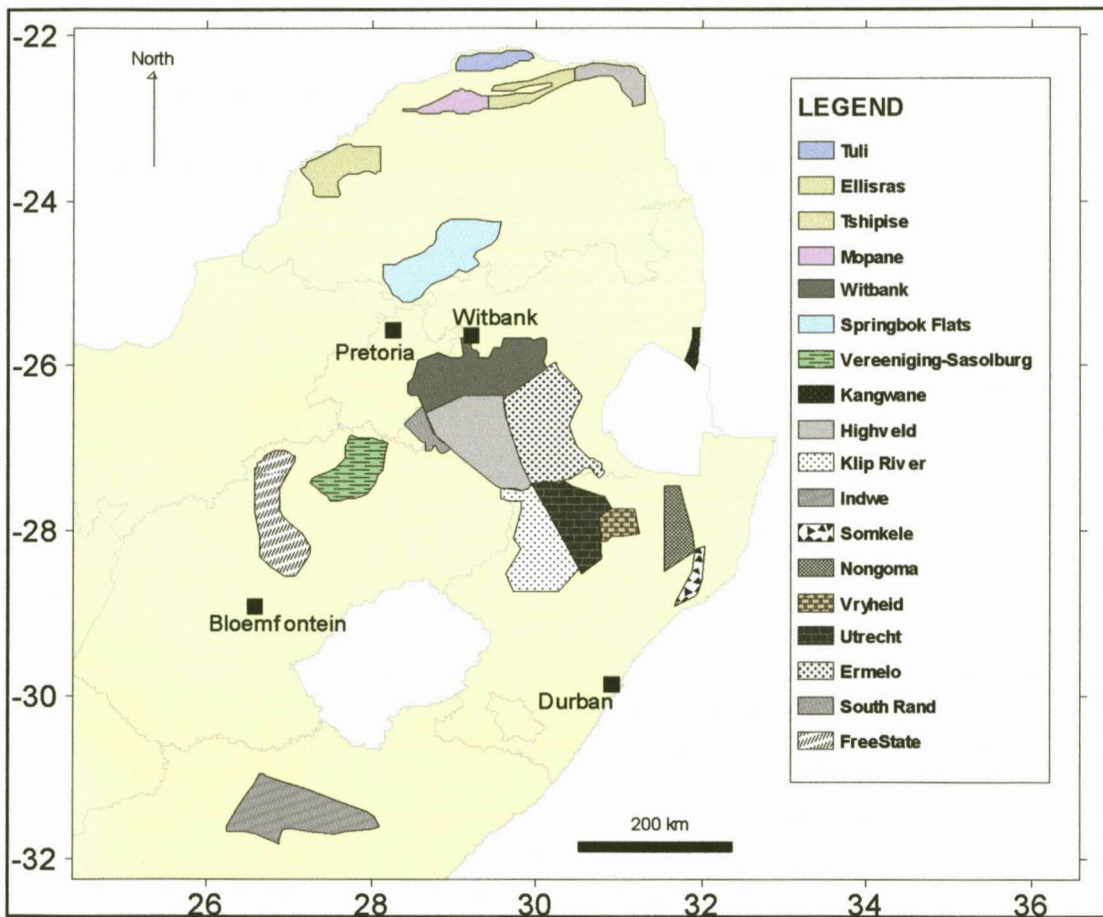


Figure 1: Coalfields of South Africa (after Snyman, 1998).

Unfortunately, associated with coal mining in South Africa, the phenomenon of Acid Mine Drainage (AMD) occurs. Acid mine drainage occurs when sulphide minerals in rock are oxidised, usually as a result 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 capacity of waste rock, overburden, pit walls, pit floor and tailings to produce acid mine drainage. Several researchers, such as Hodgson and Krantz (1998), Geldenhuys and Bell (1998), and Grobbelaar *et al.* (2002), have addressed the effects of AMD in South African Coalfields.

A variety of minerals can be found in South African Coalfields, several of which are relatively inert. Others such as pyrite (FeS_2) and the carbonate minerals such as calcite and dolomite (CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$) are more reactive and lead to elevated concentrations of different ions in coalmine waters. The most abundant minerals in the coals are clay minerals (primarily kaolinite and illite), together with carbonates (calcite, dolomite, ankerite and siderite), sulphides, quartz and glauconite (Geldenhuys and Bell, 1998). 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.

As an illustration of the impact of AMD, 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, 1998). Extrapolation to include future opencasting at existing mines can result in an escalation of the sulphate contribution to an anticipated value of 120 t/d. The latter translates into a sulphate concentration of 450 mg/L^1 in the Witbank Dam. The cumulative consequence of AMD processes on a catchment scale is therefore significant enough to warrant detailed investigation into predictive and management tools. Grobbelaar (2001) and Grobbelaar *et al.* (2002) indicate that expected post-closure sulphate loads for the Witbank Catchment are in the order of 170 - 280 t/d, based on discharges of 100 - 160 ML/d. Investigations into treatment costs of this emitting water undertaken by Coaltech 2020 indicate that, based on current figures, treatment costs will be in the order of R5,00 per m^3 and between R2,00 and R5,00 per kg of sulphate removed (Van Niekerk, 2001). There is a critical need to accurately predict the future mine water quality evolution, for both regulatory/environmental impact and economic requirements.

Acid mine drainage is a widespread phenomenon affecting the quality of water at all South African collieries. Techniques to determine the likely leachate quality are numerous and have thus far been applied without uniformity. Through this research, it is hoped that an understanding of the role of each prediction technique can be obtained, and that though the testing and refinement of methods as well as the development of new tools, more consistent and reliable results can be attained.

1.1 OBJECTIVES

This thesis 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 coal mining conditions.

The aims of this thesis therefore include:

¹ Although litre should be abbreviated to l, L is used throughout for the sake of clarity.

- To give a detailed description of hydrogeochemical prediction techniques.
- To investigate the applicability of existing global geochemical prediction technologies to South African coal mines.
- To evaluate the results from different prediction techniques.
- To enhance current testing or interpretation methods.
- To develop integrated tools to facilitate more accurate application of these tools.
- To select and recommend methodologies to be used in South African coal mines.

1.2 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 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.
- The use of several field techniques such as core boreholes, down-the-hole profiling and underground sampling in conjunction with laboratory testing.
- Development of predictive tools and interpretation methods.
- Application of the tools and techniques to case studies to compare with the field situation.

1.2.1 ABATE

The research aims are to define a suite of acid-drainage prediction, applicable to South African coal mine conditions. The thesis will highlight the use of different techniques and illustrate the benefits of applying several techniques conjunctively to arrive at a meaningful assessment of future water quality evolution at South Africa collieries.

To this end 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. While the application of a suite of techniques appears self-evident, the non-hierarchical nature of such an approach is a paradigm shift in terms of applied approach in South Africa.

Figure 2 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).

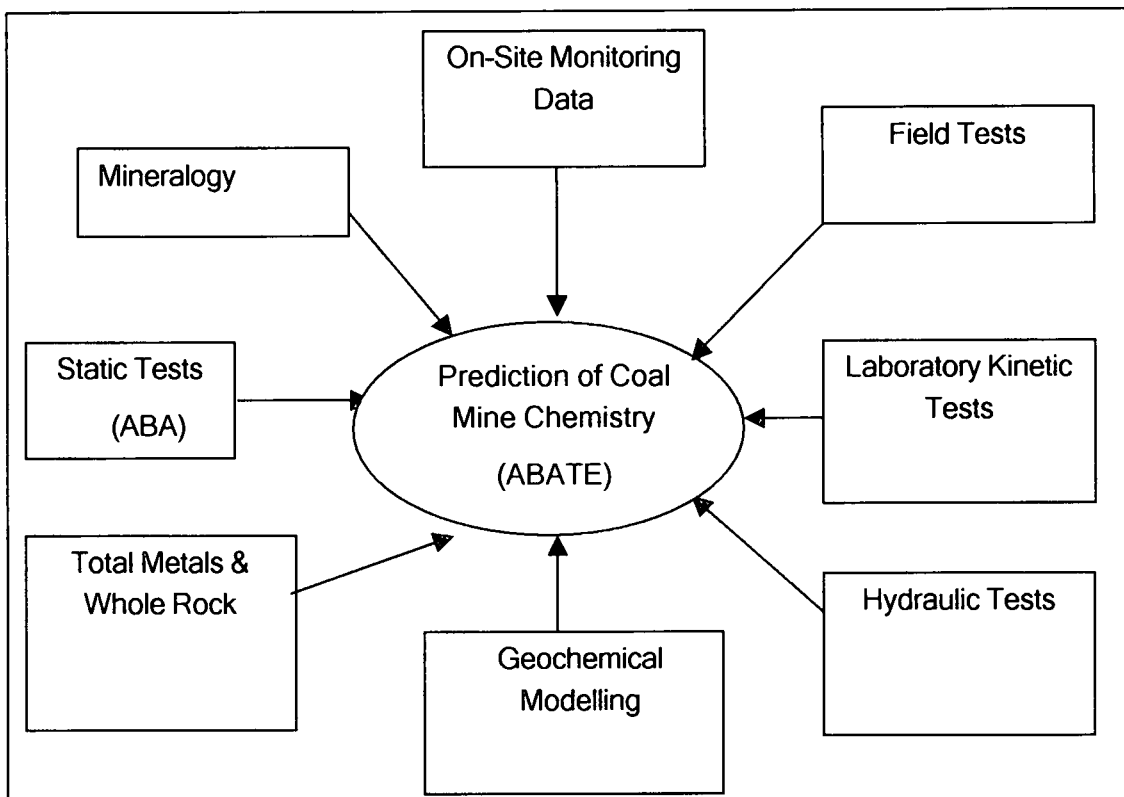


Figure 2: The Prediction Wheel for Mine Drainage Chemistry (adapted from Morin and Hutt, 1999).

This thesis will concentrate on the evaluation, development and application of these methods which make up the ABATE strategy.

1.3 THESIS STRUCTURE

The thesis is structured as follows:

- Chapter 1 is an introduction.

- Chapter 2 provides an overview of the drivers on observed water quality, including acid-generating and neutralisation reactions expected in South African Coalfields.
- Chapter 3 provides details of static, kinetic and numerical methods for the prediction and understanding of acid mine drainage in the South African Coalfields.
- Chapter 4 details the results from the testing of the methods described in Chapter 3. This chapter will give details regarding the evaluation and development of ABA methodologies to be followed (including the place and use of mineralogy), and the ABA nature of different lithological layers commonly found in the coalfields.
- Chapter 5 outlines the development of cost-effective kinetic tests and the results from the 24 kinetic tests run in the course of the research.
- Chapter 6 provides an indication of applicable field techniques to support hydrogeochemical prediction.
- Chapter 7 provides a critique of common numerical tools (geochemical modelling methods), and the application of geochemical models.
- Chapter 8 outlines the development of the ABACUS interpretation tool and the BUGEL empirical model for underground compartments.
- Chapter 9 provides details of case studies where the methods have been used, to show applicability and shortcomings.
- Chapter 10 gives overall conclusions to and recommendations relating to data collection, the use and interpretation of the methods, and key areas of research that should be targeted.

2 FACTORS INFLUENCING WATER QUALITY IN COAL MINES

2.1 INTRODUCTION

Water quality in South African coalmines is an important consideration for the long-term management of mining impacts (Hodgson *et al.*, 2001). Aspects of water management and protection in South Africa have changed considerably in the last few years, with the promulgation of laws like the New National Water Act (Act No 36, 1998), which focuses on sustainability and equality. These principles take into account:

- The basic human needs of present and future generations.
- The need to protect water resources.
- The need to share water resources with other countries.
- The need to promote social and economic development through the use of water.
- The need to establish suitable institutions in order to achieve the purpose of the Act.

As part of the impact of these laws, aspects such as waste discharge costs and the polluter pays principle have become important focuses of water management on the South African collieries (Postma and Schwab, 2002).

To deal with these issues, an understanding of the key drivers on water quality in local collieries is required. Several factors will influence the observed water quality in the short and long-term at any coalmine. The most important of these factors are:

- The conditions of coal and associated mineral formation.
- The process of acid mine drainage, which results from the oxidation of sulphide minerals to yield acidity and sulphate.
- Neutralisation of the acidity, with associated secondary mineral formation.
- The mining method employed.
- The hydrogeological influence of each mining method.

The rest of this chapter will highlight the impact each one of these influences can have on water quality, so that an understanding of the role of each portion of the ABATE strategy or the prediction wheel given in Figure 2 can be obtained.

2.2 INTRODUCTION TO AMD

Acid mine drainage (AMD) occurs when sulphide-bearing minerals in rock are exposed to air and water, oxidising the sulphide sulphur to sulphuric acid (Evangelou (1995), Evangelou and Zhang (1997), Hadley and Snow (1974), Moses *et al.* (1987) and Robertson (1996)). AMD and heavy metal pollution can poison groundwater and drinking water, and destroy aquatic life and habitat. The acid dissolves heavy metals into ground- and surface water (Hadley and Snow, 1974).

It is only relatively recently that the full implications of its impact have been acknowledged in mine planning. Nordstrom *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 from 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 constructed from acid-generating rock around the mine site (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.

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 (Evangelou, 1995). Bright orange coloured water and stained rocks are usually telltale signs of acid mine drainage. The orange colour is due to ferric hydroxide ($\text{Fe}(\text{OH})_3$) (yellow boy) precipitating from the water (Figure 3). 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 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).



Figure 3: Neutralised AMD, with precipitation of yellow boy at a South African Colliery.

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: AMD is the number one environmental problem facing the mining industry across the world (Domville *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).

2.3 COAL AND ASSOCIATED MINERALS IN SOUTH AFRICA

Coal occurs in many different coalfields across South Africa (Figure 1). The majority of production currently emanates from the Witbank, Highveld, Ermelo and Natal Coalfields. Most of the coal formed in stable tectonic conditions, along with sedimentation of the sandstones and shales of the Ecca formation (Late to Early Permian Period - 260 Ma) (Snyman, 1998).

The South African coal deposits are found in two major tectonic settings, namely stable cratonic platforms and fault-bounded rift basins. The main Karoo Basin is typical of a stable cratonic platform and the northern parts of South Africa are typical of a fault-bounded rift basin (Snyman, 1998). The coal seams in the South African Coalfields were mostly formed in this epicontinental environment and occur within the Vryheid Formation. The Vryheid Formation forms the mid-part of the Ecca Group which, in turn, is part of the Karoo Supergroup (Bullock and Bell, 1997). This formation consists of sediments deposited in shallow marine and fluvio-deltaic environments in which coal developed from peat that accumulated in swamps and marshes. The formation primarily consists of sandstones, siltstones, mudstones and shales. In order for peat to accumulate and be preserved, subsidence must occur or, alternatively, the water table must be sufficiently maintained to prevent peat destruction. Slight variations in water depth would result in thin but widespread lower quality (high ash) bands within a seam, produced by oxidation due to the lowering of the water level or drowning of the swamp by increased water depth.

2.3.1 Coal seam sedimentary processes

In general, coal seams form during periods of low sedimentary deposition when plant growth and peat accumulation occur at the same rate as the substrate. Such periods separate depositional events. In many instances, these depositional sequences took place in a deep, rapidly subsiding portion of the main Karoo Basin (Falcon, 1986).

The coal-forming environments have been subdivided into two types; the paraglacial and the epicontinental environments. The paraglacial environment is a basin edge phenomenon, which developed around the north-west and northern side of the basin as a result of the accumulation of glacialacustrine and glaciofluvial sediments on the marine-covered surfaces of the Kaapvaal Craton. These sediments were deposited at the close of the Dwyka continental glaciation. Distribution of the coal seams in this environment was controlled by post-Karoo topography, with peat accumulation predominantly occurring in low-lying land protected from active sedimentation. These coals are freshwater marsh in origin, with characteristically low sulphur content (Falcon, 1986).

The epicontinental coal-forming environment was related to the major development of sediments across the north-eastern stable shelf area of the Karoo Basin and overlying the older paraglacial sediments to the north (Figure 4). This environment

was locally subjected to marine or brackish water inundation during delta switching, resulting in a variety of geochemical (pH, salinity and Eh) environments. Such factors affect coal quality and the resultant sulphur content of the coal considerably.

Within each coal seam a range of local conditions controls the development of the coal type and facies, such as topographical controls, the local paleoenvironment, type of plant community, rate of accumulation and nature and rate of plant degradation, or biochemical coalification.

The conditions for the formation of different coal facies vary with paleo-ecological environments. The *in-situ* inertinic coals are found predominately in relatively dry environments, viz. on high ground on valley flanks, levees of rivers, upper delta, alluvial plane swamps. Drift forms occur in reworked organic detritus pieces usually transported by water and deposited on river banks or as flooded deposits in deltaic or lacustrine environments.

Vitrinite rich coals are usually associated with permanently wet or water-logged conditions as may be found in sea shore, fluvial, lacustrine, or lower deltaic/paralic back swamps (Falcon, 1986). Shallow open water, distal environments, lagoons, ponds, and distal deltaic settings typically accumulate very fine wind and water borne organic and inorganic matter and particularly algae, spores and pollens (Falcon 1986). Known as exinite, these components impart a high hydrogen and volatile matter content to the host sediment.

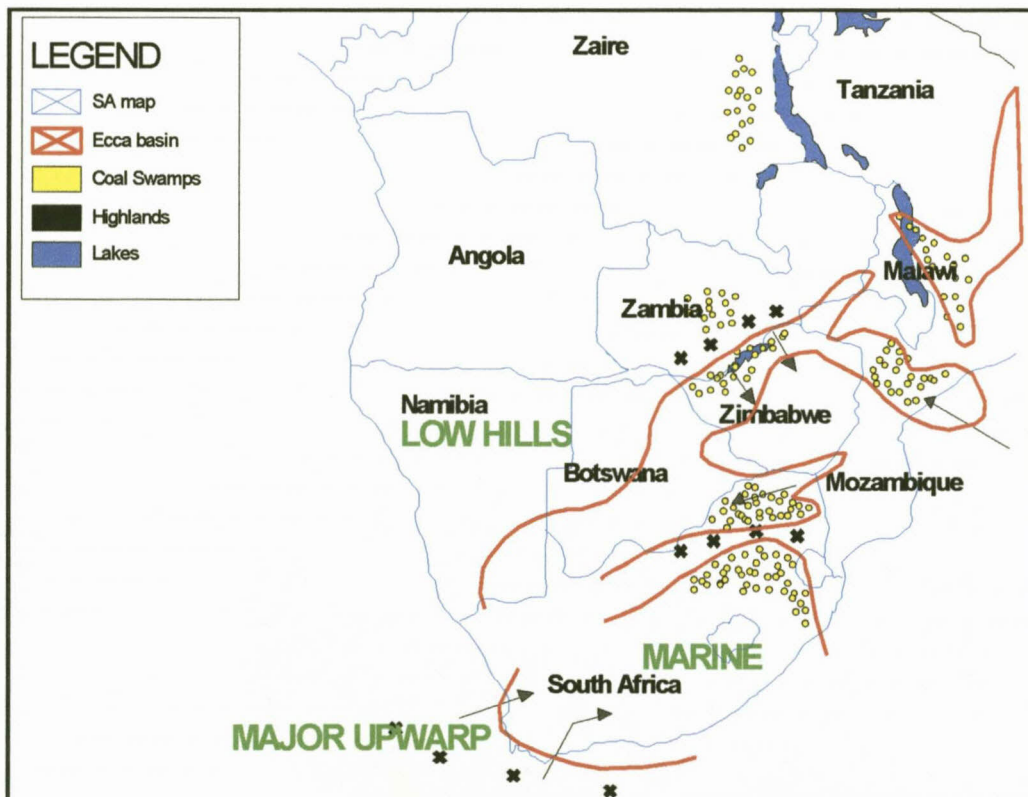


Figure 4: Ecca Basin. The tectonic situation is dominated by major upward movement in the south (after Rust, 1975).

2.3.2 Hydrochemical conditions during the deposition of South African coal

A key question when researching the AMD conditions in South African coalmines involves the co-existence of acid generating minerals and minerals that buffer acidity.

The bulk analyses of coals, when combined with a consideration of the conditions of formation, provide several clues regarding the expected mineralogy. The ash content of coal is dependent not only on the peat types and contemporaneous clastic depositional processes, but also on the swamp water pH, which is a significant parameter in the determination of the ash content of coal. The rate and degree of plant degradation during peatification is primarily pH-controlled. Microbial activity plays a critical role during the peat stage, and is to a large degree pH-controlled.

Geochemically the ash content of coal is dependent on pH-controlled levels of bacterial activity in the ancestral swamps (Cairncross and Cadle, 1987). Microbial activity becomes increasingly effective above a pH of approximately 4.5. Coals are low in mineral matter and were derived from peat that accumulated under highly acid conditions with a pH of < 4.5 . If the peat swamp pH is > 5 , then microbial activity is so vigorous that it precludes sufficient organic material to produce coal. Peat accumulation in swamps with pH > 5 would only produce black, highly carbonaceous shales or impure bone coal ($> 33\%$ ash) or, if unfavourable conditions were only short-lived, a coal parting (Cairncross and Cadle, 1987).

As microbial and bacterial activity can be temperature-dependent, the pH of the No. 1 and the No. 2 Seam swamp water may have been greater than 4.5, obtained from warm climate modern-day swamps. The cooler temperature inhibited peat degradation under higher pH-values and would therefore have suppressed bacterial activity. This would allow anions such as bicarbonate to be present in the formation water.

2.3.2.1 Pyrite and calcite formation

The pH-conditions are very important in understanding the observed minerals commonly associated with the coal seams in South Africa. If it is assumed that the conditions under which the peat were reserved were fairly anoxic (otherwise there would have been heightened bacterial metabolism of the organic material) and that the pH-conditions were such that peat preservation could occur, the presence of pyrite in these seams should be investigated. Berner (1970) outlines the following broad process for pyrite formation:

- Bacterial sulphate reduction.
- Reaction of the reduced S (probably in the form of H_2S) with sedimentary iron minerals.
- Reaction of the monosulphide iron minerals with elemental or other forms of S to form pyrite.

The important factors for pyrite formation are therefore the presence of metabolisable organic matter, the diffusion of sulphate in the reacting sediments, the total

concentration of sulphate, the reactivity of iron minerals, and the production of elemental sulphur. Figure 5 indicates the process as seen by Goldhaber and Kaplan (1982).

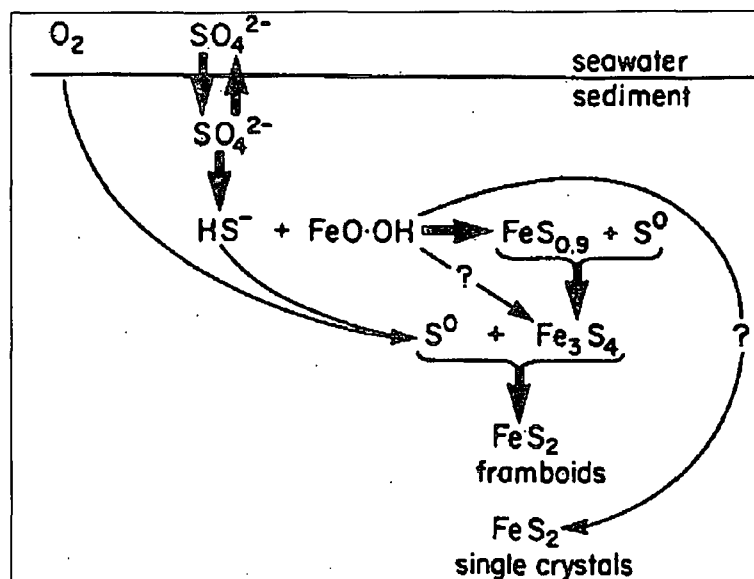
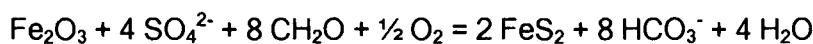
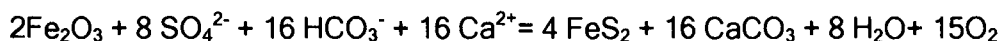


Figure 5: Pathway of sedimentary pyrite formation. (Goldhaber and Kaplan, 1982).

Pons *et al.* (1982) described this process with the following overall equation (CH_2O represents organic matter):



Written differently (in the presence of calcium, Chang and Berner, 1999):



The equation of Pons (1982) provides an explanation for the bicarbonate nature of many roof drips in the coalfields (See Section 2.3.2.2). Reported studies such as those by Gilb (1987) also indicate that where calcretions occur in mudstones, these are often of marine origin (similar to local conditions) and that in these environments, higher sulphur proportions occur. The equation of Chang and Berner (1999) provides the answer, from a chemical reaction mechanism perspective, of the co-existence of the source of acidity (pyrite) and the source of neutralisation (calcium-rich carbonates such as calcite) within coal seams.

The likely redox and pH-conditions under which pyrite is stable are also important to understanding the co-existence of these phases. The two figures below indicate the stability field of pyrite under different conditions. Figure 6 indicates the conditions under which elemental sulphur and pyrite could co-exist. This demonstrates that pore waters trapped within these coal layers are expected to have lower pH-values and be in reduced states. As time proceeds, processes such as ion exchange, reaction with the carbonate system and carbonate minerals will alter this chemistry to eventually reflect a sodium carbonate nature.

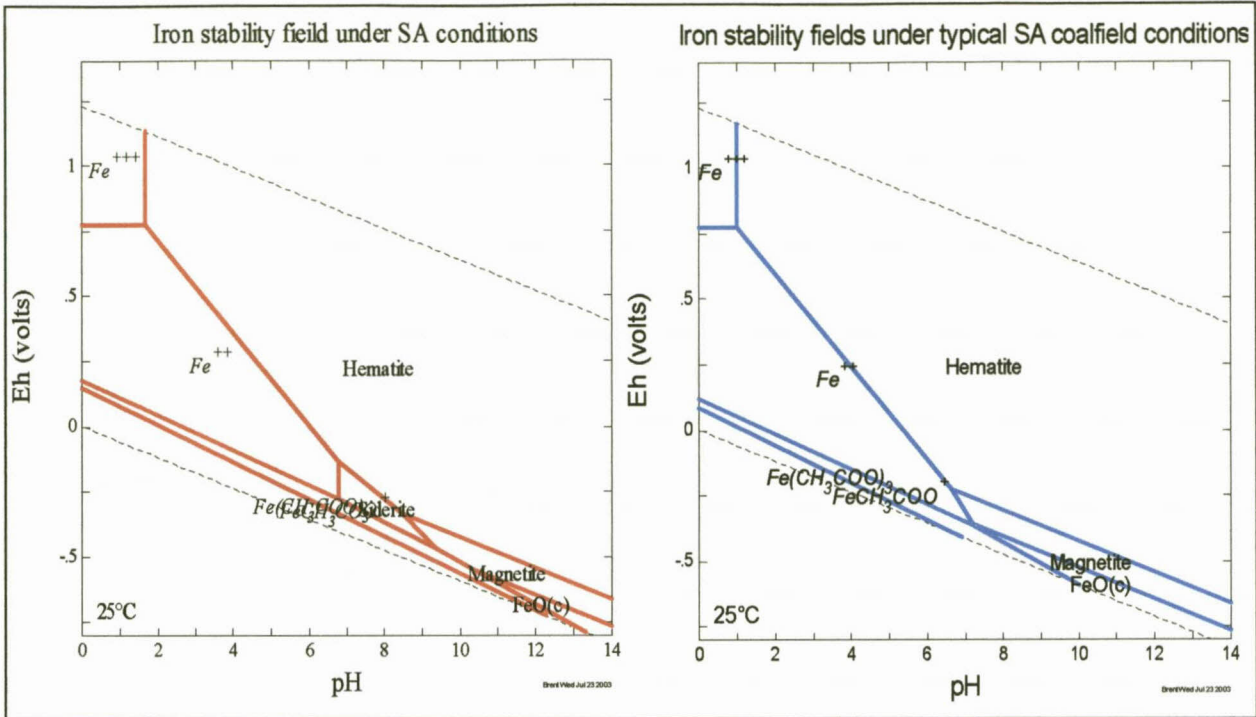


Figure 6: Stability fields of iron species under typical South African Coalfield conditions
The red trace provides the stability fields for $[Fe] = 10^{-5}$ and $[HCO] = 10^{-2}$ while the blue shows the variation under conditions where $Fe] = 10^{-2}$ and $[HCO] = 10^{-6}$.

When the effect of carbonate in the water from dissolution of calcite and/or dolomite and atmospheric CO_2 dissolution via Henry's law is taken into account, the stability fields look rather different, as is shown in Figure 6:

The pH/Eh conditions for pyrite stability with higher carbonate concentrations indicate an overlapping zone of pyrite and siderite stability; refuting the erroneous assumption that primary siderite would result in the absence of pyrite (Rose and Cravotta, 1999).

2.3.2.2 The formation of Na-HCO₃ waters

One of the enigmatic factors encountered in South African Coalfields is the occurrence of sodium-rich high alkalinity waters as mining proceeds.

In several reports, such as Hodgson and Krantz (1998), Hodgson and Usher (1999), mention is made of "sodium carbonate" as a first stage in buffering any generated acidity. The impression created in several of these reports is that sodium carbonate or bicarbonate minerals exist within the coal or overlying sediments. In many subsequent reports, however, Hodgson and others refer to the sodium carbonate nature of the connate water as a more likely explanation (Hodgson and Grobbelaar, 1998, Hodgson *et al.*, 2000). To investigate this further, a mechanism to explain the evolution of such waters is sought.

Inspection of mineralogical databases for a range of sodium containing carbonate or bicarbonate minerals yields the following possibilities (Parkhurst and Appelo, 1999):

Nahcolite($NaHCO_3$) Log $K_{sp} = -10.88$

Natron($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) $\text{Log } K_{\text{sp}} = -1.31$

Thermonatrite($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) $\text{Log } K_{\text{sp}} = 0.12$

Trona($\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$) $\text{Log } K_{\text{sp}} = -11.12$

Determining the solubility of any of these species at various partial pressures of CO_2 , shows that a very high sodium value is needed before any of these phases is likely to precipitate.

Inspection of all available mineralogical determinations done as part of this research (nine mines in three Coalfields, more than 200 samples) and studies done by Azzie (2002) and Pinetown (2003) show that none of these phases are found in the solid phase.

The question then arises, if it is not from dissolution of a mineral, how does such a solution arise? The very high bicarbonate values can be explained by the expected reactions which occurred during the coalification process. The organic material, available in high quantities, would have yielded CO_2 and water as products of the respirative oxidation of the organic material. Through Henry's law considerations, the CO_2 will dissolve in water. As seen in previous sections, pH conditions in South African coal sedimentation were not necessarily as low as in other coalfields, and the fractionation of this dissolved inorganic carbon into H_2CO_3 , HCO_3^- and CO_3^{2-} driven by the concurrent equilibria occurs (Figure 7). The presence of other carbonates such as calcite and dolomite results in neutralisation and higher pH-values, so that bicarbonate is the dominant species.

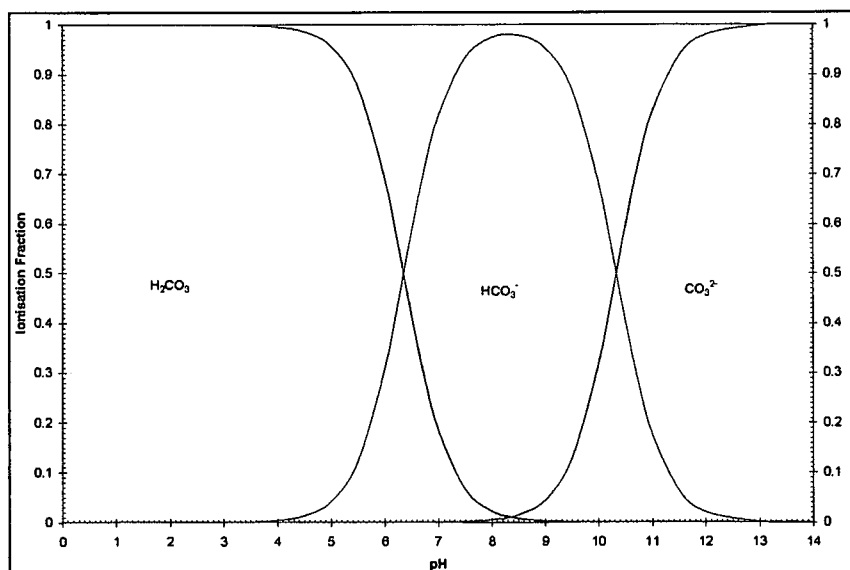
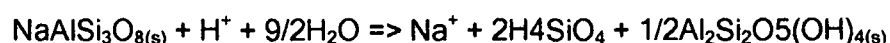


Figure 7: Distribution Diagram for the Carbonate System.

The partial open/closed nature as a result of the burial or sedimentation process allows the total CO_2 to accumulate, which can give rise to high bicarbonate concentrations. The explanation above, together with the equation of Pons *et al.* (1982) for pyrite formation (Section 2.3.2.1), could clarify the high bicarbonate values, but does not explain how sodium remains as the dominant cation.

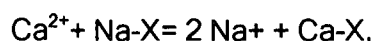
Indications are that the South African coals were deposited under marine or lacustrine conditions. Using this as a basis for consideration, it would be expected that any waters encountered would be sodium/chloride dominated. The sodium dominance is therefore not unexpected, but from collected roof drip waters, enrichment of sodium relative to chloride has occurred. Since the chloride minerals associated with the common cations are very soluble, removal of chloride through precipitation is not a likely scenario. Furthermore, sorption of chloride has not been observed to occur; thus chloride is considered conservative (Davis *et al.*, 1998).

An additional source of sodium therefore needs to be identified. An obvious source would be the sodium feldspar, albite ($\text{NaAlSi}_3\text{O}_8(\text{s})$). Albite is a slow-weathering common silicate in the coalfields. In the conditions of formation discussed previously, this would weather to yield sodium, aluminium and silica species. Under favourable conditions, kaolinite will form according to the reaction below:



Since the weathering of all the feldspars (muscovite, K-feldspar, albite and anorthite) will produce kaolinite, the presence of kaolinite cannot unequivocally be used to support this hypothesis. However, from previous studies on the mineralogy of local coalfields, kaolinite has been reported as the principal clay mineral (Azzie, 2002). Some tenuous evidence therefore exists for this situation, which also explains the enrichment relative to chloride.

From previous discussions, high Ca and Mg are also expected (for example calcite would only precipitate at high enough calcium concentrations), thus a mechanism for the relative enrichment of sodium instead of Ca and Mg also needs to be explained. The most likely explanation for this would be an ion-exchange process. Several authors such as Capo *et al.* (2001), Perry (2001) and Mayo *et al.* (2000) have undertaken detailed modelling and characterisation studies in coal mines. The phenomenon of sodium enrichment in coal mines is addressed by all of these studies. In each of these the most likely explanation put forward by the authors is that cation exchange of Ca and Mg in favour of Na is taking place. The clay minerals are ideally suited for cation exchange to occur. In studies such as Perry (2001) the evolution of high Na water via cation exchange is explained, with the generic equations as follows:



where X refers to exchange site such as a clay mineral. Many of the clays in local collieries have high cation exchange capacities (Azzie, 2002) and several of these could yield sodium while removing the divalent cations from solution. Examples would include clays such Na-montmorillonite, and zeolites such as analcime (Mayo *et al.*, 2000). It is important to note that this process would compete with H^+ ion removal at lower pH-values, which also raises pH (Appelo, Personal Communication, 2001), but in neutral to alkaline solutions, the divalent cations will more easily exchange for sodium.

A feasible model to explain the evolution of high Na/high alkalinity waters would therefore include:

- Sodium as the dominant cation in the connate water, with associated chloride dominance.
- CO₂ generation through the oxidation of organic material ongoing from coalification to the present times.
- Dissolution of calcite and dolomite to yield more bicarbonate competing with pyrite formation, which removes these species.
- Further enrichment in sodium through dissolution of sodium containing silicates such as albite, which would yield sodium and kaolinite, the most common clay in local coal mines.
- Removal of divalent cations such as calcium and magnesium to liberate more sodium through ion exchange processes.

Current research by Pinetown (2003) could provide further mineralogical evidence to resolve these processes.

Table 1 indicates the chemical composition of several roof drips encountered underground in the Highveld Coalfield:

Table 1. Typical composition of different roof waters in the Highveld Coalfield.

Site	EC	pH	Ca	Mg	Na	K	P-Alkalinity	Total	F	Cl	SO ₄
	mS/m		mg/l	mg/l	mg/l	mg/l	mg/l as CaCO ₃	mg/l as CaCO ₃	mg/l	mg/l	mg/l
Middelbult - Seam	234	8.8	8.6	4.65	600	3.81	37	1055	9	221	5.19
Middelbult - S37	236	8.78	8.44	2.89	642	3.73	38	1243	8.9	116	1.33
Middelbult - S38	167	8.81	5.05	1.61	450	2.41	34	893	13.36	57	1.65
Bos-68	449	8.7	10.4	4.89	1098	7.19	39	1345	3.53	849	0.93
Bos-1	423	8.75	9.4	3.86	1050	7.06	51	1463	3.64	682	1.54

2.4 IMPACT OF MINING TYPE ON HYDROGEOCHEMISTRY

Several authors such as Hodgson and Krantz (1998), Hodgson (2001) and Grobbelaar (2001) have dealt at length with the impact that the mining type has on the hydrogeological regime at South African collieries. This section aims to highlight several of the observations made by these researchers in such a way that the impacts on water quality are indicated.

2.4.1 Mining types in South Africa

Coal extraction has been ongoing in the Mpumalanga Coalfields for more than 100 years. (Havenga, 2003). Coal is generally mined by opencast- or underground methods in South Africa. (Grobbelaar, 2001). At depths down to 50 meters coal is normally extracted by surface mining, the extraction rate associate with type of mining being currently 85 - 90% (Hodgson and Krantz, 1998). At depths below 50 meters more conventional mining methods such as bord-and-pillar extraction have been used since mining began. Since 1973 improved underground extraction methods have

been introduced on an increasing scale in a number of South African Coalfields. Stopping, with an extraction rate of 70 - 80 %, and longwall mining with extraction rates of the order of 75 - 85 % have been introduced in several new existing coal mines (Hodgson and Krantz, 1998).

The extent of the different types of mining in the Witbank/Highveld Coalfields is given by the figure below (Figure 8) from Grobbelaar (2001) and Usher *et al.* (2002).

It is clear that most of the mining is through underground methods with almost a third currently through opencast methods. In the Witbank area, bord-and-pillar mining predominates, while in the Highveld Coalfield more extensive use is made of high extraction methods such as stopping and longwall mining.

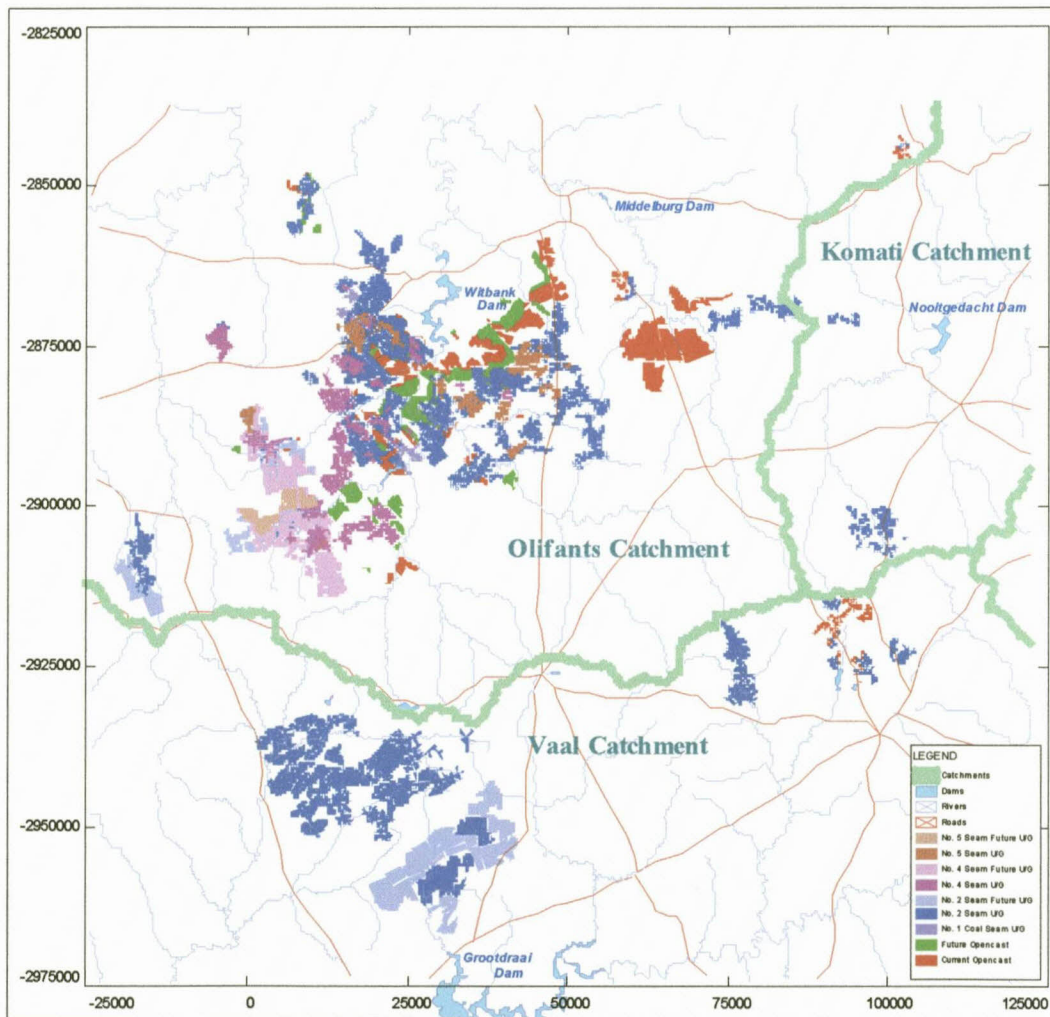


Figure 8: Mining in the Witbank/Highveld Coalfields (Grobbelaar, 2001).

2.4.1.1 Opencast Mining

Opencast coal mining has a big influence on the normal hydrological conditions associated with undisturbed strata. Factors influencing normal conditions include the exposure of unweathered strata to atmospheric conditions, increased gradients of groundwater flow and higher permeabilities of disturbed strata.

2.4.1.2 Underground mining

Two classes of underground mining can be differentiated in the South African Coalfields:

- Bord-and-pillar.
- High extraction.

Detailed discussion of these methods is available at several sources such as Snyman (1998), Hodgson and Krantz (1998) and Hodgson *et al.* (2001).

Mining is currently most often done usually continues mining techniques. For bord-and-pillar, sections of coal are left intact to support the roof and prevent collapse. Generally extraction rates for this type of mining ranges from 50% in the deeper mines such as those around Secunda, to almost 70% in shallower mines near Witbank (Grobbelaar *et al.*, 2002).

Subsidence associated with bord-and-pillar mining is less pronounced than for high extraction methods due to less collapse, although several areas of subsidence have been noted in shallower mines. This results in lower influxes of water than those found in high extraction areas.

High extraction is done principally through two methods:

- Stooing
- Longwall mining

Stooing is a further stage of the bord-and-pillar method, with increased pillar extraction. Continuous miners are generally used for this extraction process, removing pillars or parts of pillars in a particular section. The degree of extraction varies, based on the geology, coal quality and usually safety factors. (Grobbelaar, 2001). Depending on the competence of the overlying lithology and the degree of extraction, goafing or collapse can occur. The amount of subsidence at surface and the severity of cracks depend on (Hodgson, 2001):

- The depth of mining and nature of overlying rock.
- The coal seam thickness mined.
- The area stooped and panel geometry.
- The degree to which pillars have been left in the stooped area, thus still supporting the coal roof.

Longwall mining is a method by which the coal seam is removed in one operation by means of a long working face or wall. The working advances in a continuous line, which may be several hundreds of metres in length. The space from which the coal has been removed is usually allowed to collapse (goafing) or is back-filled with other material. In South Africa, the panel lengths are usually 200 m. Due to the dimensions of longwall panels, caving of the overlying strata occurs up to the surface. As a rule of thumb, subsidence at surface is usually in the order of 50% of the mining thickness (Hodgson, 2001).

As a result of this collapse a greater proportion of water is expected in high extraction areas. Schematically the effect of the collapse in high extraction areas can be portrayed by the figure below (Figure 9):

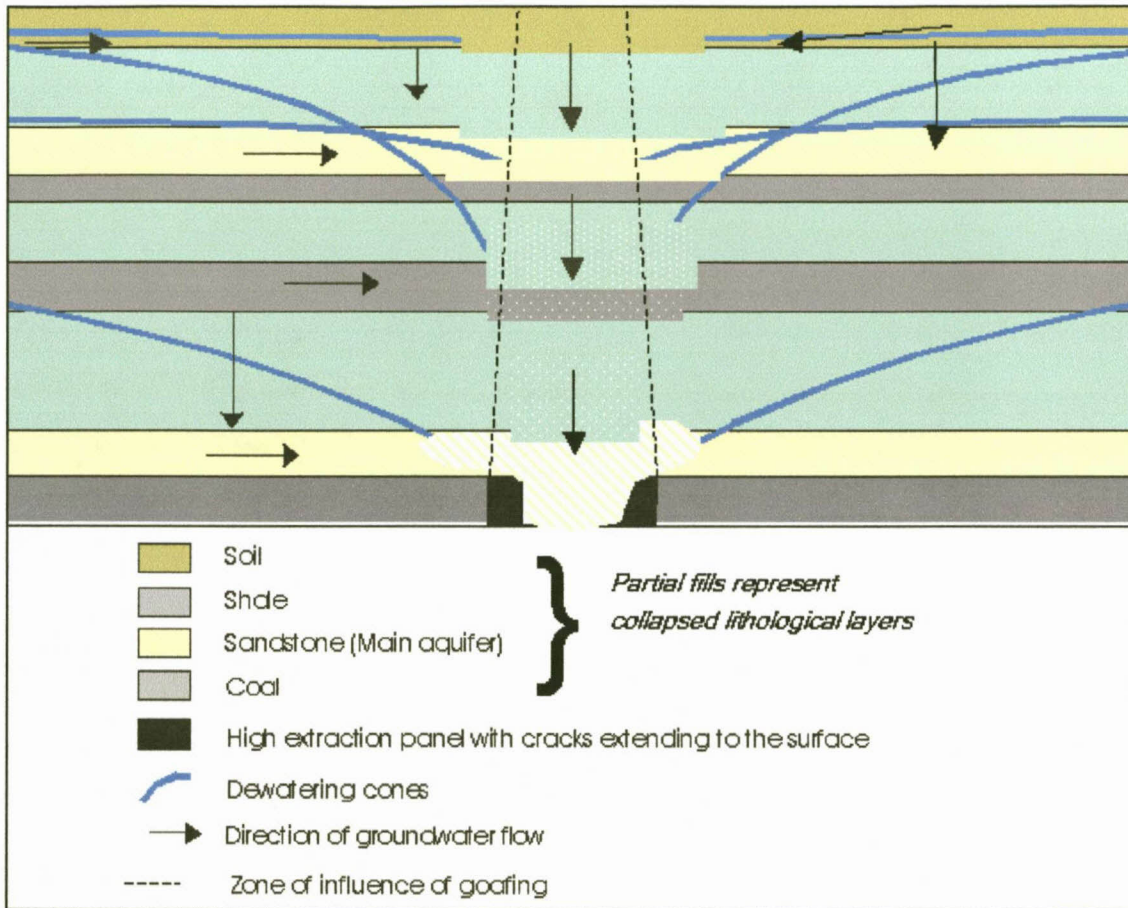


Figure 9: Zones of collapse and dewatering due to high extraction mining. (Modified after Hodgson, 2001).

In Figure 9, the relative influx from different horizons can be seen. Most of the collapse will occur in the layers immediately above the mined compartment, with fractures extending outwards from these areas to surface. The degree of interconnection, and extension of the fracture zones will largely determine the influx encountered. Where these encounter overlying surface water bodies large influxes have been experienced; indications are that these influxes decrease over time (Du Toit, 2003, Personal Communication).

2.4.1.3 Water Influx

Several sources of water influx are expected in South African collieries. In opencast areas, much of the influx is dependent on the state of the post-mining rehabilitation, while in underground mining factors such as the mining type, depth and degree of collapse and interconnectivity are important.

Figure 10 illustrates the generalised hydrological conditions associated with an opencast environment. Normal groundwater movement still takes place in aquifers. Groundwater flow directions will necessarily be directed toward the pits, due to an

artificial change in gradients on a local scale and a higher K value in spoils (Grobbelaar, 2001).

This flow, together with direct recharge into the spoils will create an artificial groundwater level in the heaped spoil until a decant level is reached. Water that decants out of the spoils as well as run-off from the surface of the spoils will follow the natural gradient and will flow to the nearest river or stream.

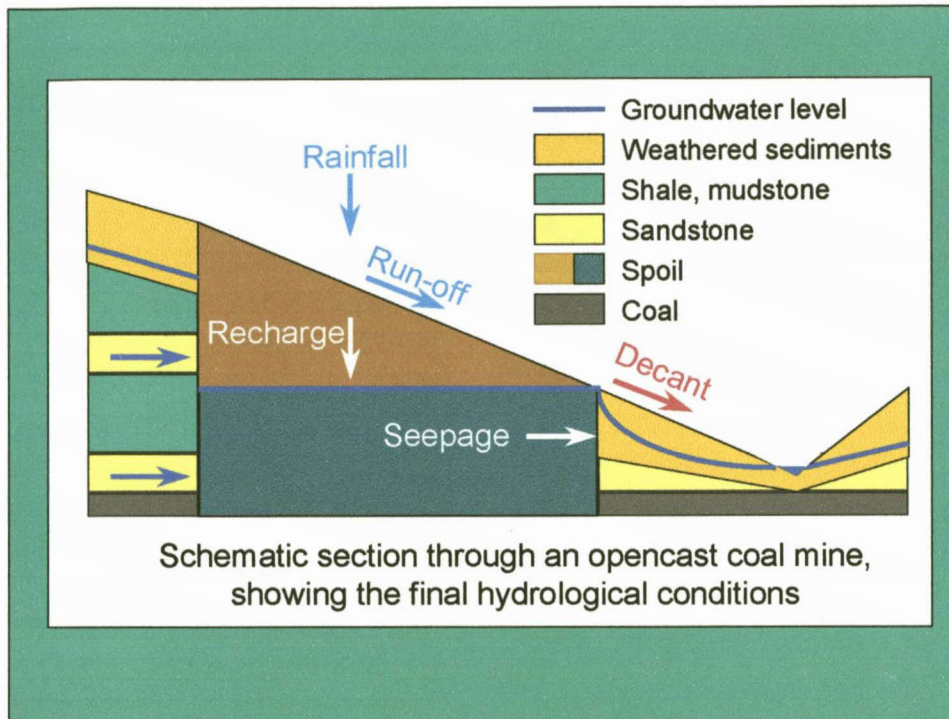


Figure 10: General geohydrology of opencast pits (Grobbelaar, et. al., 2001).

In terms of expected sources of water, the table below (Table 2) from Hodgson and Krantz (1998) summarizes, the most important information:

Table 2. Water recharge characteristics for opencast mining (Hodgson and Krantz, 1998).

Sources which contribute water	Water sources into opencast pits	Suggested average values
Rain onto ramps and voids	20 - 100% of rainfall	70% of rainfall
Rain onto unrehabilitated spoils (run-off and seepage)	30 - 80% of rainfall	60% of rainfall
Rain onto levelled spoils (run-off)	3 - 7% of rainfall	5% of rainfall
Rain onto levelled spoils (seepage)	15 - 30% of rainfall	20% of rainfall
Rain onto rehabilitated spoils (run-off)	5 - 15% of rainfall	10% of rainfall
Rain onto rehabilitated spoils (seepage)	5 - 10% of rainfall	8% of rainfall
Surface run-off from pit surroundings into pits	5 - 15% of total pit water	6% of total pit water
Groundwater seepage	2 - 15% of total pit water	10% of total pit water

The high recharge percentage of around 20% is due to a multitude of factors such as ponding, areas of spoils exposure, restabilisation cracks and influx into ramp areas. Several researchers have confirmed these high recharges through decant measurements (Hodgson, 1999, Van Tonder *et al.*, 2003). The high influx is naturally an important driver on the observed water quality in opencast pits.

In underground mines the following sources of water could be encountered:

1. Water encountered in the seam as mining commences. This is fairly low except where fractures, or fissures as they are known within the mining industry, are encountered.
2. Recharge through the roof lithologies. The magnitude of this varies depending on mining - induced fracturing of the overlying sediments.
3. Direct recharge where cracks from the collapse of mining areas, usually due to high extraction mining, run through to the higher yielding transmissive aquifers nearer surface.
4. Regional groundwater flow, which will usually flow along the coal horizon, due to its higher hydraulic conductivity compared to the surrounding sediments.
5. Influx through the floor lithologies. This can play an important role in areas where the floor is transmissive, but in where the mining floor is close to the Dwyka such as where the No. 1 Seam or No. 2 Seam are mined, such influxes are negligible.

Schematically these can be seen in Figure 11:

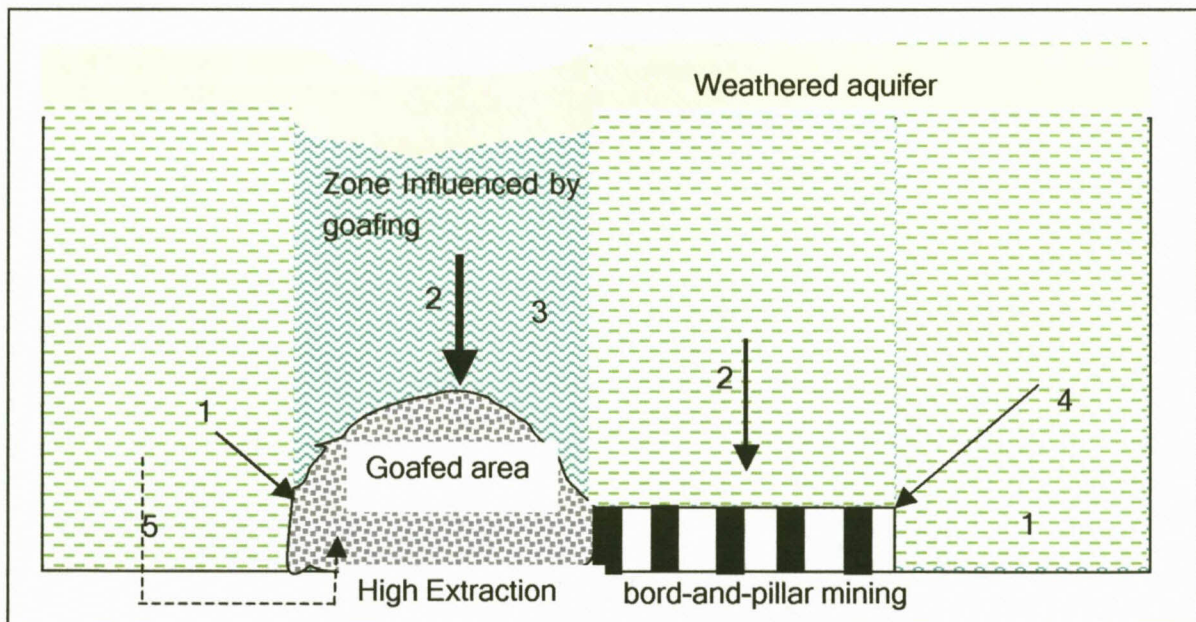


Figure 11: Schematic representation of influxes of water (Numbers refer to sources of water; thickness of line gives relative magnitude).

The water encountered as mining continues will subside over time. In bord-and-pillar areas, where mining has been completed, features such as roof bolts, drilled to stabilize the roof during mining, act as local sinks for water to drain to. Where such a roof bolt intersects horizontal or vertical fractures, increased influx is experienced. This is particularly problematic in areas adjacent to water storage compartments, where seals are installed to accommodate a head in excess of the mining height. As the water level rises, intersection of the naturally occurring bedding plane fractures occurs. These act as more transmissive conduits which allow the water to flow more

freely toward the locally created sink (the roof bolt). The photograph, below, from an underground compartment in the Highveld Coalfield illustrates this phenomenon:

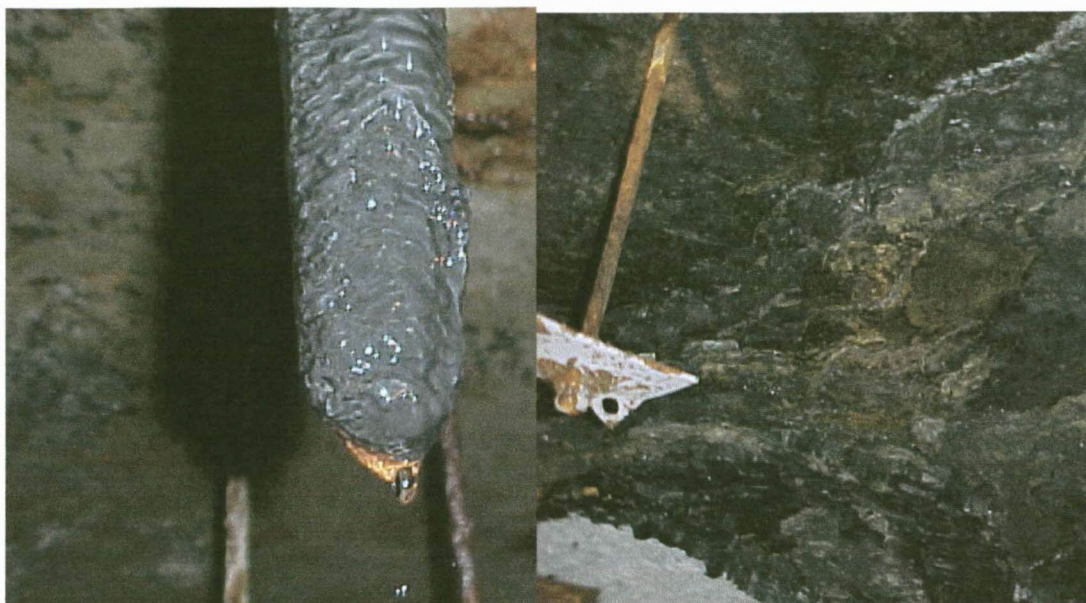


Figure 12: Water flow through a roof bolt, and the weathering of the roof shales due to the increased water flow.

2.4.1.4 Impact on water quality

Two dominant types of natural groundwater influx are encountered:

- The Na-Cl-HCO₃ type water would be associated with the marine sediments including mudstones and shales. These are typically connate waters, which have undergone enrichment with bicarbonate and sodium. These waters are often high in dissolved constituents.
- The Ca-HCO₃ or Ca-Mg-HCO₃ type water is typically associated with recharge water, where rainfall water percolates through the overlying geology into the underground workings. The greater the recharge, the more rapidly this type of water, which is encountered in the shallow weathered aquifer, will find its way into the mine void. These waters are usually far more dilute than the sodium-bicarbonate waters, except where there has been some stress put on the system by oxidation in the overlying sediments. In these cases, the neutralization through carbonate minerals will result in elevated concentrations of the major ions in solution.

Depending on the depth of mining, the nature of the recharge and the overlying geology, the influx water will tend more strongly to one of these two types.

2.4.1.4.1 Bord-and-Pillar mining:

Recharge into these areas is lower than for high extraction areas due to the roof being kept intact through support by the pillars. This will result in slower fill rates allowing the build-up of oxidation products. The reactive surface area of these areas is the lowest of all mining types. Although entire walls are exposed in each pillar this

area is far smaller than for opencast or high extraction areas. The lower recharge rates means that the rate of alkalinity added to the underground workings from the recharge water is also slower. Over time scaling of the coal pillars fracturing and partial collapse of the roofs within the bords results in increased reactive surface area.

2.4.1.4.2 High Extraction mining

The recharge into these compartments is higher than bord-and-pillar, but usually less than rehabilitated opencast pits. This gives faster filling rates, reducing the time for oxidation products to build-up, and reducing the pyrite oxidation rates. Where the recharge water is high in alkalinity, this will enhance the neutralization potential of the compartment. However, the goafing results in a far higher reactive surface area, therefore reactions can proceed far quicker if the mineralogy is similar to the bord-and-pillar area.

2.4.1.4.3 Opencast pits

In opencast pits, the material that remains is extremely heterogeneous, ranging from boulders down to very fine particles (See Section 7). This provides a high reactive area when compared to underground mining, and if large quantities of pyrite remain in the spoils high sulphate generation rates can be obtained. The recharge rate is far higher than underground mining, thus dilution is an important mechanism within such a system. Localised areas of acidity (hotspots) will occur, which serve as initiators of large-scale pyrite oxidation. The decant elevation in these pits is of prime importance; where this elevation is at a point where most of the spoils will be submerged, the water quality is expected to improve over time. Where largely unsaturated conditions subsist, the likelihood of acidification and poor quality water with high sulphate increases.

2.4.1.5 Summary

The different mining types each have conditions, which promote poor quality water, and others that should ameliorate the effects of pyrite oxidation. In all of the mining types, however, the local mineralogical conditions provide the most important driver on water quality. Newbrough and Gammons (2002) emphasize the importance of understanding the relationship between mine drainage chemistry and the mineralogy of the surrounding rocks, and how these relationships can vary on a district scale.

Later in this thesis, in Chapters 7 and 9, trenches dug in the spoils clearly indicate the validity of this observation. In underground mining, this is no less important. A case study at an underground compartment shows that the roof sediments have got a higher probability of acidification than the coal seam itself, implying that the high extraction areas pose the greatest risk. The balance between the increase recharge, with addition of alkalinity and faster inundation, against the higher surface area and lower net neutralizing potential (Chapters 3 and 4) will determine what the final water quality will be.

Figure 3 summarises some of the key issues from a hydrogeochemical perspective:

Table 3. Key processes in different mining types that affect water quality.

	Rehabilitated Opencast	Bord-and-pillar	High Extraction
Recharge	15%-25%	1%-8%	5%-15%
	<i>Dilution can occur</i>	<i>Build up of oxidation products</i>	<i>Rapid inundation with some dilution; also often an additional source of alkalinity</i>
Relative Surface Area	High	Low	Medium
	<i>Faster reactions; high salt loads</i>	<i>Slower reactions; high concentrations still possible</i>	<i>Higher salt generation than in bord-and-pillar</i>
Porosity	25%	In line with extraction: 50-65%	20% over the collapsed height
	<i>Flooding can occur to prevent excessive salt loads</i>	<i>Large amount of water- high water: rock ratio</i>	<i>Smaller volume of water distributed over greater height</i>
Coal Removal	90%	50-65%	90%
	<i>If coal seams are the most likely to acidify, it reduces the risk</i>	<i>If coal seams are the most likely to acidify, it has the greatest probability of generating acid</i>	<i>If coal seams are the most likely to acidify, it reduces the risk</i>
Decant	Likely	Unlikely	Rare
	<i>Outflow can occur with small amount of material flooded</i>	<i>In most cases the workings will eventually flood</i>	<i>In most cases the workings will eventually flood</i>

These aspects are all dealt with again in Chapters 6, 7, 8 and 9.

2.5 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 sufficient 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 13). These 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 stages are mineralogically dependent, and in South Africa the observed quality of water is often near neutral with a high salt content due to carbonate buffering. Once this has been depleted, pH-values tend to fall relatively rapidly, leading to the bimodal distribution of pH in coal mine waters. Table 4 shows some of the more important buffering phases encountered.

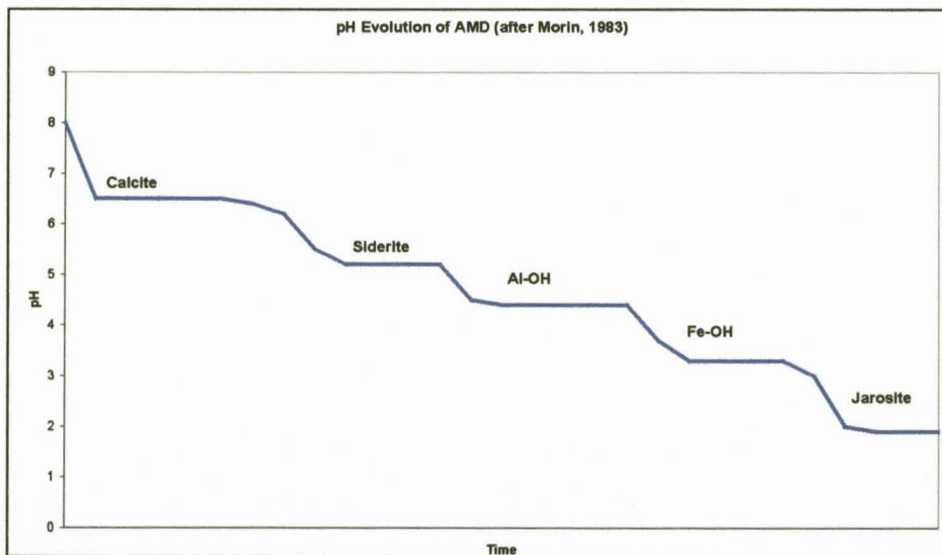


Figure 13: Stages in pH-evolution as a result of different buffering minerals (after Morin, 1983).

2.6 BASIC CHEMISTRY OF AMD GENERATION

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. These heavy metals include 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 (Figure 14). When exposed to water and oxygen, it can react to form sulphuric acid (H_2SO_4). The following oxidation and reduction reactions the pyrite oxidation that leads to acid mine drainage.

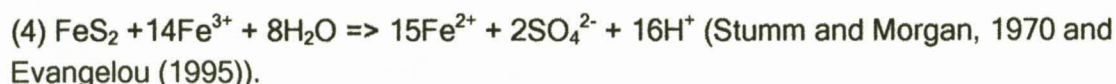
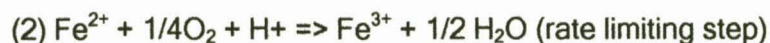
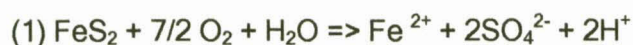


Figure 14: Part of a borehole core showing pyrite inclusions.

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 oxidises 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 15 and Stumm and Morgan (1981) in Figure 16. 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).

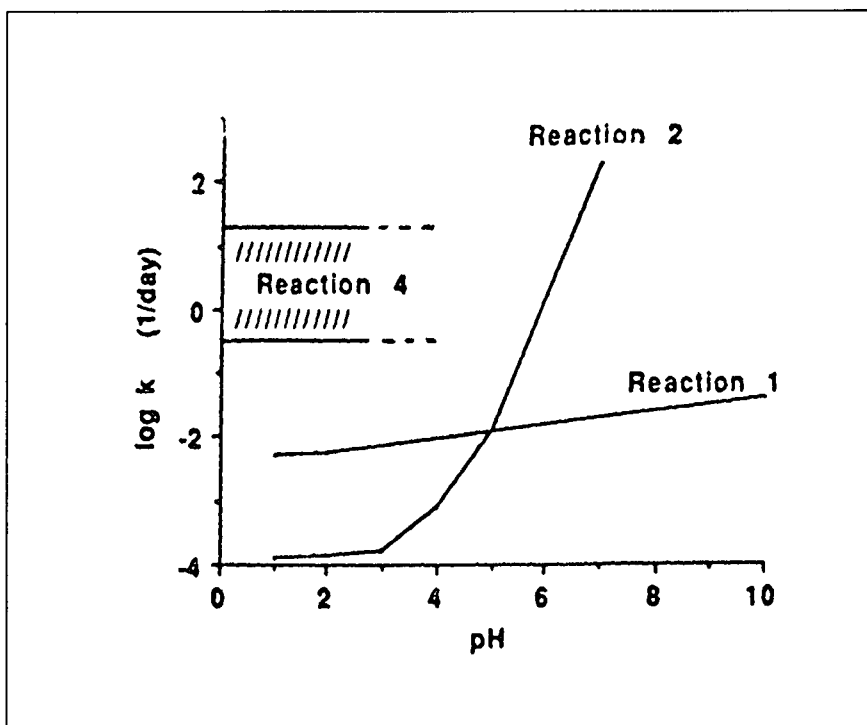
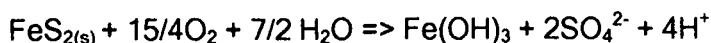


Figure 15: Comparison of rate constants as a function of pH for Reactions 1, 2 and 4 (after Nordstrom, 1982, Evangelou, 1995).

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 ($\text{Fe}(\text{OH})_3$) formed during Reaction 3 (Banks *et al.*, 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:



In the above reaction, every mole of pyrite yields four moles of acidity (Durkin and Herrmann (1996), Kempton *et al.* (1997) and Morin and Hutt (1994)). The necessity for air and water is clear (although the process can occur in a dry environment) (Cohen, 1996). Reactions 1-4 can also be seen in the model (Figure 16) by Stumm and Morgan (1981).

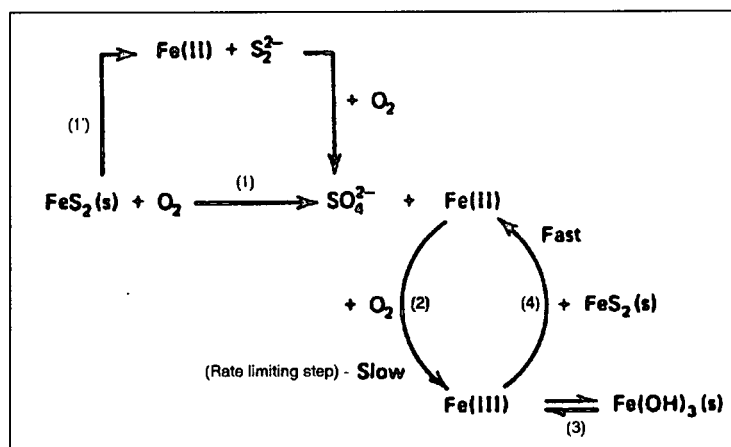


Figure 16: Model for the oxidation of pyrite (Stumm and Morgan, 1981).

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 16 for the oxidation of pyrite (Stumm and Morgan, 1981) and in the following reaction (Evangelou and Zhang, 1995):



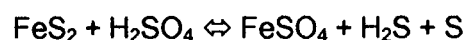
It has been reported that pyrite in mining waste or coal overburden is initially oxidised by the atmospheric O_2 , producing H^+ , SO_4^{2-} and Fe^{2+} . The Fe^{2+} can be further oxidised by O_2 into Fe^{3+} that in turn hydrolyses and precipitates as amorphous iron hydroxide releasing additional 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. Holmes and Crundwell (2000) indicate, through electrochemical studies, that the oxygen in the produced sulphate is mostly produced from water and not oxygen. Factors such as pH, P_{O_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 consequences 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 Evangelou (1995):



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 (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, the ferric iron ion is capable of dissolving many heavy metal sulphide minerals, including those of lead, copper, zinc and cadmium, by the general reaction:



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 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).

2.6.1 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+} may 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.

2.6.2 The Role of Micro-Organisms

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).

2.6.2.1 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, and 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+}).



Ferric iron is a powerful oxidising agent. Even at a $\text{Fe}^{3+}/\text{Fe}^{2+}$ 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 very slowly with sulphuric acid in the absence of ferric iron (Roman and Benner, 1973).

The effects of bacteria upon the rate of dissolution of sulphate from pyrite are highly pronounced, as demonstrated by Scharer *et al.* (1991). (See Figure 17 below).

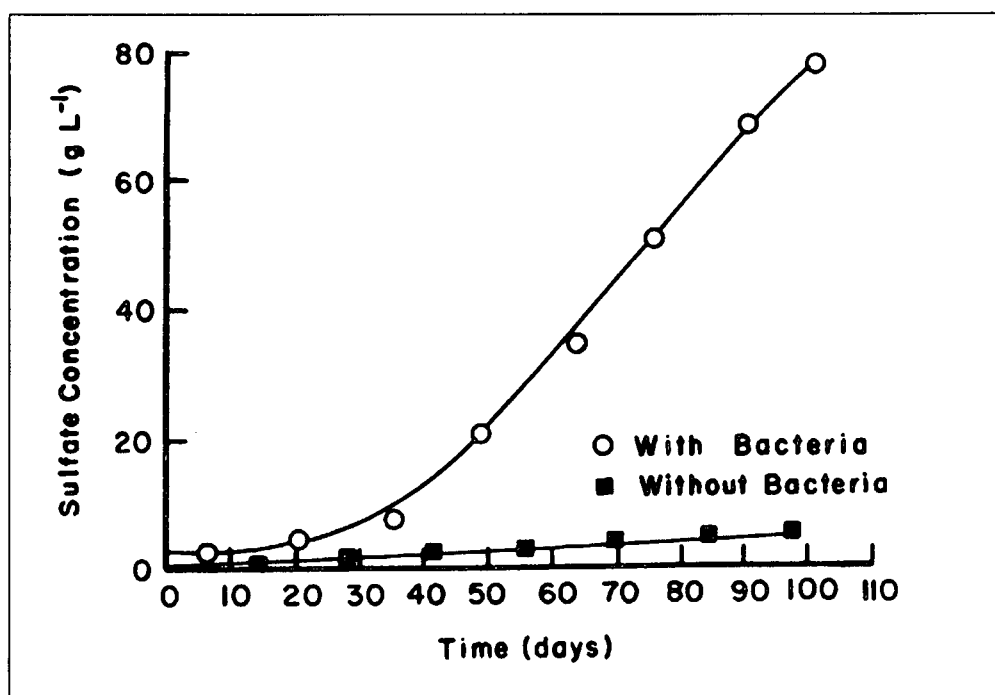


Figure 17: Pyrite oxidation kinetics in mine waste at 21°C and pH 3 in the presence and absence of bacteria (Scharer *et al.*, 1991).

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 18), whereas minimum activity is reached at approximately pH 1.5 and pH 5 (Jaynes *et al.*, 1984).

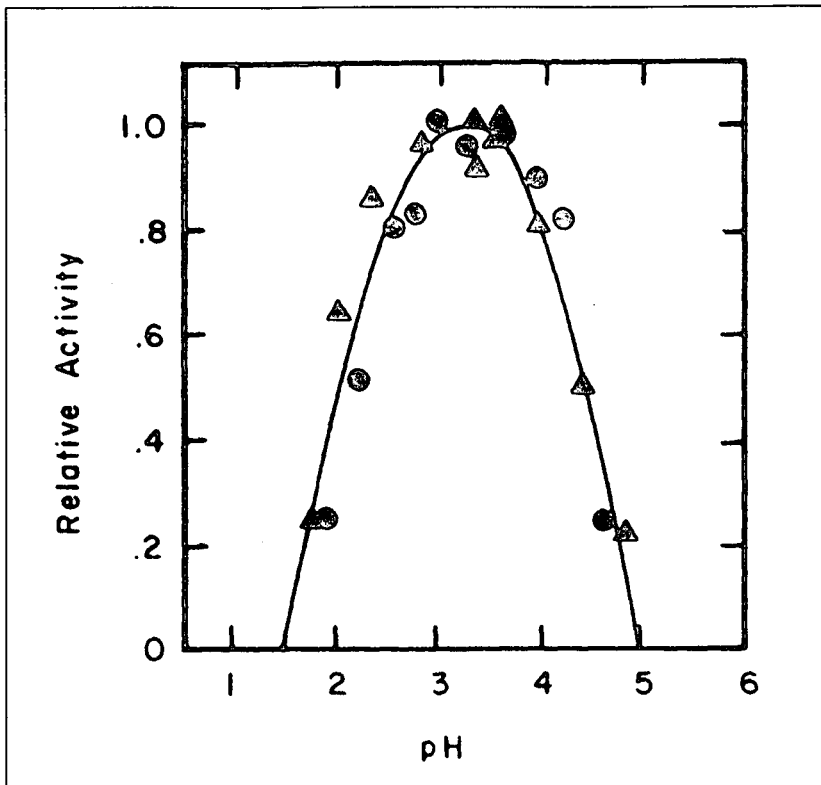


Figure 18: Influence of pH on relative activity of *T. Ferrooxidans* (Jaynes *et al.*, 1984).

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)).

The data in Figure 19 show that *T. ferrooxidans* (obligate aerobes) activity ceases when O₂ is depleted. However, bacterial activity resumes even under extremely small increases in O₂ content, and reaches a maximum at approximately 0.01 mole fraction of O₂ or 1% (Jaynes *et al.*, 1984).

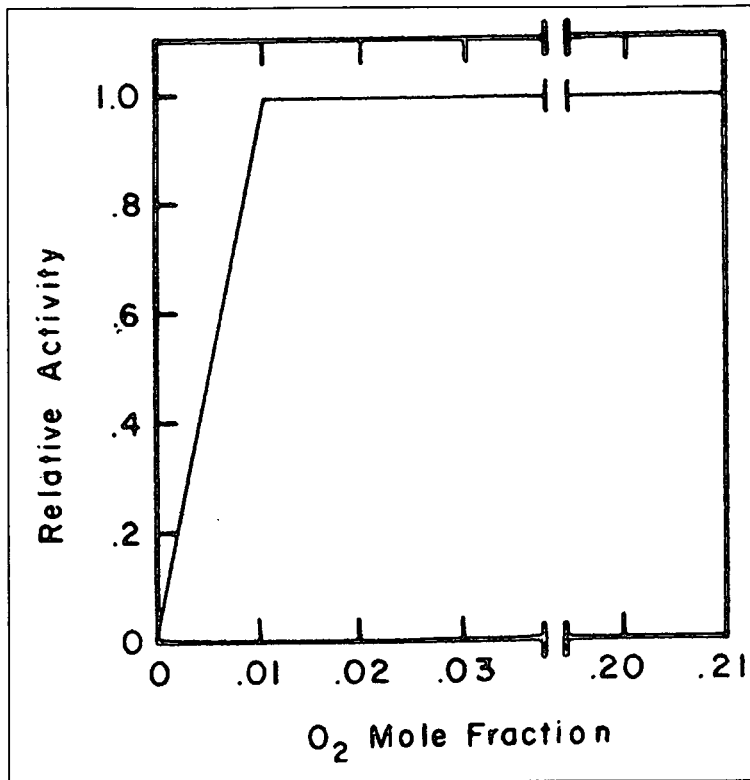


Figure 19: The influence of O₂ concentration on relative activity of *T. ferrooxidans* (Jaynes et al., 1984).

The kinetics of acid generation can be seen in Figure 20 below. In the absence of biologically catalysed oxidation, oxidation rates are relatively slow for all pH-conditions (Robertson, 1996).

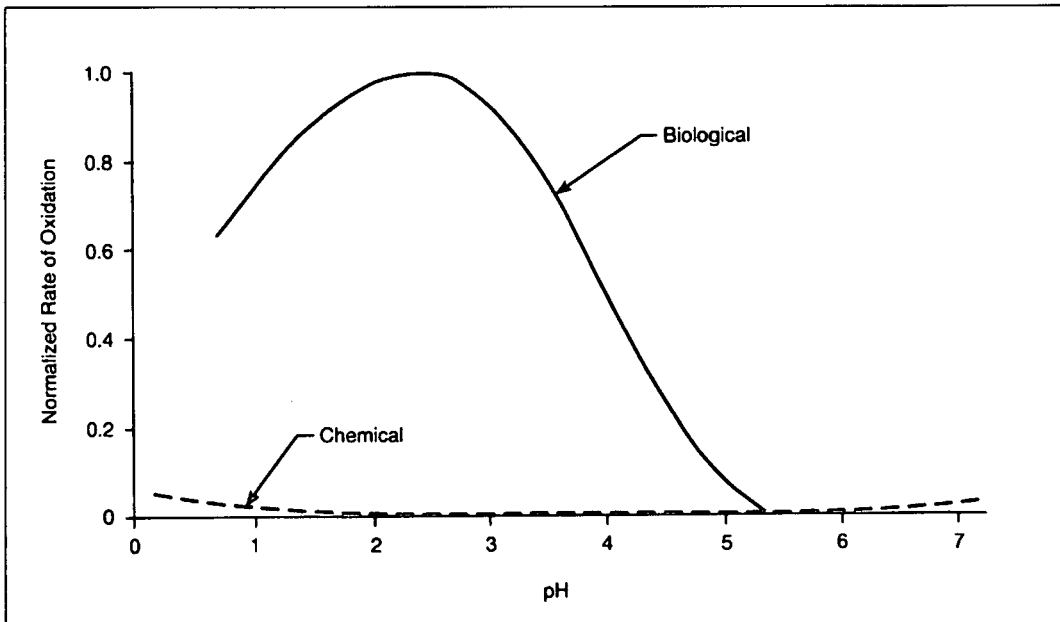


Figure 20: Kinetics of acid generation (Robertson, 1996).

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 the 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).

Kirby *et al.* (1999) reinvestigated Fe(II) oxidation in AMD and found that from pH 2.8 to approximately pH 5, Fe(II) oxidation rates are negatively correlated with pH and catalysed by *T. ferrooxidans*. From pH 5 to 6.4, Fe(II) oxidation appears to be primarily abiotic and is positively correlated with pH. Above pH 6.4, oxidation appears to be independent of pH. This can be graphically illustrated in Figure 21:

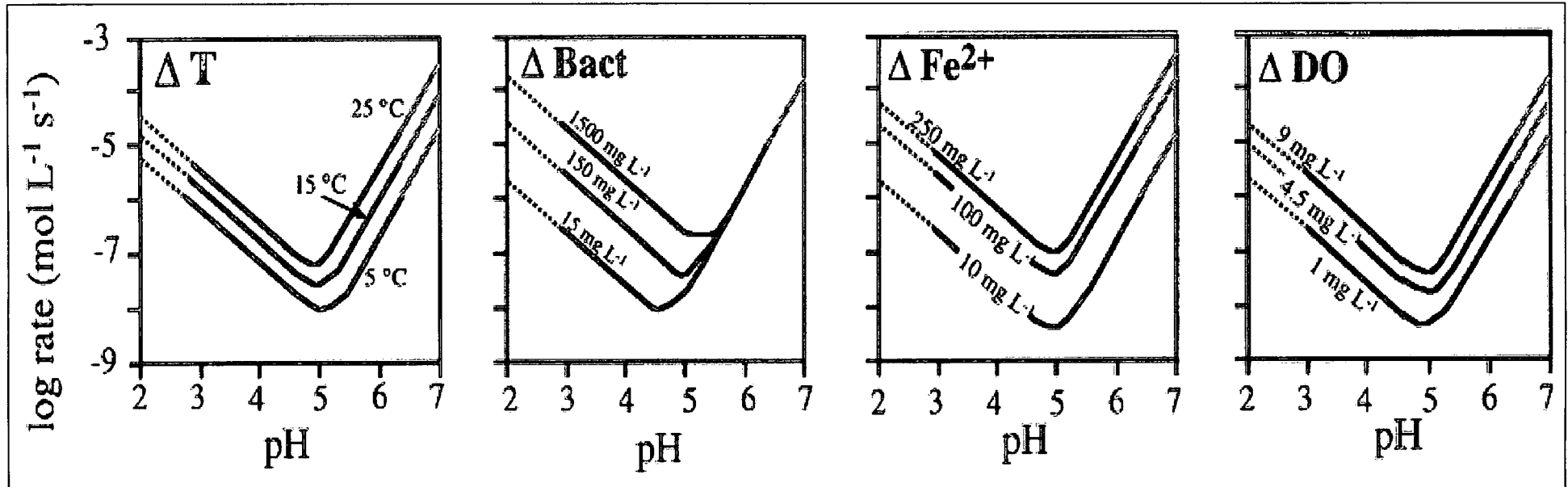
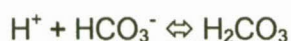
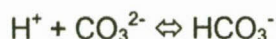


Figure 21: Predicted effect of varying pH, temperature, *T. ferrooxidans*, Fe(II), and dissolved oxygen on the rate of Fe(II) oxidation.

Unless otherwise specified, calculations are based on Fe(II)=100 mg L⁻¹, *C*_{bact}=150 mg L⁻¹, DO=9 mg L⁻¹, and T=20°C. Dashed lines indicate pH-range over which the model has not been field-checked. Grey lines indicate pH range where oxidation appears to be slower than predicted by the abiotic rate law (Kirby et al., 1999).

2.7 NEUTRALISATION REACTIONS

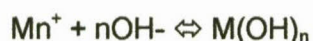
Acid mine drainage depletes the buffering ability of water by neutralising carbonate and bicarbonate ions to form carbonic acid (H_2CO_3) (Drever, 1997).



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 (Drever, 1997).



If the pH of AMD is increased, as would happen in contact with basic minerals such as calcite (CaCO_3) or dolomite ($\text{CaMg}(\text{CO}_3)_2$) 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:



where: OH^- = hydroxyl ion; $\text{M}(\text{OH})_n$ = 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 ($\text{CaMg}(\text{CO}_3)_2$), and acid produced from pyrite is neutralised *in situ* by these minerals.

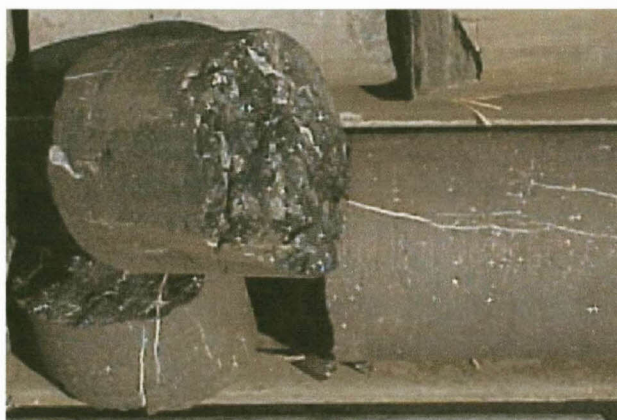


Figure 22: Calcite veinlets commonly observed in cores from coal horizons.

The sulphate most commonly formed is gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), 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

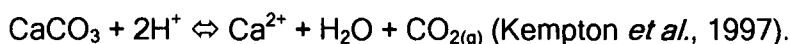
present in the waste, can buffer the acid produced in the unsaturated zone (Morin *et al.*, 1998).

Factors that determine the neutralisation rate by carbonate and silicate minerals include: pH, P_{CO_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).

2.7.1 Carbonate Systems

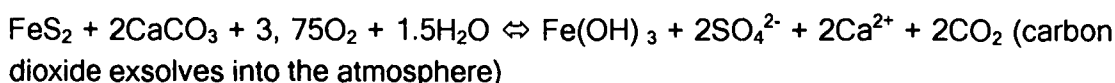
The carbonate system is predominant in controlling the buffering intensity and neutralising capacity of natural waters, and represents a complex system involving the transfer of carbon among three phases: solid, liquid and gas. When $CO_{2(g)}$ is brought into contact with water, it will dissolve and form 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_3 ($pH < 6.3$); 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. 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:



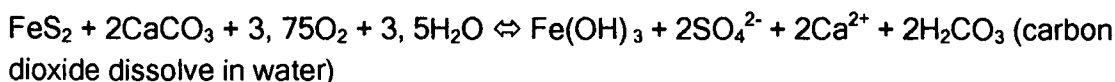
The S: C ratio for complete neutralisation of acid from sulphide S by carbonate C (AP: NP) can range between 1: 1 and 1: 2 (Kempton *et al.*, 1997).

In an open system:

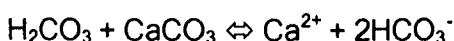


Acidity produced from 1 mole of FeS_2 (64 g sulphur) is neutralised by 2 moles of $CaCO_3$ (200 g) or 1 g sulphur: 3.125 g $CaCO_3$ (Brady *et al.*, 1994).

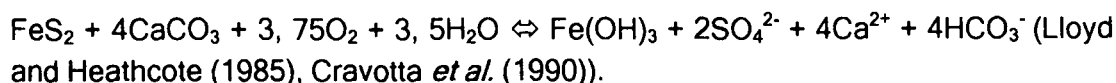
In a closed system:



H_2CO_3 reacts with carbonate in the following reaction:



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

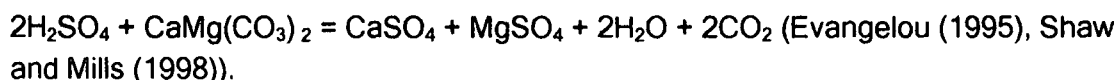


In this reaction 1 mole of FeS_2 is neutralised by 4 moles of CaCO_3 , which results in a mass ratio of 1 g pyrite: 6.25 g calcite. Maximum Potential Acidity (units of kg CaCO_3/t) is therefore calculated as percent sulphur times 62.5 (Brady *et al.*, 1994). To neutralise the pyrite-derived acidity to 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 high 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):



Dolomite neutralisation reaction (dolomite dissolution by sulphuric acid):



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

2.7.2 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 change by orders of magnitude as the temperature is varies). The reason for this lies in the exponential dependence on the temperature of the reaction rate constant, which can follow the Arrhenius equation:

$$K = A e^{-(E_a/RT)}$$

where A is the pre-exponential factor and E_a 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

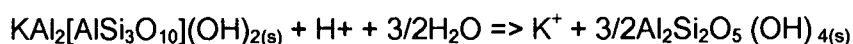
state that in AMD solutions, the presence of significant cation and sulphate concentrations could lead to a decrease in carbonate solubility.

2.7.3 Other Minerals

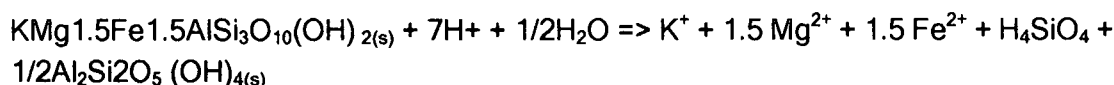
Other minerals, including some silicates such as plagioclase feldspar, may also neutralise acid produced by sulphide mineral oxidation. Under certain conditions the outflow quality is controlled by depletion of sequential buffering phases - carbonates, hydroxides (such as gibbsite) followed by aluminosilicates (Jurjovec, Ptacek and Blowes, 2000). Usually neutralisation rates of non-carbonates can be orders of magnitude slower than acid-production rates and the oxidation reactions will dominate (Shaw and Mills (1998), Sherlock *et al.* (1995)). The fact that the non-carbonate minerals react too slowly to prevent acidification is illustrated by the fact that in many coalfields a bimodal frequency distribution of pH is found; waters are either neutral or acidic with very few values in between (Cravotta, *et al.*, 1999).

Reactions of other gangue minerals may also contribute to the neutralisation potential of the 'system' under specific pH-conditions (Ritchie, 1994), for example:

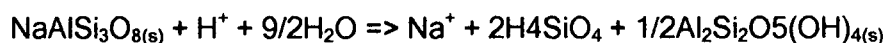
Muscovite dissolution:



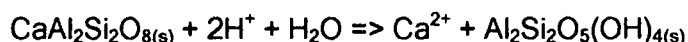
Biotite dissolution:



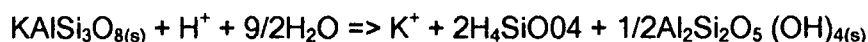
Albite dissolution:



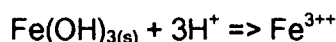
Anorthite dissolution:



K-feldspar dissolution:



Iron oxy-hydroxide dissolution:



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 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 4) has appeared in several publications regarding AMD (SRK (1991), Hodgson and Krantz (1998), James (1997) and van Niekerk (1997)):

Table 4. Buffering pH of some common minerals as reported in several publications.

Mineral	Composition	Buffer pH
Calcite	CaCO_3	5.5 - 6.9
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	5.3 - 6.8
Siderite	FeCO_3	5.1 - 6.0
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	3.7 - 4.3
Gibbsite	$\text{Al}(\text{OH})_3$	3.7 - 4.3
Ferric hydroxide	$\text{Fe}(\text{OH})_3$	3.3 - 3.7
Goethite	$\text{FeO}(\text{OH})$	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_{CO_2} is misleading, as this has a major influence on the pH at which buffering occurs. This will be expanded upon in Section 2.8.

The science and understanding of AMD generation is still developing and there are several mining operations 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.

Kwong (1993) suggested that all of the minerals in the Dissolving, Fast and Intermediate weathering groups (Table 5) 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.

Table 5. Relative Mineral Reactivity at pH5 (from Sverdrup (1990), Kwong, (1993)).

MINERAL GROUP	TYPICAL MINERALS	RELATIVE REACT- IVITY 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, gntophyllite, 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

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.

2.8 DETERMINATION of pH BUFFERING OF DIFFERENT MINERALS

In 2.7 the buffering capability of various minerals is referred to. The tabulated buffering levels of different minerals are often somewhat misleading.

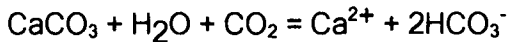
Neutralisation of acid generated by AMD processes occurs due to (Hodgson and Krantz, 1998):

- The alkalinity of the water itself.
- 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.

2.8.1 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):



An illustration of this phenomenon is shown below in Figure 23:

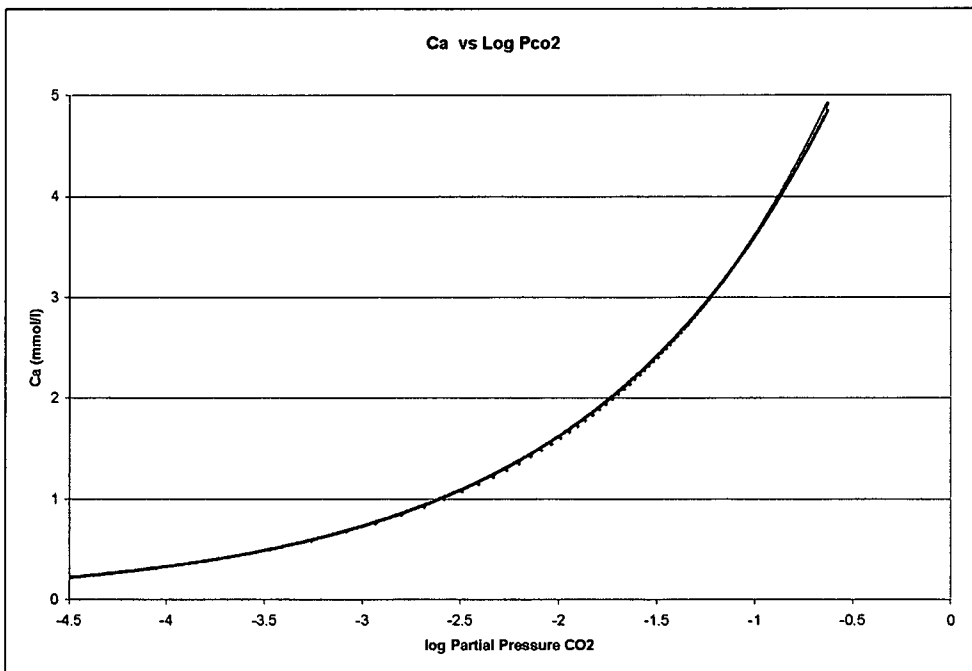


Figure 23: Calcite dissolution as a function of P_{CO_2} .

With an increase in partial pressures of CO_2 , more calcite dissolves and consequently the alkalinity will also increase (Figure 24). However, increased P_{CO_2} does not directly cause an increase in alkalinity, as has been implied in certain publications. The increased dissolution of carbonate minerals results in more bicarbonate in the water, increasing the alkalinity.

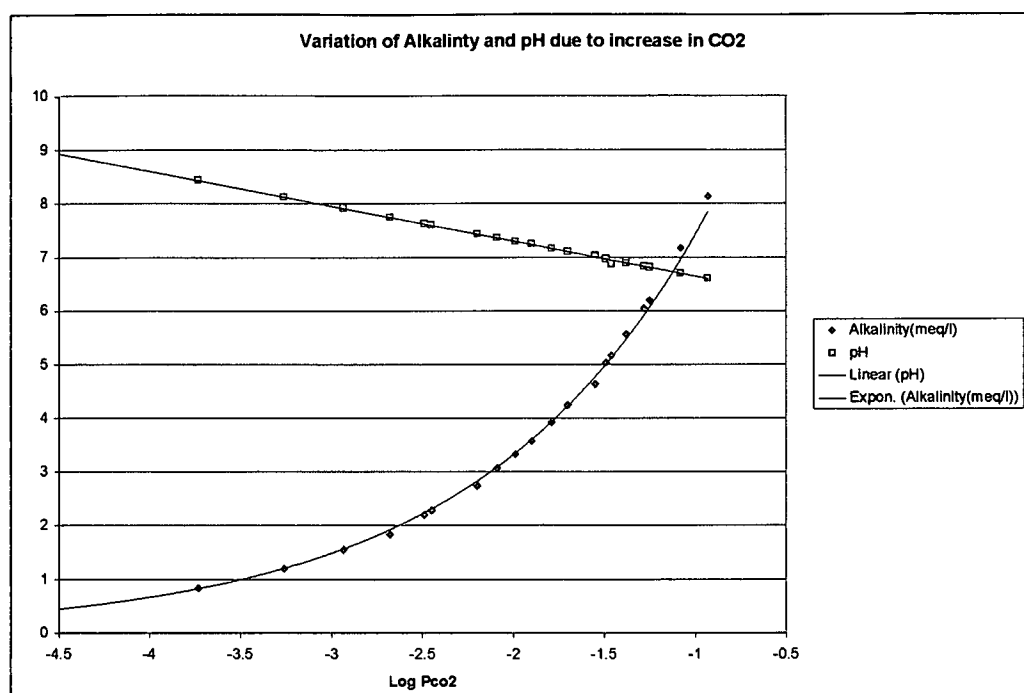
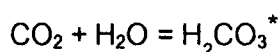
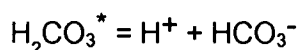


Figure 24: Variation of Alkalinity and pH as a function of calcite dissolution at varying P_{CO_2} .

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



The amount of $H_2CO_3^*$ formed is a function of the P_{CO_2} pressure within the spoil.



The $H_2CO_3^*$ dissociates to form bicarbonate which, it has been argued, causes increased alkalinity of the water (Hodgson and Krantz, 1998).

This argument is incomplete and may be misleading. 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:

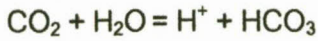
$$\text{Alkalinity} = mHCO_3^- + 2mCO_3^{2-}$$

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 P_{CO_2} because neither the P_{CO_2} nor the uncharged species H_2CO_3 is involved directly in the charge balance equation. Although an increase in P_{CO_2} will cause an increase in HCO_3^- , the reaction is either (Drever, 1997):



or



In the first case, the alkalinity gained by increasing mHCO_3^- is exactly balanced by the alkalinity lost by decreasing mCO_3^{2-} . In the second case, the increased HCO_3^- is exactly balanced by H^+ , so the net effect on alkalinity is zero. Thus the increase in alkalinity due to the variation in P_{CO_2} is due to the increased carbonate mineral dissolution.

2.8.1.1 FURTHER INFLUENCES OF P_{CO_2}

The buffering level of any of the carbonate minerals present in the spoils is dependent on the partial pressure of carbon dioxide. Thus this must be considered when determining/reporting on minerals responsible for maintaining the pH at a specific level in areas affected by mining. Near 1 atm pressure fugacities and partial pressures are very similar (Stumm and Morgan, 1981), and under particularly underground colliery conditions partial pressure approaches are a valid assumption.

The simulation was done using the geochemical modelling code PHREEQC (Parkhurst and Appelo, 1999).

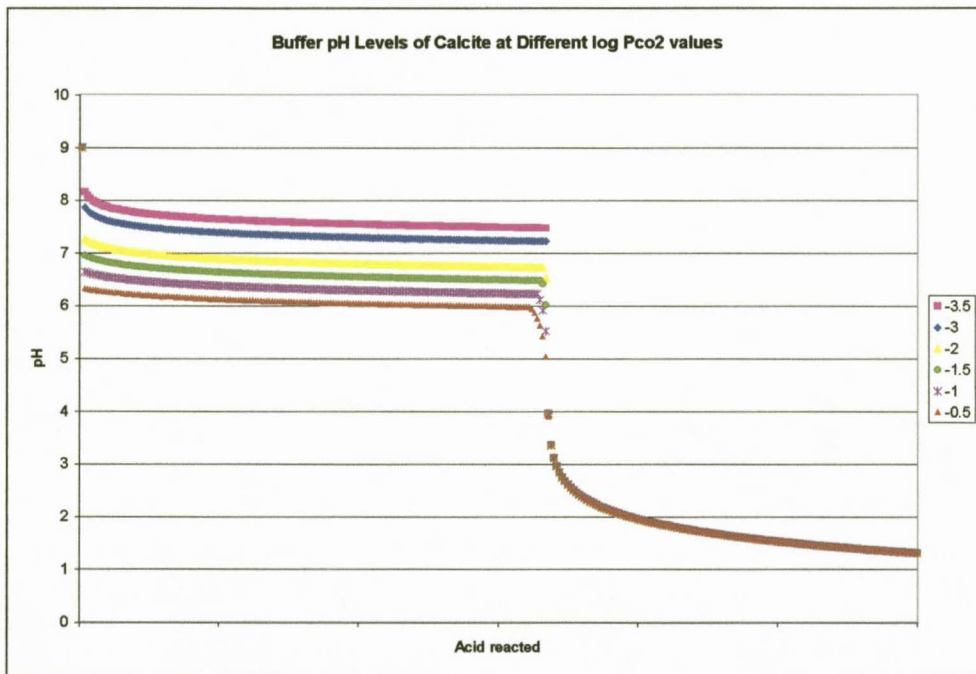


Figure 25: Calcite buffering level as a function of P_{CO_2} .

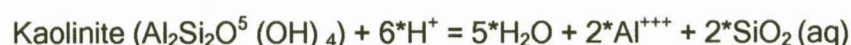
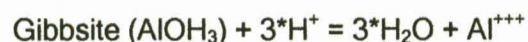
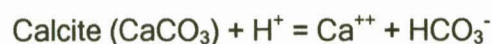
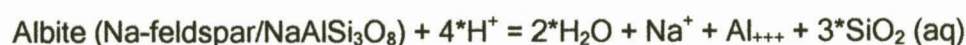
Figure 25 above shows how, under different P_{CO_2} conditions, the buffer level can vary up to two pH-units. This is very important in interpreting conditions on site. In mining waste facilities such as exposed tailings impoundments and waste rock piles, depending on factors such as carbonate contents, sulphide contents, sulphide oxidation rates, and 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).

2.8.2 Contribution of Individual Species

Several minerals are credited with the ability to cause buffering in some cases, or consumption of produced acidity. The carbonates are often credited with the greatest influence, however it is clear that, in 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):



Shown in Figure 26 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 7.2.6 and 7.2.3 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.

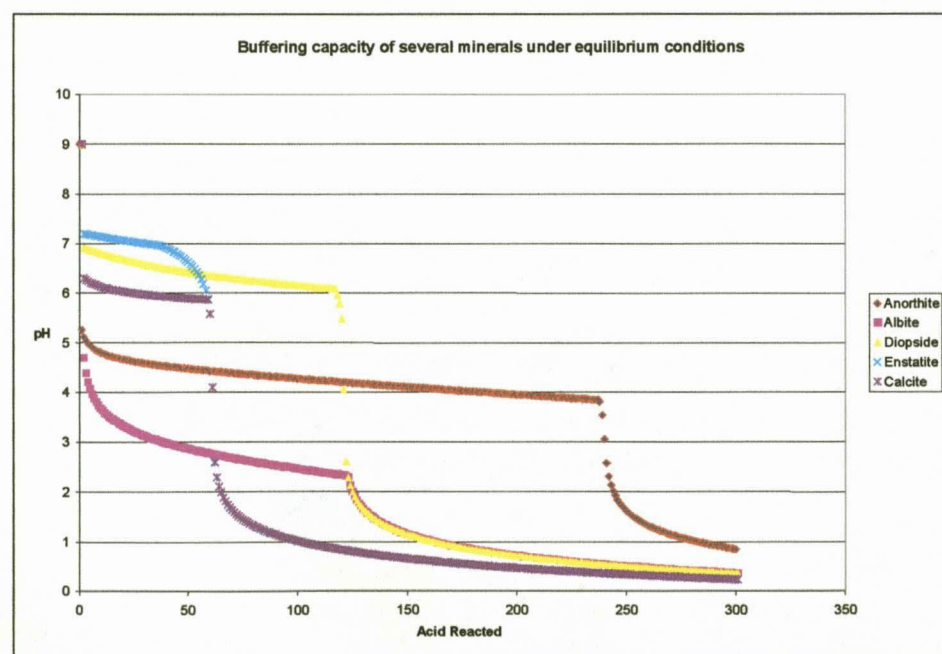


Figure 26: Equilibrium buffering levels of different minerals in an open system.

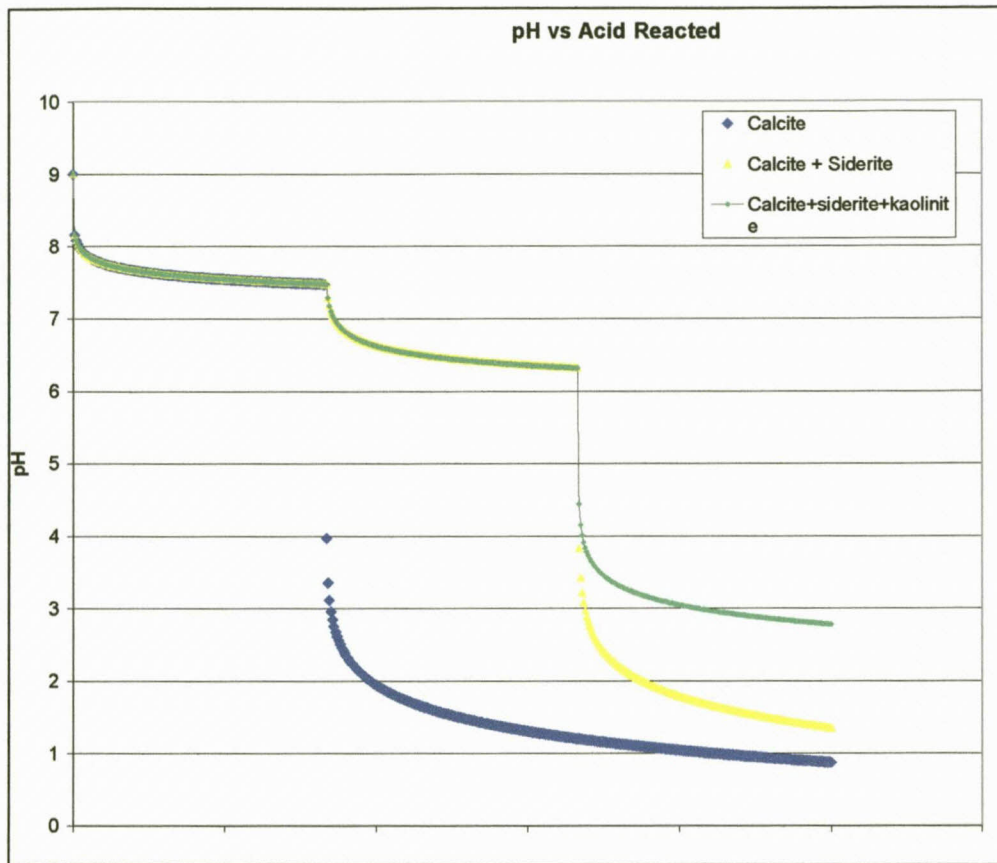


Figure 27: Combined buffering profile of equivalent amounts of different common minerals.

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 1.

2.9 SECONDARY MINERAL PRECIPITATION.

One of the most important controls on the observed water quality in South African coalmines is the formation of secondary minerals as products of the pyrite oxidation and subsequent neutralisation thereof.

From the overall reaction of calcite as buffering mineral, the formation of iron precipitates, is evident, as is the fact that calcium and sulphate will increase in concentration:



This increase in Ca^{2+} and SO_4^{2-} can only occur up to a point, where the aqueous solubility of these ions becomes limited by the solubility of gypsum ($\text{CaSO}_4 \cdot 10\text{H}_2\text{O}$). Eary (1999) indicates that in nearly all pit lakes or rehabilitated opencast pits, SO_4 is the dominant solute, but is limited by gypsum solubility. He furthermore suggests that fluorite, calcite, and barite are also important solubility controls. The fact that partially soluble iron minerals form, results in the observed iron concentrations being far lower than the total iron produced. As the acidity in the water increases, dissolved iron concentrations will rise accordingly (Younger, 1999).

Some previous investigations in the coalfields have suggested that gypsum precipitation does not play an important role in controlling the observed sulphate concentrations in South African coalmines (Hodgson and Krantz, 1998). Field observations at several mines, and detailed investigation into the saturation state of coalmine waters over the Witbank/Highveld Coalfield suggest that this is an erroneous assumption. Shown on the figure below () is gypsum growth observed at an underground compartment at a mine in the Highveld Coalfield.

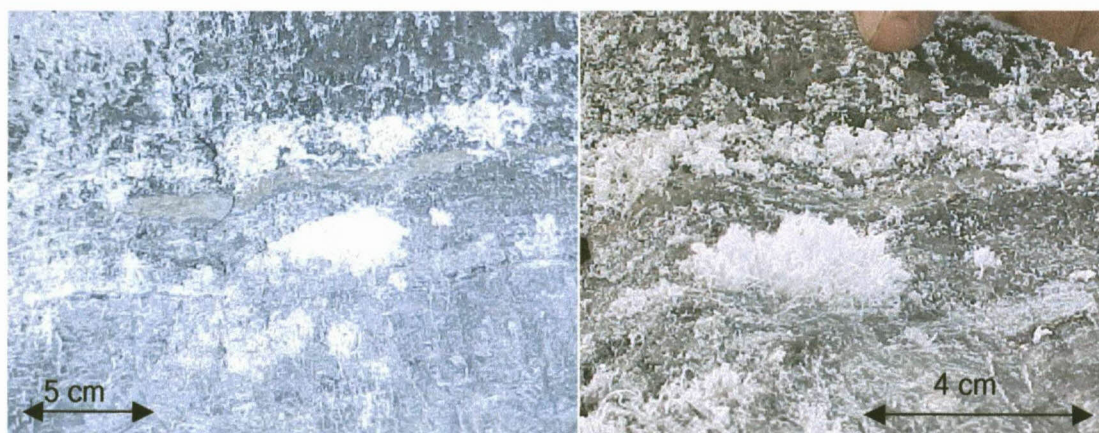


Figure 28: Gypsum shown in situ and close-up with sample above ground.

To further investigate this, use was again made of PHREEQC. In this case, almost 8000 samples from over the entirety of the Witbank and Highveld Coalfields were used to ascertain the degree of saturation with gypsum (Figure 29). On this figure the saturation state is represented by the saturation index (SI), which describes the state

of any solution relative to the mineral being evaluated (Appelo and Postma, 1993). The maximum solubility of each mineral at equilibrium is given by its theoretical solubility (the K_{sp} value). The measured concentrations in solution are used to determine whether this condition is met. Further discussion on this aspect is given in Section 8.3.3.

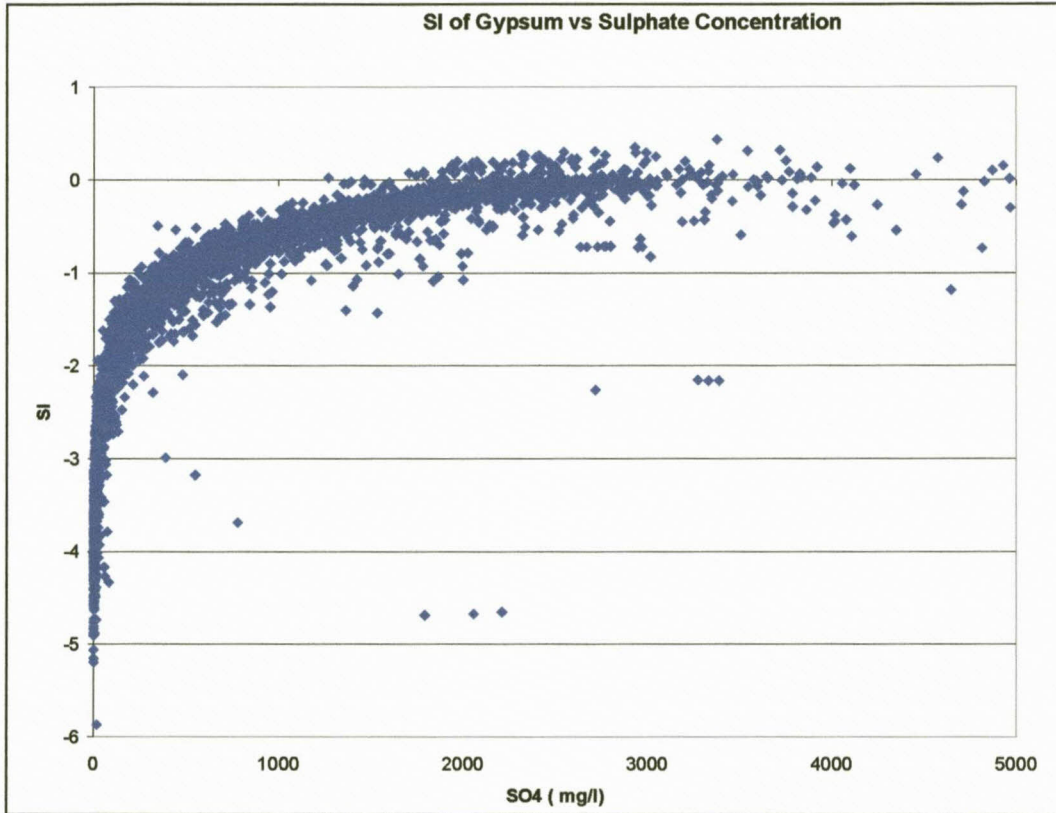


Figure 29: Saturation state of gypsum plotted against sulphate concentration.

A value of 1700 mg/L was used as a lower cut-off to ascertain solubility controls. Out of the 1071 samples in the obtained data set that exceeded 1700mg/L SO_4 , almost half had SI values approaching equilibrium (a value of 0.1 was used as a cut-off). Therefore, although not all the values in the higher ranges are at, or approaching equilibrium, indications are that gypsum saturation is an important control on the upper limit of sulphate values that can be obtained.

This observation has several implications:

- Determination of gypsum saturation should form part of any hydrogeochemical assessment in the coalfields.
- Calcium values should be measured on a regular basis so that these assessments can be made.
- The observed sulphate generation rates often reported (Hodgson and Krantz, 1998, Van Tonder *et al.* 2003) should be reported with an indication of possible gypsum saturation.

This last point could be significant for the generalised assessments often made e.g. that rehabilitated opencast pits yield between 5 kg/ha/day and 10 kg/ha/day

sulphate (Hodgson and Krantz, 1998). This rate appears to be fairly constant despite differences in degree of spoils saturation, age of spoils or regional impacts. It is therefore possible that the observed rates, as derived from flow and concentration calibration, reflect a maximum sulphate concentration with a consistent recharge. The maximum sulphate concentration is determined by the gypsum solubility. Hodgson in subsequent reports has suggested that gypsum precipitation will play a role under low flow conditions (Hodgson, 2000).

Values from water at Optimum Colliery clearly indicate this observation. In Figure 30 the sulphate concentration over time for the decant water where previous determinations regarding the sulphate generation rate were based on, is shown together with the relative saturation of gypsum.

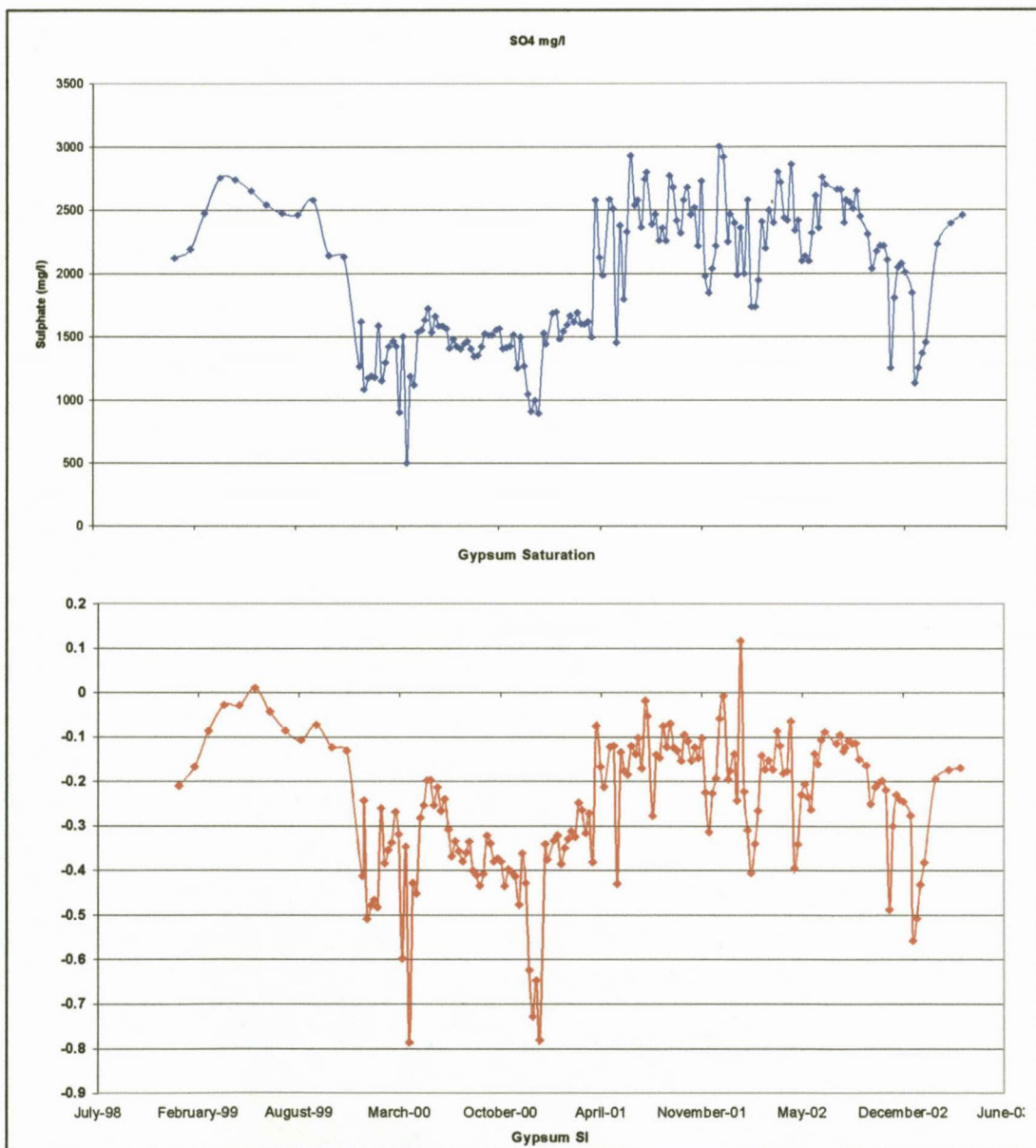


Figure 30: Sulphate concentration and gypsum saturation for decant water from Optimum Colliery.

The SI values indicate that the sulphate values are limited by gypsum precipitation, with values close to saturation as soon as concentrations rise. This could imply that true sulphate generation rates are greater than those derived from flow and concentration measurements. (Van Tonder *et al.*, 2003).

Another effect of secondary mineralisation, is that where neutral conditions are re-established, more sulphate may be released. This is due to the desorption of sulphate from the iron hydroxide precipitates as reported by Rose and Elliot (2000). As pH rises the surfaces on the iron precipitates become less positive and sulphate can easily desorb leading to further sulphate release (Figure 31). The authors go on to suggest that in natural systems, the best way to avoid this is where gypsum precipitation occurs.

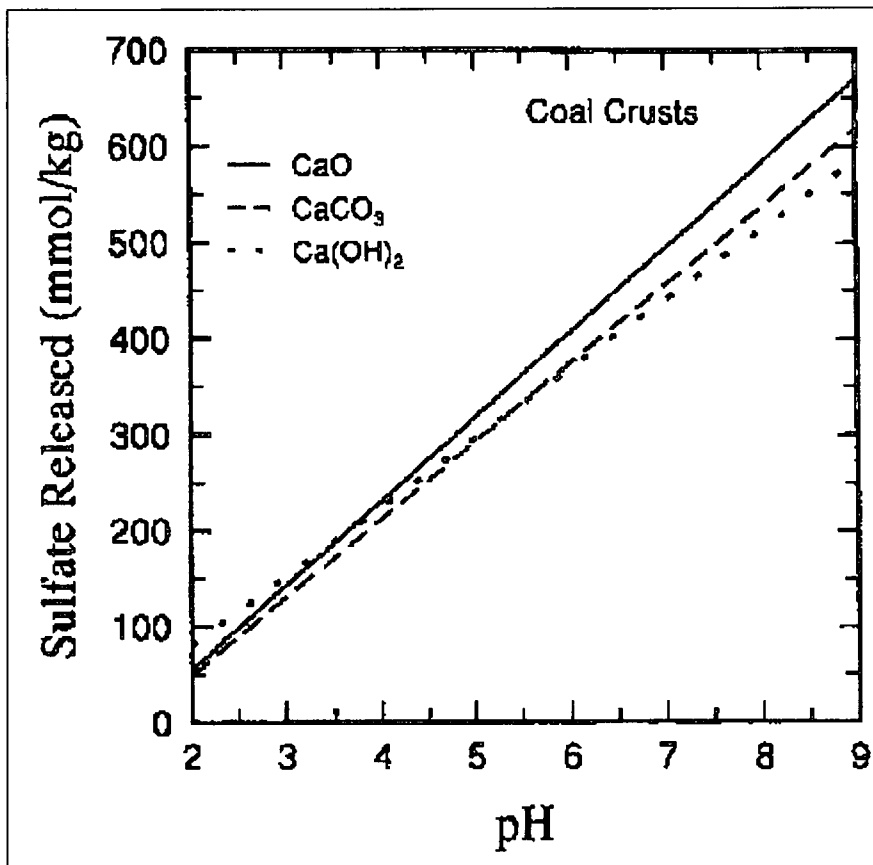


Figure 31: Release of SO_4 from iron precipitates on coal crusts as pH rises. (Rose and Elliot, 2002).

The effect of secondary mineral formation is an important control on water quality in South African collieries.

3 OVERVIEW OF PREDICTION METHODS

"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).

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 may 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):

1. Initial assessment and site reconnaissance.
2. Sampling.
3. Chemical, mineralogical and physical analyses.
4. Short-term leaching tests.
5. Geochemical static tests.
6. Geochemical kinetic tests.
7. 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 thesis aims to address.

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):

1. Identify and describe all geological materials excavated, exposed or otherwise disturbed by mining.
2. 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.
3. 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). The challenge lies in the fact that 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, the so-called static methods 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), 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. 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 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, 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), 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. In South Africa the use and application of ABA data is not yet a regulatory requirement, although for most collieries the EMPR and other licensing process usually include ABA as an integral step.

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

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

The principal disadvantages of Acid-Base Accounting are:

- 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.
- Acid-Base Accounting assumes that all acid production can be attributed to iron disulphide minerals (chiefly pyrite) and that no acid is produced by sulphate or organic sulphur forms.
- Measurement of neutralisation potential though some methods utilises a hot acid extract to measure carbonates and bases. Recent work suggests that this extraction procedure may overestimate neutralisation potential and that a modified method may be needed (Hunter, 1997b).

Application of the 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 in the northern Appalachians, and probably of 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). It 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).

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

3.1.1 Static Geochemical Methodologies

Static tests are typically simple and inexpensive procedures to provide 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 coalmine 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 predicting mine drainage quality in the northern Appalachians.

Cruywagen (1999) and Usher *et al.* (2001) report extensively on the testing of different static test methodologies and the selection of recommended methods as will be expanded on in Chapter 4.

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 in an 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 (Chemex Labs (1997), Mills (1998g)). 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 and columns, which are the most commonly used methods of determining kinetic AMD characteristics of drill core, waste and other rock samples and tailings (Mills, 1998). 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 to 15 kg. The most commonly used procedure is the ASTM standard (1996). 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).

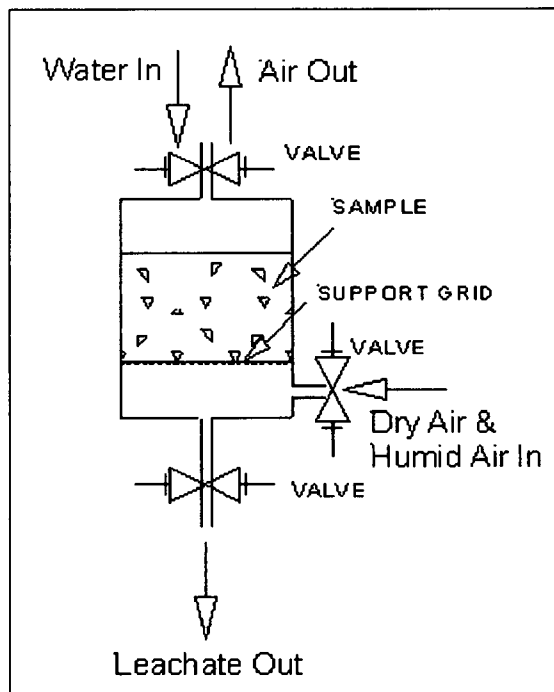


Figure 32: Generic schematic diagram of a humidity cell (Mills, 1998).

The main advantages of kinetic tests:

- Test 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 mine sites 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 still uncertain.
- Data interpretation requires a 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 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 objectives also apply. In addition, it may be necessary to add the following objectives to facilitate the selection of mitigation methods and for the development of a closure plan:

1. Evaluation of the extent of oxidation.
2. Evaluation of the extent of neutralisation.
3. 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 ranging from the ASTM suggested 20-week period to more than 2 years. 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 rehabilitated spoil or existing waste conditions. 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), Caruccio (1984). 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).

3.3 HUMIDITY CELLS

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 15 μ m (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, 1998). This is also true for South African collieries.

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 1 kg 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).

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, 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. 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, and nutrient supplies 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).

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

3.3.1 Other Kinetic Tests

There are several other kinetic tests commonly used. These are dealt with in detail in Cruywagen, 1999 and Usher *et al.*, 2002. Some commonly procedures include:

- column tests.

- accelerated kinetic tests.
- bacterial oxidation tests.
- soxhlet extraction.

Field tests can include:

- Test waste rock piles.
- Small tailings deposits.
- Wall rock leaching.
- minewall washing procedure ("MINEWALL").

3.4 APPLICATION OF HUMIDITY CELL DATA

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 pertaining to that point. The IOR is a function of many variables such as oxygen concentration, sulphide sulphur concentration, temperature, pH, pyrite morphology and microbial ecology 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 that are judged to be important (Bennet, Comarmond and Jeffrey, 2000). This is essentially what kinetic tests hope to achieve.

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 on oxidation rates from field test piles (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 that is submerged.

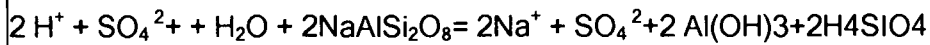
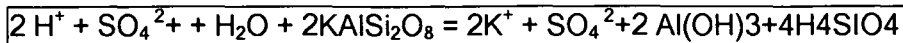
It is apparent that greater surface areas do not necessarily yield greater amounts of sulphate and that the range of surface areas varies from very low (i.e. larger fractions) to very fine material. Hollings *et al.* (2000) also found no correlation between grain size and sulphate release rate in humidity cells to extrapolate rates to the field. In addition there was no correlation between grain size and oxygen consumption. Section 5.3.10 further investigates some of these relationships.

3.4.1 Calculations

The key objectives of laboratory kinetic tests are (a) long-term stable reaction rates under kinetic conditions and (b) depletion times for acid-generating, acid-neutralising, and metal-leaching minerals. Therefore, interpretations of the tests focus on calculating these values. Recommended equations are listed in Table 6.

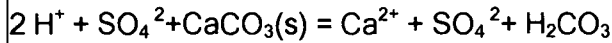
Table 6. Calculations for Humidity Cells (from Morin and Hutt, 1997).

Acid generation
Acid Production Rate (mg CaCO ₃ /kg/wk) = Acidity (mg CaCO ₃ /L)* Volume Leachate Collected /Sample Weight
Sulphate Production Rate (mg/kg/wk) = Sulphate (mg/L)* Volume Leachate Collected/ Sample Weight
Remaining S _{total} (% of original) = {Initial %S-[(Cumulative Sulphate Production Rate(mg/kg)*32.06/96.06/1000)]/Initial S total as %S}*100%
Remaining S _{sulphide} (% of original) = {Initial %S _{sulphide} -[(Cumulative Sulphate Production Rate(mg/kg)*32.06/96.06/1000)]/Initial S _{sulphide} as %S}*100%
Sulphate Production Rate by Surface Area (mg/m ² /wk) = Sulphate Production Rate (mg/kg/wk) /Surface Area (m ² /kg)
Molar Ratios
Carbonate Molar Ratio = [(Ca mg/L)/40.08) + (Mg(mg/L)/24.31) + (Sr(mg/L)/87.62)] / (SO ₄ (mg/L)/96.06)
Feldspar Molar Ratio = [(Ca (mg/L)/40.08)+ (K(mg/L)/2*39.1)+ (Na(mg/L)/22.99)] / (SO ₄ (mg/L)/96.06)
Acid Neutralisation and NP Consumption
Alkalinity Production Rate(mg CaCO ₃ /kg/wk) = Alkalinity (mg CaCO ₃ /L)* Volume Leachate Collected/ Sample Weight
Carbonate Ratio NP Consumption (mg CaCO ₃ /kg/wk) = Carbonate Molar Ratio *Theoretical NP Consumption (mg/kg/wk)
based on:
$2\text{H}^+ + \text{SO}_4^{2-} + (\text{Ca}_x, \text{Mg}1-x)\text{CO}_3(\text{s}) = x\text{Ca}^{2+} + (1-x)\text{Mg}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{CO}_3$
or $2\text{H}^+ + \text{SO}_4^{2-} + 2(\text{Ca}_x, \text{Mg}1-x)\text{CO}_3(\text{s}) = 2x\text{Ca}^{2+} + (2-2x)\text{Mg}^{2+} + \text{SO}_4^{2-} + 2\text{HCO}_3^-$
Feldspar Molar Ratio Total NP Consumption (mg CaCO ₃ /kg/wk) = Feldspar Molar Ratio *Theoretical NP Consumption (mg/kg/wk) based on:
$2\text{H}^+ + \text{SO}_4^{2-} + \text{H}_2\text{O} + \text{CaAl}_2\text{Si}_2\text{O}_8 = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{Al}(\text{OH})_3 + 2\text{H}_4\text{SiO}_4$



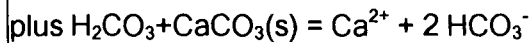
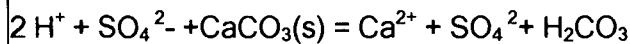
Theoretical NP Consumption at pH 6 (mg CaCO_3 /kg/wk) = Sulphate Production Rate (mg/kg/wk) * 100.09/96.06

based on:



Empirical Open-System NP consumption around neutral pH (mg/ CaCO_3 /kg/wk) = Theoretical NP Consumption (mg/kg/wk) + Alkalinity Production Rate (mg/kg/wk) - Acidity Production Rate (mg/kg/wk)

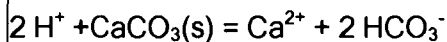
based on:



minus un-neutralized acidity

Theoretical Closed System NP consumption pH 6.5 (mg/ CaCO_3 /kg/wk) = [Theoretical NP Consumption (mg/kg/wk) * 2] - Acidity Production Rate (mg/kg/wk)

based on:



minus un-neutralized acidity

Remaining NP (% of original) + {[Initial NP (t CaCO_4 /1000 t) - Cumulative NP Depletion Rate (mg/kg/1000)] / Initial NP (t CaCO_4 /1000 t)} * 100%

Metal Leaching

Metal Leach Rates (mg/kg/wk) = Metal Concentration (mg/L) * Volume of Leachate Collected (L) / Sample weight (kg)

Remaining Metal (% of original) = {Initial Metal content (mg/kg) - [(Cumulative Metal Leach Rate (mg/kg) / Initial Metal Content (mg/kg)]} * 100%

Notes: At the later stages of some testing programs, analyses for sulphate, alkalinity and metals are not done on a weekly basis, but may be decreased to monthly. In this case weekly values for rates can be calculated through interpolation of the proceeding and subsequent measured values.

From these equations the long-term rates and lag times until acidity can be determined (Li, 1997). For this to be done, detailed and high quality ABA is necessary. The extrapolated rates are compared with the ABA values to determine whether acidity will be generated, and also when this will occur. In broad terms, if the acid potential outlasts the total neutralising potential, based on these cells, then acidity is expected. In this case the period in which the material remains neutral is deemed the lag period (*ibid*). The two most important problems in determining these lag times are the uncertainties in the available total NP (the validity of the ABA determination) and assumption that all the NP is available for neutralisation before the onset of acidity. The method proposed by the IGS for NP determinations (Usher *et al.*, 2002, Cruywagen *et al.*, 2003) addresses several of these uncertainties. The lag time calculation can give incorrect answers if the minerals contributing to NP are very slow-reacting. The combination of the mineral assemblage and ABA data is thus more likely to give consistent answers. An integrated approach to the prediction, as suggested by Morin and Hutt (1999) and later on in this thesis, reduces the incorrect application of lag time calculations. A more generic approach to this is to subtract a value from the determined NP value (e.g. 10-15 kg/t CaCO_3 after Morin, 1996).

Chapter 5 of this thesis indicates several cells where the theoretical onset of acidity showed good correlation to acidification in several humidity cells. In these cells the mineralogy should indicate that the contributing phases were fast reacting carbonates; thus there was less discrepancy in the values. The other important aspect to note is that these cells were run for longer than the ASTM 20-week period. Li (1997) used the 20-week data when the cell discharge was still neutral, and correctly identifies this as a major reason for the inaccurate lag time prediction, again emphasizing the fact that stabilised rates need to be used if these cells are to be considered in prediction programs.

3.4.2 Upscaling the results from humidity cells

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).

Of great concern to most practitioners is the upscaling of the results from humidity cells. Few field calibration studies and screening criteria for kinetic tests are published (Kleinman, 2001). Although several papers have been published regarding kinetic tests, there is not a large volume of published data on this upscaling thereof. Much of this is due to the large variations in kinetic test methodologies, lending weight to the arguments by Hornberger and Brady (1999) that these tests should be standardised. Papers such as Morin and Hutt (1994 and 1997), Stromberg and Banwart (1994 and 1998), Frostad *et al.* (2000), Lin *et al.* (1997) and Bennet *et al.* (2000) present examples of upscaling kinetic test results to field scale.

Of these Morin and Hutt (1997) present the most detailed discussion of methods to use. Using this rationale the following points are pertinent:

- The stabilised oxidation or reaction rate of any particular component is a good analogue of the field reaction.
- The most important caveat to this is the availability of oxygen. The authors use the basic assumption of a rate limiting concentration, above which the measured rate is regarded as constant.
- This limitation is valid to waste where the material is too fine to allow advection of diffusion of oxygen to the reactive surface and then in submerged areas, such as flooded underground areas.
- In the case where oxygen is unavailable, rate adjustments need to be made. These adjustments can ignore or include possible anoxic oxidants such as ferric iron.
- Where there are possible limits to oxygen consumption, two scenarios need to be considered:
 - The rate of oxygen supply exceeds the rate of consumption.
 - The rate of oxygen supply is less than the rate of consumption.

In areas where the former scenario is expected above the water table (or in unflooded areas) the rate obtained from humidity cells can be used without adjustment. This rate therefore represents the expected fundamental release or production rate. The units of this rate are expressed as mass of product per unit time as a function of surface area or mass. Where fine material makes up more than 20% of the reacting mass (such as in the rubble zone found on the floor) the expression as a function of mass should suffice, since the reactive surface area will be largely determined by the finer and more reactive fraction. Thus if the stabilised humidity cell rate (RHC) has been obtained (often only after a period of a year or more of humidity cell operation), then this can be scaled up directly. The difficulty then lies in obtaining field estimates for the mass or reactive surface area of the material in the field.

In cases where there is no continuous oxygen source available, once the oxygen has been depleted, the rate will either decrease to the dissolution rate of minerals such as gypsum, or the oxidation rate of ferric iron needs to be considered. In a conventional humidity cell this cannot be evaluated. The site characterisation needs to ascertain if such oxidation is a likely scenario. Should site-specific rates for this be required, alternative kinetic tests need to be designed to obtain these rates and the order of the reaction with respect to ferric iron as example. The most basic assumption would be that these do not play a role, as would be the case if the situation remained circa neutral.

For a more detailed prediction of the field rate, the total weight of a component that has adequate oxygen nearby is multiplied by the humidity cell rate:

$$\text{Rate1} = \text{OWT} \times \text{RHC}$$

Where Rate1 = total reaction rate for the reactive component in mg/wk

OWT = Total weight of oxidising material in kg

RHC = humidity cell rate in mg/kg/wk

If the flow rate can be determined, the hypothetical concentration can be obtained by dividing this rate by the flow rate. It is important to check the obtained concentration to see if it would not be constrained by the saturation level of likely minerals in the assemblage.

The release rate in such a case becomes:

$$\text{Rate2} = \text{EQC} \times \text{Flow}$$

Where Rate2 = total release of a component in mg/wk

EQC = equilibrium concentration in mg/L

The availability of oxygen and the transport thereof is of importance in determining which scenario to use. In the case of waste, much work has been done by various researchers such as Ritchie (1994 and 2000), Stromberg *et al.* (1994), Henry *et al.* (2000) and, locally, James (1996).

In the underground scenario it can be assumed that oxygen levels are above the rate limiting values in unflooded portions. In flooded areas various factors will determine the availability of oxygen. These include:

- The amount of oxygen in the air in the unsaturated area adjacent or above the flooded portion.
- Henry's Law.
- Diffusion into the water according to Fick's Law (approximately $2.1 \times 10^{-9} \text{ m}^2/\text{s}$ for oxygen in water).
- Oxygen consuming processes in the saturated portion (mostly redox processes; in coal mines the oxidation of organics could compete with sulphide oxidation reactions for this oxygen).
- Water flow.

An equation that could be useful for estimating the flux of the oxygen into and the concentration of dissolved oxygen with depth in a water column is the following (Morin and Hutt, 1997 after Morin 1993):

$$\text{DO}(z) = \text{DO}(\text{in the upper most water}) \exp\{-z[0.17 \times 5 \text{PYRx}(1-n) \times \tau / (dxn)]^{0.5}\}$$

Where DO(z) = concentration of DO at depth z below the water rock interface (mg/L O₂)

z = depth below interface(m)

n = porosity

%PYR = percentage of pyrite in material

d = average particle diameter

τ = tortuosity factor

Morin and Hutt (1994) present a method of estimating the resultant concentration in a typical flushing of a mine waste rock pile. In this very simple method the stabilised humidity cell rate for a metal for example, is multiplied by the mass of material reacting and divided by the amount of flow out of the pile. In the case of a flooded compartment this method has no validity, as there will be factors such as residence time to consider. However, if a steady state "saturated" rate can be obtained, this can be used as a rate for upscaling.

Frostad *et al.* (2000) present a comparison between sulphate production rates in laboratory and at field scale. Several difficulties are pointed out by these authors when scaling up. These include:

- Taking temperature differences into account. The use of the Arrhenius equation that is sensitive to the pH in the cell and on site is proposed.
- Quantifying micro-environments within field piles. It was found that in the laboratory tests rates were in some cases lower than for field piles. This is ascribed to microclimates existing in the field where acid generation occurs (cf. Chapter 7, where hotspots within South African spoils are discussed).
- Accounting for complex hydrology in the field.
- Particle size might be more important in certain scenarios than suggested by Morin and Hutt (1994) or Bennet *et al.* (2000).

The findings are that (ibid) laboratory rates should be corrected for field temperatures and surface areas, but that for several of these cells this upscaling could not be done with confidence, for the reasons outlined above. They also suggest that cumulative sulphate production may be more useful than the neutralisation potential depletion method.

Lin *et al.* (1997) provide details of a model that can be used to estimate the field situation based on laboratory characterisation. A new development at the University of Utah is the AMDHC model (Version 4.16, Lin *et al.*, 2002). The model assumes that the ASTM method is used, and is dependent on the detailed characterisation of the material purports to predict the humidity cell response. This could provide an additional verification of any humidity cells operated.

3.4.3 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 indicating 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, 1998).

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 the surface area, can comparisons be accepted as valid (Mills, 1998).

3.5 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

capabilities 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, the 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 capabilities. 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.

The most important 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).

3.5.1 Data Requirements for Most Detailed Models (from the ICM)

The Water Research Commission-sponsored website "Internet Service Centre for Mine Related Water Models" gives the following generalised data requirements for geochemical models (Howard and Heymans, 2000):

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.

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 (K_d) 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).

These aspects are addressed in Sections 7 and 8.2 in more detail.

4 EVALUATION OF EXISTING STATIC LABORATORY PREDICTION TECHNIQUES

4.1 Static Methods

The static methods are usually synonymous with acid-base accounting. 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. Procedures such as mineralogy can also be included as part of the static test suite of techniques.

4.1.1 ABA Terminology

AP (Acid Potential) = $S\% \times 31.25$

NP (Neutralisation Potential) - the capacity of a sample to consume acid

NNP (Net Neutralising Potential) = $NP - AP$

NPR = NP: AP

Units: Usually these parameters are expressed in kg of CaCO_3 equivalent per ton of rock.

4.1.2 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 (after Boer, 1999) illustrates some of the factors that impede the extrapolation of ABA results to the field situation through uncertainty.

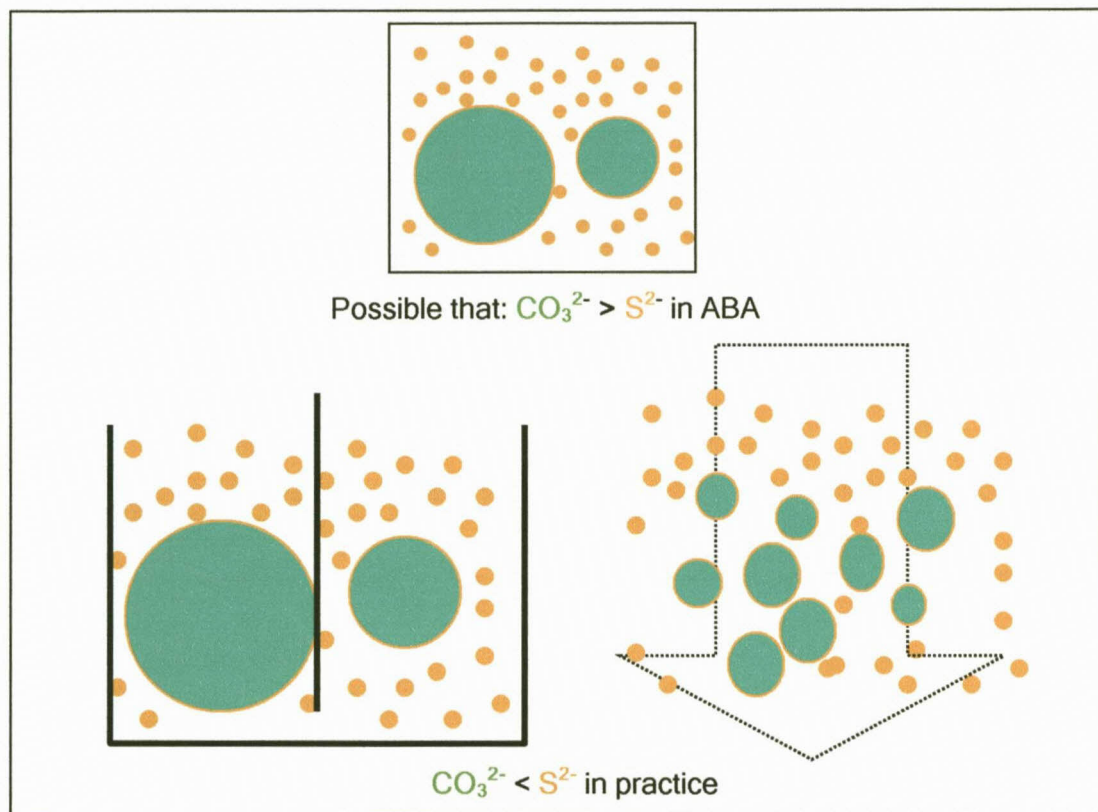


Figure 33: Comparison between laboratory occurrence and field conditions.

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 what is predicted in the laboratory. This approach is analogous to that of an equilibrium approach used in classical chemistry since 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 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 were to be set at, for example, 20 kg CaCO_3 equivalent/tons of material (Errington, 1991). Several papers such as Stromberg and Banwart (1994 and 1999), Puura and Neretnieks (2000), show how silicates can be effective in consuming acidity. However, all these papers show that this is only effective at pH-values of below 3.5, except in extremely low pyrite-bearing materials).

- 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 in the spoils and assessments in underground compartments a > 10% fines ratio is a valid assumption in South African conditions, therefore this limitation is a minor consideration in spoils. Holmstrom *et al.* (1999) show that this coating effect also occurs on pyrite surfaces, decreasing their effectiveness over time. From an ABA point of view these two effects could be balanced in most field situations; however, from a predictive point of view such as geochemical modelling, these factors have to be brought into account. Stromberg and Banwart (1999) also indicate that in very fine material such as tailings the inter-particle diffusion rates could be too slow for calcite to contribute fully to neutralisation; again in most coal mining applications this is not excessively problematic).
- 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 an 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.

4.2 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 the H_2O_2 method.
- Neutralising Potential using sulphuric acid.

The recommended methods are discussed in detail in Usher *et al.*, 2001 (part of which is included as Appendix 5) and Cruwagen *et al.*, 2003, and brief supporting evidence for the selection will be outlined below.

4.2.1 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 reason for this is that with the more dilute solution, incomplete oxidation can result. The 30% H_2O_2 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:

1. Only reactive species will oxidise and result in acid generation. Jennings *et al.* (2000) show that for ABA to be used with confidence an indication of the true sulphur reactivity is required, rather than a total S value.
2. 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 $\text{NNP} > 20$ is generally not acid producing and $\text{NNP} < -20$ kg/t CaCO_3 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)).
3. Some quality control can be done, since low pH-values should also have far more acid potential than the neutralising potential.
4. The resultant reaction product can be analysed to give an indication of the expected heavy metal content and final water quality that could result.
5. The method yields very good reproducibility.

The sections that follow show several of these factors.

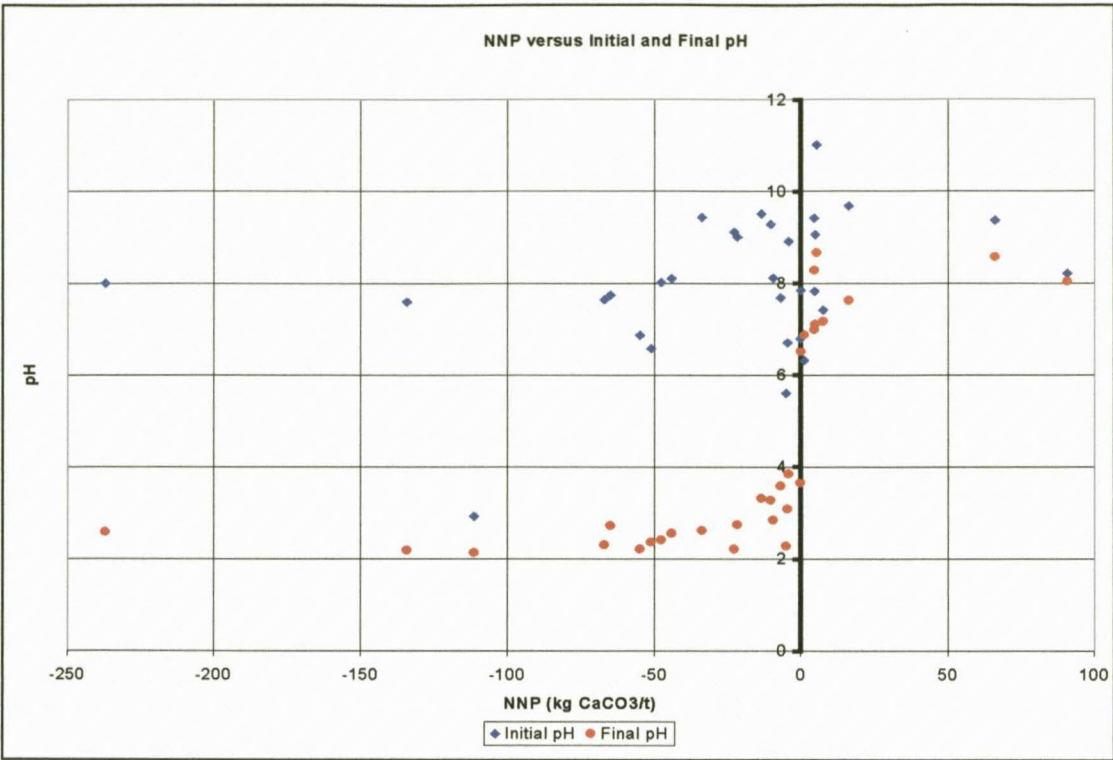


Figure 34: Results of NAG tests used as quality control.

4.2.1.1 COMPARING LECO %S WITH 30% H₂O₂ %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 (e.g. organic S, sulphate, sulphide) (Kania, 1998). There is a good correlation between the Leco methods and the hydrogen peroxide method, as shown in the graph below (Figure 35).

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. Duplicate samples were analysed by Leco and by the 30% H₂O₂ method. The results obtained from both methods are shown below (Figure 35 and Figure 36).

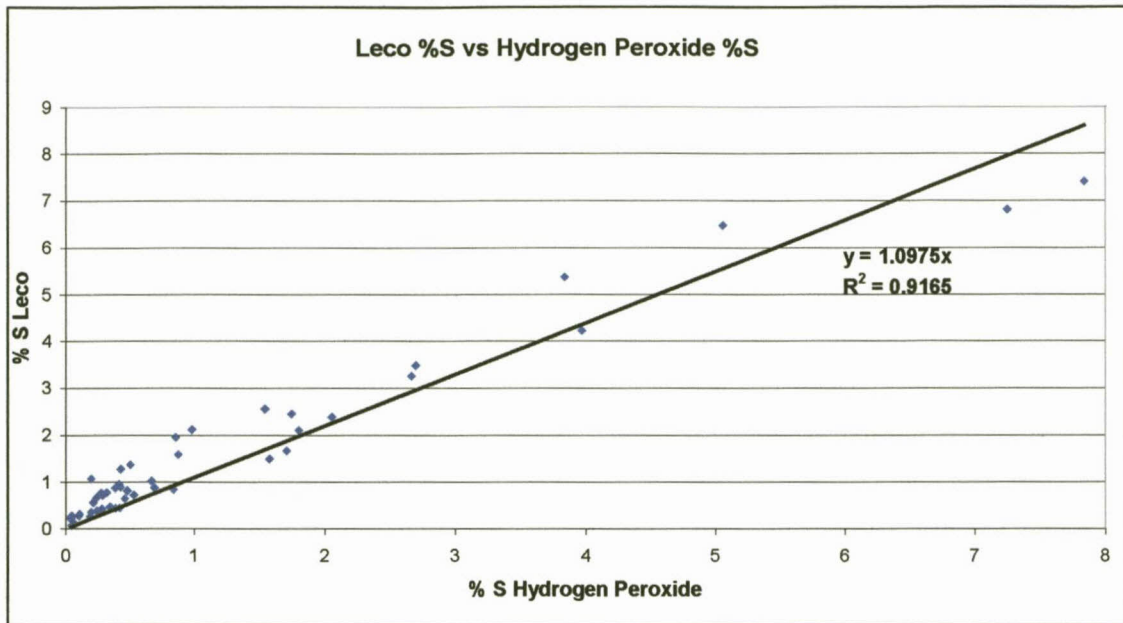


Figure 35: Comparison of percentage sulphur determined by the Leco analyser and the 30% H_2O_2 method.

From this regression graph, H_2O_2 gives higher %S for values of over 5%, whereas 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 from the Leco analyser. This can be seen from the regression co-efficient of almost 92% between the 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. Acidity is produced that cannot be accounted for by the pyrite (sulphide S was used to determine the AP) and organic sulphur that were present, giving additional acidity after oxidation processes in the mine were completed. Thus, complete peroxide oxidation will include the contributions of all species that might be acid-forming in the waste rock, leading to better assessment of the true acid generating potential.

4.2.1.2 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 36 and Figure 37 that the repeatability of this method is acceptable.

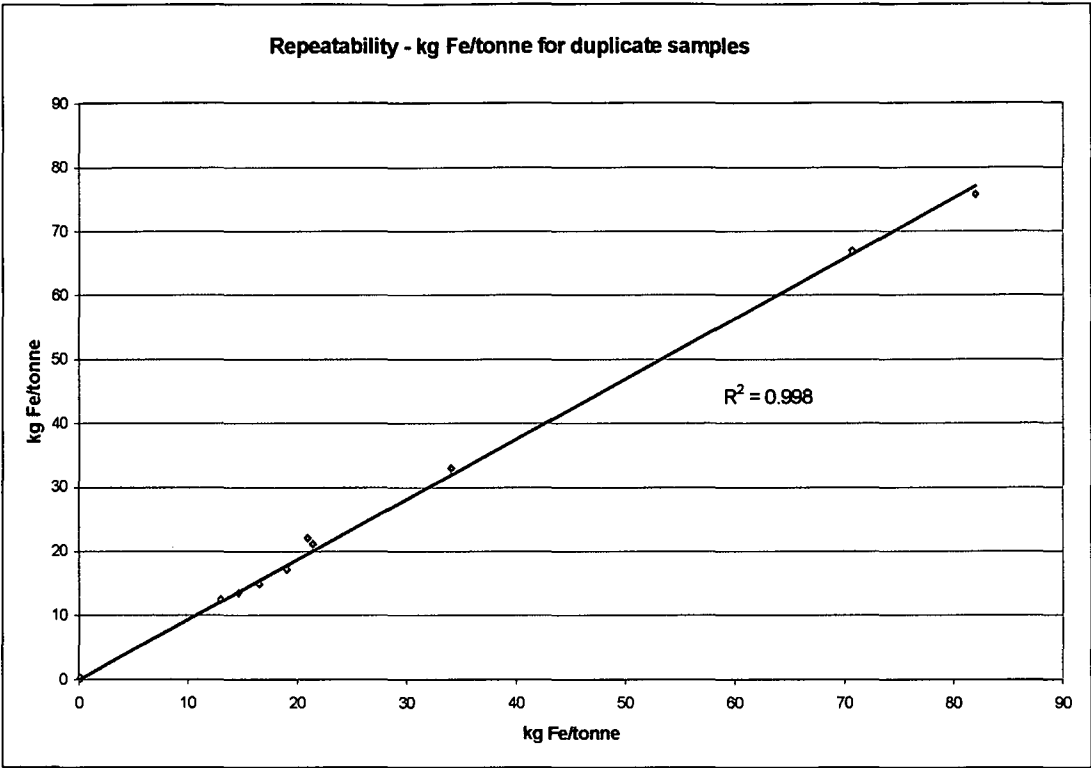


Figure 36: Comparison of Fe obtained for duplicate samples to show repeatability.

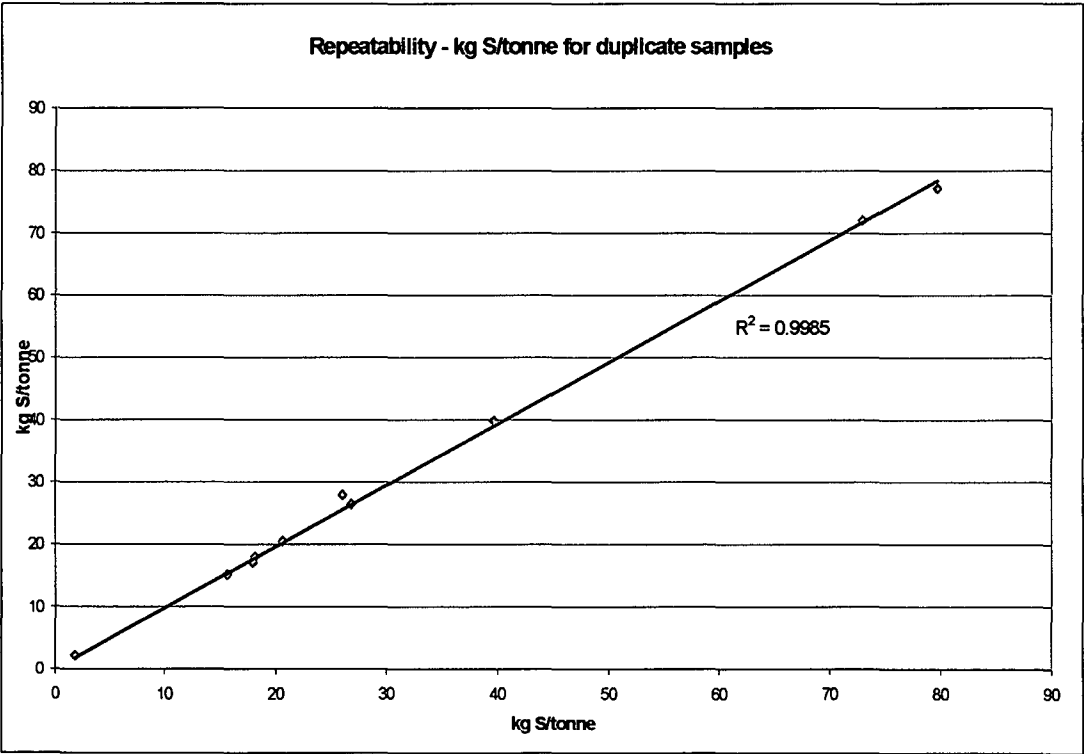


Figure 37: Comparison of S obtained for duplicate samples to show repeatability.

4.2.2 Release of constituents under oxidative and acid leach conditions

An evaluation of the release of constituents under complete oxidation (hydrogen peroxide oxygen) and by acid leaching is shown below:

Table 7. 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

For most of the constituents the amount released by a strong acid leach clearly exceeds that of oxidation. The implication is that if any material is to be used as buffering or backfill, the potential for release under acidic conditions should be determined.

Table 8. Constituents released by 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 illustrates this graphically for several more common constituents.

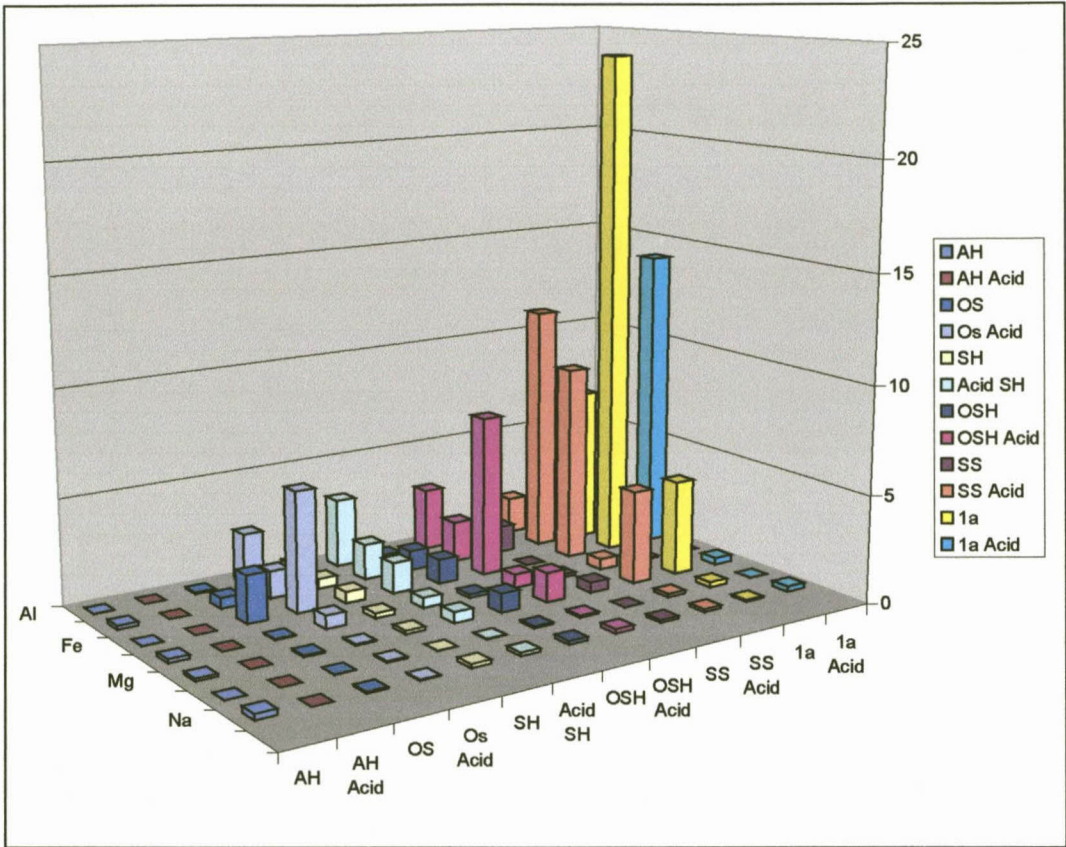


Figure 38: Comparison of constituents released in complete oxidation and acid digestion.

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 acid digestion. The conclusion 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, determining acid leachable metals is essential to provide an indication of the mobilisation that will occur.

4.2.3 Comparing NAG pH to overall ABA.

Schafer (2000) reported the use of the NAG method to classify uncertain samples from ABA results. To ascertain the validity thereof, 546 samples, on which ABA was done, were assessed to determine the correlation between the NAG pH and the ABA results. Table 9 below, summarises some of these findings. Based on this comparison, using an NAG pH of 5, 4.5 and 4 as cut-off, it can be seen that with a NAG pH below 5, more than 86% of samples will have NNP values of less than 0 kg/t CaCO₃ or NPR values of less than 1. When pH 4.5 is used as a cut-off value, it provides a reliable evaluation of the situation in almost 95% of the cases tested. Of

the 546 samples, only 61 had eventual NNP values of greater than the 20 kg/ton CaCO_3 margin. Of these samples, only two have NAG pH-values of less than 5.5.

Table 9. NAG pH compared to ABA.

	NNP <0	NPR<1	NPR<2
NAG pH <5	86%	87%	>100%
NAG pH <4.5	93%	95%	>100%
NAG pH <4	>100%	>100%	>100%

4.2.4 Neutralisation Potential Method

Full details of the testing of the proposed NP method are given in Usher *et al.* (2002) and Cruywagen *et al.*, (2003).

HCl is widely used as titrant in the testing of a samples ability to buffer an acid, after the Sobek *et al.* (1978) method to acidify the sample for NP determination. Tests were run where HCl and H_2SO_4 were used to compare results. After the addition of acid the sample is stirred for 30 minutes and left for 24 h for digestion. No heat treatment is done, as this is a harsh step and not likely to be found naturally. The pH of this slurry must be below 2.5 after 24 h, but not lower than pH 2 according to Lawrence and Day (1997) and Lawrence and Wang (1997). Additional acid is added until the pH remains below 2.5 for at least 24 hours. Back titration to a pH of 7 is started with NaOH. The comparison between the results obtained with the two acids on 32 samples can be seen in Figure 39. With a regression coefficient of 0.9971, there is thus no major difference in either acidifying the pulverised sample with HCl or H_2SO_4 . AMD predominately contains H_2SO_4 and it is therefore justifiable to use sulphuric acid, as it should provide a better simulation of field conditions.

Titration are done by hand and are only terminated when less than 0.05 mL of NaOH are needed after two consecutive days, to get the pH back to seven. This lag period has been shown to eliminate siderite buffering and thus the accuracy of the answers is enhanced. (Cruywagen, 1999).

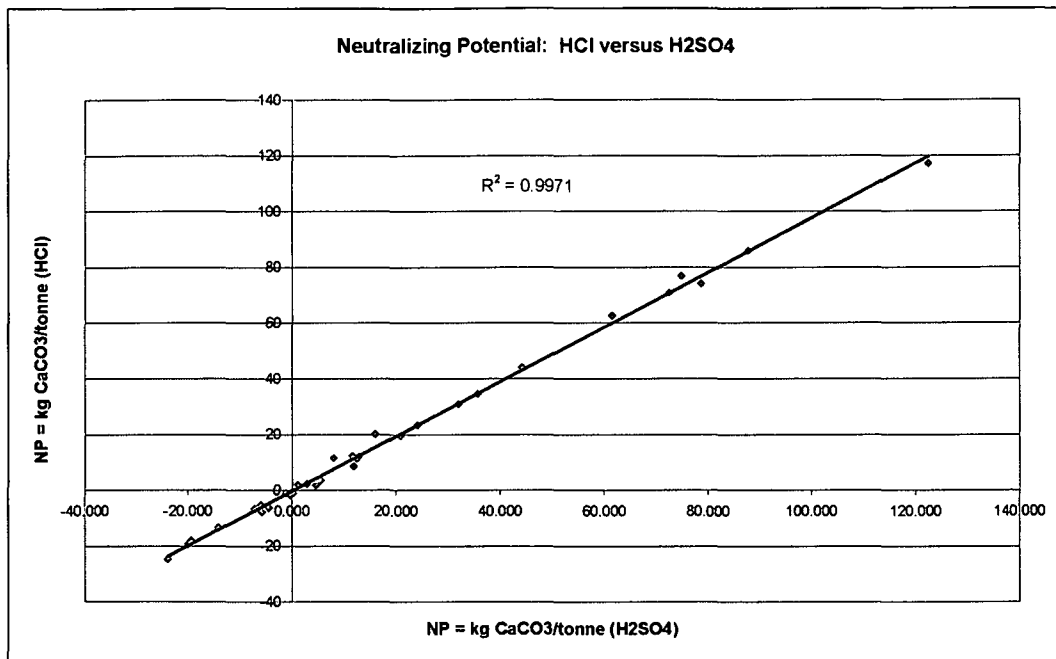


Figure 39. Comparison of HCl and H₂SO₄ for determination of Neutralising Potential.

Comparison between back-titration to pH 7 and 8.3 was also done. This showed some minor variations, but based on arguments in Cruywagen (1999) and Usher *et al.* (2002) a back-titrated value of 7 has been selected.

4.2.4.1 CONCLUSION

This section has detailed the findings from an evaluation of suggested ABA methods. From 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 coalmines. The improvements suggested 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 coalmines of Southern Africa.

4.2.5 Screening Criteria

One of the major advantages of static tests is that fairly well-defined sets of screening criteria have been developed to interpret the tests. Although these criteria can sometimes provide slightly contradictory interpretations, their combined use can lead to a good classification of tested samples into classes of 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). While one has to agree with this sentiment it is felt that until there is a large enough, comparable Acid-Base Accounting database in South Africa, 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.

4.2.5.1 NET ACID GENERATING TEST (NAG) pH

This set of criteria is based on the final pH obtained in the NAG test. The 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.

4.2.5.2 NET NEUTRALISING POTENTIAL (NNP)

The use of NNP most often leads to uncertainties. The reason for this is that research and experience have shown that 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 (Price *et al.*, 1998):

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.

4.2.5.3 NEUTRALISING POTENTIAL RATIO (NPR)

Guidelines for screening criteria based on ABA (from Price *et al.*, 1998).

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 very reactive sulphides in combination with insufficiently reactive NP
None	>4: 1	No further testing required unless materials are used as alkalinity source

The criteria above can also be plotted to give a visual indication of the likelihood of acid generation, as shown in Figure 40 below.

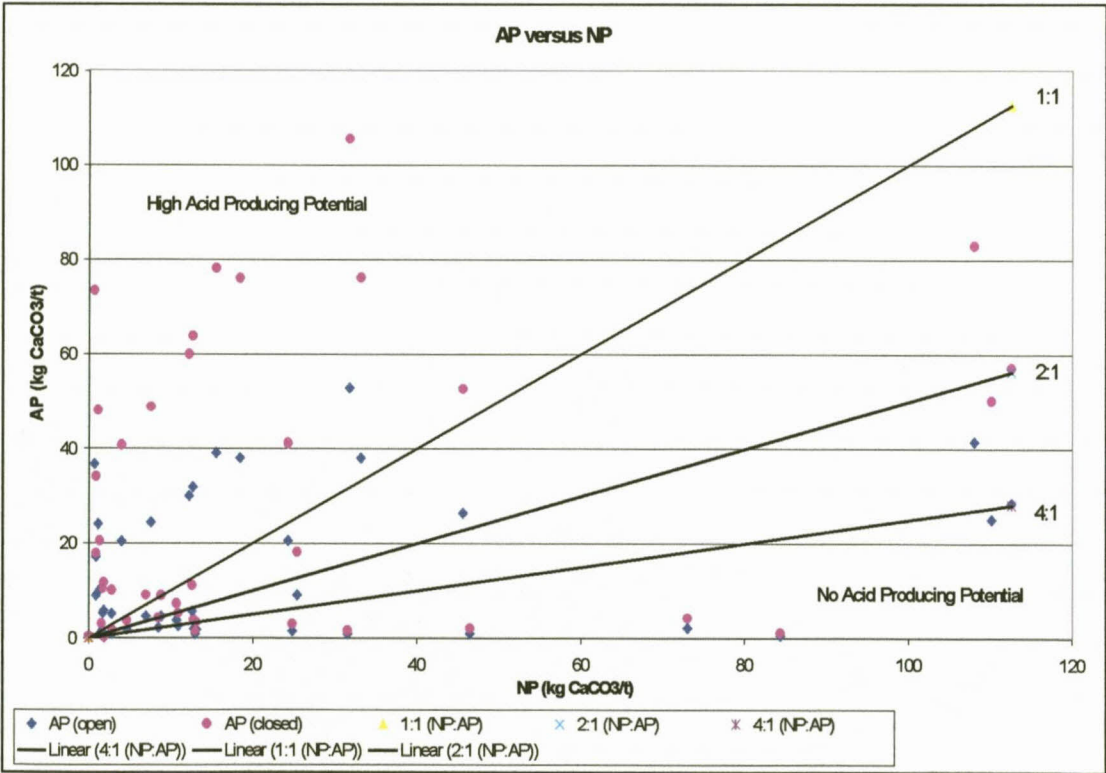


Figure 40: Plot showing different categories of acid-generation potential based on NPR.

4.2.5.4 % S AND NPR

A set of rules, which has been derived from 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 showing a high likelihood of acid generation, the green low and the grey region uncertain (See Figure 41). Samples would only plot in the white region if a high S-value occurs in a rock with very high neutralising capabilities.

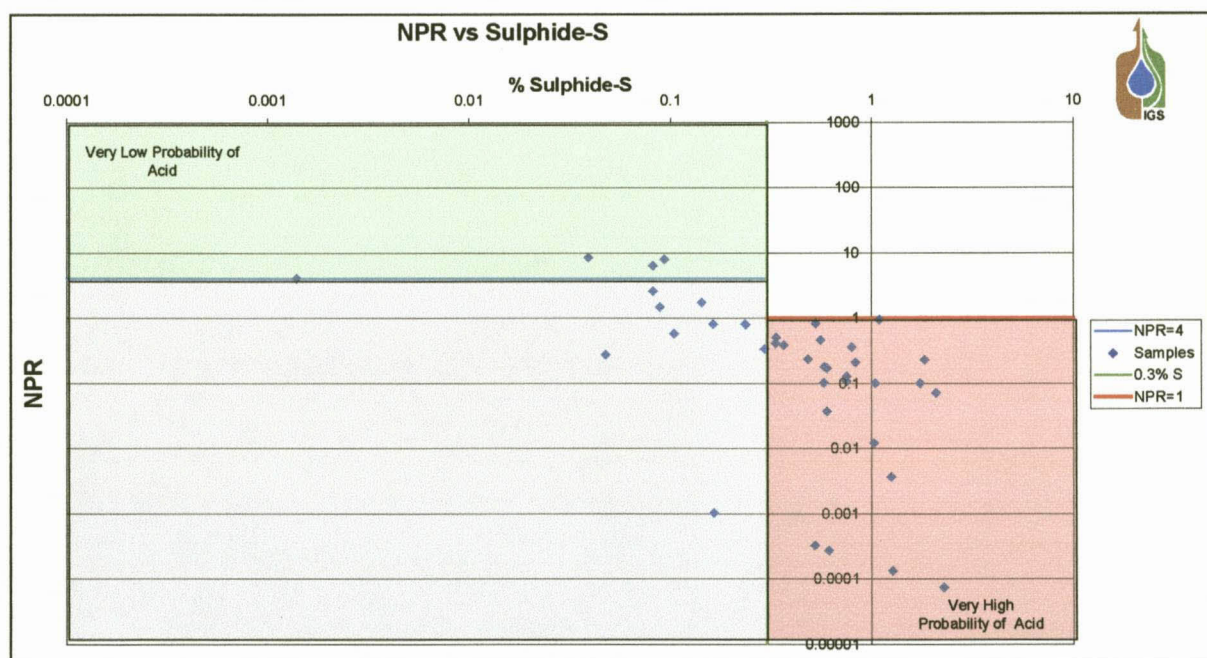


Figure 41: Evaluation plot using %S and NPR to differentiate samples.

4.2.6 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 in Chapter 8 or the WISH format.

4.3 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. Ambiguities on the interpretation of ABA results can also be greatly reduced by including mineralogical results (Paktunc, 1999).

In Section 5.3.2.1, XRF and XRD results for samples used for humidity cell testing are given. These results also indicate that the humidity cells' water qualities are consistent with the determined mineral assemblages.

4.3.1 XRD of unoxidised and oxidised samples

Cruywagen (1999) reports on comparative mineralogical assessments done before and subsequent to ABA. X-ray powdered diffractometry (XRD) was completed on untreated and 30% H₂O₂ treated samples. The presence of each mineral is indicated by a + sign, while a - sign indicates the mineral has been consumed by the oxidation process or release of acidity as a results.

The minerals that dissolve due to the oxidation (marked with - signs) are summarised in Table 10. All the pyrite, and portions of the dolomite, siderite and calcite, depending on the ABA balance, is removed during oxidation, indicating complete oxidation procedures.

Table 10. XRD results on 30% H₂O₂ treated (-) 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	+	-	-			+

Table 10 Continued. XRD results on 30% H₂O₂ treated (-) and untreated samples.

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				+	+

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

4.3.2 Neutralising Potential vs. XRF determinations

The NP from 75 samples was compared to the XRF data for the same samples. The XRD results for these samples and previous investigations such as Azzie (2002) have indicated that the major carbonate species in the South African Coalfields are calcite and dolomite. On the graph (Figure 42) the correlation between the reported CaO and MgO and NP is given. A very good correlation between CaO and NP is evident.

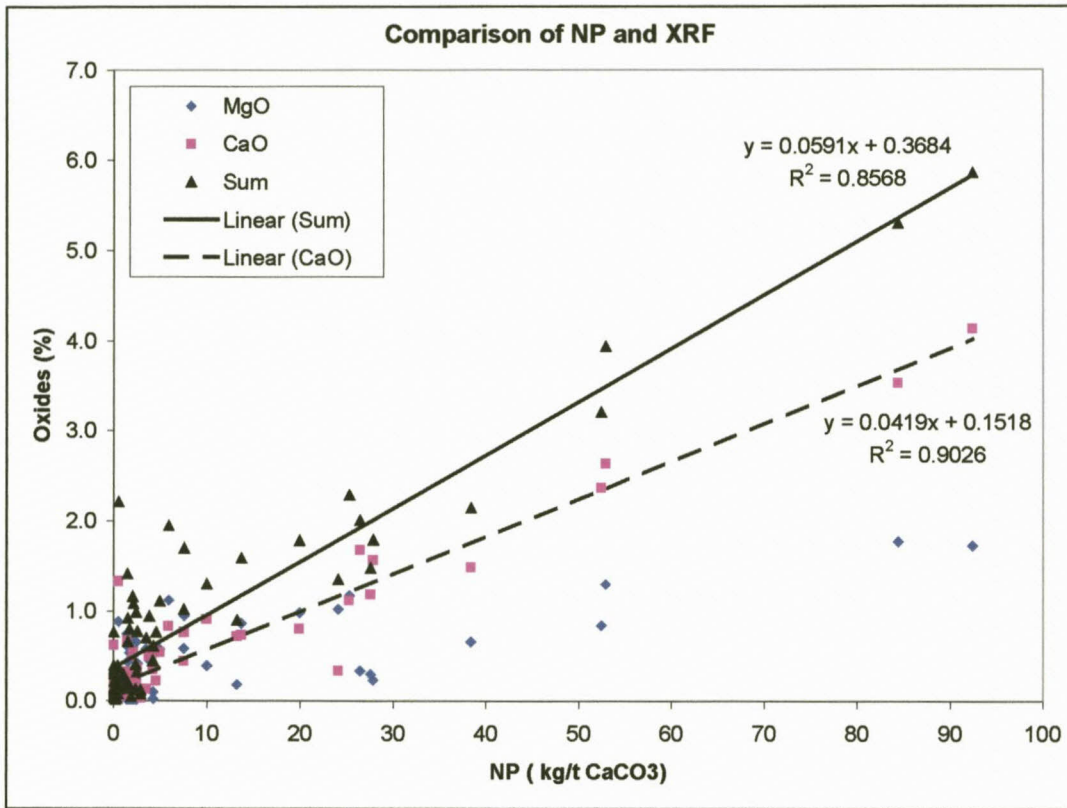


Figure 42: Comparison between XRF and NP results.

In the determination of the water and salt balance for Eikeboom Colliery, use was made of ABA, mineralogy, empirical and simplified kinetic geochemical modelling. (Usher *et al.*, 2002).

It was observed in this investigation that a good correlation between mineralogy and ABA existed. A graphical representation of this is shown in the comparisons of the ABA parameters determined with depth in various cored boreholes. Figure 43 and Figure 44 are a selection from this study.

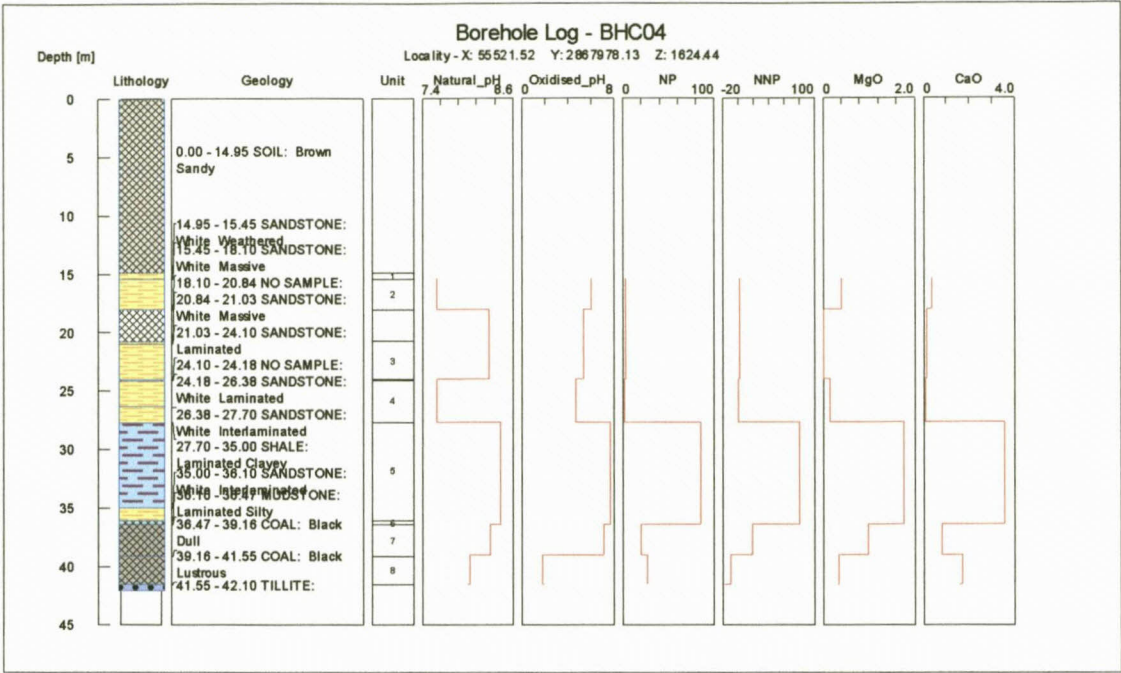


Figure 43: Relationship between NP, NNP, CaO, MgO and calcite in selected borehole.

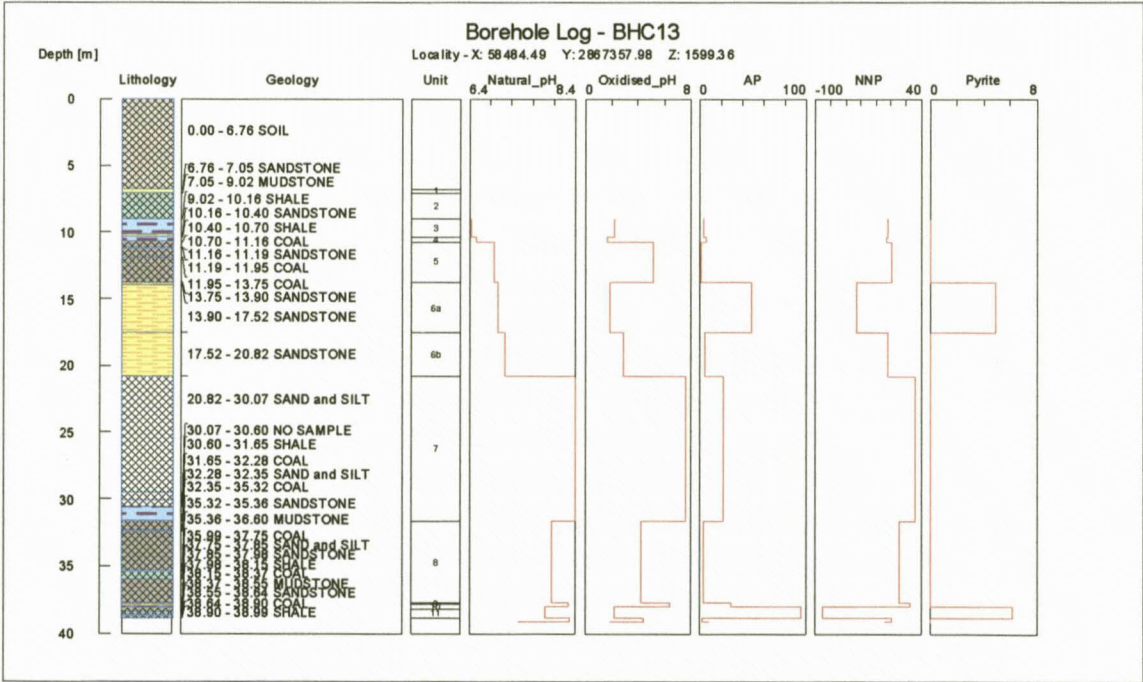


Figure 44: Relationship between AP, NNP and pyrite in selected borehole.

4.4 The ABA Characteristics of Different Lithologies in the Witbank Coalfield

In order to obtain an indication of the contribution of different lithological layers to the overall acid-base account, ABA done as part of various projects was consolidated into a single database. Only approximately a quarter of all ABA results that could be obtained by researchers such as Hodgson (1996, 1997, 1998), Hodgson and Krantz (1998), Hodgson and Grobbelaar (1998) and Usher *et al.* (2000, 2002) have been sampled and analysed according to clearly defined lithological layers.

A total of 515 ABA samples were selected, which could be clearly recognised as belonging to a specific lithological unit. The broad subdivisions used in this evaluation are as follows:

Table 11: Explanation of code used to describe ABA data.

Code	Explanation
W	Weathered sediments
5	Layers above the 5 seam
5 seam	No. 5 coal seam
4	Layers above the 4 seam
4 seam	No. 4 coal seam
2	Layers above the 2 seam
2 seam	No. 2 coal seam
1	Layers above the 1 seam
1 seam	No.1 coal seam

The overall statistics for the layers are as follows:

Table 12: Average values for each layer.

	Initial pH	Final pH	AP (Open) kg/t CaCO ₃	AP (Closed) kg/t CaCO ₃	NP kg/t CaCO ₃	NNP Open kg/t CaCO ₃	NNP (Closed) kg/t CaCO ₃	Count
W	7.23	5.34	1.34	3.59	7.22	5.88	4.54	41
5	8.70	5.83	2.35	4.69	4.44	2.10	-0.25	7
5 seam	6.23	2.10	39.83	79.66	5.48	-34.34	-74.18	4
4	7.35	4.31	12.27	24.68	9.79	-2.47	-14.74	138
4 seam	6.97	2.84	49.94	29.38	19.69	-29.43	-80.19	62
2	7.82	5.09	10.72	22.19	18.15	7.43	-3.29	155
2 seam	7.52	2.87	40.10	29.37	14.49	-24.77	-65.72	65
1	7.68	3.72	9.64	16.95	7.73	-1.91	-11.55	25
1 seam	7.63	2.50	21.63	19.50	6.24	-15.39	-37.02	18

This table is informative as far as identifying the most important characteristics of each layer. It can be seen that the upper two layers are relatively inert with low average NP and AP values. This suggests that the reactive portions have been

leached from these layers. This is an expected phenomenon, since the water table would fluctuate in the upper regions, leading to depletion in the reactive species over time. It can also be seen that the coal seams can be considered the most problematic in the Witbank Coalfield as far as acid potential is concerned. The layer between the 2 and 4 Seams has the most beneficial contribution in terms of neutralising acidity. Again, the reasons for this are probably as much due to hydrogeological response of the system as the sediments mineralogy. The layers between the 2 and 4 Seams have lower pyrite content than the seams, but unlike the layers above the 4 Seam the carbonates have been leached out to a lesser degree by circulating groundwater.

In terms of acid potential (and by implication pyrite content) the No. 5, No. 4 and No. 1 Seams show very similar characteristics from an average point of view. Once again, the average NP values are very similar. Bearing in mind the criteria ABA is interpreted with, it is also noteworthy that under open system conditions the NNP values for all the layers are very close to the uncertain area of -20 to 20 kg/t. However, under closed system conditions for all the coal seams, the average values suggest that acidification is likely. The importance of proper characterisation, especially in opencast spoils conditions, is therefore apparent.

Although the average values provide a good overview, a graphical representation of the data is more informative. Shown in Figure 45 are the average pH-values, clearly indicating the layers that show the greatest propensity toward acidification.

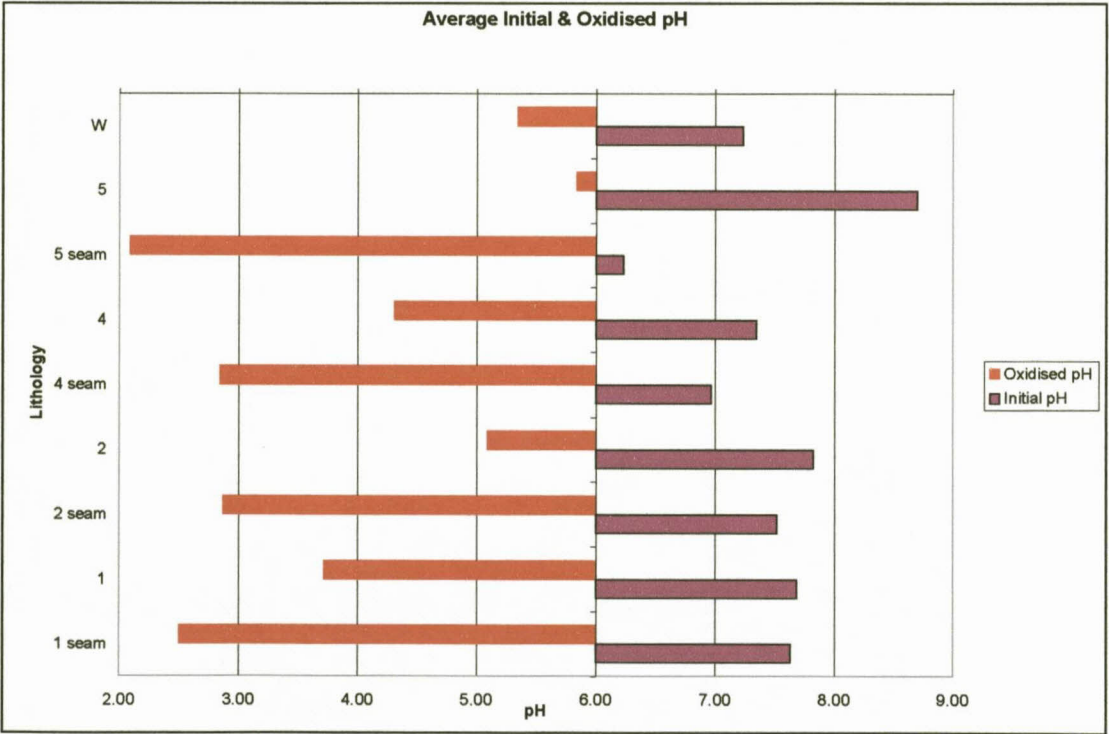


Figure 45: Average Initial and Oxidised pH by lithology.

In Figure 46 below the determined AP and NP for each layer are compared. It is clear that the AP exceeds the NP for all the coal seams and that the upper layers have low values of both parameters, with a slight excess in NP in most cases.

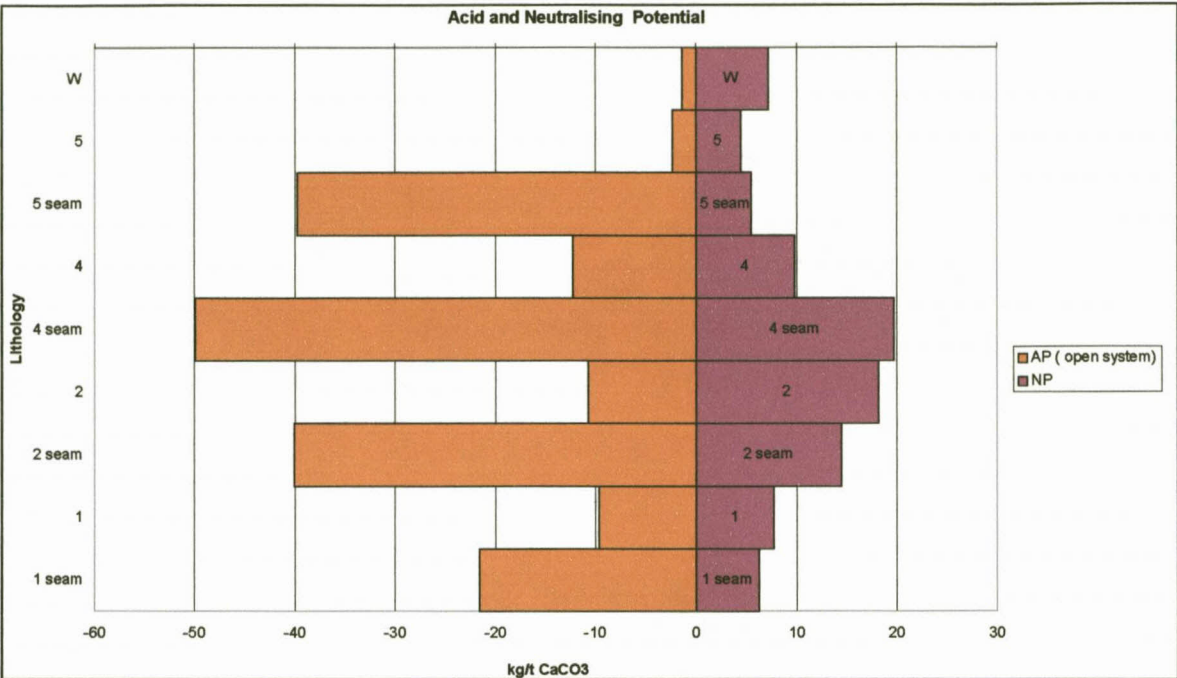


Figure 46: Average NP and open system AP (kg/t CaCO₃).

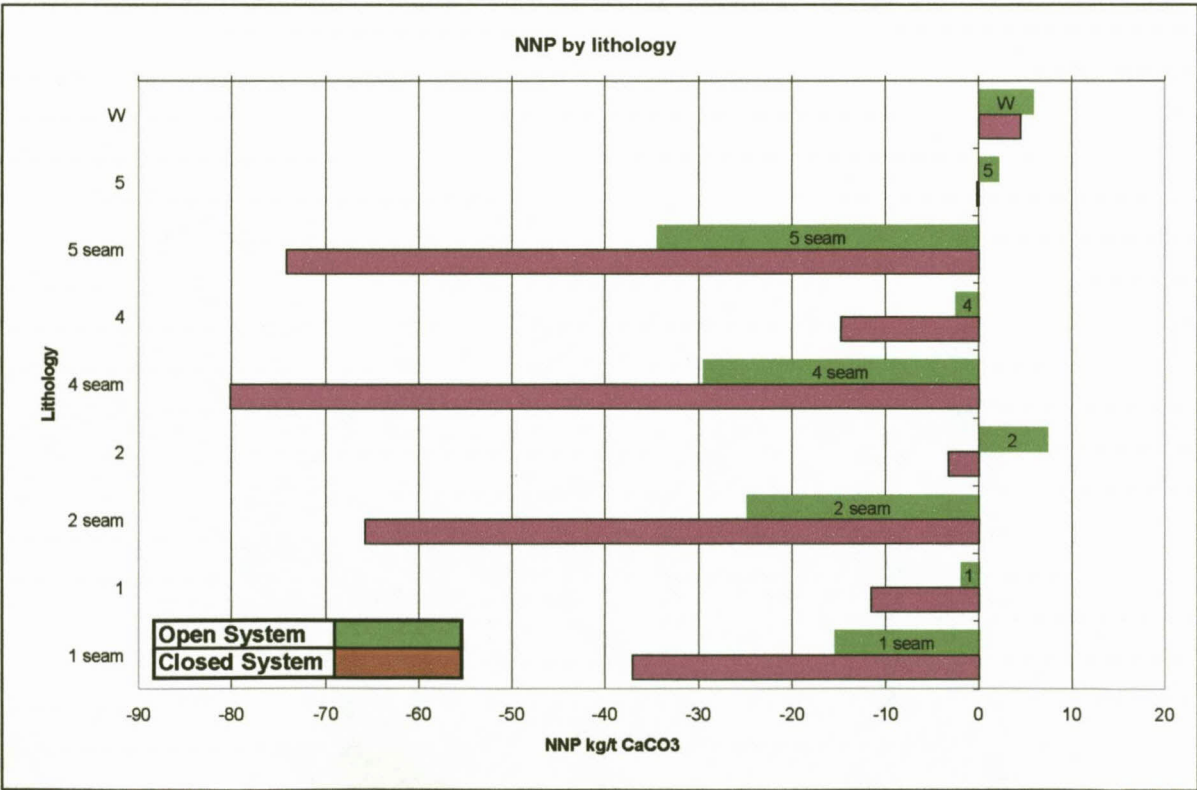


Figure 47: NNP by lithology.

In the Figure 47 above the closed system vs. open system comparison can be seen, and the deductions are in line with the early ones relating to the tabled values.

A statistical representation of each parameter using box-and-whisker plots provides more meaningful information in terms of the variation in each parameter by lithology. The box-and whisker plots of the NP, AP and NNP of each lithological layer are given in Figure 48, Figure 49 and Figure 50 respectively.

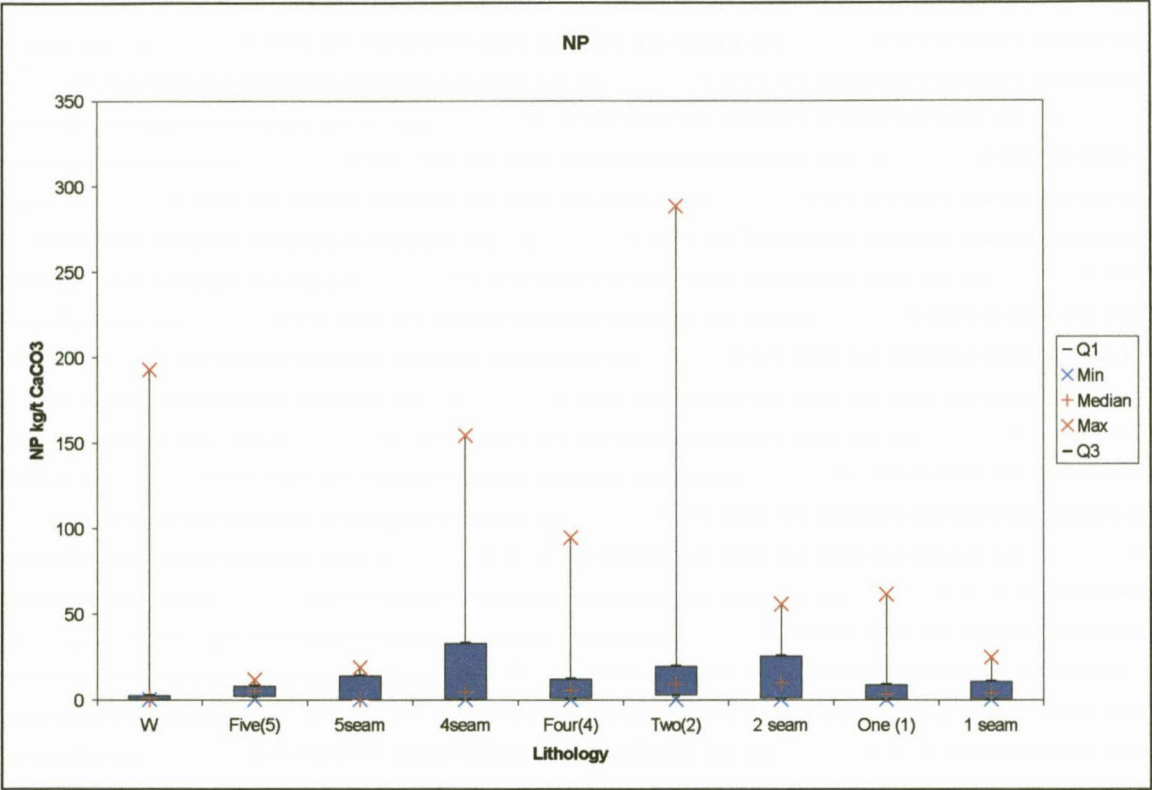


Figure 48: Variation of NP per lithology.

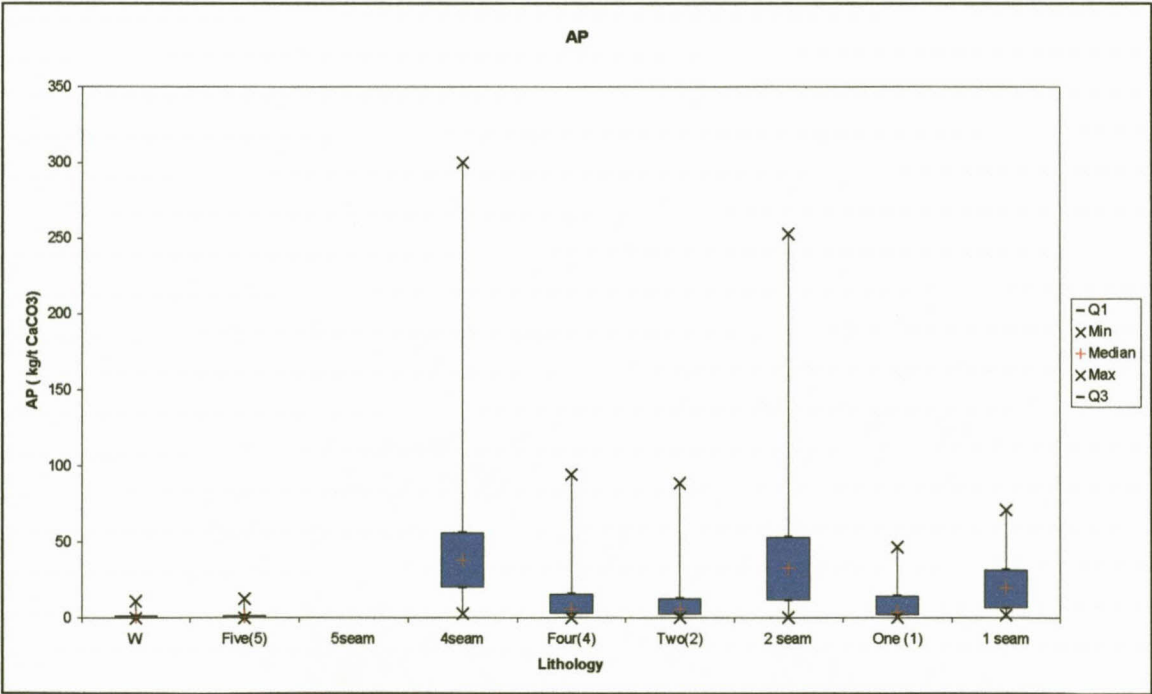


Figure 49: Variation of AP with lithology.

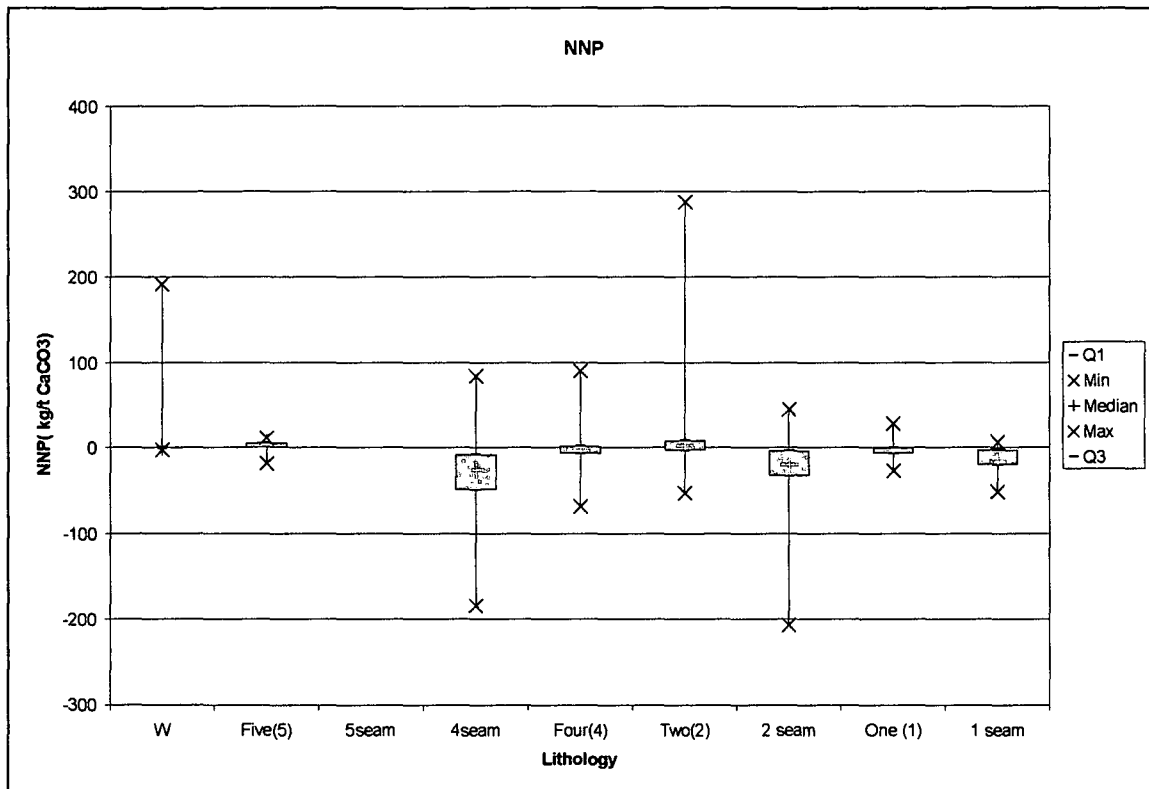


Figure 50: NNP per lithology.

The last figure (Figure 50) is insightful in understanding the behaviour of the system. The coal seams all have large variations in likely NNP, driven by the presence of pyrite nodules and the irregular occurrence of calcite, often as veinlets. The interbedded sediments have a far narrower range of probable values, with all averaging very near to zero. Conclusions drawn from this would be that these values have a far smaller contribution to the overall acid-base account. This is, however, not entirely true; in spoils only 10% coals are present, and thus the associated sediments are the controlling factor in the overall behaviour. As discussed in Chapter 9, localised areas of acidity, as found through trenching into spoils, determine the observed qualities. In underground collieries they are no less important, since where stooping or other high extraction mining techniques are practised, the overlying sediments will predominate in the reactive portion of the mine.

While these values provide an overall picture of what is expected from each broad lithology, it is also evident that the exact localised conditions will be critical in determining how the system will react over time.

5 THE EVALUATION OF STANDARD KINETIC TESTS, THE DEVELOPMENT OF ALTERNATIVE METHODOLOGIES AND COMPARISON TO OTHER METHODS

5.1 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), 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 submerged system. These tests can therefore be used as valuable tools in the ABATE strategy to predict drainage water quality.

5.1.1 Types of Kinetic Tests

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

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.

5.1.1.1 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).

5.2 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 with the dimensions 10 cm diameter by 20 cm in length, and has a nominal capacity for 1 kg of rock. The rock sample is typically crushed to grain sizes of less than 6 mm in diameter and is placed on a perforated plate to permit the flow of air 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 mL 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.

As part of the research for this thesis, humidity cells with the following construction (Figure 51) are currently used at the Institute for Groundwater Studies (IGS).

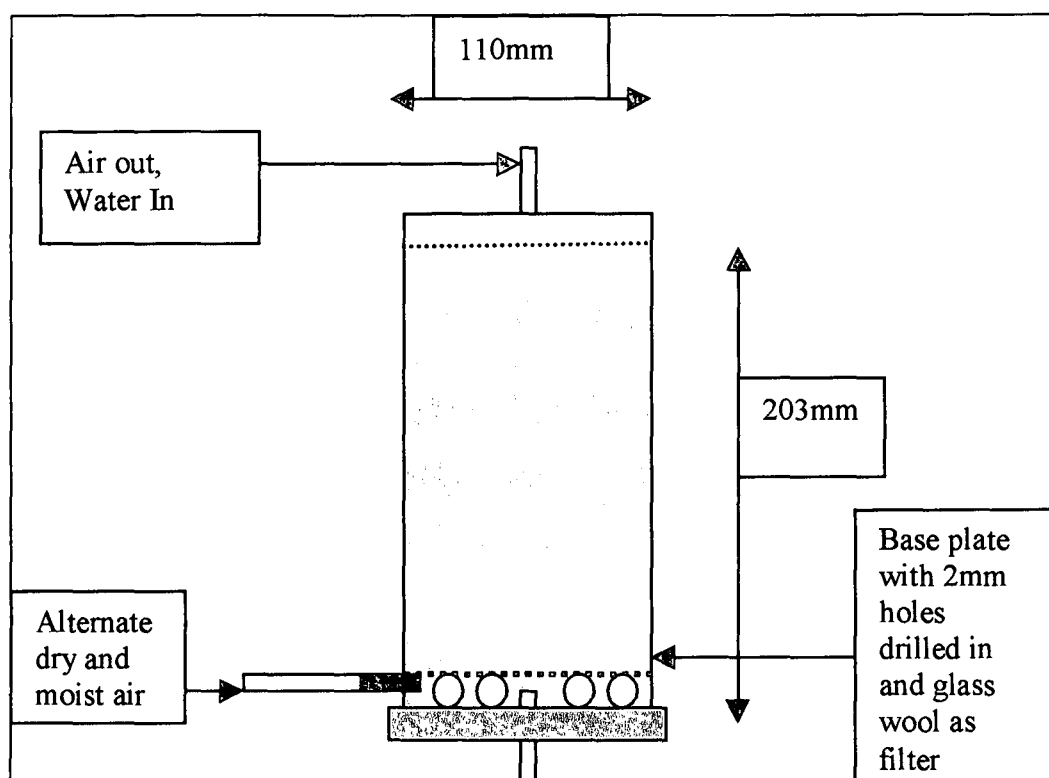


Figure 51: Humidity cell configuration used at the IGS.

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).

5.2.1.1 BACTERIAL ADDITION TO CELLS

Cravotta (1995), states that he has never obtained a soil, sediment or sludge sample that 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 bacteria of interest.

5.3 RESULTS OBTAINED

5.3.1 Methodology

In this research attempts have been made 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.

Figure 52, Figure 53 and Figure 54 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 more widespread use and application, if costs are minimised.

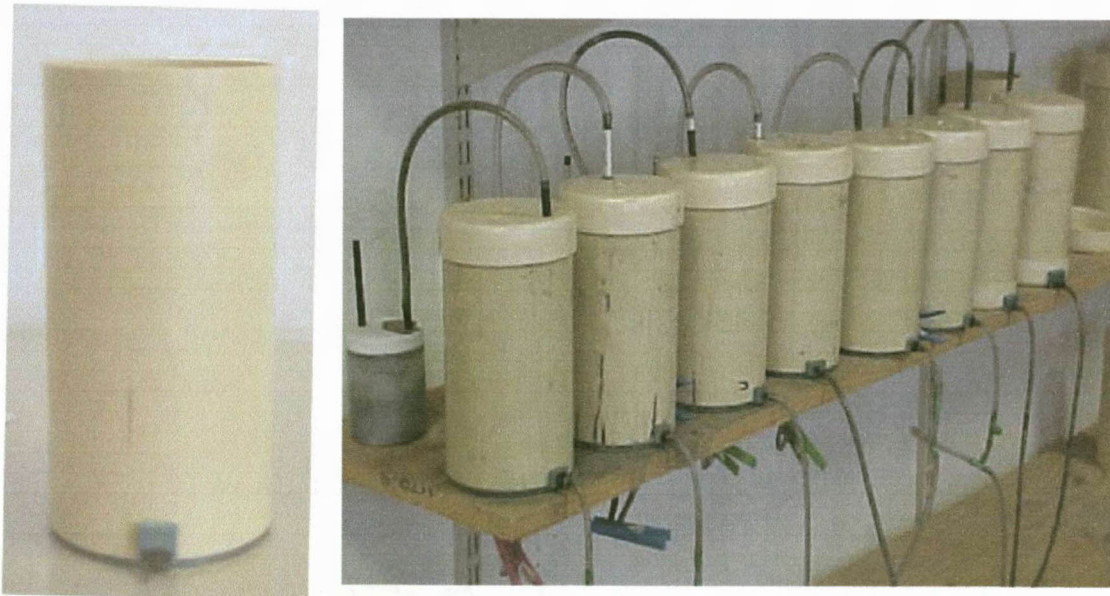


Figure 52: An IGS humidity cell, left and an array of cells set up at the IGS, right.



Figure 53: 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 following 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. In this research the same methodology was employed, with 500 mL additions of de-ionised water each week. (Lawrence and Day, 1997).

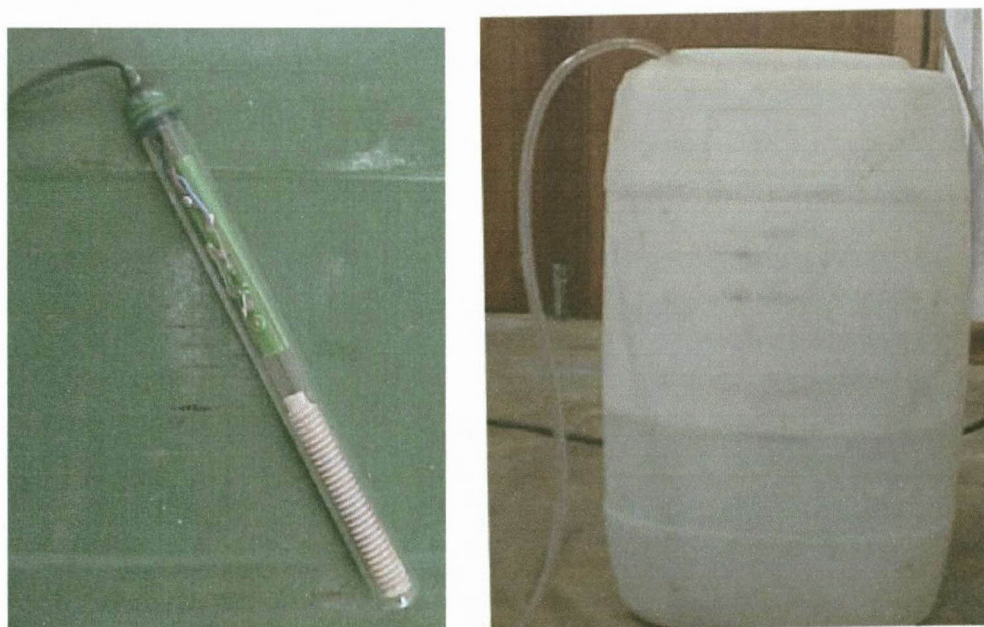


Figure 54: Modified humidifier components: A fish tank heater, left and a 20-litre drum with fish aerator and tubing, right.

5.3.2 Static test results for samples used in humidity cells

Table 13 shows the static ABA done on the samples used for kinetic testing. These samples were obtained from cored boreholes and the trenches dug in spoils at three different collieries. 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 as determined by ABA, would acidify in a cell.

Table 13. ABA results for samples used in kinetic tests (kg/t CaCO_3 where appropriate).

Cell	Initial pH	Final pH	AP (Open)	AP (Closed)	NP	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

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

5.3.2.1.1 INTRODUCTION

Seven rock samples, representing the initial samples used in the kinetic tests (See Section 5.3) were submitted to the University of the Free State's Geology Department, with the request that they be investigated mineralogically and chemically. X-ray fluorescence and X-ray diffraction testing was undertaken.

5.3.2.1.2 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 analysis. The powdered samples were analysed with a Siemens D-5000 X-ray diffractometer using monochromatic $\text{CuK}\alpha$ -radiation and the PC-PDF2 computer programme for mineral identification.

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

The results of the Major Element Analyses in wt % as determined from the XRF investigation are listed in Table 14, with trace elements given in Table 15.

Table 14. Results of XRF determination on samples for kinetic testing (weight %).

	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	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 15. 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

5.3.2.1.4 XRD RESULTS

5.3.2.1.4.1 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)

5.3.2.1.4.2 RESULTS

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

Sample SS1: 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 clinocllore and the mica muscovite. According to the mineralogical composition, the sample could be an impure feldspathic sandstone or quartzite.

Sample OS1: 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.

5.3.3 Repeatability

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 Figure 55 to Figure 58 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.

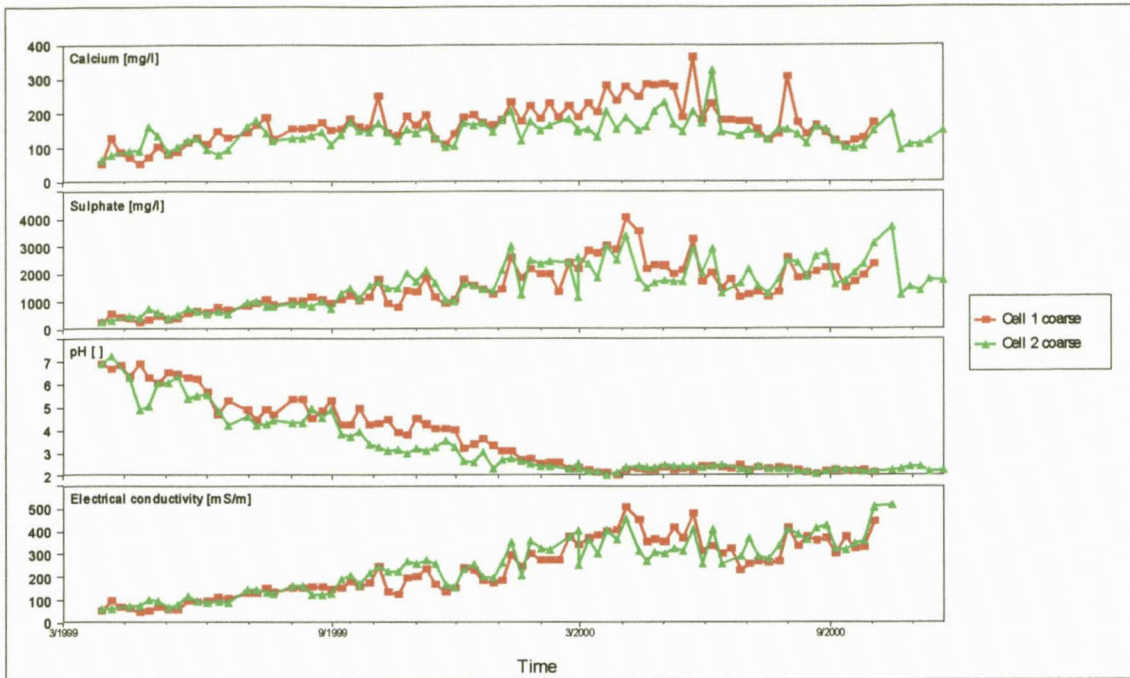


Figure 55: Repeatability.

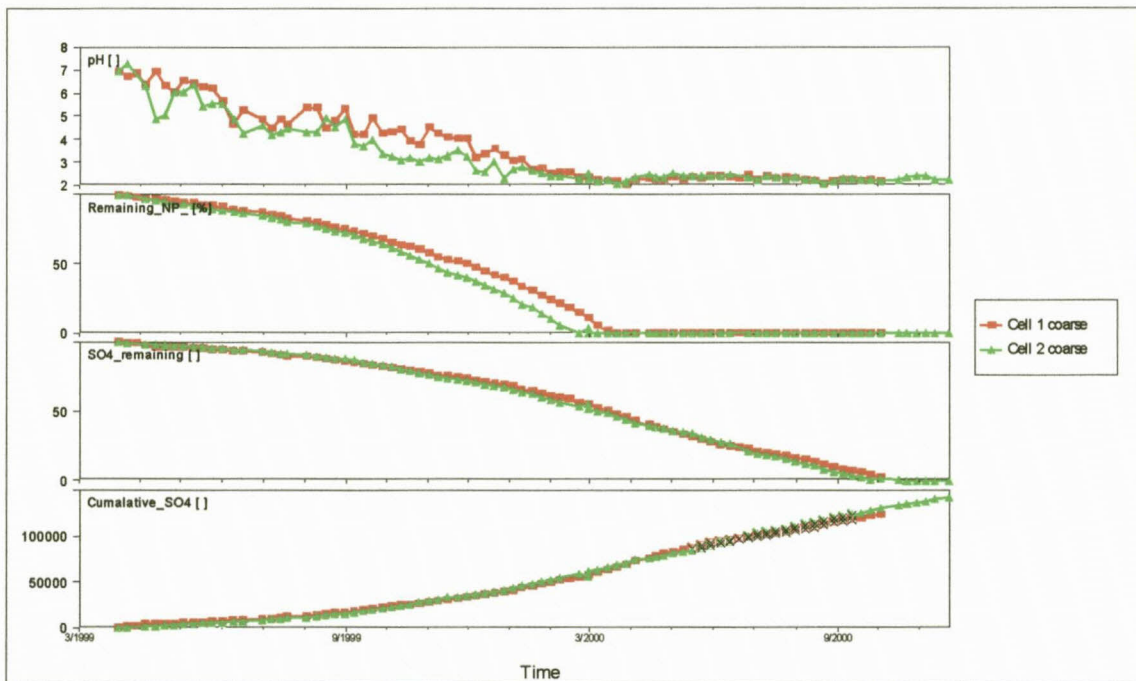


Figure 56: Comparison duplicate cells' cumulative sulphate production, remaining S and NP depletion.

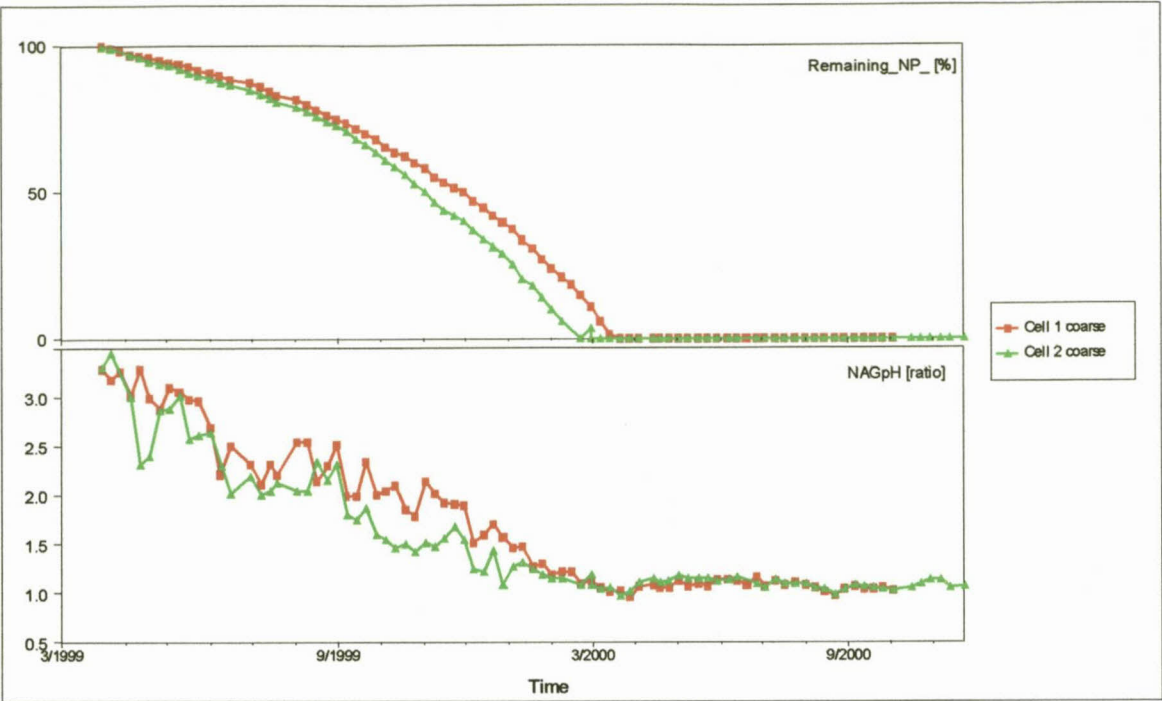


Figure 57: Comparison between ratio of NAG/final pH and outflow pH with time.

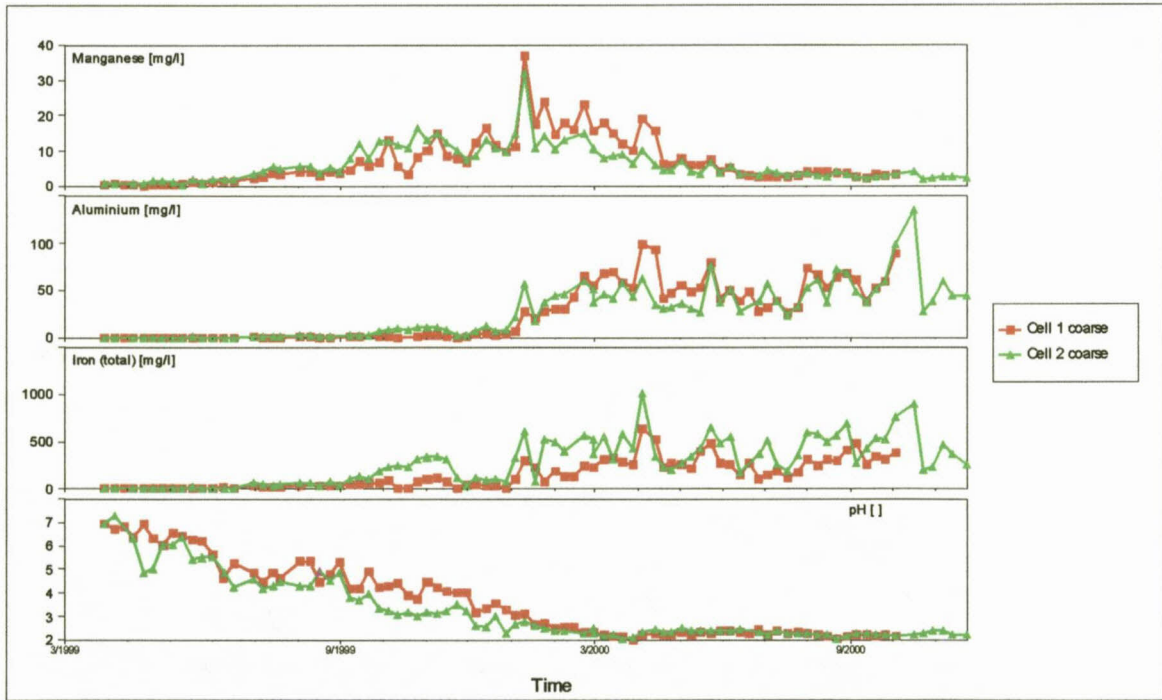


Figure 58: Duplicate cell's metal production rates compared to pH.

It is clear from the figures above that the 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.

5.3.4 Depletion of NP and pH observed

Figure 56 above shows the depletion of neutralisation capacity over time. The cumulative increase in sulphate and depletion of overall SO_4 capability are also indicated. The depletion shows that the cells have almost run to completion and have yielded most of the sulphates available from the pyrite generation.

Figure 57 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 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 final pH and the depletion of the neutralisation capability 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 58 and Figure 60 that it is at this point that 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 solubility curves, as shown in Figure 59 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 buffering phenomena.

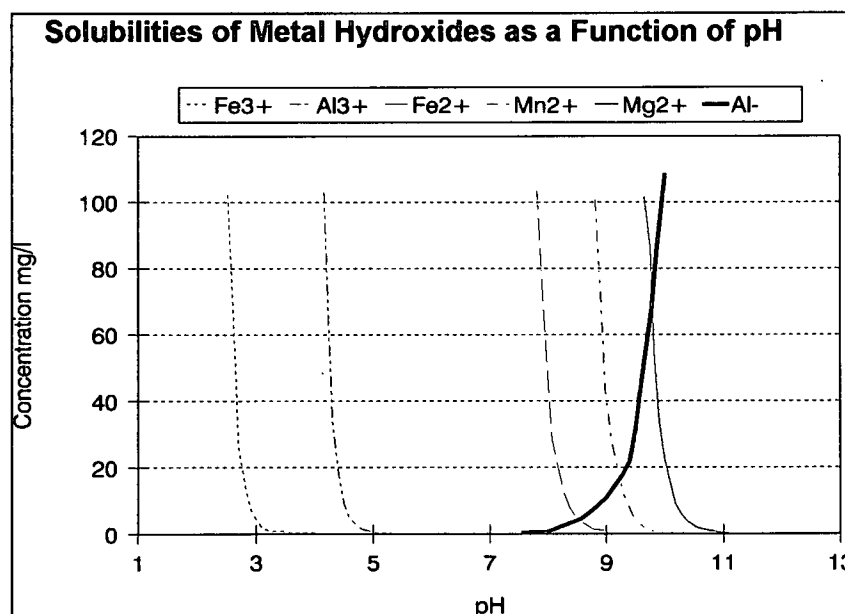


Figure 59: Solubility of selected metal hydroxides as a function of pH.

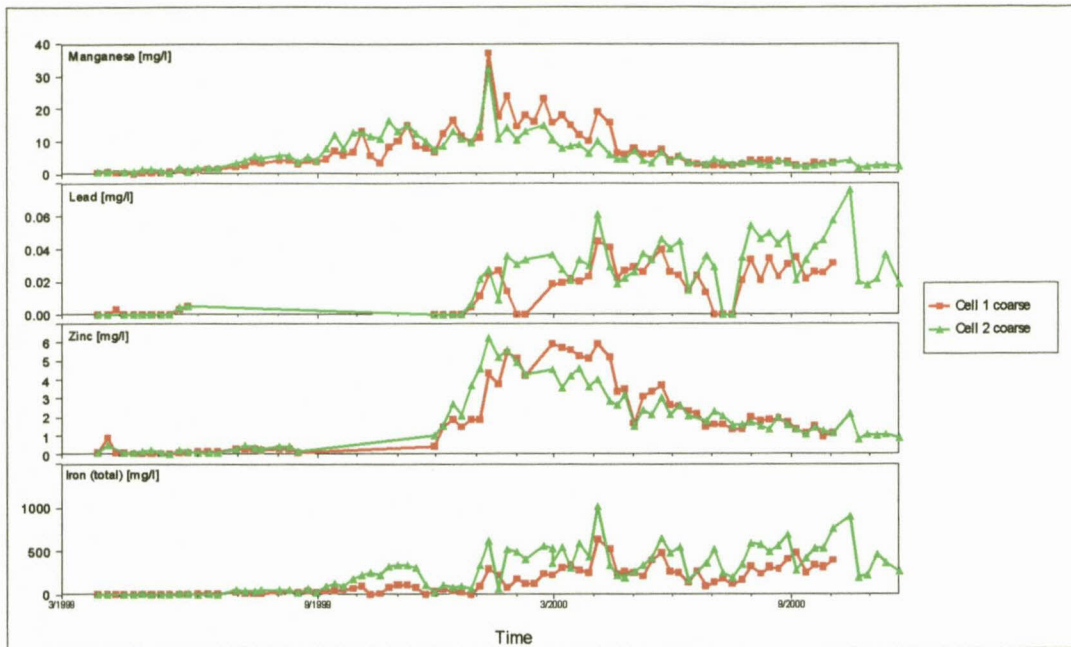


Figure 60: Correlation between iron concentration and that of other metals.

The correlation between iron and the other metals (Figure 60) indicates the metal solubilisation phenomenon via iron, as discussed in Chapter 2.

5.3.5 Reaction rates from humidity cells

Several authors have proposed the use of kinetic tests for investigating the most important controls on the rates of production. As part of this research 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 61 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 64. 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 (Morin and Hutt, 1997).

The depletion in NP as a result of more humid conditions is also clear. Over the period of testing, 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 slightly negative NNP determined by ABA, and lends credence to the ABA results.

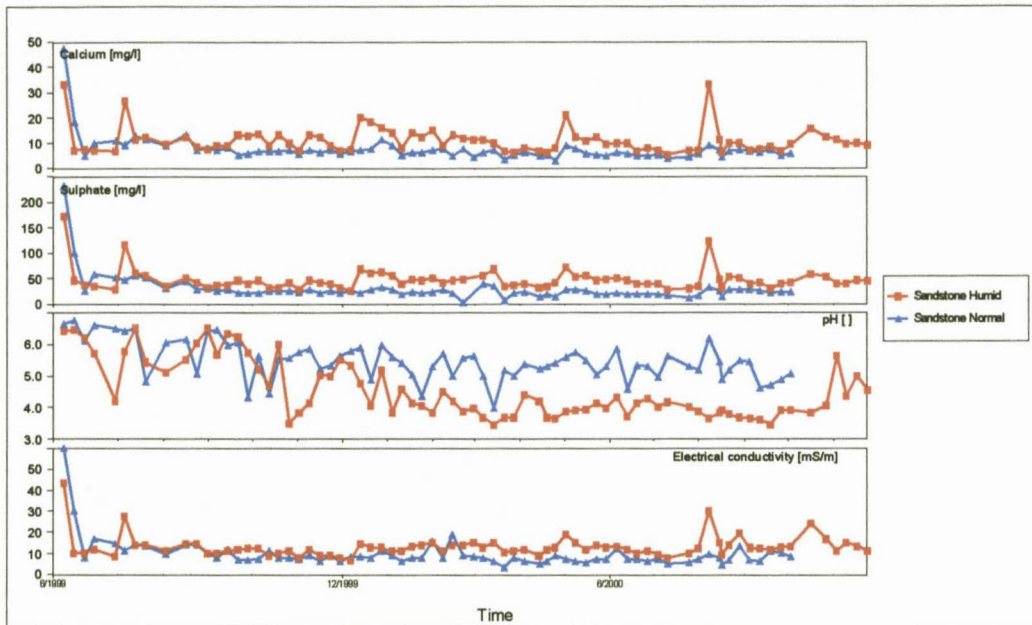


Figure 61: Comparison. Alternating dry vs. continuous humidified air.

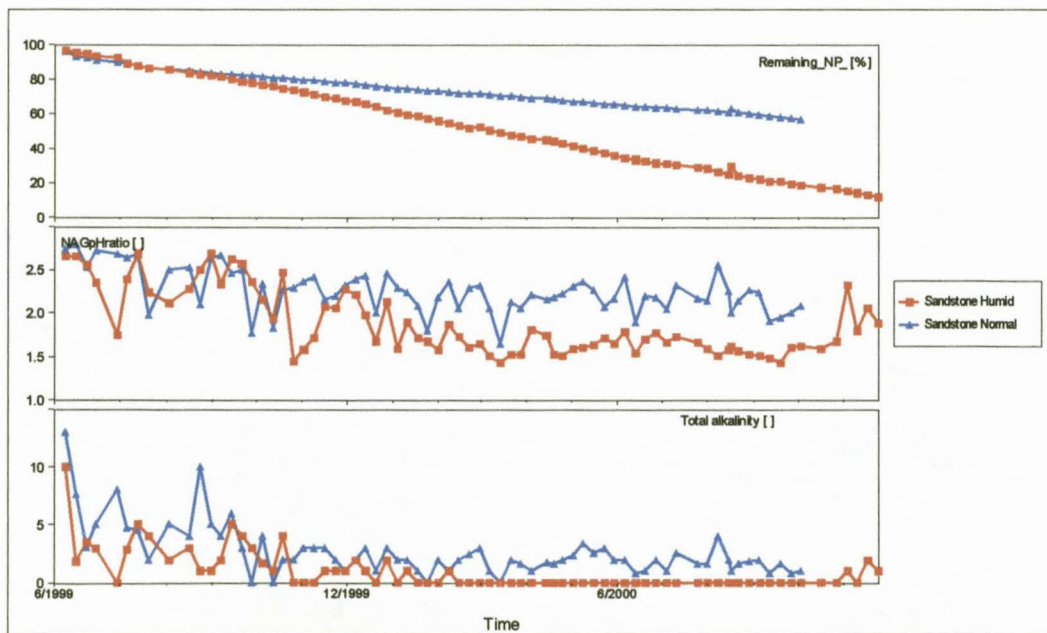


Figure 62: Comparing humid vs. normal cycles, showing more rapid depletion in NP and quicker acidification (sandstone).

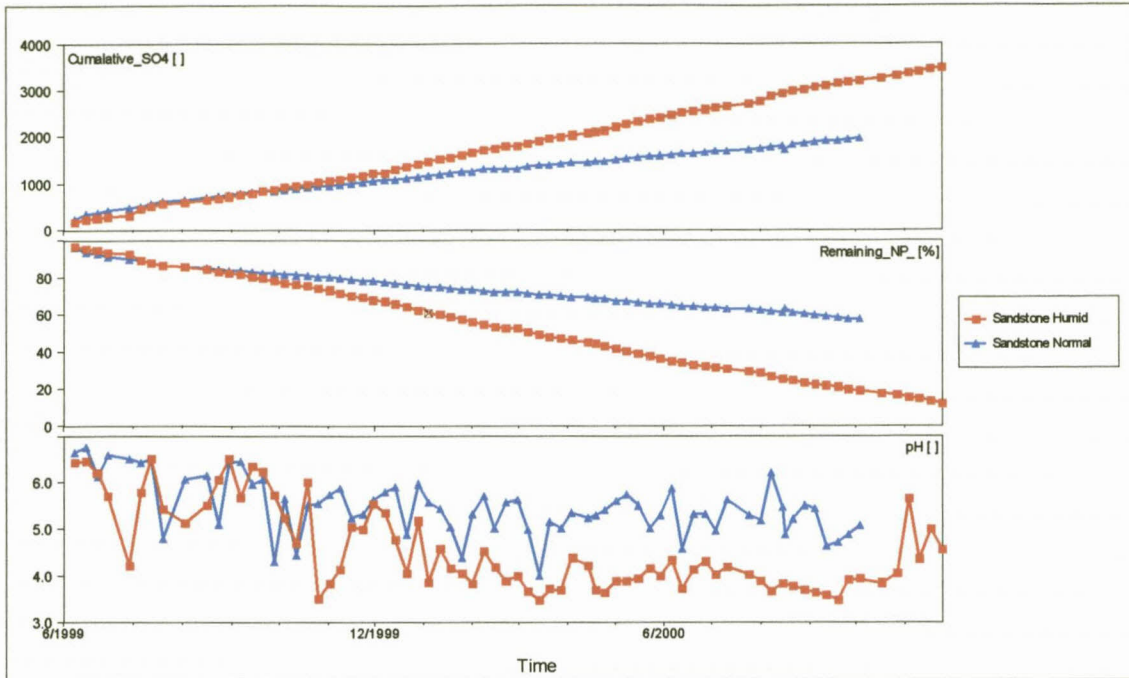


Figure 63: Comparing humid vs. normal cycles, showing higher SO_4 production, more rapid depletion in NP and quicker acidification.

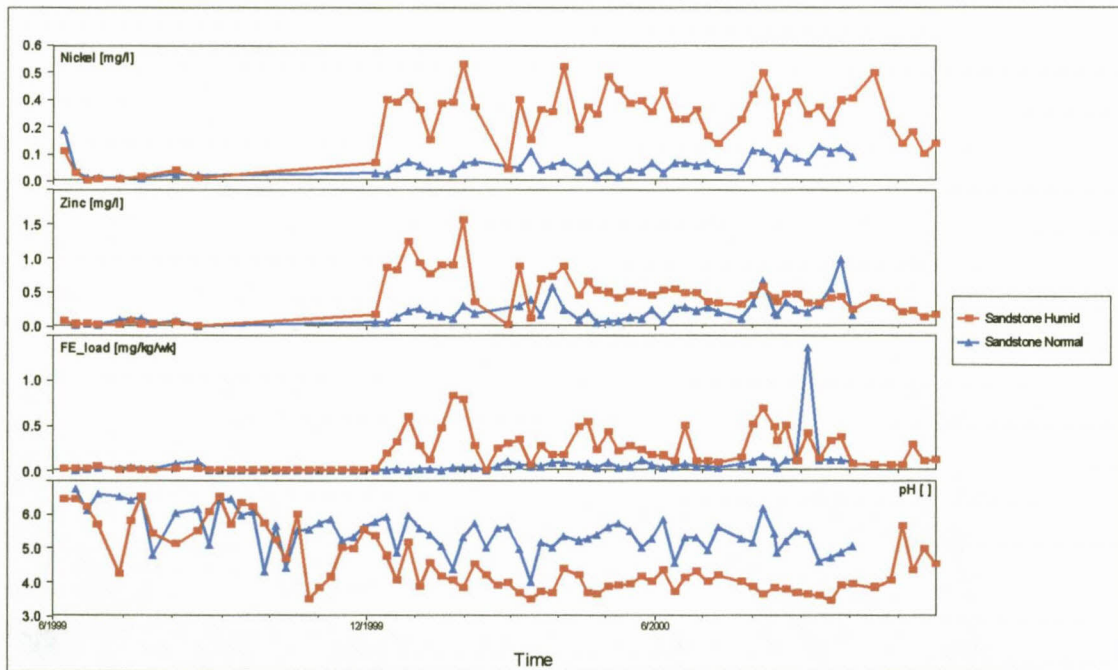


Figure 64: Comparison between metal loadings for humidified and normal cycles in sandstone.

Duplicate humidified and normal protocol testing was also done on shale samples (Figure 65 and Figure 66). 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 show 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; as can be seen from these four cells, this cannot be determined at the outset of the research.

The shale samples remain 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 13) 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 5.3.2.1) 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 (See Section 5.3.6).

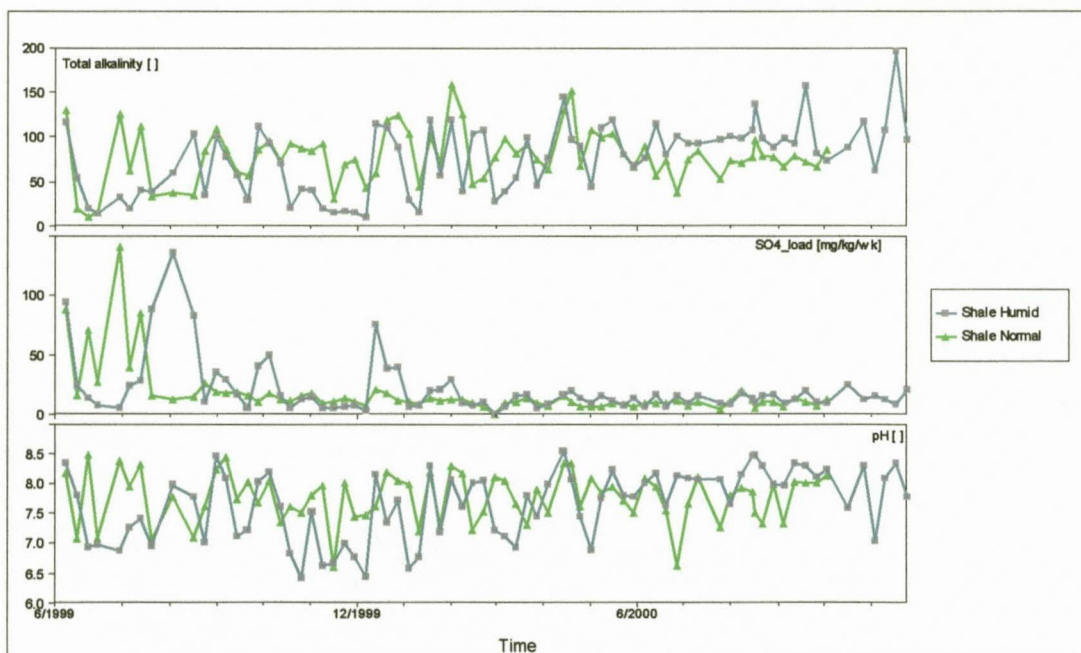


Figure 65: Comparison of the two protocols for the shale sample.

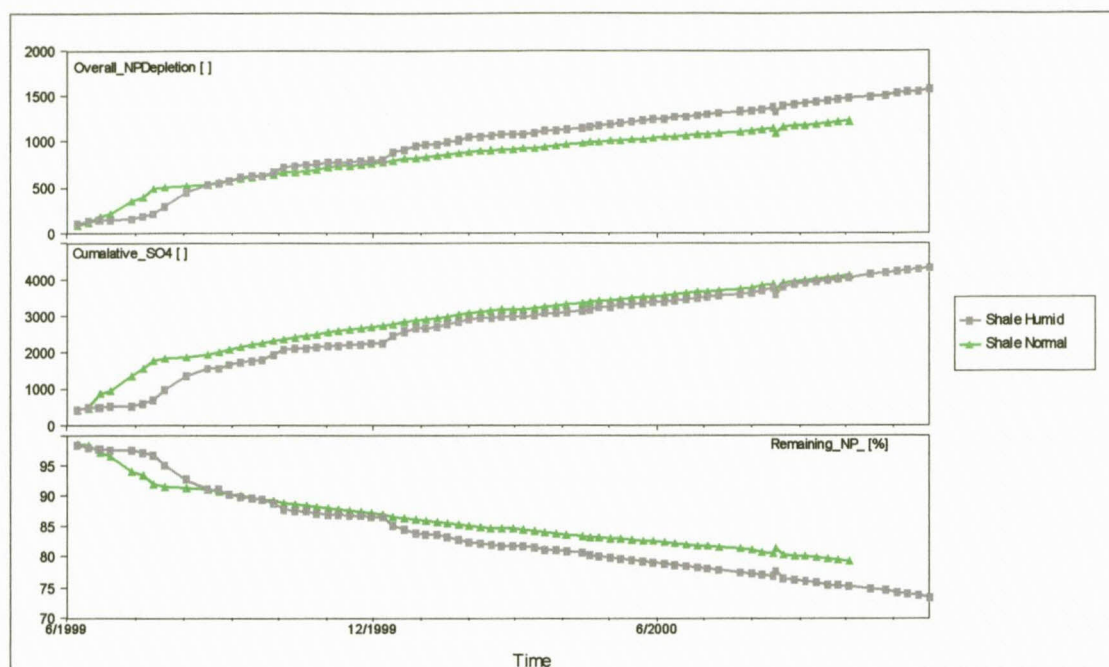


Figure 66: Comparison of the two protocols for the shale sample, showing very slightly higher leaching for the humid protocol.

5.3.6 Flushing of secondary products

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 use to indicate any mineralogical control on the observed outflow chemistry. For this shale sample, it was clear that the trace amounts of calcite/dolomite were sufficient to buffer the system under the influence of open system carbon dioxide. Figure 67 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 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 68 for all the cells and Figure 69 for the cells that produced the most sulphate. In the field flushing rates are lower and gypsum precipitation is a likely control on observed water quality. 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 for iron species

due to the slow kinetics of formation, as reported by Williams and Smith (2000), or due to true supersaturation.

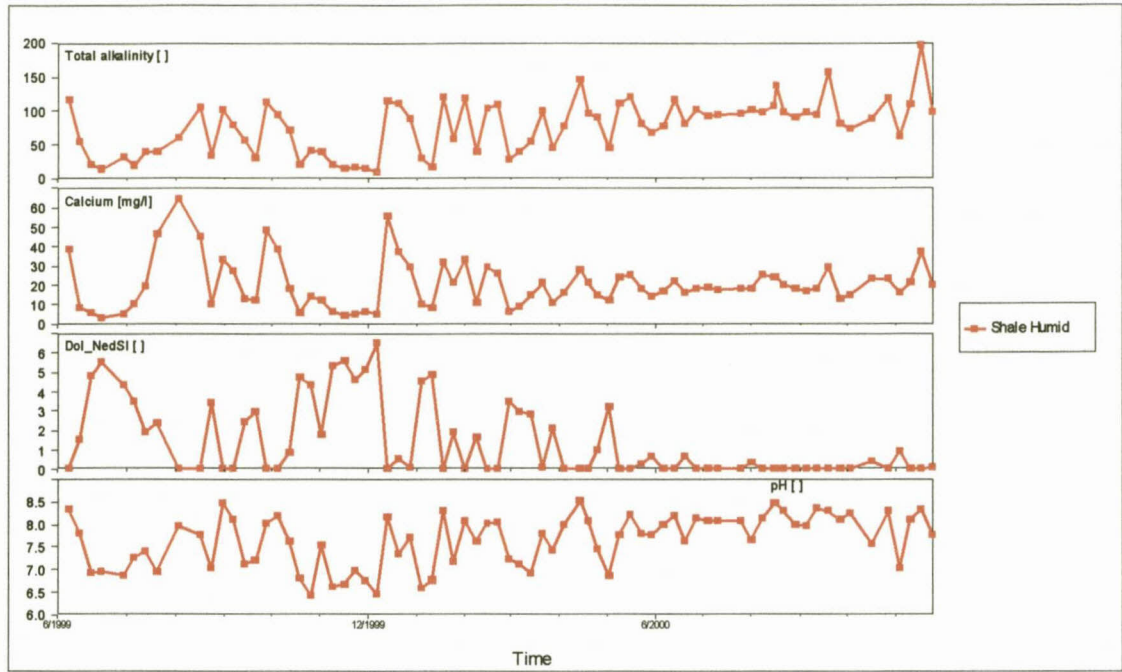


Figure 67: Comparison of observed pH, alkalinity, calcium and the saturation index of dolomite.

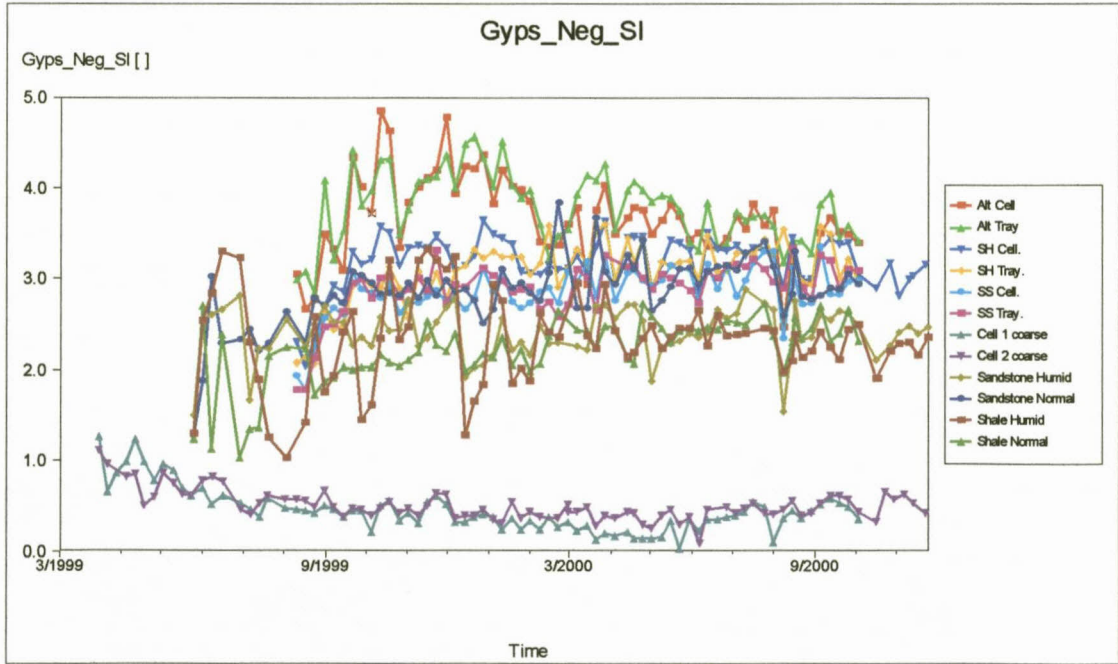


Figure 68: Gypsum saturation for all cells.

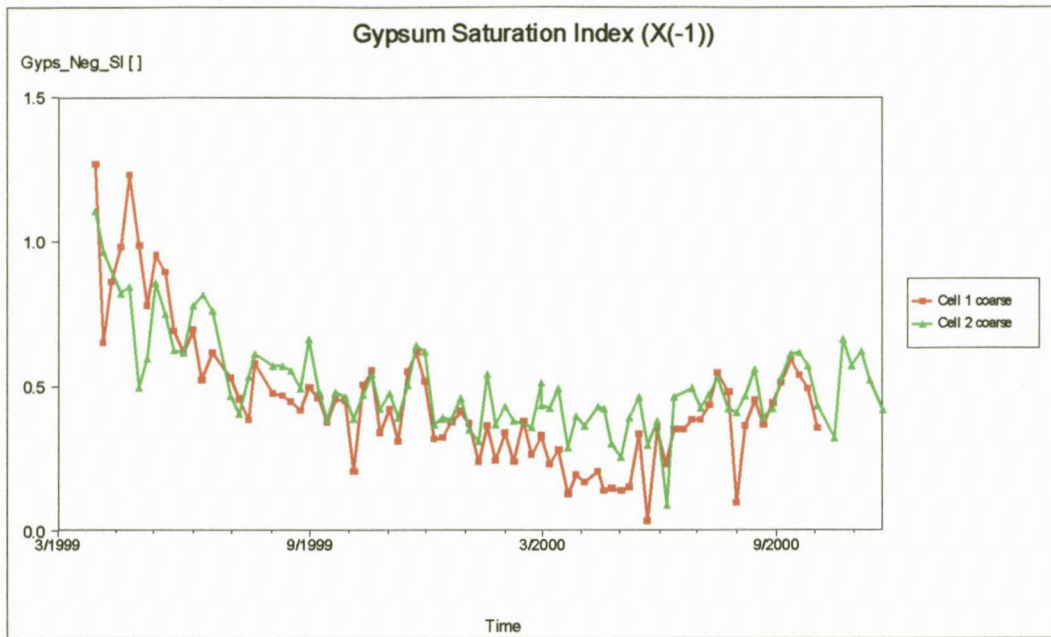


Figure 69: Gypsum saturation for cells 1 and 2, showing that saturation is approached but never reached.

5.3.7 Humidity cells compared to aerated trays

As part of the research, the use of aerated trays was also investigated (Figure 70). In these trays, duplicate samples for certain humidity cells were 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 70: 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 were 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 of sample material 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 deionised 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 (Figure 71 to Figure 74.) There is thus the potential of using this methodology, which is less capital- and labour-intensive, to obtain equivalent results to those obtained by more conventional humidity cell methods. The results from the cells are also in line with the ABA done on these samples.

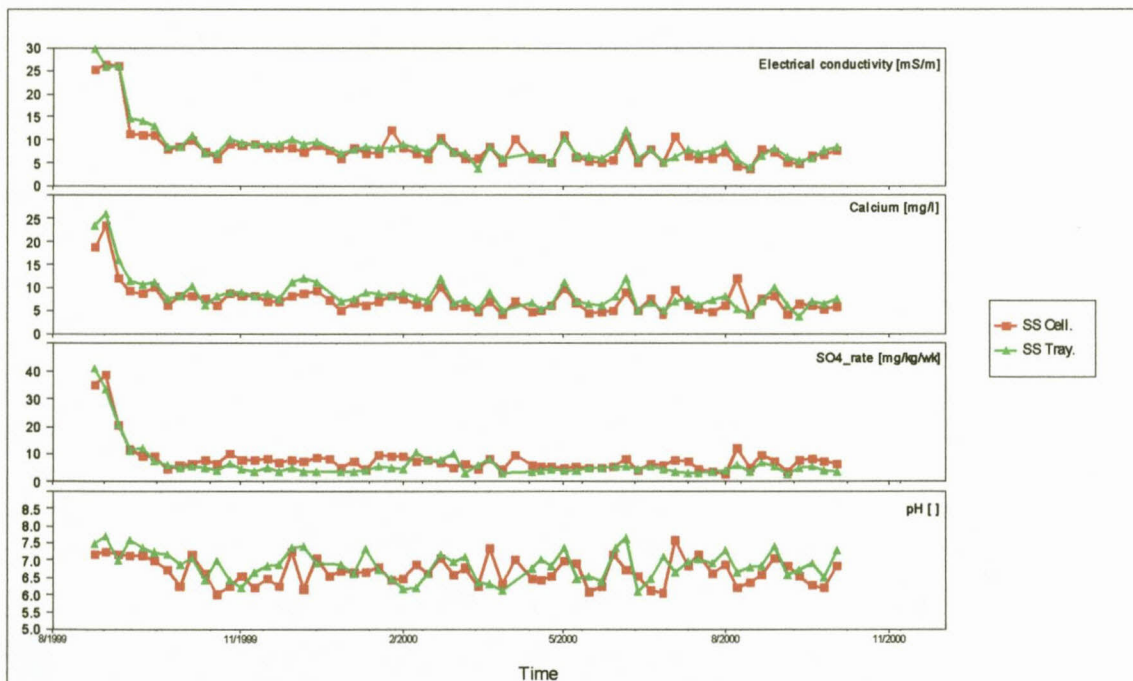


Figure 71: Comparison: Humidity cell vs. aerated tray for major constituents (sandstone.)

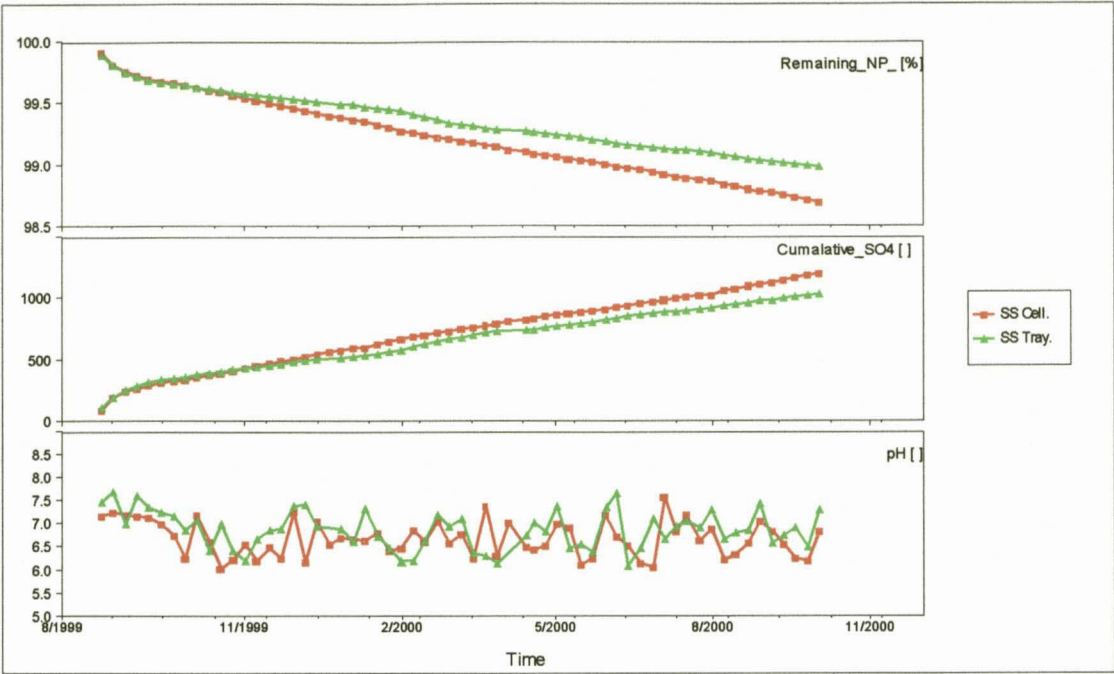


Figure 72: Humidity cell vs. aerated tray for sulphate produced and remaining NP vs. pH (sandstone).

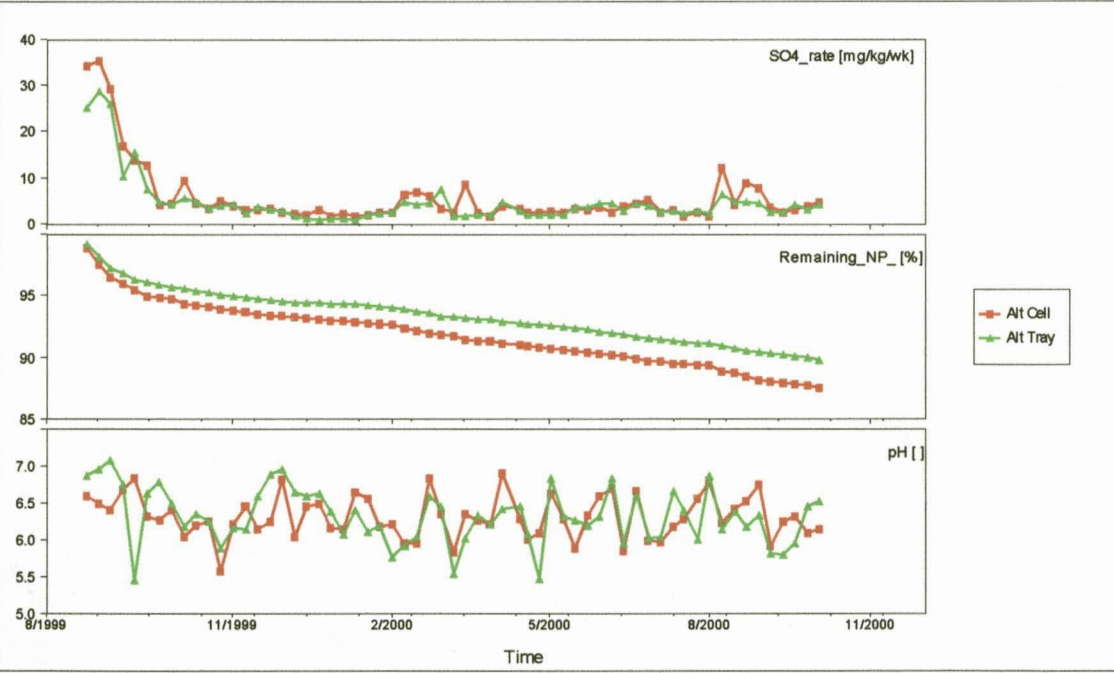


Figure 73: Comparison: Humidity cell vs. aerated tray (Alternating sandstone/shale cell).

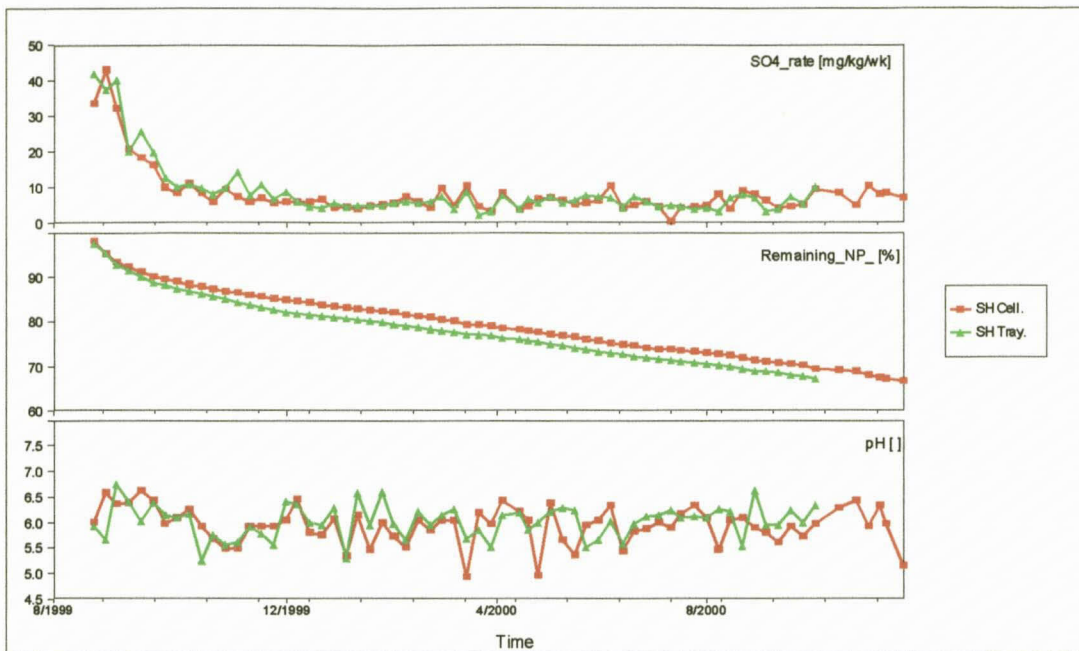


Figure 74: Comparison: Humidity cell vs. aerated tray for major constituents (shale cell).

5.3.8 Testing period

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 fewer are sufficient.
- At high SO_4 production rates, 36 may be too few.

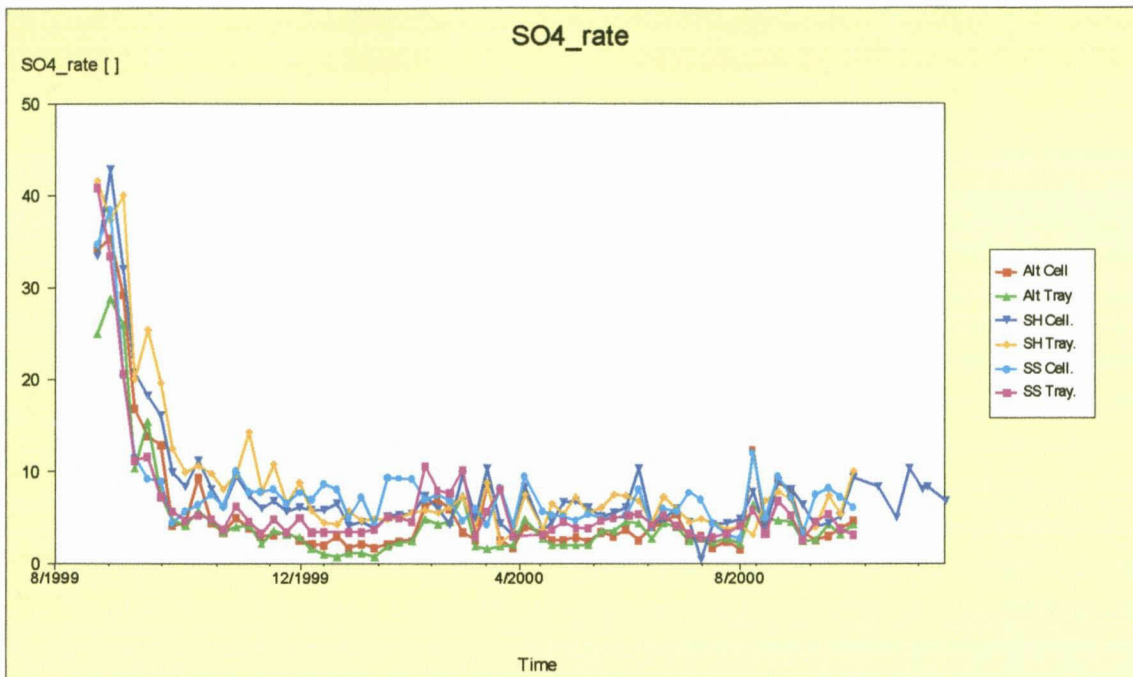


Figure 75: Sulphate production rate for all the core samples tested for conventional and aerated trays.

The figures that follow (Figure 76 to Figure 77) show the sulphate production rates for various cells under normal and humid protocols. 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, according to 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 flushing out 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.

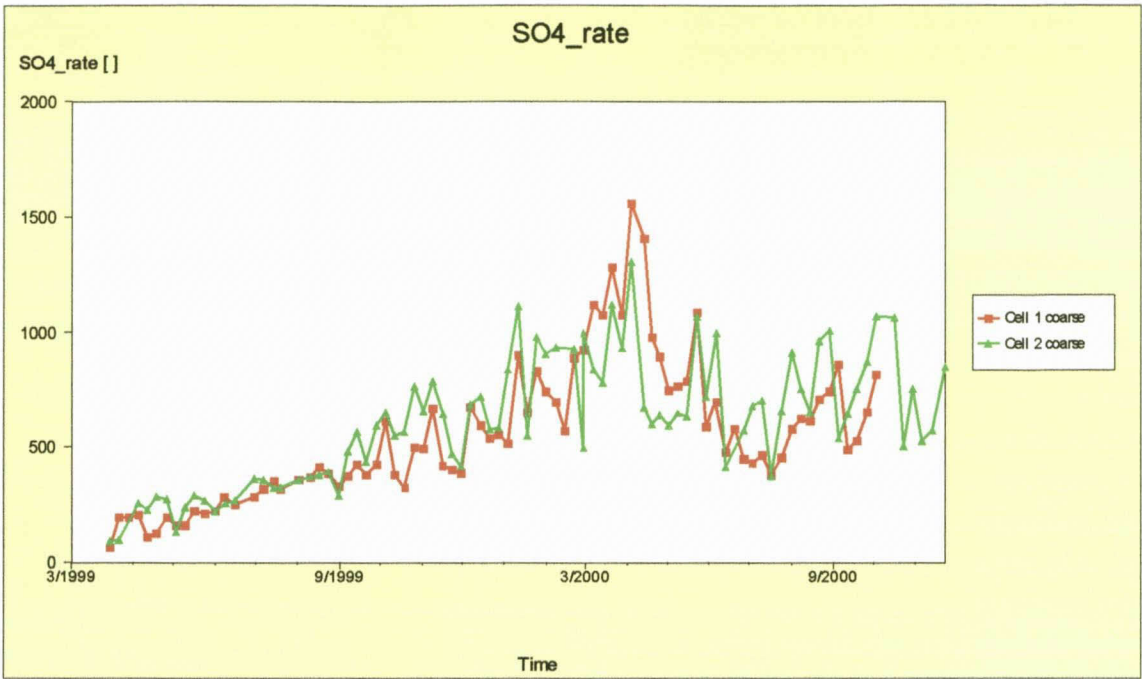


Figure 76: Sulphate production rate for the shale samples.

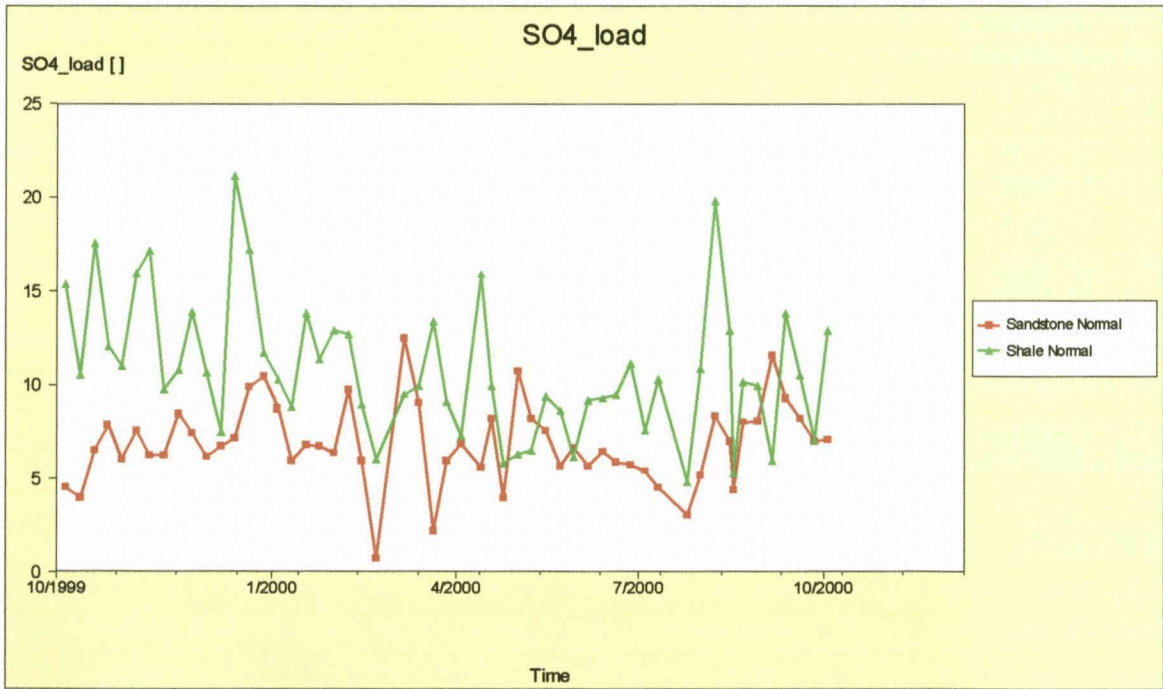


Figure 77: Sulphate production rate for the conventional humidity cells in the humid vs. normal test.

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. This is consistent with their higher reactive sulphide content as determined by ABA.

5.3.9 Raw samples tested by different methods

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 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 at the 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 16 gives the ABA results from these samples.

Table 16. 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



Figure 78: Incubator used for trays.

The results from the kinetic tests are given in the Figure 79 to Figure 84.

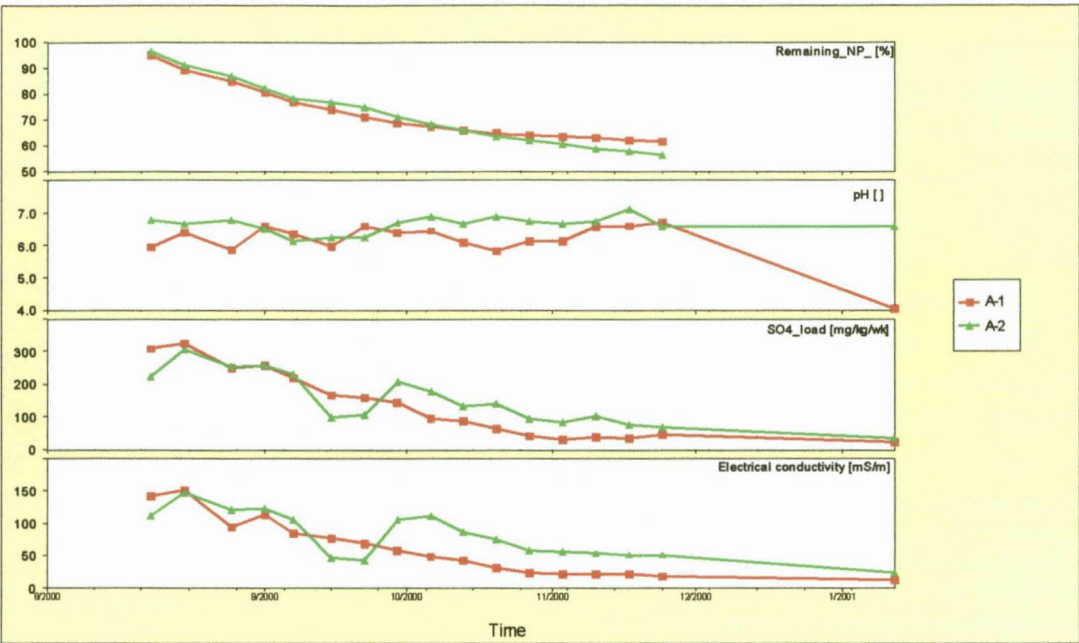


Figure 79: Results from spoil sample A, from the different methodologies.

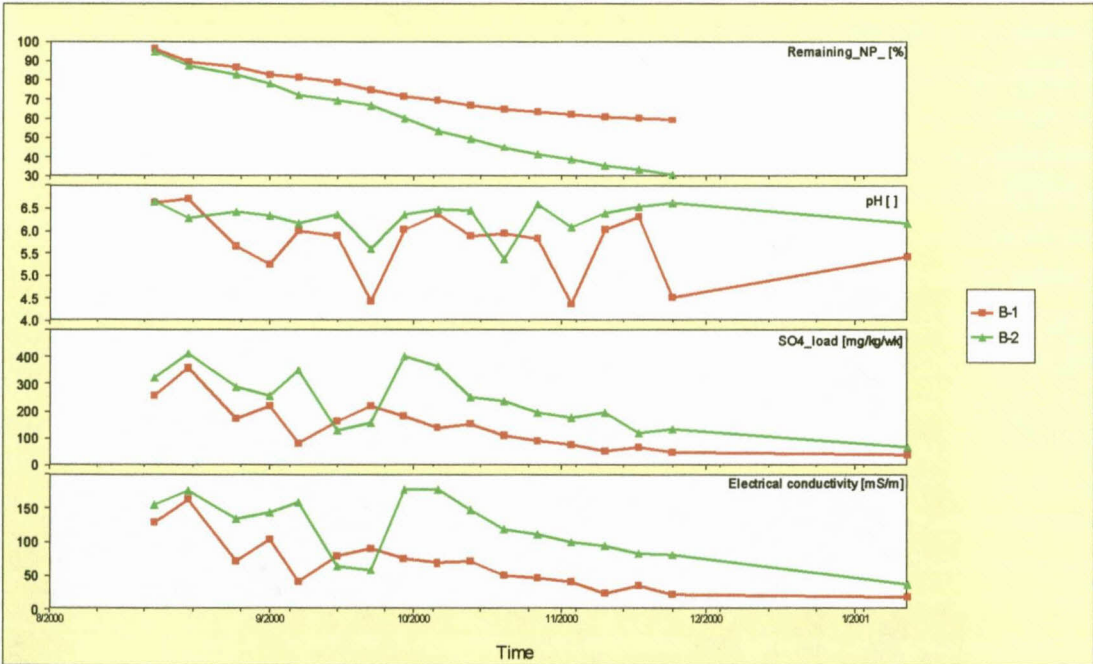


Figure 80: Results from spoil sample B, from the different methodologies.

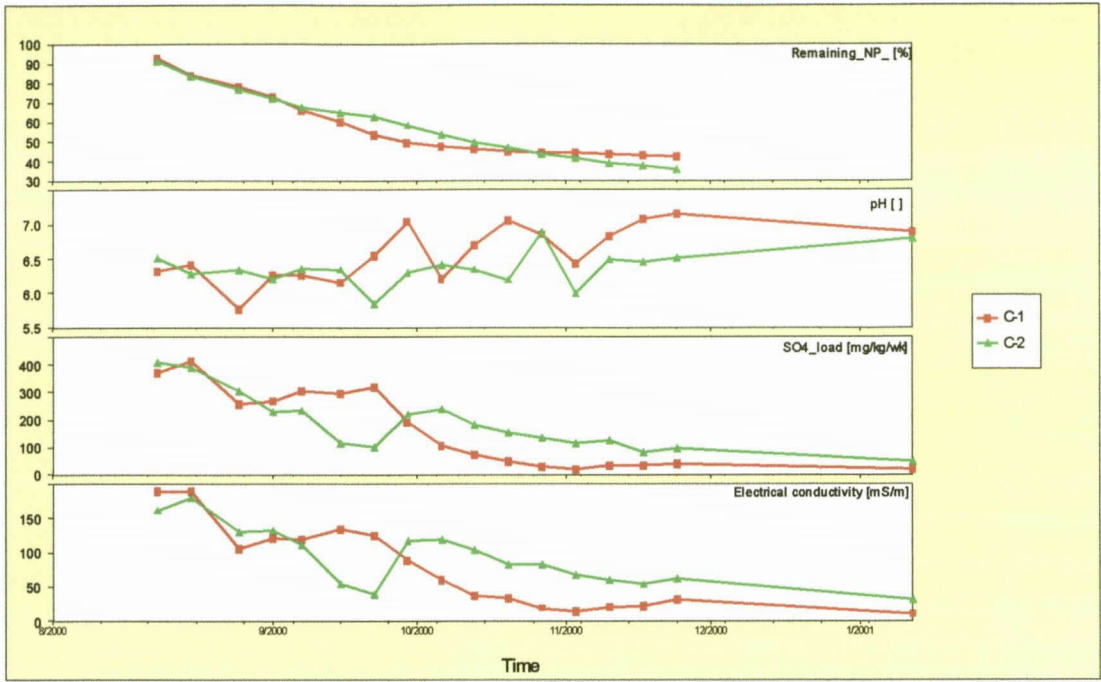


Figure 81: Results from spoil sample C, from the different methodologies.

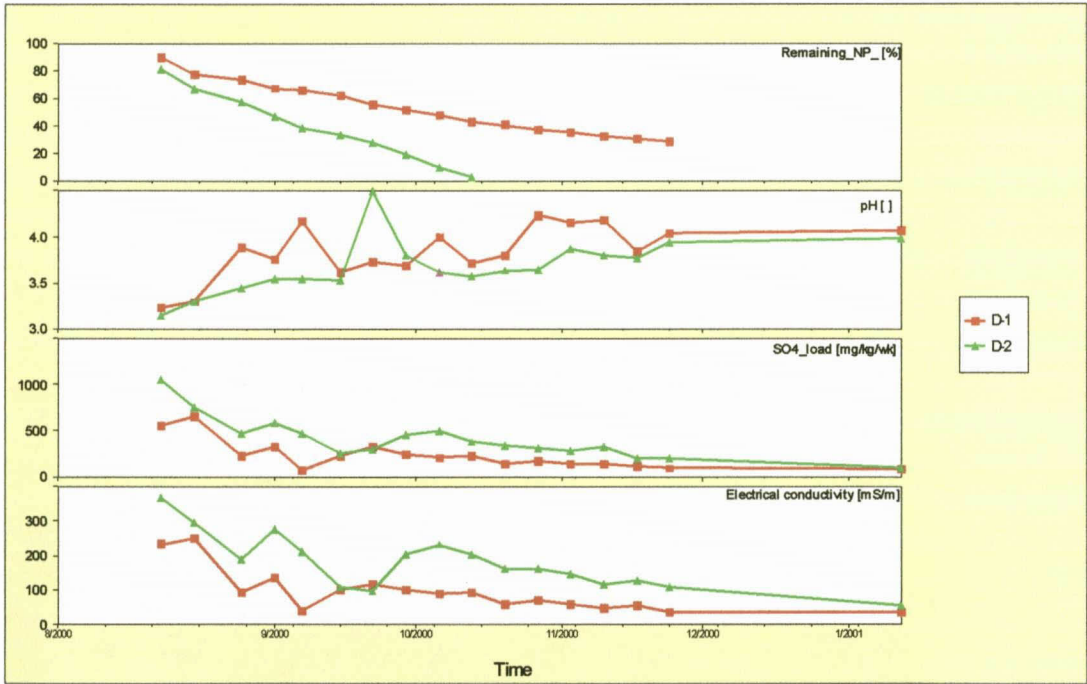


Figure 82: Results from spoil sample D, from the different methodologies.

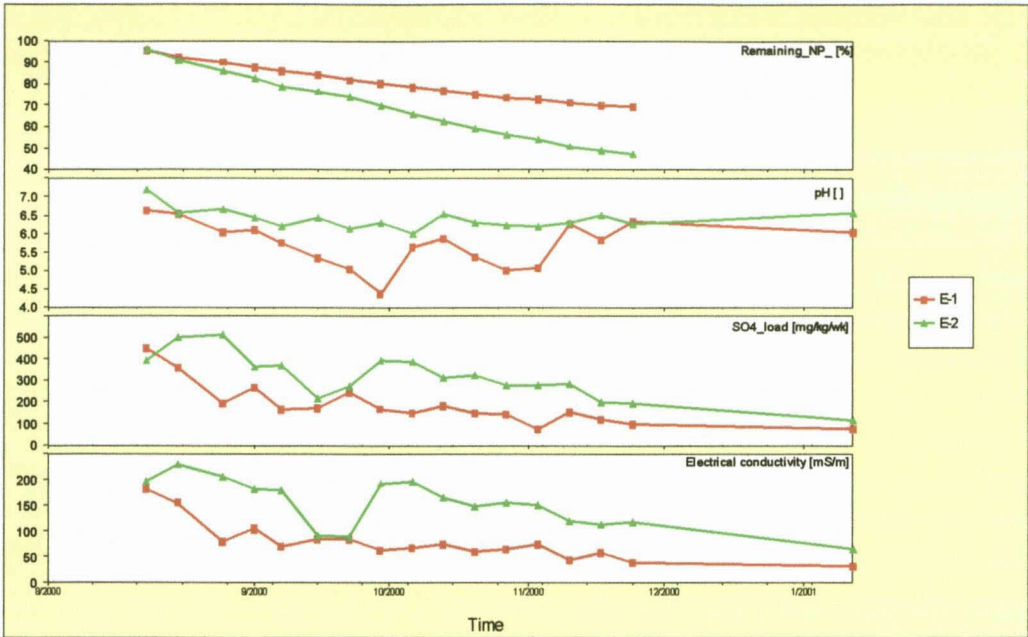


Figure 83: Results from spoil sample E, from the different methodologies.

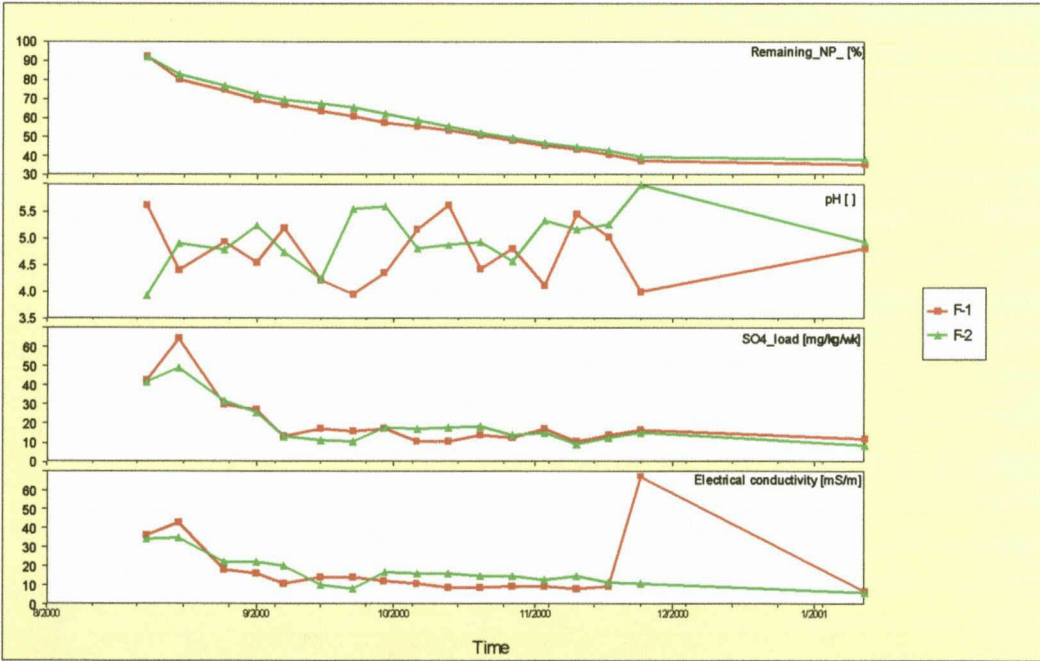


Figure 84: Results from spoil sample F, from the different methodologies.

The 12 sets of results show that the standard methodology and the modified methodology using the trays give comparable results. In F the single high EC value is a likely anomaly, which is unlikely to be a realistic portrayal. 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 evident acidification 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), 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.

5.3.10 Observations from the International Kinetic Database

The International Kinetic Database (IKD) (MDAG, 2000) was consulted to identify trends observed in humidity cells operated worldwide. Morin and Hutt (1999 and 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 derived from 64 mines and 475 cells.

Figure 85 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 field. 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. The Intrinsic Oxidation Rate (Ritchie, 2000) may limit higher values of sulphate, while without full analyses the secondary mineral controls eg gypsum solubility can not be evaluated. In the IKD, only the overall surface area is provided. It is therefore also possible that the fine fractions in each cell are providing the necessary reactivity in the testing period, and that most of the cells have only been run for the 20-week minimum as prescribed the ASTM methodology.

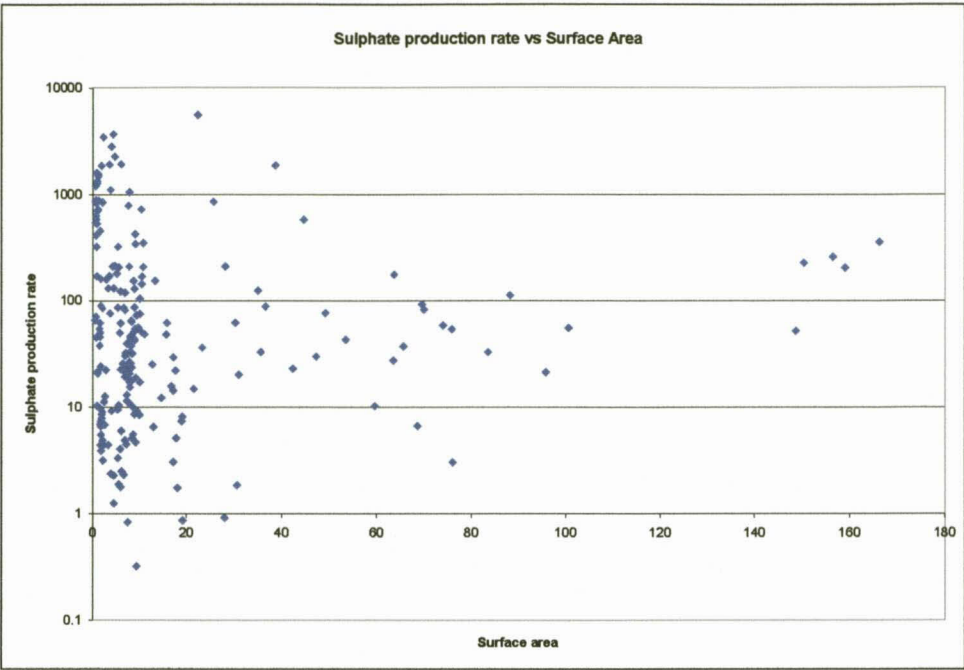


Figure 85: Surface areas vs. sulphate production rate (IKD, 2000).

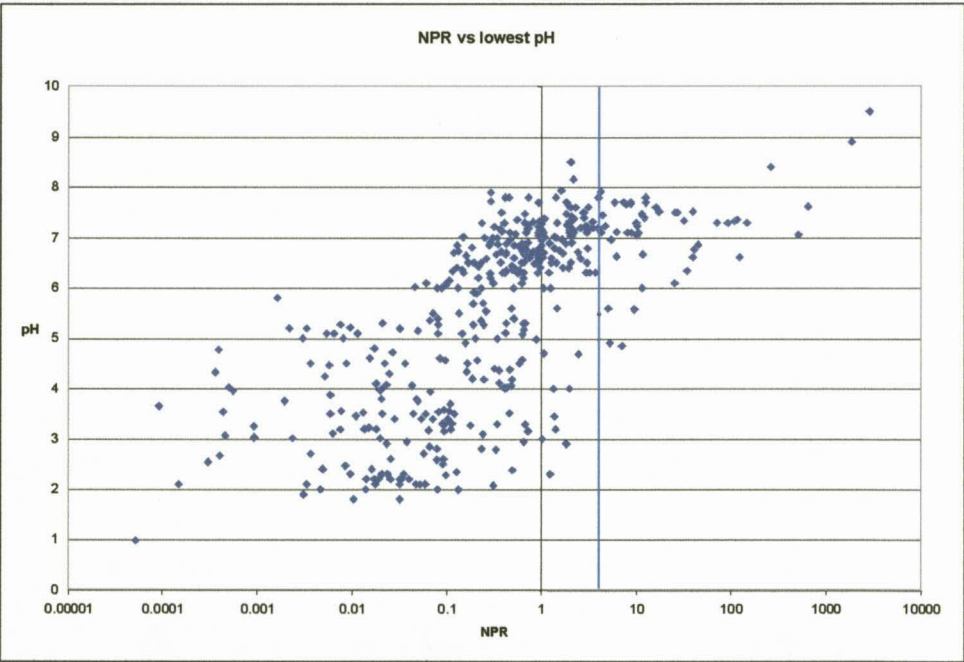


Figure 86: NNP vs. lowest pH (IKD, 2000).

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 86) 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 87 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, 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.

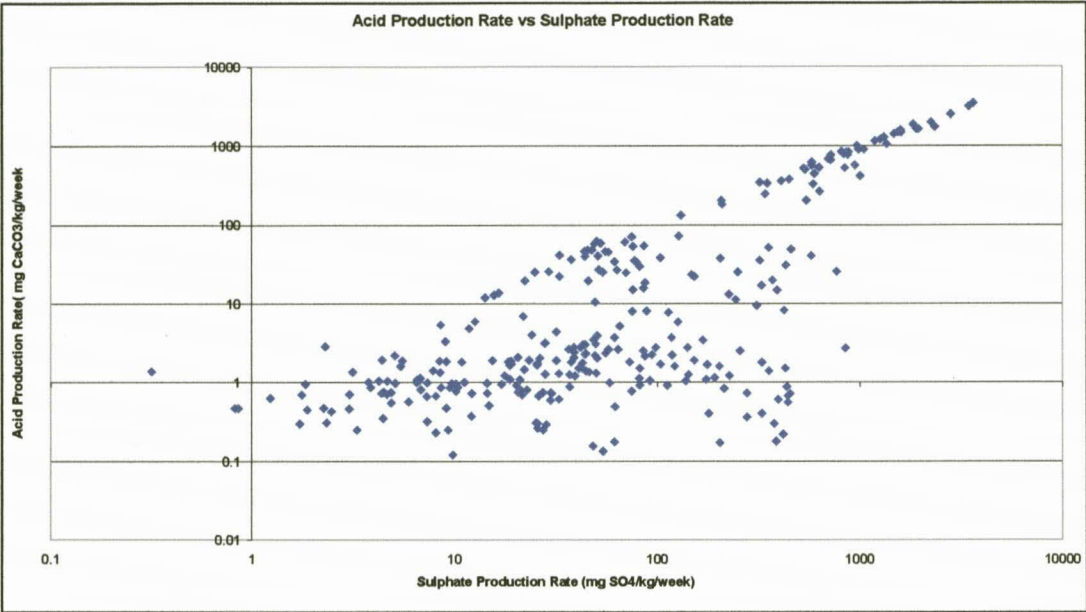


Figure 87: Acid production rate vs. sulphate production rate (IKD, 2000).

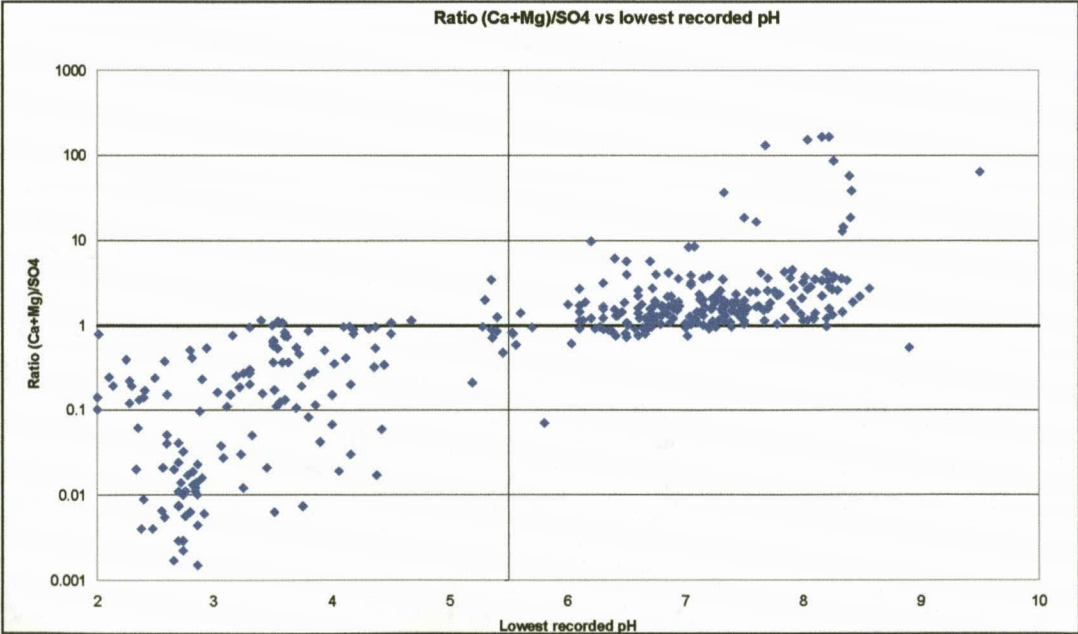


Figure 88: "Base cation/acid anion ratios" vs. lowest pH (IKD, 2000).

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 88). In most cases, once the sulphate concentration exceeds the concentration of these two cations, the pH drops. This has important implications for the interpretation of observed values at mines, and can possibly act as an early warning mechanism.

This ratio was also used in the evaluation of the kinetic tests done as part of this thesis. The depletion of this ratio in the cells that acidified over the testing period indicates that the ratio could be a very useful indicator to predict the onset of acidification (Figure 89).

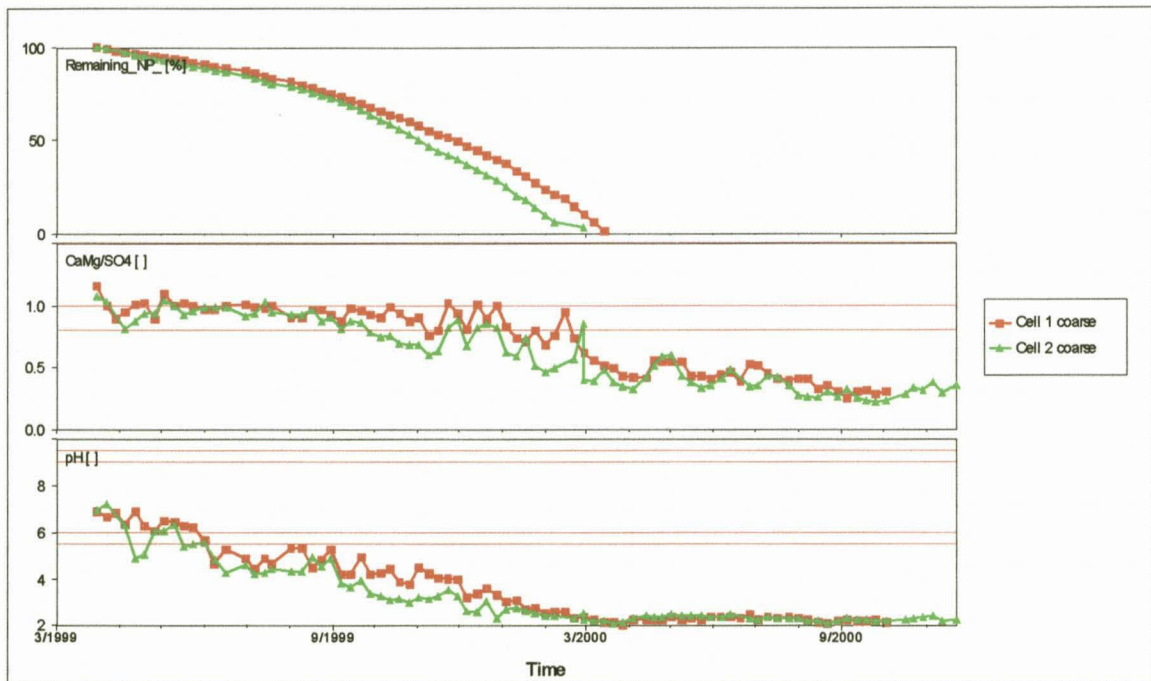


Figure 89: Comparison of "Base cation/acid anion ratio" vs. pH and Remaining Neutralising Potential on humidity cell.

A defunct mine where acidification has already occurred was used to further explore this phenomenon. There was again a good correlation between the low pH and the depleted calcium + magnesium against sulphate ratio. Figure 90 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 the ratio as a monitoring and evaluation tool.

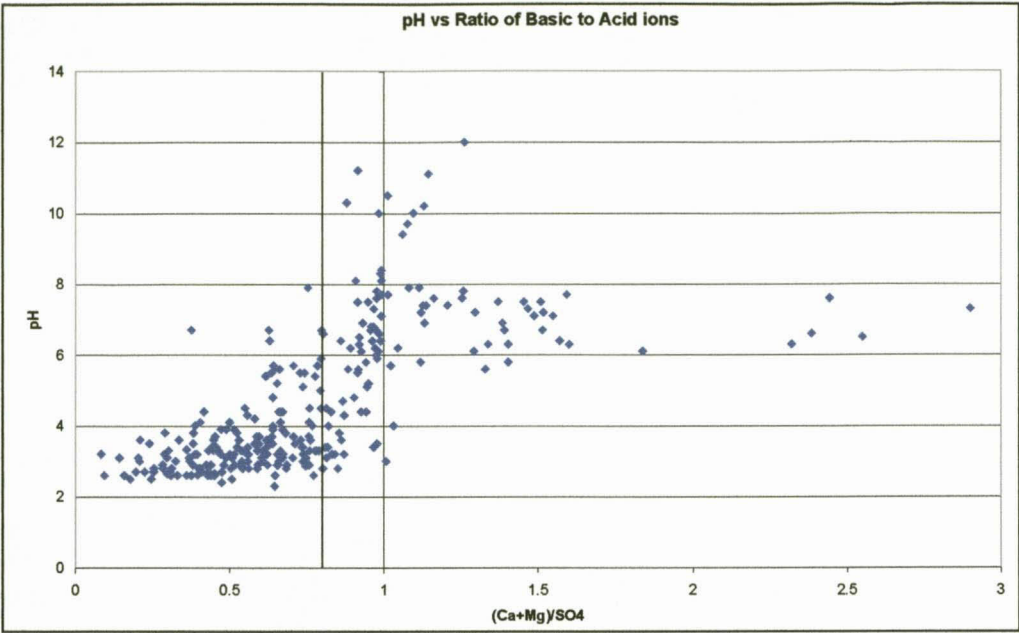


Figure 90: Comparison of "Base cation/acid anion ratio" vs. pH at defunct coalmine.

The figure below (Figure 91) 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.

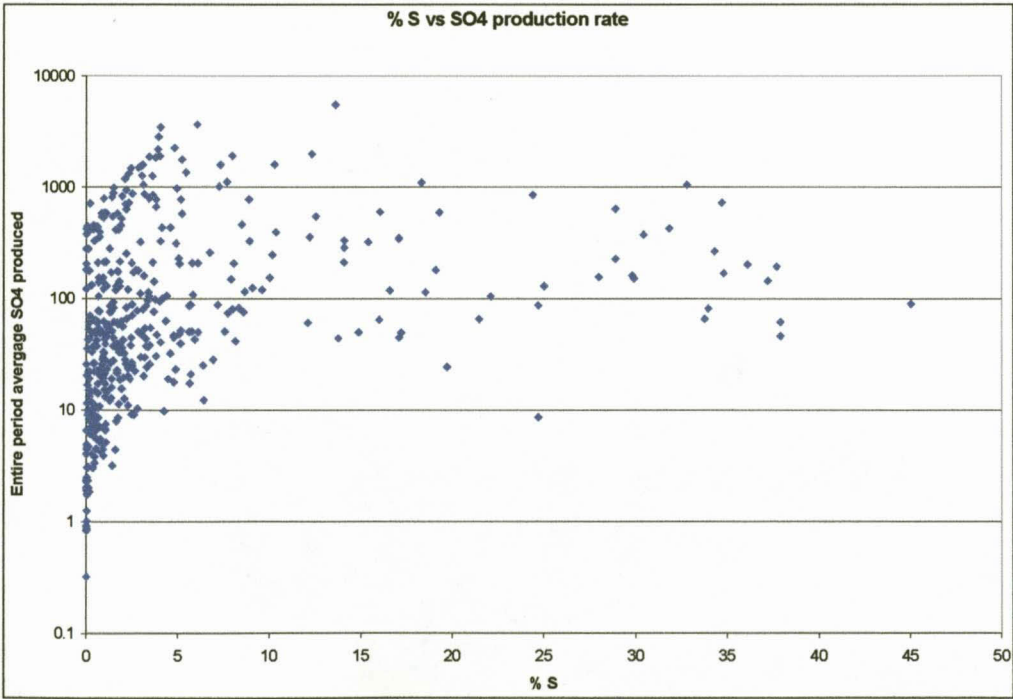


Figure 91: % S vs. SO₄ production rate (IKD, 2000).

There appears to be a very poor correlation between the total sulphide and lowest recorded pH (Figure 92).

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 that 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 for a brief phase in the cells' hydrochemical evolution.

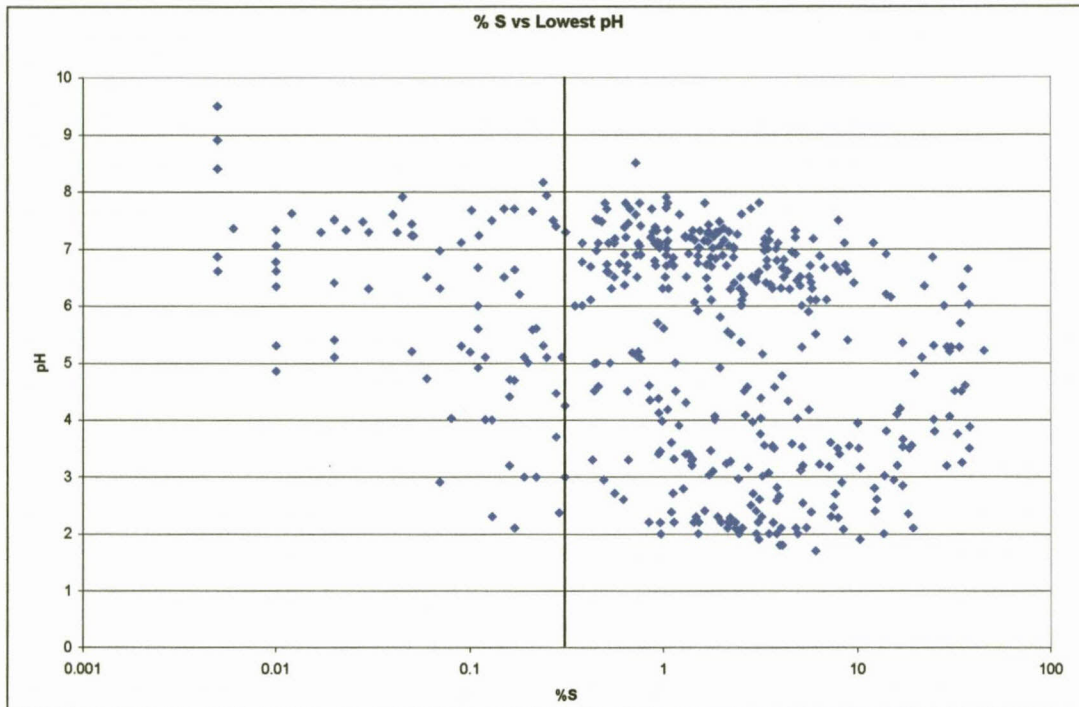


Figure 92: % S vs. lowest recorded pH (IKD, 2000).

5.4 CONCLUSIONS

Humidity cells are excellent kinetic tests to 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:

- 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.

- 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.
- 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.
- 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.
- 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 a volumetric ratio of 1:1 and preferably 0.5 L water to 1 kg sample.
- 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.
- Samples should not be agitated excessively once the test is underway. Test protocols that 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).
- 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.
- 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)).
- 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 thesis it is recommended that humidity cells should be used as the method of choice for laboratory kinetic tests.

The standard methodology should be as follows:

- Use 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.
- Use appropriate methods to maintain the temperature of these tests at 30°C.
- Leach with deionised water, collect and analyse for pH, sulphate, alkalinity and the parameters of choice (with Fe, Mg and Ca as minimum).
- Pass air through on a cyclic dry/humidified cycle for three days each.
- Leach with deionised water on the seventh day, using flushing volumes equal to half of the test sample, collect leachate and analyse.
- 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 (Appendix 5).

This thesis and other investigations, 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 therefore, the standard humidity cell method should be used as far as possible and where deviating from this, duplicate standard methods should be used for purposes of evaluation.

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

1. practical to construct and operate.
2. of reasonable time and cost requirements to encourage widespread acceptance and use.
3. representative of the physical, chemical and biological conditions in the mining environment (i.e. in conformance with the preceding 8 principles).
4. 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) on standardisation of the methodology are briefly discussed. These authors feel that two major advantages of developing standard kinetic procedures are that almost everyone, especially for mine permitting purposes, would use 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:

- The upscale 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 considered important within a complete prediction program such as contained in the ABATE strategy since:
 - They provide rates of production under test conditions.
 - They provide expected reaction sequences.
 - 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.

6 FIELD METHODS TO SUPPORT HYDROCHEMICAL PREDICTION

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

The most important field methods suggested are the following:

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

6.1 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 t of material used in ABA can be compared with the testing of 1 apple for a 300 ha orchard (Tarantino and Shaffer, 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 Samples

- 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 93, examples of cores from exploration boreholes and random sampling respectively can be seen.



Figure 93: 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 (Figure 94) 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):

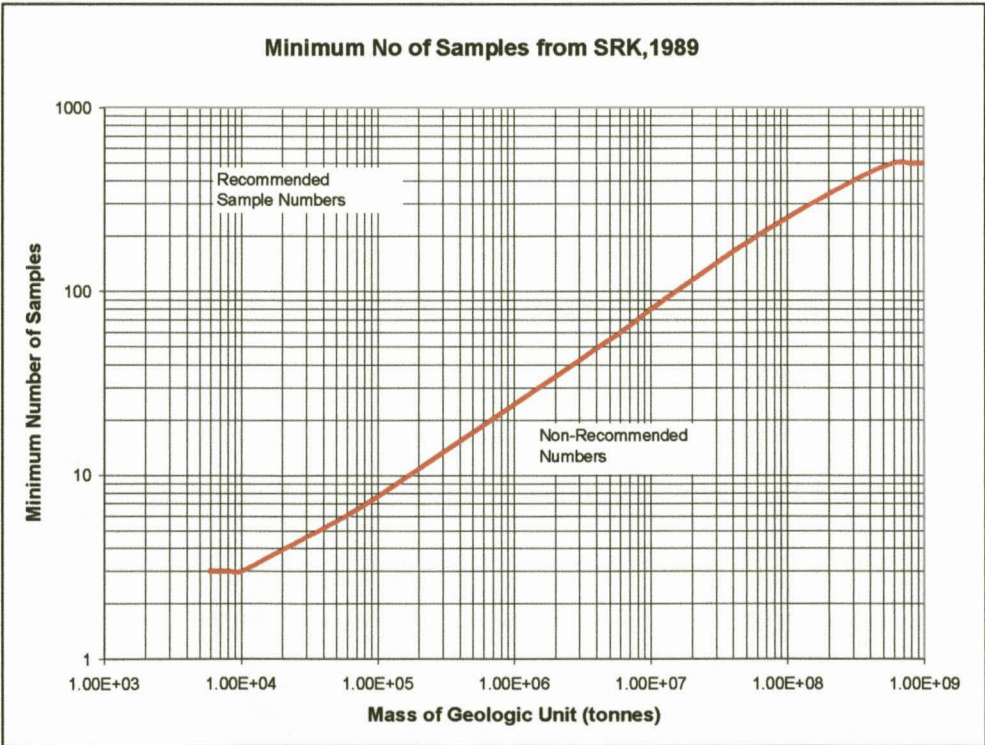


Figure 94: Minimum No. of samples based on mass of geologic unit (from SRK, 1989).

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 be conducted in a stepwise fashion and that the representativeness of the sample set be determined. Once a more complete database is available for South African coalmines, analysis of the data should be able to provide a more generic areal guideline for sample numbers.

There are many statistical methods to determine the adequacy of sampling. Several of these methods are very intricate and cumbersome in application, and their 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).

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

The following examples will indicate the concepts more clearly. Table 17 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 17. 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 18 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 18. Potential error estimate for number of samples used, 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

Figure 95 visually displays this data

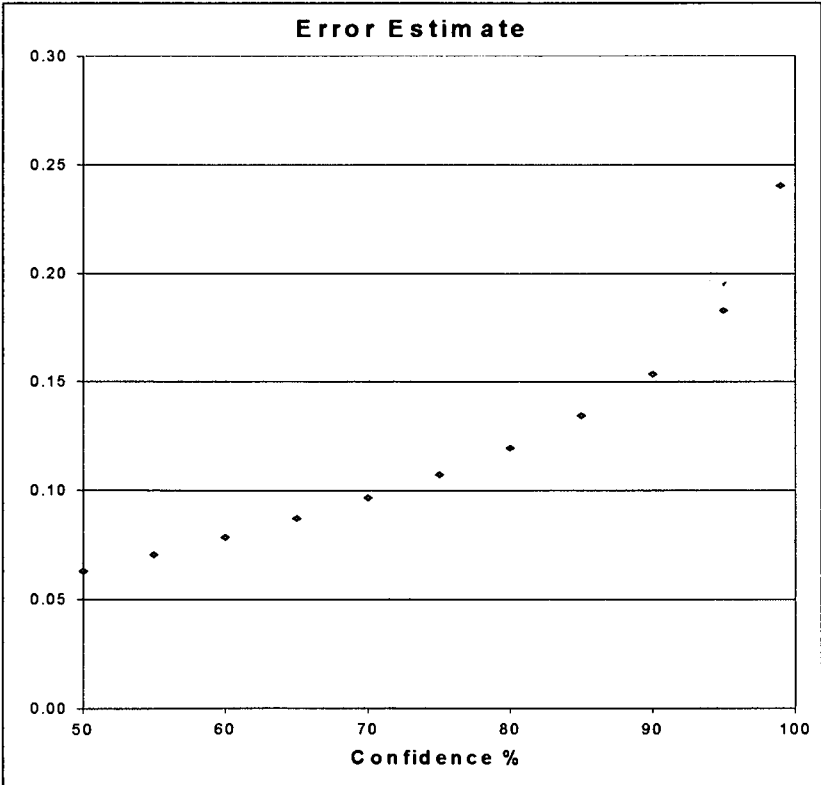


Figure 95: Increase in error with increasing desired confidence level, based on current data set.

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. Table 19 and Figure 96 describe the estimated sample size needed based on the available data set on the acid potential, as obtained from ABA.

Table 19. Required number of samples for mine 1, based on required confidence level.

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

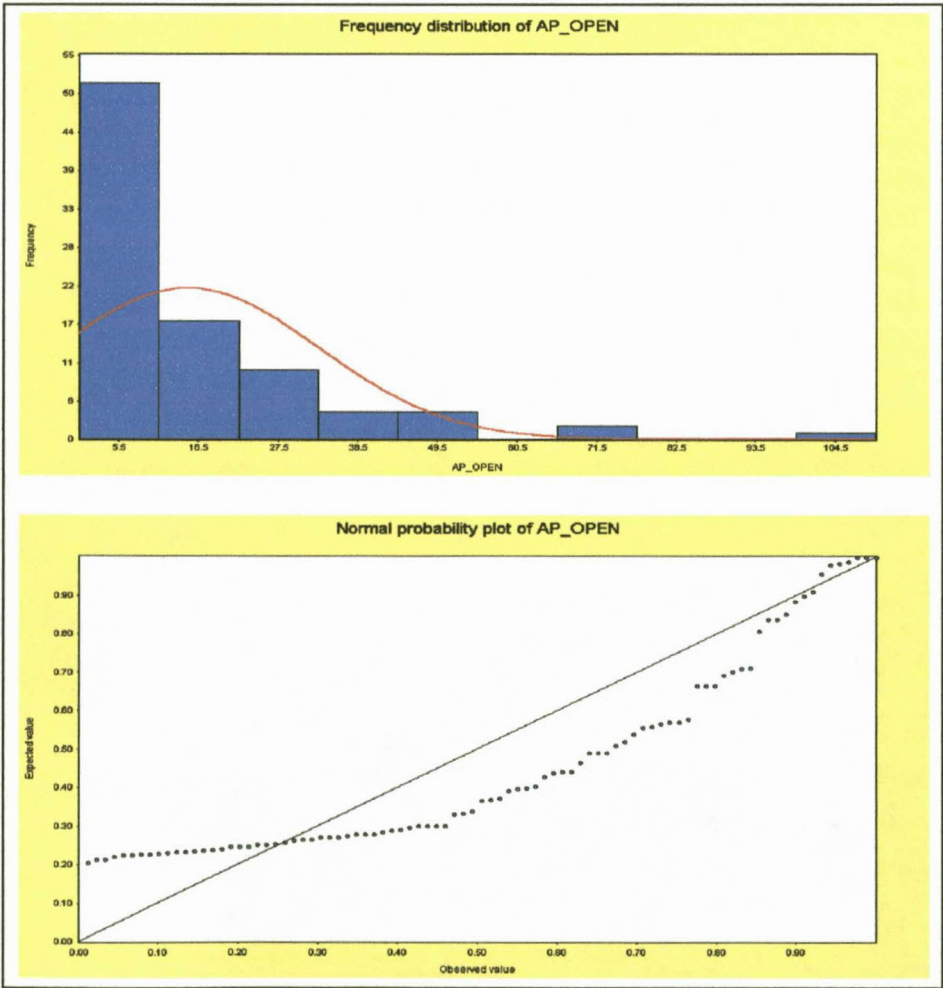


Figure 96: Distribution of AP values and normal probability plot of raw AP data.

It is evident from the preceding figure that the AP data do 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 coalmine sites (Morin and Hutt, 1997).

Log transforming the data yields the following results and distribution (Figure 97). Note that for the estimate of a sample adequacy of 80% for example, a tenth of the determined mean of the transformed data is again used as acceptable error.

Table 20. No of samples required for each confidence level after log transformation.

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

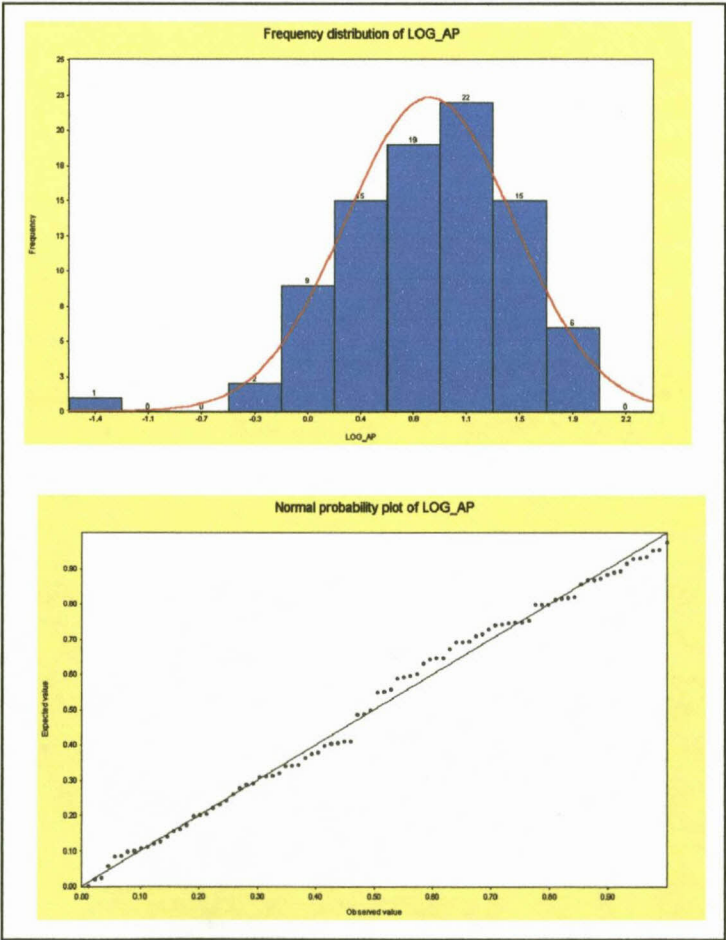


Figure 97: Distribution of values and normal probability plot of log transformed AP data.

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 by 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. A major caveat to all of this is a test of normality or log normality that must be determined. Riemann and Filzmoser (2000) suggest that the assumption of log-normal distribution is the exception rather than the rule in field data, and that most statistical methods widely used in geochemistry are based on an incorrect premise of normality or log normality.

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 (1998), Rose and Cravotta (1998)). Any sampling program to determine the characteristics of the spoil and make predictions as to its behaviour will need 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 required to find these hotspots. Using the assumption, based on the evidence gathered from the field work in this research, 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.

6.1.1 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.

Linking 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:

- Representativeness is very important for the rest of the process.
- Core and random sampling can yield good results.
- Core sampling 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.

6.2 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 by 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 (1998) 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 as Weaver (1992), Hodgson (1998) (DWA&F Waste Management series) and Karkins (1996). Plumb (1999) details specific requirements for mine contaminant monitoring.

Monitoring data is also useful for the determination of field rates and to determine the relationship between different analytical data sets and the true behaviour of the system. This aspect is explored in Section 8.2.

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 (See Figure 98). The parameters 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 and many other factors 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.
- Provide site-specific input for geochemical models.

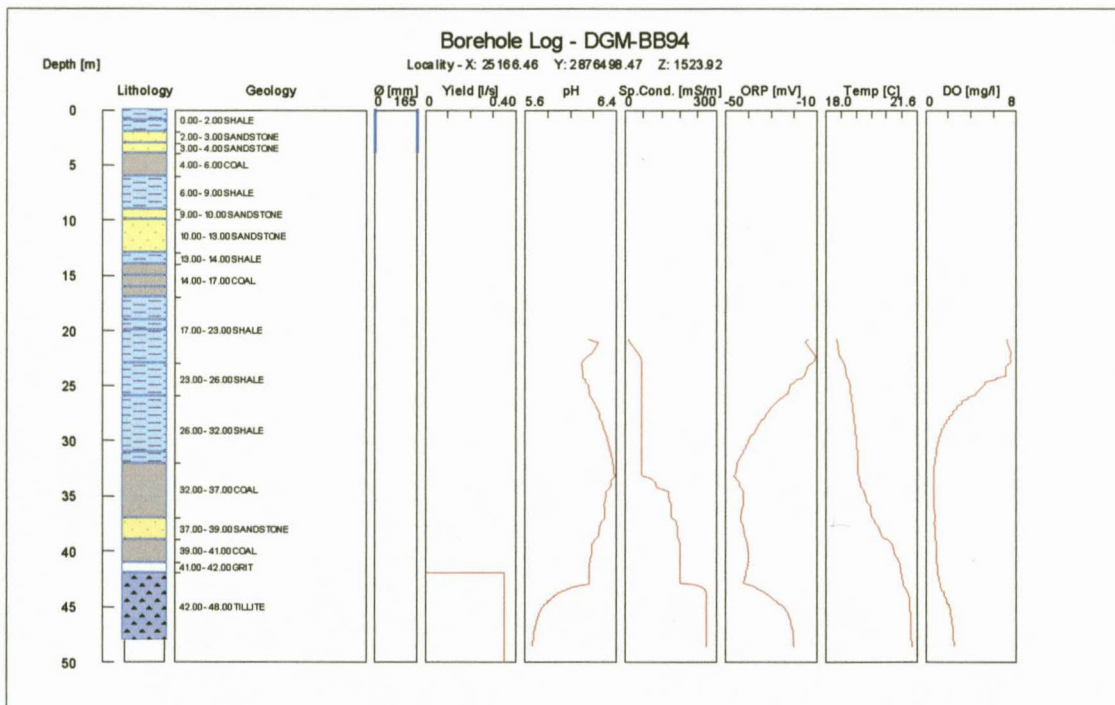


Figure 98: Example of a depth profile and comparison to geology and water strike.

6.3 TEST PITS

An excavator was used to dig the inspection pits in rehabilitated spoils at three different collieries to depths in excess of 3 m (Figure 99). 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 the samples.



Figure 99: Excavator and removed spoils in an inspection pit.

- Visual inspection of the exposed sides was done to note any salient features (Figure 100).
- The depth of the topsoil was measured or averaged where a variation existed over the extent of the 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 100: Two profiles - a non-acidic pit on the left and an acidic pit on the right.

The spoils contain various types of material (Figure 101). A proportion of the material has burned, and portions of the dumps were still burning at the time of excavation. Along certain sections, coal slimes have often been interdisposed with spoils.



Figure 101: 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 103).



Figure 102: 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 103: Surface rehabilitation at the acidic sites.

From observations in the pits, the following observations are pertinent:

- The hydraulic characteristics of dumps vary greatly. Some areas exist from where salts will mobilise, and at others 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 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 that 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 acidic 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 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 of around 20°C have been recorded. In several of the 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 significantly higher temperatures, 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 21.

Table 21. Results from inspecting pits in 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		

6.4 DETERMINATION OF MASS DISTRIBUTION OF DIFFERENT PARTICLE SIZE FRACTIONS

As part of the detailed site characterisation of the S7 underground compartment in Brandspruit Colliery, an assessment of the amount of floor rubble was made. This data is vital for the understanding of the observed reactions and as input to kinetic geochemical models which are to be done on the compartment. No previous record of such a characterisation in South African collieries is available.

6.4.1 Sample protocol

6.4.1.1 Aim and tasks of the floor sampling

The overall aim of this floor sampling exercise was to provide useful information for geotechnical, mineralogical and geochemical studies for the geochemical prediction research project. The final results through underground investigation, sampling and laboratory analyses will be used for computer geochemical modelling for long-term water quality prediction.

To achieve this goal, the following detailed tasks were undertaken:

1. Quantify and estimate the amounts of waste left on the floor from the collapsing of the pillars, and roof together with the coal residues within the bords.
2. Determine the grain size fractions by sieving the samples into >12 mm, 2-12 mm and <2 mm fractions and record the weight of each fraction.
3. Record and describe different lithologies, e.g. sandstones, shales and coal in the coarser fractions (>2 mm).

Take the fine fraction (<2 mm) samples for laboratory tests.

6.4.1.2 Procedures for floor waste sampling

Detailed procedures for measurement and estimation of the amounts of wastes are as follows (after Zhao, 2002):

- 1) Measure the geometrical parameters of the waste piles around the pillars and on the floor in order to quantify the amount of rubble, coal fines and crushed coal materials between the pillars.
- 2) Take measurements in a representative section as indicated in Figure 106. The sections to be measured are approximately A = 2m, B = 3m, C = 2m. Weigh each portion in-situ and record the weights.
- 3) Sieve and weigh the size fractions using a scale: >12 mm, 2-12 mm, <2 mm at the section (A, B, C) record these values.
- 4) Proportionally composite (combine) the three samples < 2 mm (A, B, C) into one with a total weight of 10 kg per sample for further size fraction and other analyses.

6.4.2 Sampling procedure

The exact locations of the sample localities at compartment S7, also known as Johannes se Dam (JSD), where the solid phase characterisation was done is given by Figure 104 and Figure 105.

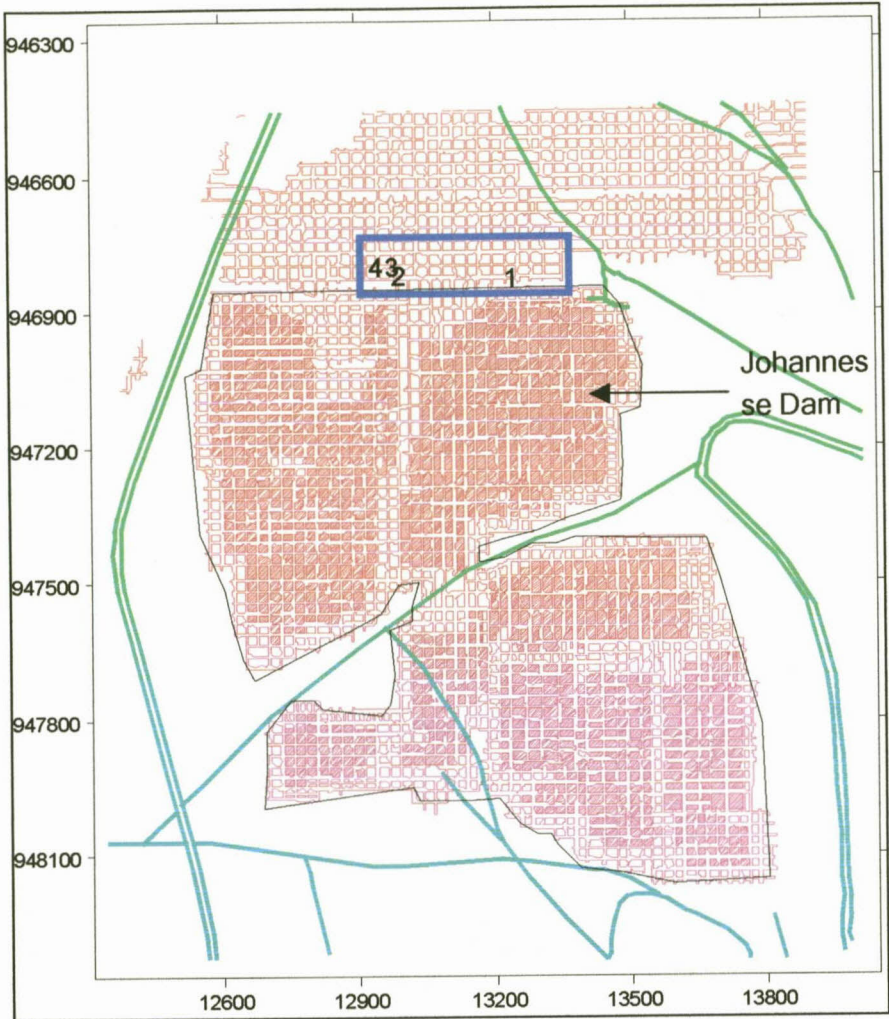


Figure 104: Positions where solid sampling was done shown in blue block.

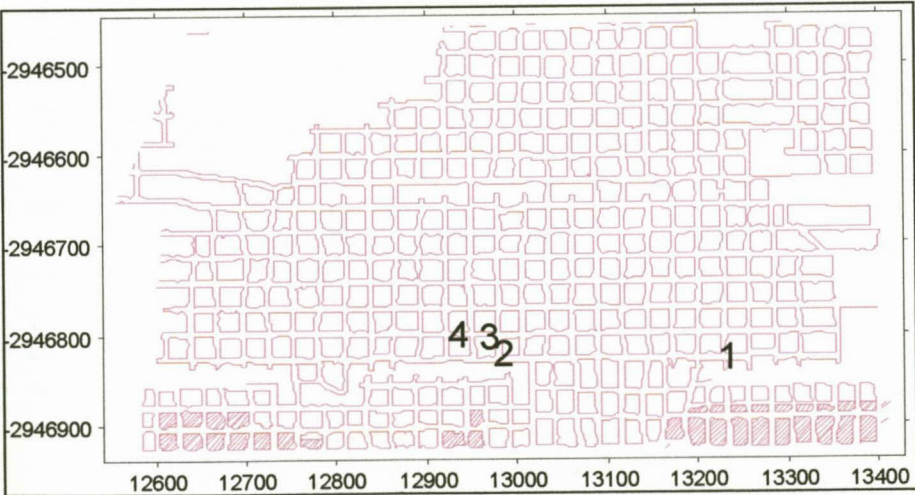


Figure 105: Positions of solid phase sampling.

The objective was to obtain an indication of the grain size distribution between pillars in the mined-out areas. The sections between the pillars were divided into three distinct areas as seen in Figure 106.

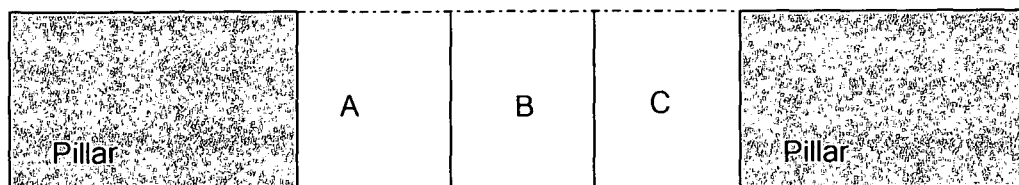


Figure 106: A, B and C each containing fractions 1(>12 mm), 2(12 - 5 mm) and 3(<5 mm) are areas between the pillars where sampling took place.

In each section the volume and mass of boulders or rocks which could not easily be weighed, were estimated where possible. This was the largest fraction while the other three fractions consisted of grains >12 mm, 12 - 5 mm and <5 mm. The >12 mm fraction was obtained by putting an estimated percentage of rock in the specific area A, B or C, through a 12 mm sieve. Everything remaining on the sieve was seen as the >12 mm fraction and was placed in a basin in order to estimate the weight. Material less than 12 mm was put through a 5 mm sieve to separate the 12 - 5 mm from the <5 mm fraction. The weight of each fraction was also estimated. Only the <5 mm fraction was sampled for further analysis.

All the samples obtained were named JSD1 to JSD 4, with A to C referring the position relative to the pillar.

6.4.3 Results

6.4.3.1 Locality 1 - Johannes se dam1 (JSD 1)

Pillar width next to A = 11.5 m; Pillar width next to C = 15.6 m; Distance between pillars = 6.8 m; Volume of material used = 0.5 m x 0.5 m x 0.3m.

Boulders taken into consideration were approximately 50% of the total mass in section A and weighed about 35 kg. Boulders made up approx. 10% and 40% of the total material in section B and C, respectively.

Material used to determine fraction 1, 2 and 3 made up 15% of the total rock in section A. Sections B and C were not estimated.

Section B consisted of mud thus no estimations were made.

	A	B	C
Fraction 1	8 kg	-	11 kg
Fraction 2	7 kg	-	5 kg
Fraction 3	5 kg	-	2 kg

These types of assessments were done in a further three bord areas to obtain an indication of variability.

6.4.4 Mass determinations per section

Based on the data collected above the following mass determinations could be made (Table 22):

Table 22. Mass determinations for each bord evaluated.

JSD 1					
	Mass A kg	Mass B kg	Mass C kg	Total mass per size fraction (kg)	Incl Boulders (kg)
>12 mm	1090	0	381	1471	2942
5-12 mm	953	0	334	1287	1287
<2mm	681	500	238	1419	1419
Total mass per section	2724	500	953		
Total mass of bord area				4177	5648
JSD 2					
	Mass A kg	Mass B kg	Mass C kg	Total mass per size fraction (kg)	Incl Boulders (kg)
>12 mm	757	947	265	1969	3544
5-12 mm	663	284	232	1179	1179
<2mm	473	379	166	1018	1018
Total mass per section	1893	1609	663		
Total mass of bord area				4165	5740
JSD 3					
	Mass A kg	Mass B kg	Mass C kg	Total mass per size fraction (kg)	Incl Boulders (kg)
>12 mm	1985	1191	695	3872	6400
5-12 mm	662	397	232	1291	1291
<2mm	1158	695	405	2258	2258
Total mass per section	3805	2283	1332		
				7421	9949
JSD 4					
	Mass A kg	Mass B kg	Mass C kg	Total mass per size fraction (kg)	Incl Boulders (kg)
>12 mm	2206	1324	772	4302	5592
5-12 mm	1103	662	386	2151	2151
<2mm	1324	794	463	2581	2581
Total mass per section	4633	2780	1621		
Total mass of bord area				9034	10324

From the details above it is clear that the distribution of material is extremely heterogeneous and that typical quantities of rubble lying on the floor of compartments in the Highveld Coalfield vary between 5t and 10 t. This is a conservative estimate. From observations in nearby compartments where more moisture is present, it was estimated from visual inspection that the amount of floor material was in the order of three to six times more than this compartment.

As far as could be ascertained, an attempt to characterise the particle size fraction of rubble at underground compartments has not been done previously in South Africa. The small data set in this section is therefore of great interest, but further work is required on this aspect.

6.5 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 field measurement. 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, are more problematic due to heterogeneity and unsaturated conditions. The following table outlines the key techniques and their usefulness for understanding the site:

Monitoring technique	Key parameter		
	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 7, without these parameters, accurate prediction of mine drainage evolution over extended periods into the future is fraught with uncertainty.

6.6 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 mine site is the full-scale operation of minesite components".
- In situ field rates using drainage chemistry are the best measure of the conditions and should be used concurrently to any other method. (Al *et al.*, 2002).
- 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.

7 ASSESSMENT OF GEOCHEMICAL MODELLING FOR LONG-TERM WATER QUALITY PREDICTION

As part of the development of the ABATE methods, a short review of geochemical modelling is included. Geochemical modelling is increasingly seen as the method of choice for the prediction of long-term drainage from mines and a thorough understanding of its strengths and limitations will place the answers obtained from such models in context.

The following section highlights the advantages, requirements and limitations of 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 (Howard and Heymans, 2000). Since a full evaluation of several of the commonly used codes is available there, 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), 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). These are 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 collecting input data for the model of choice, including full characterisation of waste rock pile with respect to its chemical and physical properties, meteorological information and any other information required. 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 (Li, 2000).

All the geochemical processes included in geochemical models need accurate data and detailed simulation for a model to approximate the field situation.

There are seven basic model classes; these have been discussed in detail in Section 3.5:

- 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.

- 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 the 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).

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 Tests, 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 aspect, 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 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. Where long-term predictions of loadings are made, these models should have some field verification to show validity.

7.1 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 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 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) 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 emphasized that, although the 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 or 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. Younger (2000) stresses the importance of mineralogical composition of the aquifer matrix as necessary initial conditions in reactive contaminant transport models.

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), 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)) utilise only a subset of the species/minerals to obtain results. Thus any system where species are present, and not included in the dataset, will be modelled with decreased confidence. 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; thus all thermodynamic data and reaction constraints have to be defined by the modeller. This makes such models 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. This also is true for pyrite oxidation rates as reported by Scharer *et al.* (2000) while the use of kinetic rate constants obtained from the literature for simulating the dissolution of primary mineral phases such as the carbonates and alumino-silicates will likely overestimate the actual rates (Al *et al.*, 2002).

Research on geochemical kinetics has revealed a wealth of possible mechanisms and rates by which minerals, organisms and aqueous species may interact (Steeffel 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:

$$K = Ae^{-E_a/RTk}$$

where

A = Arrhenius pre-exponential factor

E_a = Arrhenius 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 not sufficient to represent most chemical processes under field conditions realistically (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 and 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 while 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 with a roughness of four, which has a reactive surface of 300 000m² while one side of a block of the same material will have a reactive surface area of 2m². Thus channelling is a very important factor that leads to uncertainty. This phenomenon will be expanded on in the following section.

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 problem with codes that can accommodate these features, is that they cannot 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 is 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, this is often a component that is neglected. More emphasis is therefore 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. Bain *et al.* (2000) indicate that 10 years of water quality and mineralogical determinations were used in support of their model. For accurate long-term prediction, a 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. 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 P_{CO_2} is discussed in more detail in Section 2.8.1.1.

Hendry (Personal Communication, 2000) states that, to obtain accurate field rates for use 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 the 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 that 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 vital variables 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 and other required hydraulic parameters in each portion of the system should be obtained and, if required, detailed modelling 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.

7.1.1.1 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 accuracy has been established, the uncertainty can be limited by doing probabilistic and sensitivity analysis to quantify uncertainties, so that they 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, producing an interval as the result of the simulation. In addition, the conceptual model may be crucial (Ekberg, 1999).

7.2 THE INFLUENCE OF DIFFERENT VARIABLES ON THE REACTION SEQUENCE

In an attempt to indicate the influence of the different variables to be taken into account when modelling reactive systems, a simple system consisting of a single reactive node/cell will be used. Generalised values, as obtained from case studies, 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 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 dissolved quantities of the common macro elements, some alkalinity and a pH of 7.2 is used. The minerals considered are calcite, pyrite and illite as the clay mineral. 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 cm² 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 (Figure 107). The Geochemist's Workbench (Bethke, 1996) was used for all simulations.

The values used in these simulations are within the range expected at many South African coalmines. These simulations serve as an illustration of what is likely, should the uncertainty for any key parameter be large.

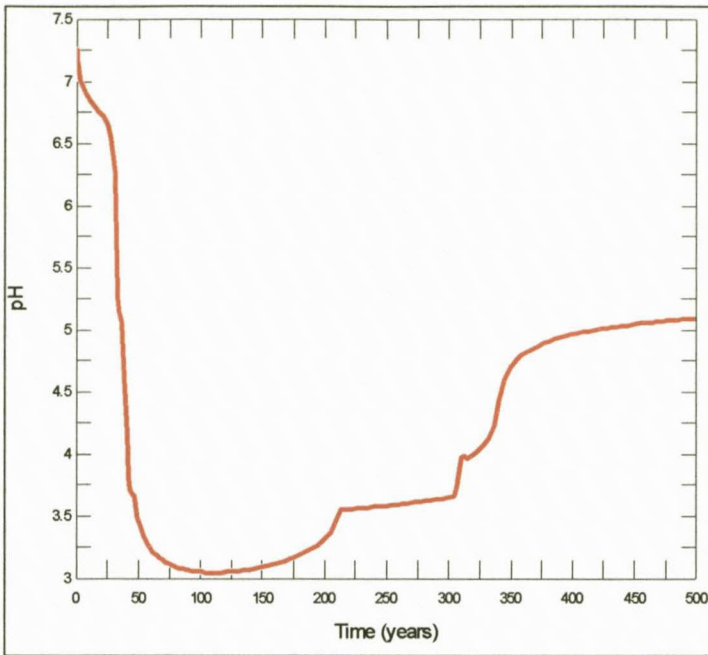


Figure 107: pH-profile vs. time for base case simulation.

The profile above shows rapid acidification within less than 50 years, followed by a fairly long period of circa pH-3 conditions before the clay mineral can adequately start consuming sufficient acidity to increase the pH again.

7.2.1 Reactive Surface

The pH-profile obtained from doubling the total reactive surface area is shown in Figure 108. The natural consequence of this is to double the effective reaction rate, and therefore the pH-profile shows a similar shape. The rate is however accelerated so that the acidification and eventual return to higher pH-values occur in a shorter time period (Figure 108).

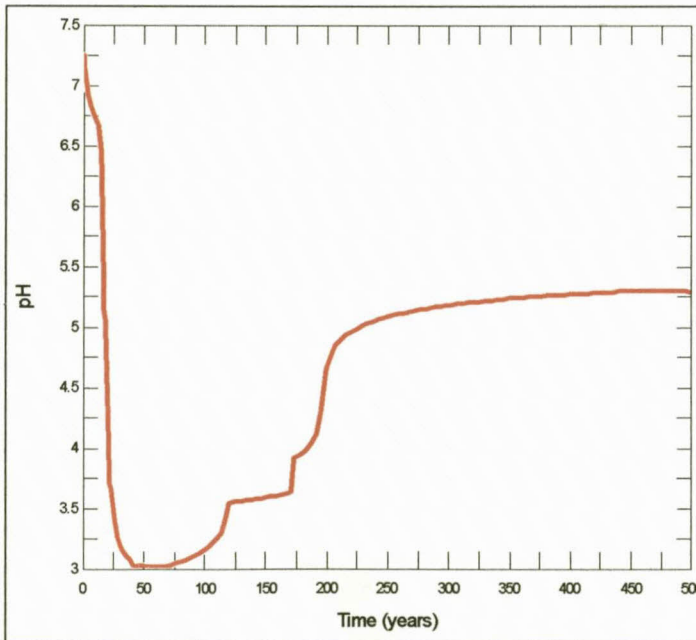


Figure 108: pH-profile vs. time with a doubling of reactive surface area.

7.2.2 Molar Quantities

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 (Figure 109).

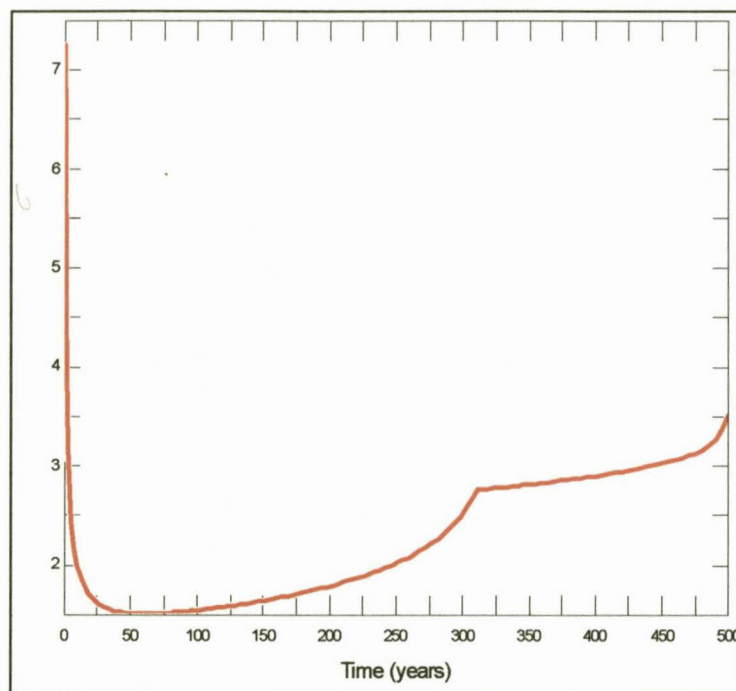


Figure 109: Doubling pyrite quantity (and thus reactive surface).

A more realistic simulation is shown below (Figure 110), with a 25% increase in pyrite as opposed to the original. This simulation demonstrates 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 and trace 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.

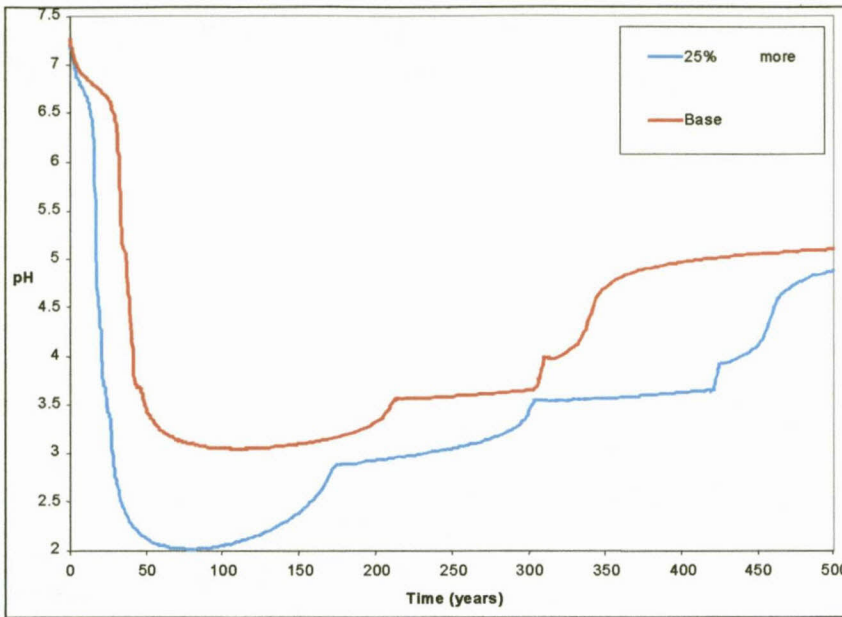


Figure 110: pH-profile with 25% increase in pyrite compared to the base case.

7.2.3 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 (e.g. Bethke, 1996) 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.

In the figure below (Figure 111), 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 is dire.

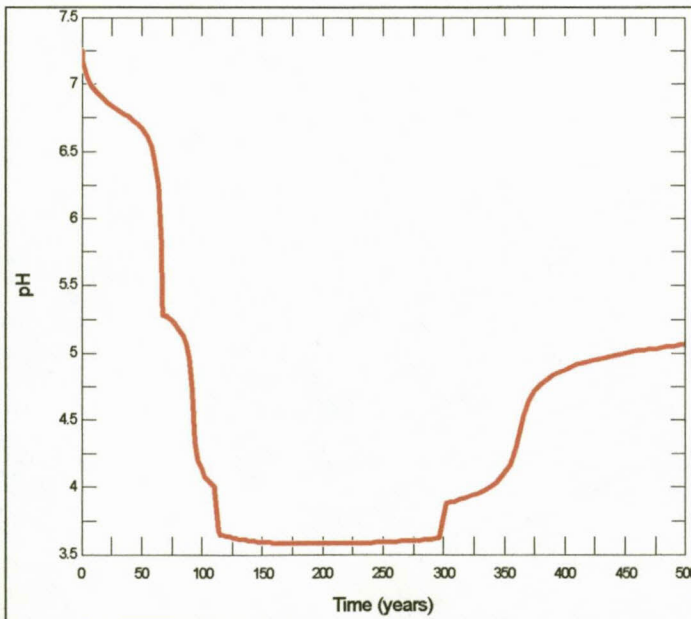


Figure 111: pH-profile with a halving of original pyrite reaction rate.

7.2.4 Flushing of the System

Figure 112 below shows the influence of inaccurate flow determinations in even the most simple of systems. The flow rate in any system 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 the reactive modelling of acid drainage, and any model purporting to correctly quantify the drainage chemistry must accurately model the heterogeneous flow obtained in mining environments.

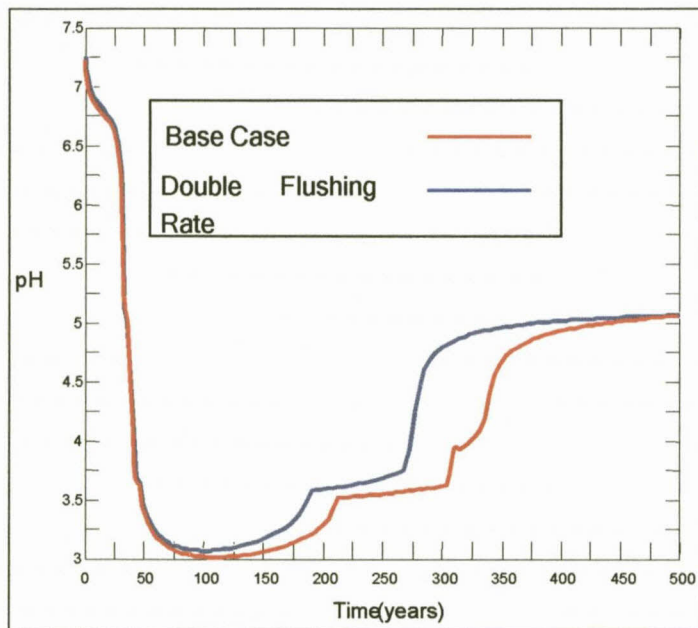


Figure 112: Influence of doubling of flushing rate.

7.2.5 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 following section will illustrate the influence of relative reaction rates on the reaction of a system 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

As can be seen from Figure 113, 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, slow, after Kwong, 1997), one could simulate the field situation more realistically. Figure 114 and Figure 115 show the concentrations of dissolved species and the mineral contributions assuming all the minerals react according to equilibrium conditions.

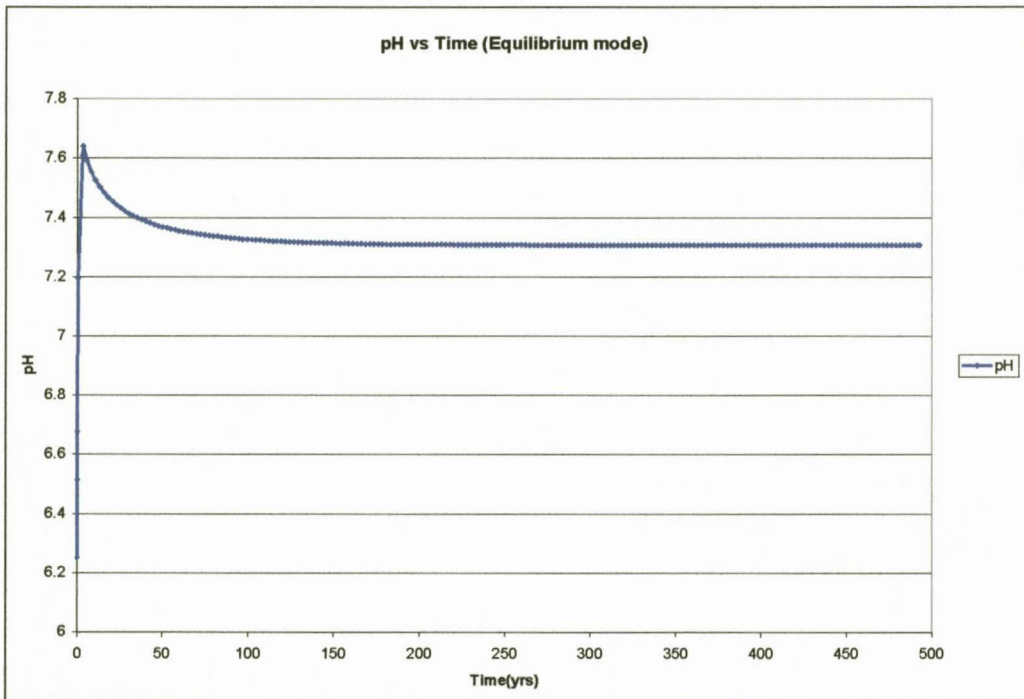


Figure 113: pH-profile in equilibrium reaction.

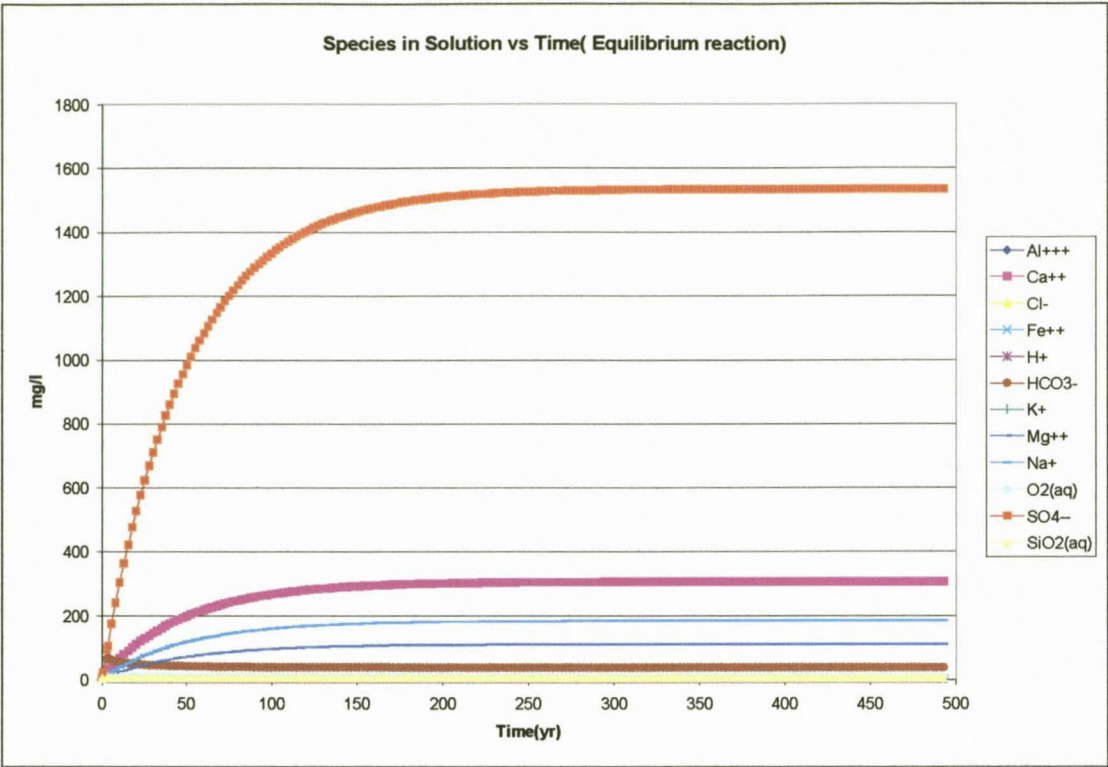


Figure 114: Species distribution over time assuming all minerals reacts to equilibrium rapidly.

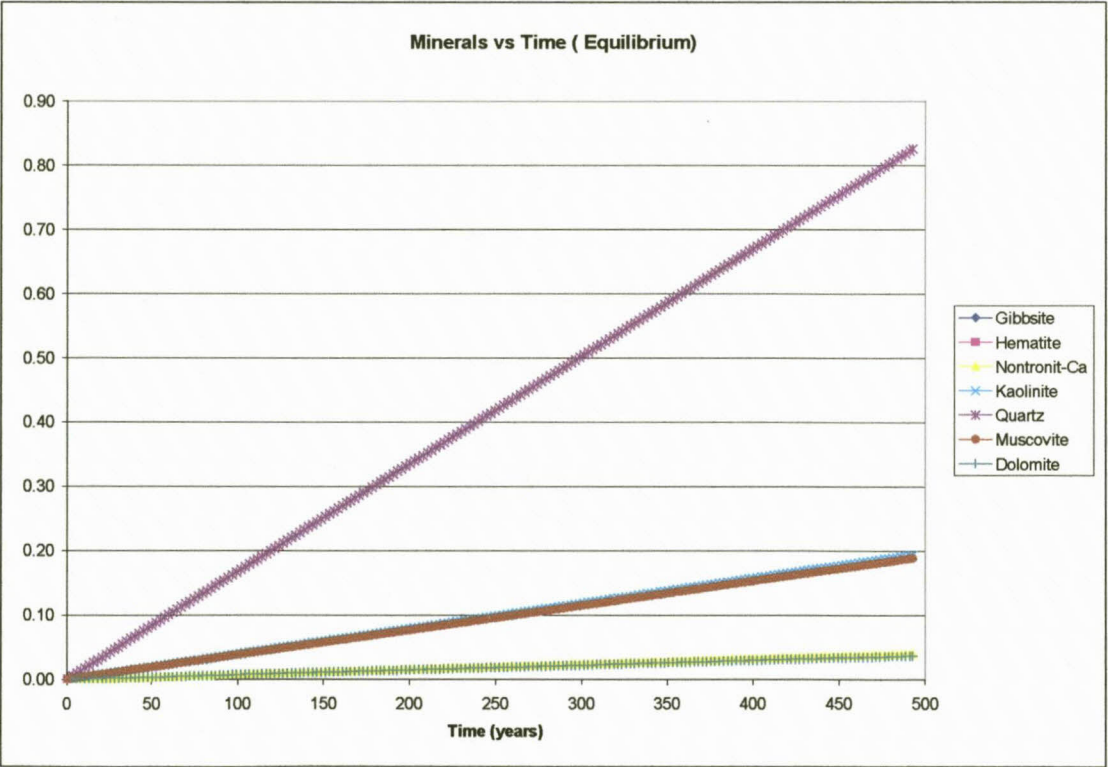


Figure 115: Mineral distribution over time assuming all minerals reacts to equilibrium.

7.2.6 Kinetic Considerations

Should it be assumed that the minerals all react in a kinetic fashion, the water quality evolution is expected to be very different. 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 116) 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 that 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 <i>et al.</i> (1981)
Diopside	1.4e-10	Schott <i>et al.</i> (1981)
Nepheline	2.8e-9	Tole and Lasaga (1983)
Anorthite	5.6e-9	Fleer (1982)

Based on these reaction rates, the mean lifetime of a 1 mm crystal for each mineral under these conditions can now be determined.

Table 24. Mean lifetime of a 1 mm 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 $O_2(g)$ 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 $8e-10 \text{ mol/m}^2/\text{s}$ under optimal conditions.

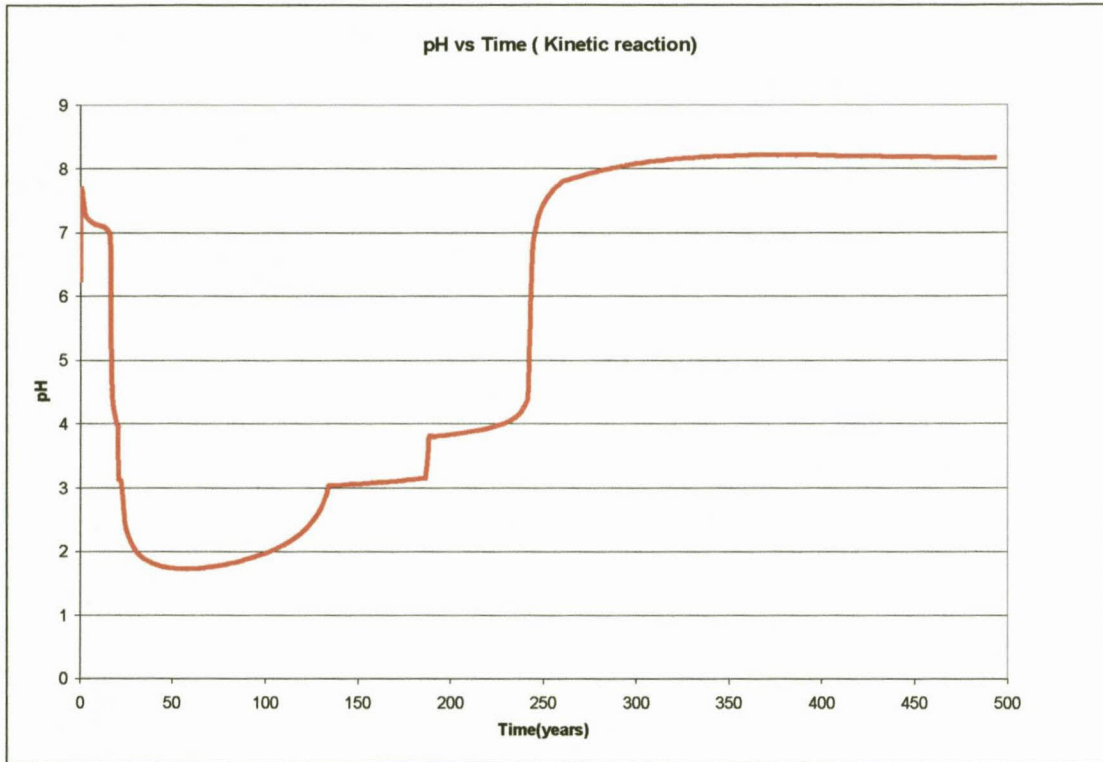


Figure 116: pH-profile for kinetic reaction, under constraints discussed.

One of the most important observations is that the pH drops relatively rapidly once the carbonates have been depleted (shown below in Figure 117). This reiterates the observation in Section 2 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. Puura and Neretnieks (2000) have also shown in experimental studies that alumino-silicate buffering can only occur at low pH values. Using PHREEQC in combination with their experimental observations they also show that illite undergoes incongruent dissolution, meaning total illite content can't be used to calculate the low pH neutralization. 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 118 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 below (Figure 117), it is clear that acidity can occur in a short time, 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.

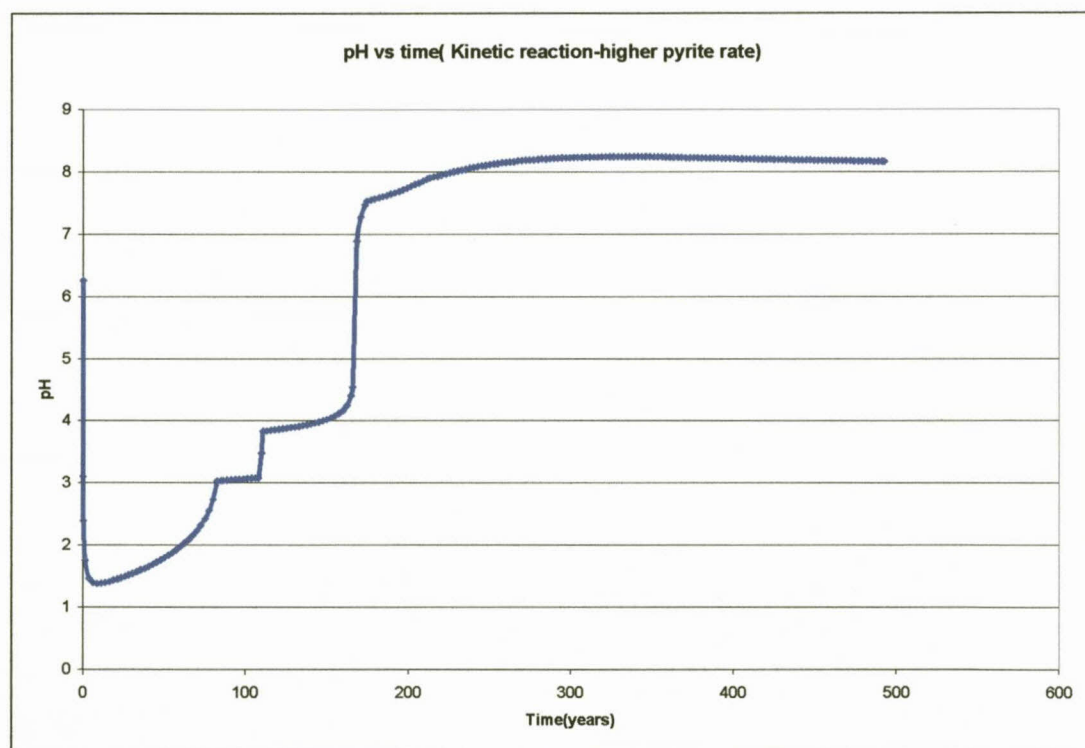


Figure 117: pH-profile at higher pyrite reaction rate.

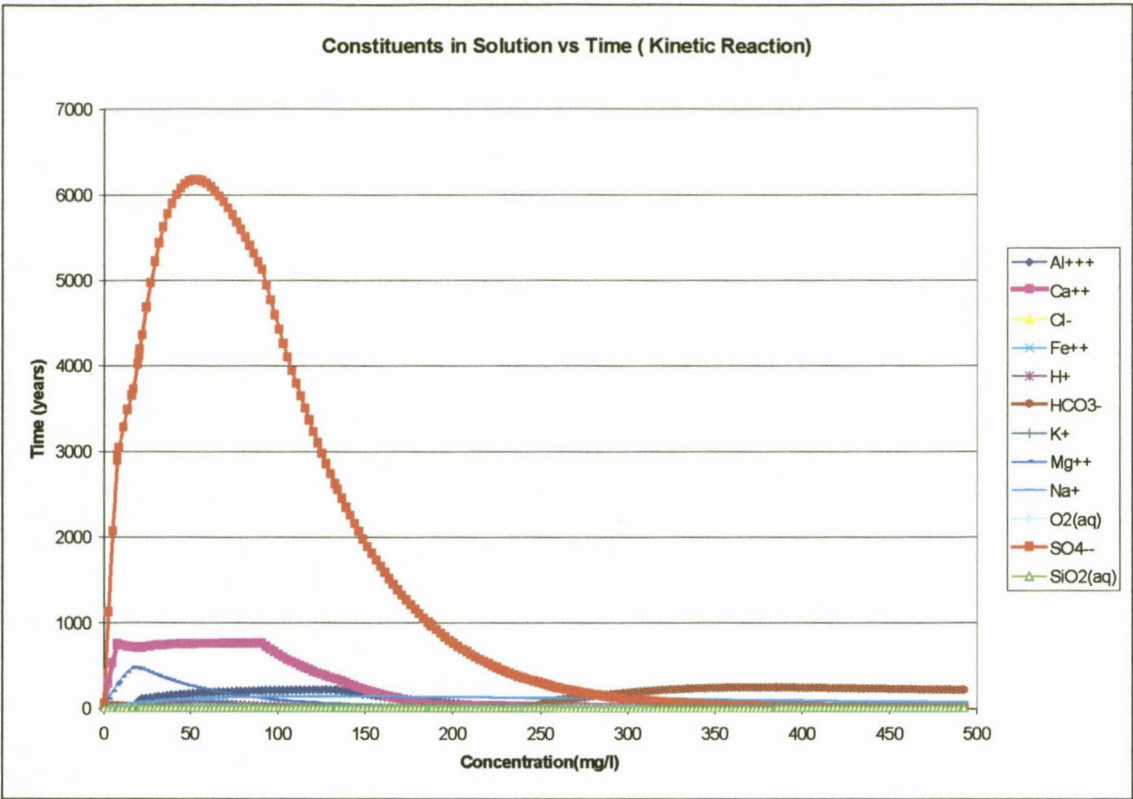


Figure 118: Distribution of different species over time.

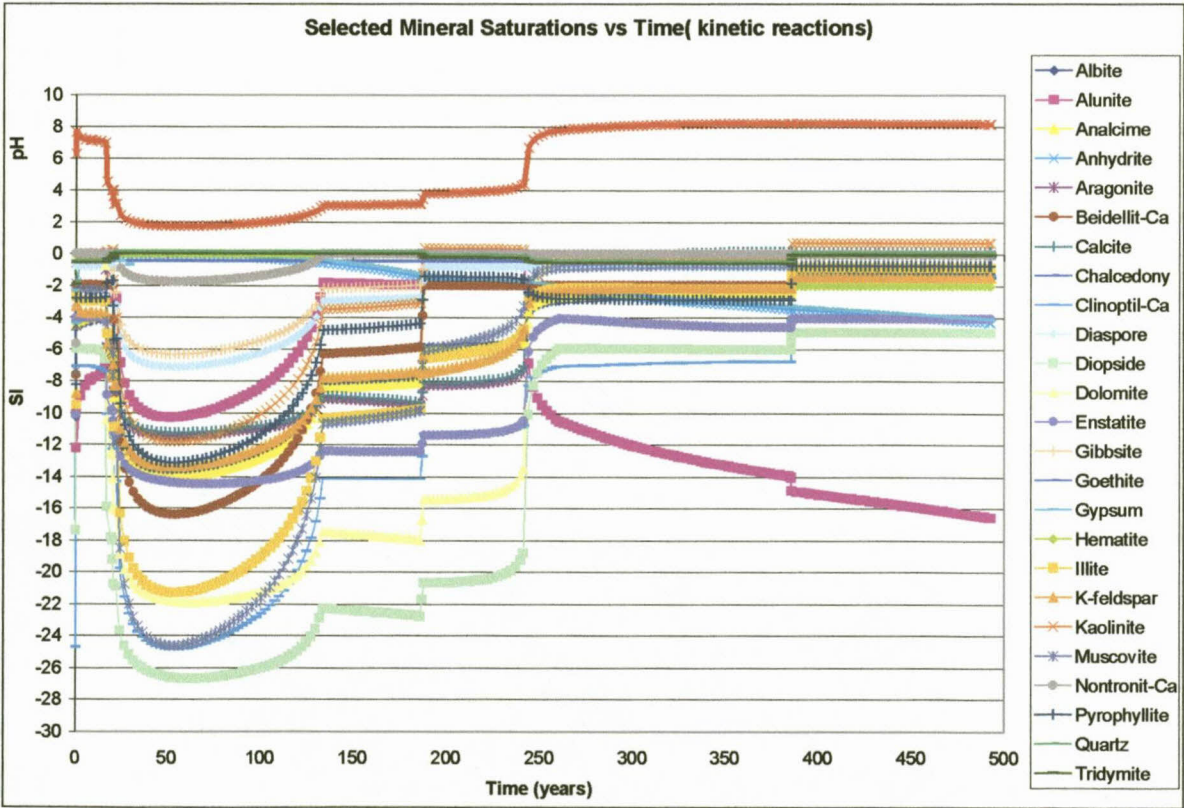


Figure 119: Mineral saturation related to the simulated pH-profile.

The profile above (Figure 119) 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 2, which includes the pH-variation over time and the related mineralogical changes occurring 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 insufficiently detailed input data. No single model is yet available to adequately address all 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 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.

7.2.6.1 SIMULATING HUMIDITY CELL RESPONSE

The humidity cells discussed in Section 5 were modelled to determine the possibility of simulating the cells' response. This modelling indicated the extreme sensitivity of a simple system to changes in rate, particle size and the 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:

1. Use the mineralogical data for the cell (Section 2.8) and assign values to each mineral.
2. Use the ABA data to quantify the pyrite and carbonate contribution.
3. Use oxygen and CO₂ as fixed fugacity buffers.
4. Allow the quantity of water drained from the cell over the testing period to "flush" the system.
5. Employ rates as described above.

6. 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 120 to Figure 124) were dealt with in the same manner. An example for the sandstone cell is shown in Figure 125 to Figure 126.

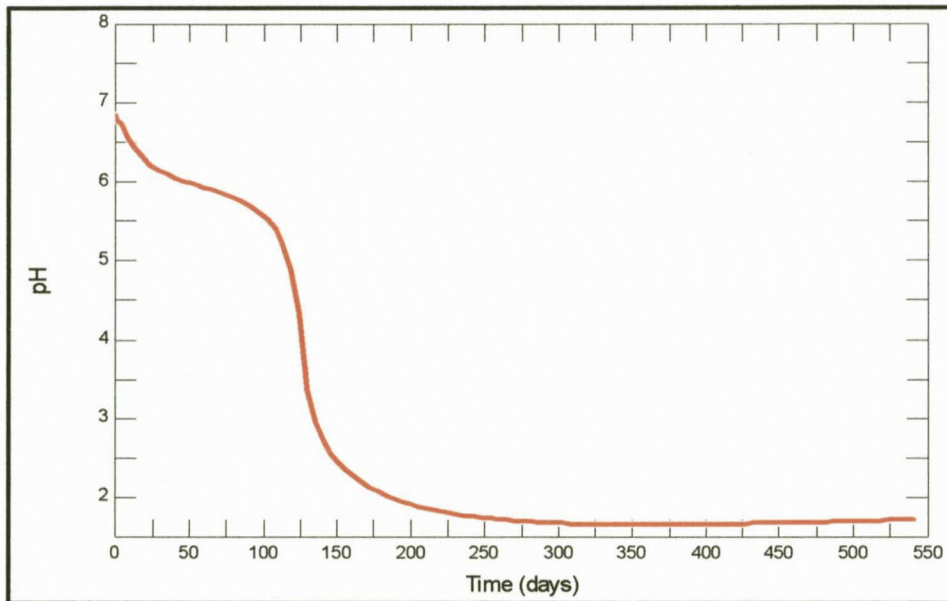


Figure 120: Simulated pH-profile for humidity cell.

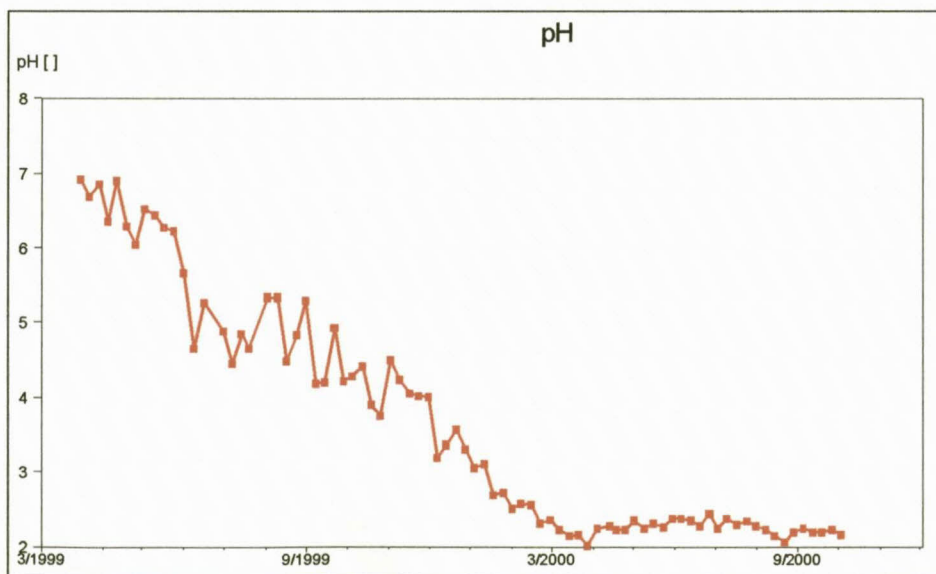


Figure 121: Observed pH-profile from humidity cell.

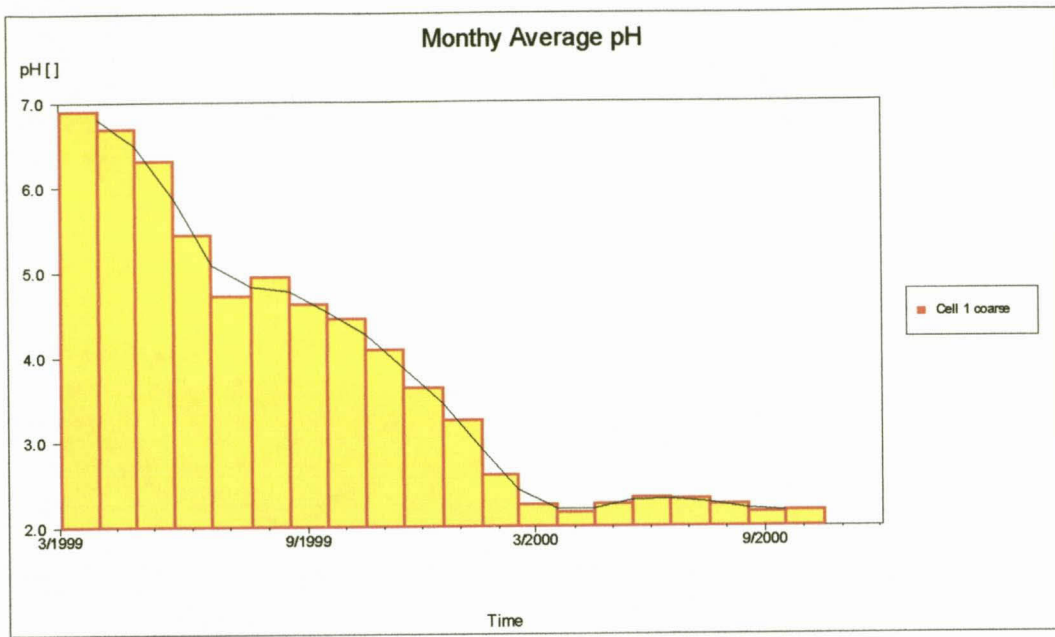


Figure 122: Observed pH as a monthly average, with the two-month moving average line shown.

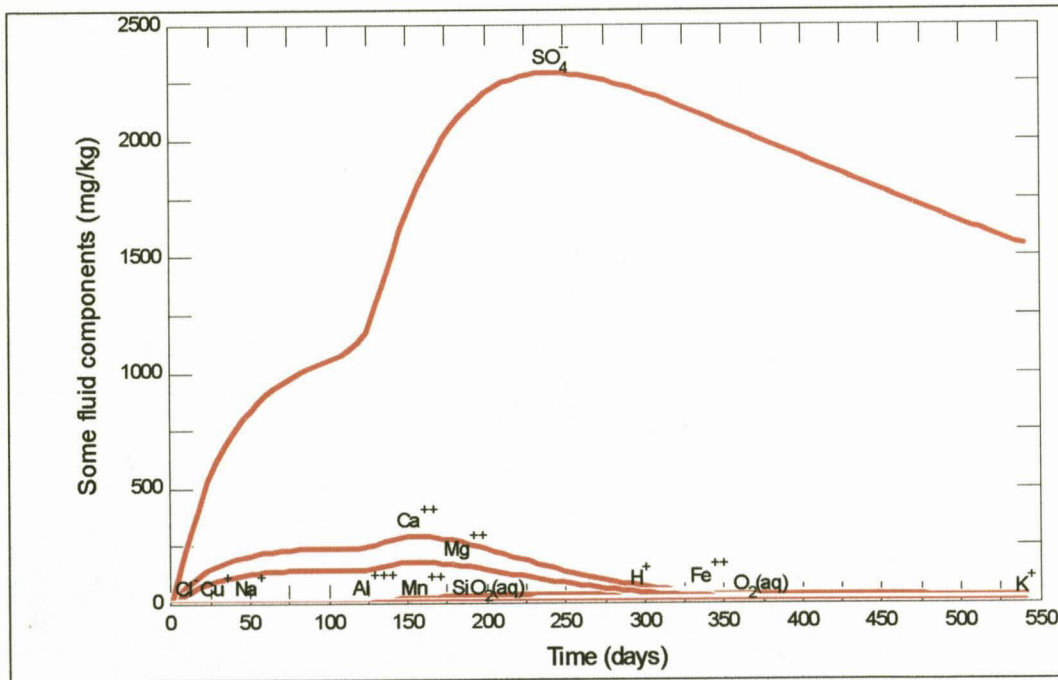


Figure 123: Simulated aqueous components for humidity cell.

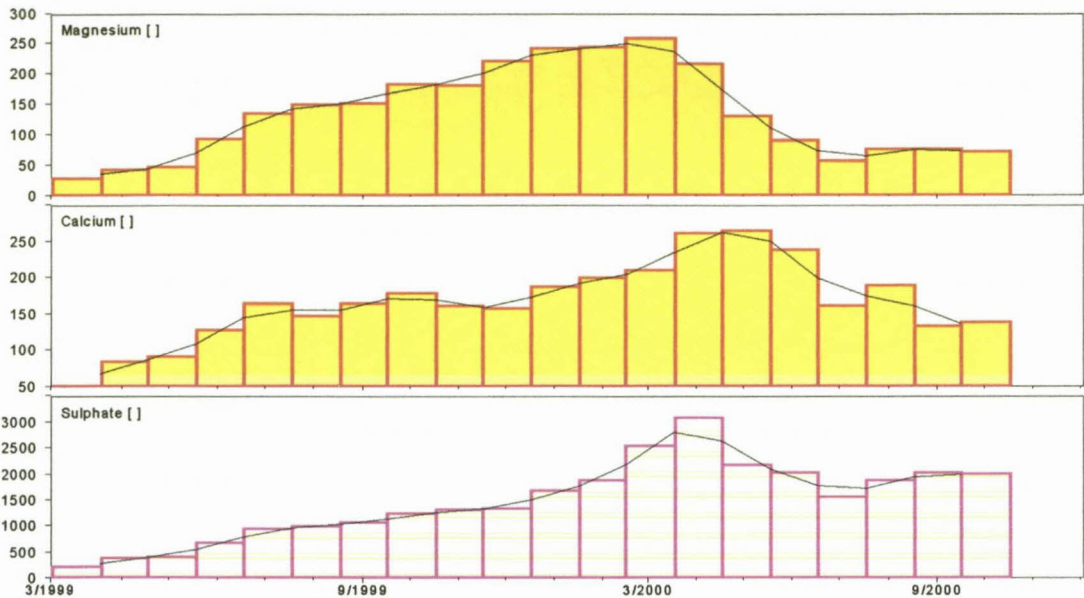


Figure 124: Observed aqueous components expressed as a monthly average, with the two-month moving average line shown.

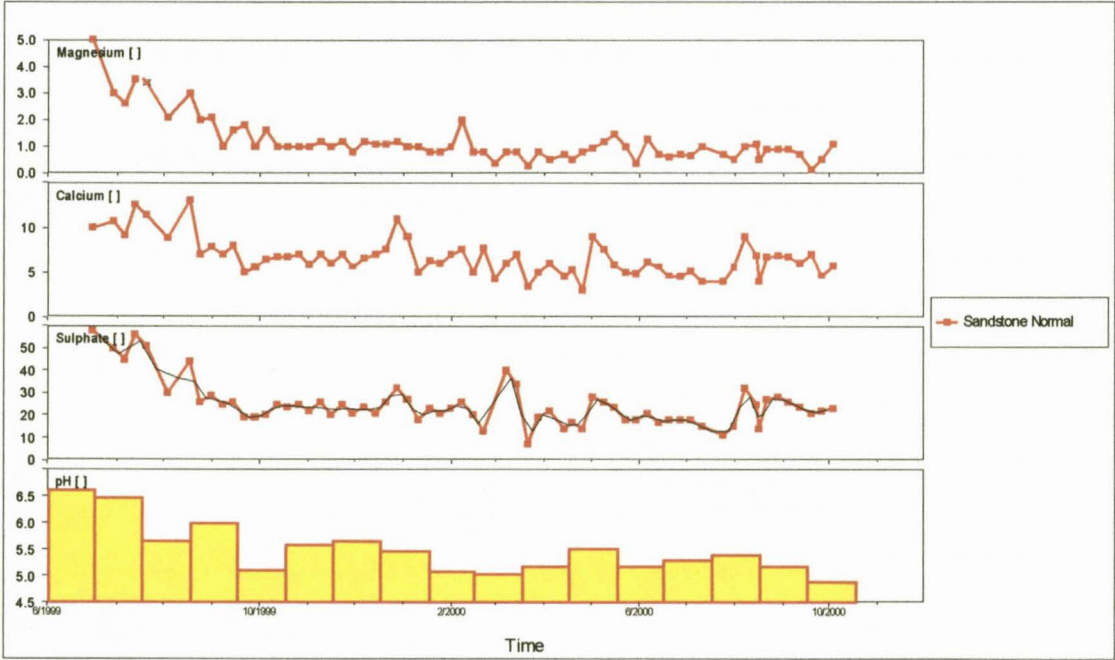


Figure 125: Outflow data from the sandstone cell.

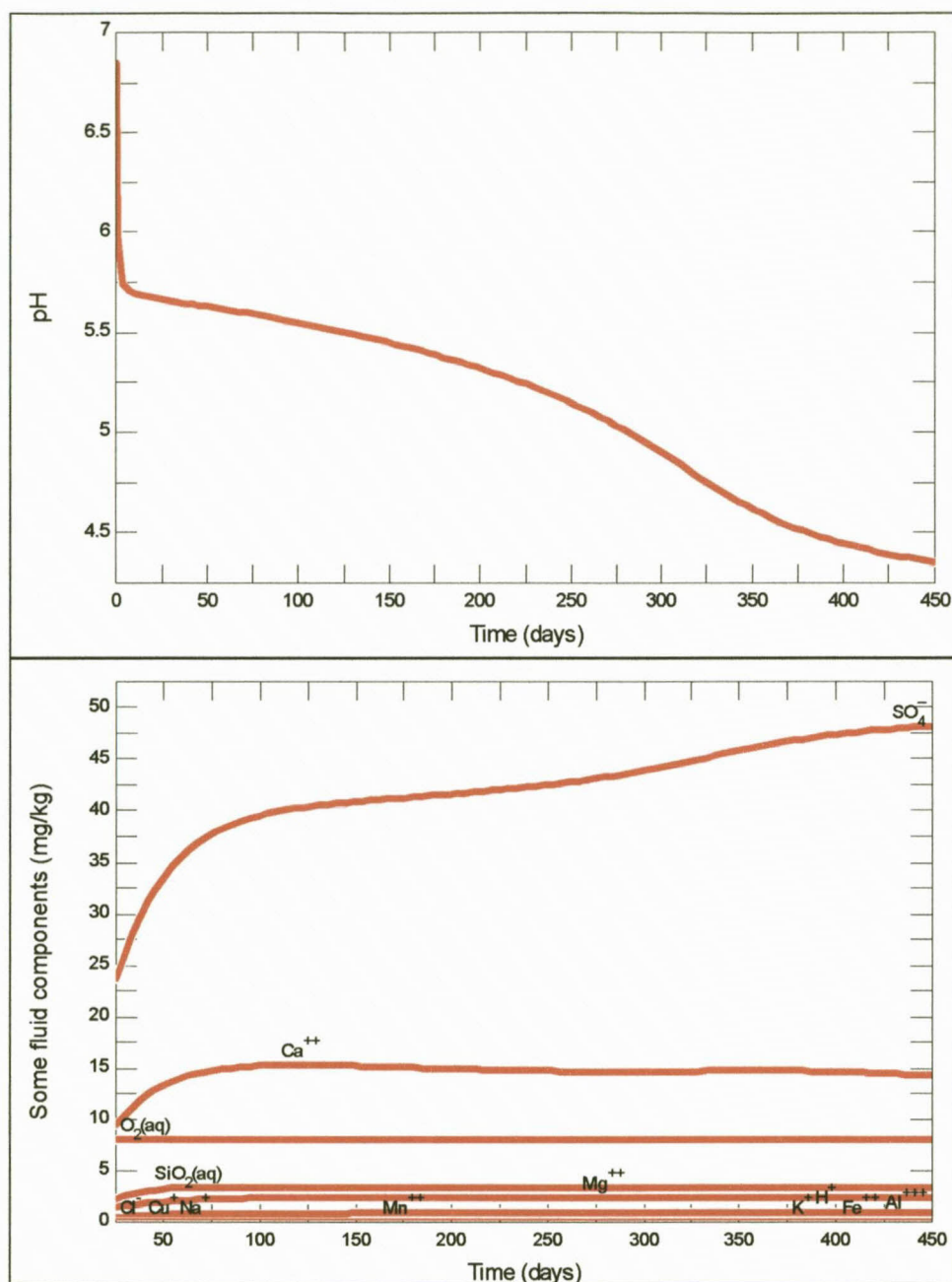


Figure 126: Simulated profiles from the sandstone cell.

From the above simulations, it would appear that it is possible to simulate the system's response over time, if data are available on the mineralogy, rates, flushing rate and quantity of pyrite and fast-reacting species. However, it must be pointed out that the solutions shown are not unique; a variation of several parameters (e.g. relative amounts of each mineral, surface areas) can give a similar response. Care must therefore be taken in trying to extrapolate this to the field too readily.

7.2.7 General Modelling Methodology

The following is a generic approach to the steps that need to be taken in geochemical modelling (adapted from Boer, 2000):

1. Collect and review site data.

2. Identify objectives, including required detail and confidence in model.
3. Select, adapt or develop model(s).
4. Start at simplest level that meets objective.
5. Prepare model inputs and parameter estimates.
6. Calibrate model to field data.
7. Perform simulations. Interpret the results.
9. Identify controlling processes.
 - Compare to concentrations at other sites.
 - Compare to estimates obtained using alternate approach.

The flow chart below (Figure 127) illustrates the iterative nature of these steps.

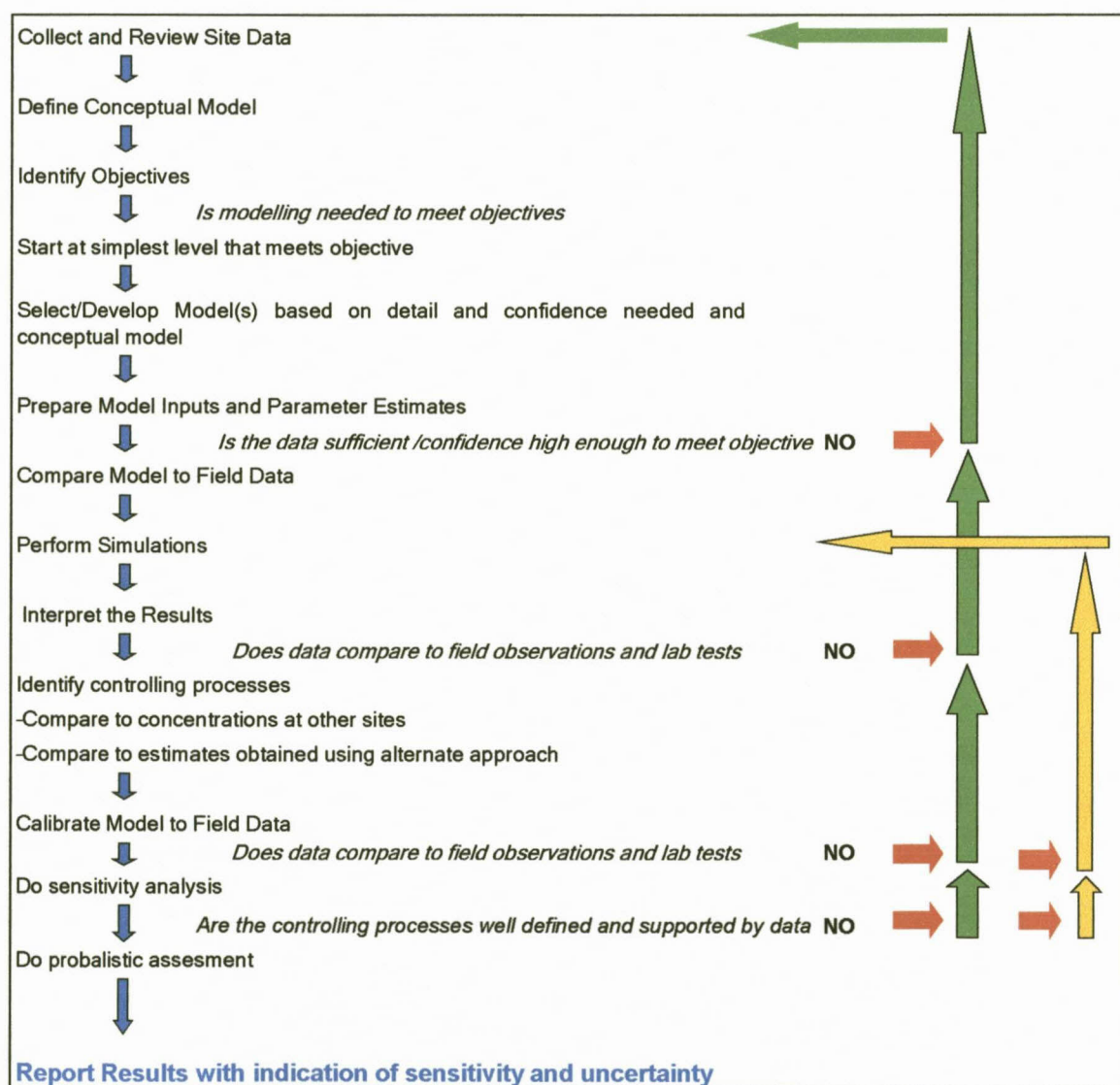


Figure 127: Suggested iterative flow path for geochemical modelling.

7.2.7.1 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 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.

7.2.7.2 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 issues in selection of a model package(s) (ASTM, 1999) are:

1. The algorithm(s) used to model each fate and transport pathway and the inherent limitations of each model in terms of applicability.
2. Degree of documentation, validation and general acceptance of algorithms incorporated in the package.
3. 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?).
4. How the model results or output from individual fate and transport models are reported and linked to other model components.
5. 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).

Table 25 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 coalmines.

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	Equilibrium, 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	Only 1-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			

7.3 CONCLUSIONS FOR GEOCHEMICAL MODELS

Geochemical models are important tools in the ABATE process, when used appropriately. This chapter has shown that geochemical modelling:

- Needs many input parameters, which are 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 many uncertainties, wherein small changes to any one of the important input parameters can alter the results drastically (See Section 8.1.1 and 8.2).
- Can be assisted by field and laboratory validation to decrease uncertainty.
- Is valuable to obtain an understanding of the key processes, rather than precise temporal prediction of water quality evolution at a colliery.
- 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.

8 DEVELOPMENT OF USER-FRIENDLY INTERPRETATION AND PREDICTION TOOLS

In the preceding chapters, focus was on extensive testing of common methodologies for coalmine water quality prediction. In this chapter the development of two tools to assist practioners in arriving at accurate answers is discussed. The ABACUS tool was developed to ensure that consistent ABA interpretation is done, and to maximise the understanding that can be obtained from such testing. The BUGLE tool is a water quality prediction scheme for underground coal compartments.

8.1 ABACUS TOOL FOR INTERPRETING ABA DATA

8.1.1 Development

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 in Section 4.2.5 and incorporates several of the graphic 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.

The tool is Microsoft Excel-based and has been developed to cater for the entire range of users (Figure 128).

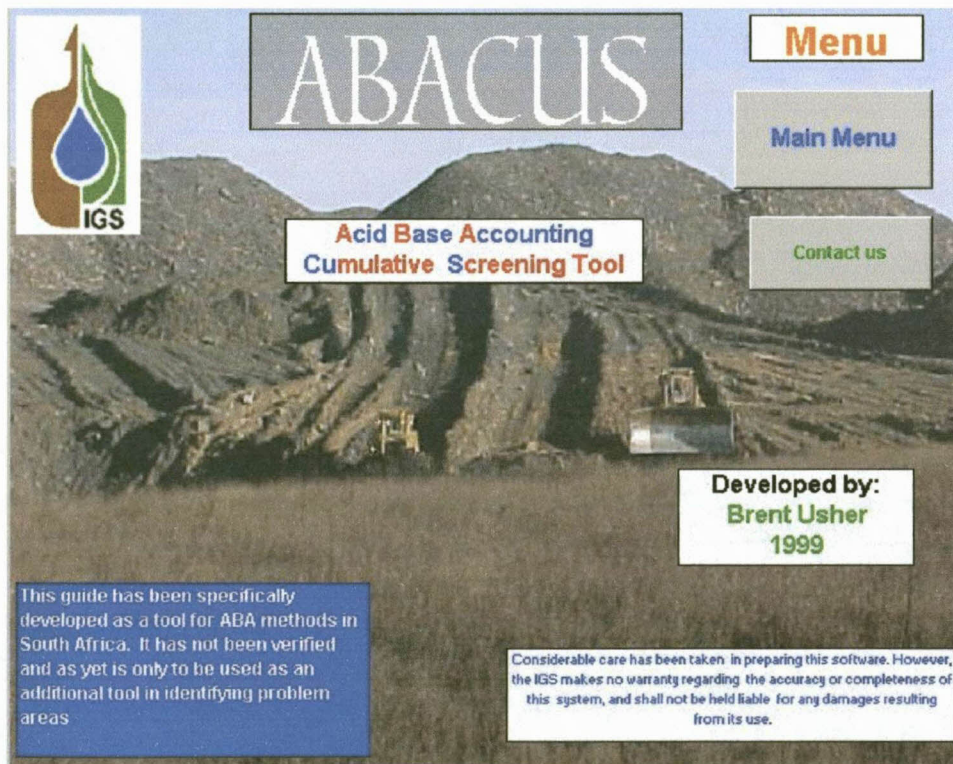


Figure 128: ABACUS entry screen.

8.1.2 Operation

The tool is very simple to apply and is menu/button-driven, with macros programmed to guide the user and lead users to the correct interpretation (Figure 129).

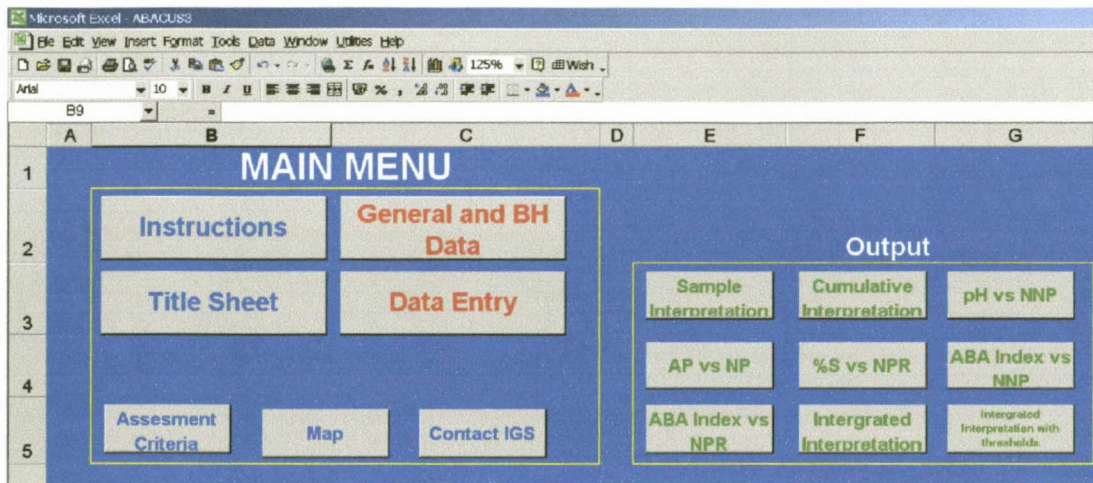


Figure 129: Menu for ABACUS, within MS-Excel.

8.1.2.1 Instructions

Full step-by-step instructions are provided with the ABACUS tool, with button-driven links to each item within ABACUS. Figure 130 shows the instruction sheet and buttons:



Figure 130: Screenshot of the instruction screen of ABACUS.

8.1.2.2 Inputs

The inputs required are the following (Figure 131 and Figure 132):

- Sample number.
- Neutralising potential.
- Acid Potential or % S.
- Initial and oxidised pH (if available).

If use is made of cored boreholes or depth-specific sampling at different localities, volumetric calculations can be made to provide an overall assessment of the area.

Main Menu		Data Input	
MINE NAME: Mine X			
No	Borehole Name	Area Represented (Ha)	Total Depth
1	Core1		250
2	Core 2		300
3	Core3		500
4	Core4		600
5	Core5		700
6	Core6		800
7	Core7		900
8	Core8		1000
9	Core9		500
10	Core10		200
ABACUS can currently be used for 10 coreholes and 300 samples			
Threshold values			
Acid Potential		10	
Neutralizing Potential		20	

Figure 131: Input for borehole-related data.

Main Menu		Back to Instructions		General and BH Data					
Either value									
Site	Core/Hole No	Site/Sample Name	Paste/Initial pH	Final pH	% S	Acid Potential (Open System) kg/t CaCO ₃	Base Potential kg/t CaCO ₃	Lithology	Depth Bottom
Mine X	1	BG1-1	7.95	4.54		10.00	10.00	SNDS	13.610
Mine X	1	BG1-2	6.95	1.86	0.5		0.00	SNDS	18.090
Mine X	1	BG1-3	7.57	3.37	1		6.19	SNDS	24.150
Mine X	1	BG1-4	8.08	2.79	2		8.96	SNDS	35.530
Mine X	1	BG1-5	6.51	2.21	1.2		0.28	SNDS	39.580
Mine X	1	BG1-6	8.26	1.79	0.35	10.94	8.43	SHLE	43.180
Mine X	1	BG1-7	8.22	1.94		9.90	8.12	SNDS	45.950
Mine X	2	BG2-1	7.19	6.09	0.1		3.64	SOIL	21.31
Mine X	2	BG2-2	8.71	7.17		2.45	12.62	SNDS	33.320
Mine X	2	BG2-3	8.35	7.64		15.75	25.92	SNDS	39.900
Mine X	2	BG2-4	8.06	1.73		54.94	25.83	SNDS	40.410
Mine X	2	BG2-5	7.83	2.33		52.05	10.31	SNDS	42.830
Mine X	3	BG3-1	7.38	7.63		4.29	14.98	SNDS	14.980
Mine X	3	BG3-2	7.33	1.63		22.51	5.65	SNDS	17.770
Mine X	3	BG3-3	8.28	2.75		17.49	6.33	SNDS	26.41
Mine X	3	BG3-4	8.21	2.12		17.98	6.11	SNDS	31.050
Mine X	3	BG3-5	8.02	6.16		7.02	11.02	SNDS	34.540
Mine X	3	BG3-6	9.11	8.05		32.70	61.11	SNDS	38.100
Mine X	3	BG3-7	7.58	4.64		4.84	7.82	SNDS	46.840
Mine X	3	BG3-8	8.75	7.8		2.44	31.21	SNDS	51.880
Mine X	3	BG3-9	8.41	1.63		14.38	6.84	SNDS	57.420
Mine X	4	BG4-1	6.63	3.58		1.42	0.79	SNDS	8.980
Mine X	4	BG4-2	6.36	1.94		8.75	5.89	SNDS	9.700
Mine X	4	BG4-3	3.40	1.96		68.14	0.00	SNDS	12.660
Mine X	4	BG4-4	6.02	2.7		4.90	0.00	SNDS	20.760
Mine X	4	BG4-5	7.99	2.98		23.86	16.78	SNDS	23.330

Figure 132: Input for ABA data.

8.1.3 ABACUS Outputs

Based on these inputs the following output is given (Figure 133 and Figure 134):

- Open system NNP.
- Closed system NNP.
- Net Neutralising Ratios (NPR).
- Interpretations based on the screening criteria given in the preceding section.
- Interpretive graphs will be generated automatically.

<div> Main Menu Back to Data Sheet Go to Instructions </div>							
Site Number	pH values	Net Neutralising Potential	NPR (Open System)	NPR (Closed System)	%S and NPR Method(Soregall and Lawrence,1997)	ABA INDEX	VERDICT
061-1	Medium Risk Acid Generation	Verify with other tests	Likely Acid Generator	Likely Acid Generator	confirm with other testing	8	Do Further Testing
061-2	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	46	High Acid Potential
061-3	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	24	High Acid Potential
061-4	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	28	High Acid Potential
061-5	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	30	High Acid Potential
061-6	Higher Risk Acid Generation	Verify with other tests	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	11	High Acid Potential
061-7	Higher Risk Acid Generation	Verify with other tests	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	11	High Acid Potential
062-1	Lower Acid Risk	Verify with other tests	Acid under certain conditions	Likely Acid Generator	Too little S to create sustained acidity	0	Do Further Testing
062-2	Lower Acid Risk	Verify with other tests	No Acid Potential	Acid under certain conditions	Too little S to create sustained acidity	-16	Very Low Risk
062-3	Lower Acid Risk	Verify with other tests	Acid under certain conditions	Likely Acid Generator	confirm with other testing	1	Do Further Testing
062-4	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	22	High Acid Potential
062-5	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	26	High Acid Potential
063-1	Lower Acid Risk	Verify with other tests	Acid under certain conditions	Acid under certain conditions	Too little S to create sustained acidity	-17	Very Low Risk
063-2	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	21	High Acid Potential
063-3	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	30	High Acid Potential
063-4	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	18	High Acid Potential
063-5	Lower Acid Risk	Verify with other tests	Acid under certain conditions	Likely Acid Generator	Too little S to create sustained acidity	-1	Do Further Testing
063-6	Lower Acid Risk	Verify with other tests	Acid under certain conditions	Likely Acid Generator	confirm with other testing	6	Do Further Testing
063-7	Medium Risk Acid Generation	Verify with other tests	Acid under certain conditions	Likely Acid Generator	Too little S to create sustained acidity	-2	Do Further Testing
063-8	Lower Acid Risk	Probably Excess Neutralising Minerals	No Acid Potential	No Acid Potential	Too little S to create sustained acidity	-18	Very Low Risk
063-9	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	16	High Acid Potential
064-1	Medium Risk Acid Generation	Verify with other tests	Likely Acid Generator	Likely Acid Generator	Too little S to create sustained acidity	3	Do Further Testing
064-2	Higher Risk Acid Generation	Verify with other tests	Likely Acid Generator	Likely Acid Generator	Too little S to create sustained acidity	11	High Acid Potential
064-3	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	59	High Acid Potential
064-4	Higher Risk Acid Generation	Verify with other tests	Likely Acid Generator	Likely Acid Generator	Too little S to create sustained acidity	36	High Acid Potential
064-5	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	15	High Acid Potential
064-6	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	21	High Acid Potential
064-7	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	18	High Acid Potential
064-8	Lower Acid Risk	Verify with other tests	Acid under certain conditions	Acid under certain conditions	Too little S to create sustained acidity	-14	Very Low Risk
064-9	Lower Acid Risk	Probably Excess Neutralising Minerals	No Acid Potential	No Acid Potential	Too little S to create sustained acidity	-20	Very Low Risk
064-10	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	47	High Acid Potential
065-1	Medium Risk Acid Generation	Verify with other tests	No Acid Potential	No Acid Potential	Too little S to create sustained acidity	-10	Very Low Risk
065-2	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	26	High Acid Potential
065-3	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	54	High Acid Potential
065-4	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	22	High Acid Potential
065-5	Lower Acid Risk	Verify with other tests	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	9	Do Further Testing
065-6	Lower Acid Risk	Verify with other tests	No Acid Potential	No Acid Potential	Too little S to create sustained acidity	-14	Very Low Risk
065-7	Higher Risk Acid Generation	Potential Acid Generator	Likely Acid Generator	Likely Acid Generator	Additional Confirmation of Acidity	33	High Acid Potential

Figure 133: Comparative interpretation sheet.

The graphs the ABACUS generates includes:

- a pH vs. NNP graph.
- a S% vs. NPR graph.
- a graph of AP vs. NP with categories of expect acid-generation.

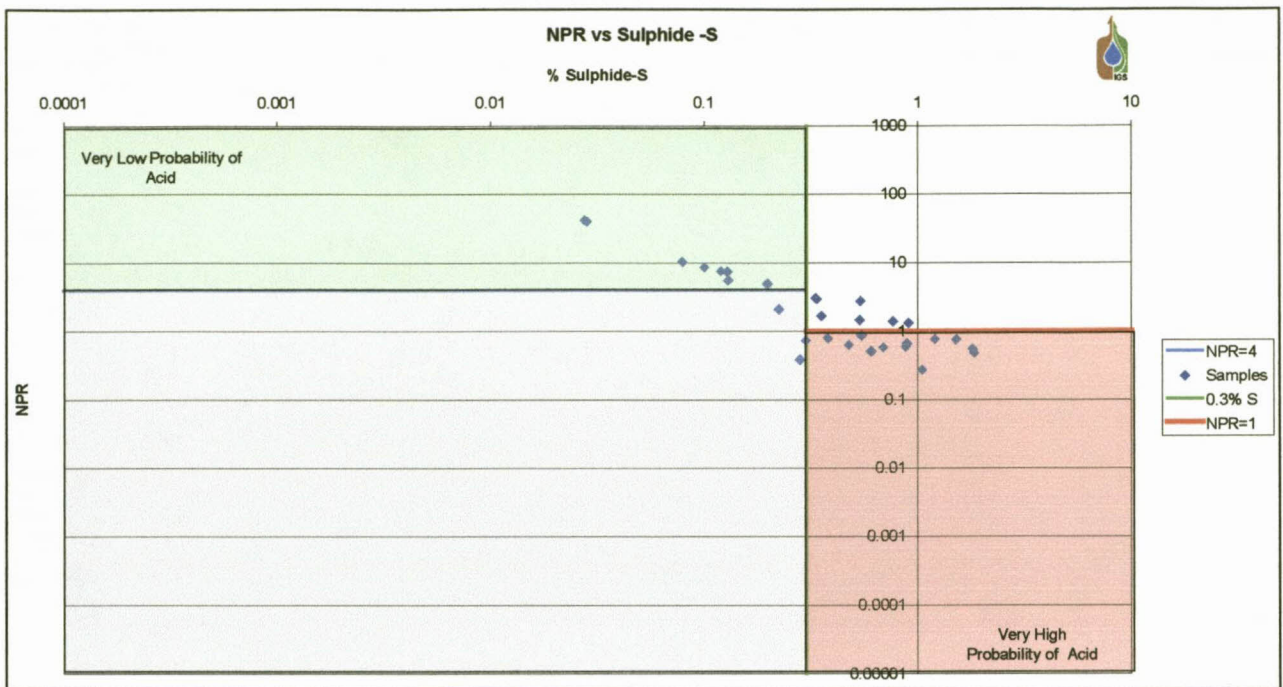


Figure 134: Example of interpretative graphs produced by ABACUS.

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 for interpreting 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 assigned based on present understanding, but tests have been performed for sensitivity and output generated with various real and hypothetical values.

The system can accommodate volumetric calculations in cases where depth-specific information is available for the area under investigation. This volumetric approach is widely used in non-South African Coalfields. The approach is for example used by the Pennsylvanian authorities in the Appalachians (Brady, Personal Communication, 2001). Application of such volumetric calculations is given in Section 9.2.

8.1.3.1 Integration of an approach to consider entire mined area to obtain a volumetric assessment in ABACUS

One of the most serious criticisms against ABA is that the results are often difficult to extrapolate to a field scale. This section will explain an extrapolation technique that can be used if lithological samples have been tested across the extent of the mine.

The Thiessen polygon technique is used by the Pennsylvanian State authorities to assist in the evaluation of opencast coal mines (Perry, 1998). The Thiessen polygon method is commonly used in hydrology to assign the area of influence of a rain gauge and provides an excellent method for weighting the influence of each borehole on which ABA is done. When the entire extent of the borehole has been tested, as is recommended in this thesis, it provides a relatively easy, yet powerful, volumetric calculation to predict what would happen at an opencast mine.

The subdivision of Optimum Colliery, using the Theissen polygon method, is shown in Figure 135 below. An extension is available in ARCVIEW (ESRI, 1999) with which these polygons can be determined for any particular area.

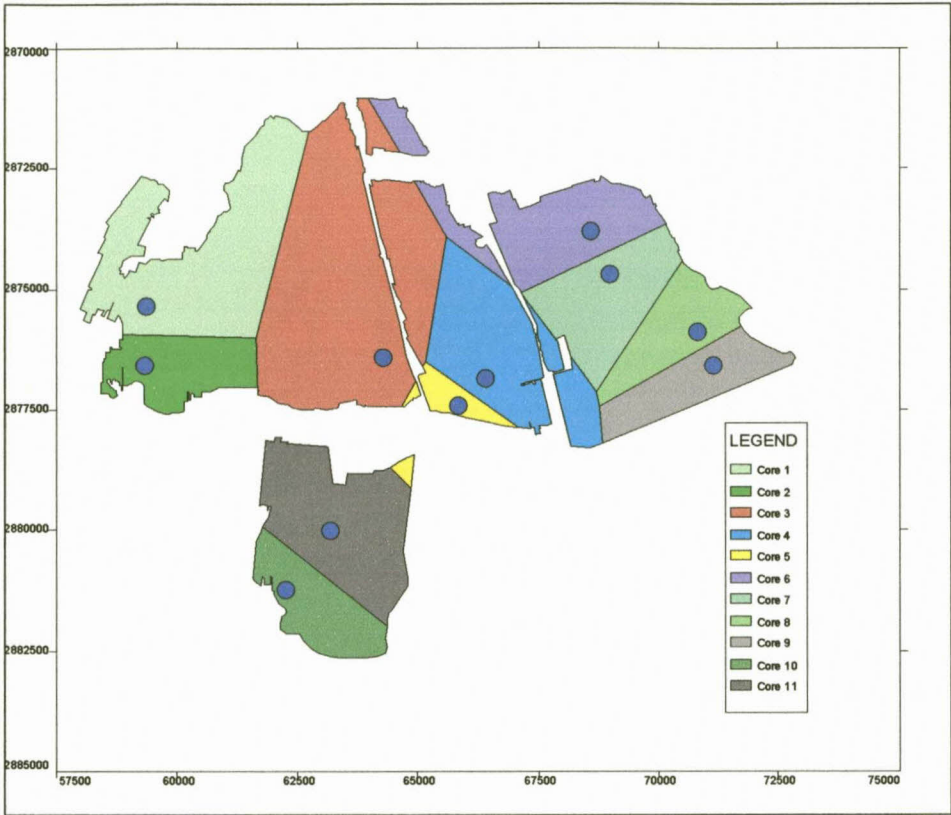


Figure 135: Subdivision of different areas using the Theissen polygon method.

The areas that each borehole “represents” can therefore be calculated and is given in Table 26 below.

Table 26. 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 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 27.

The results are based on a volumetric calculation 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 an accurate determination of the overall characteristics of the spoiled overburden, provided the boreholes can be regarded as representative of the area (See Figure 136 and Table 27).

This technique is a very important component of overall ABA interpretation, especially in spoils, since an accurate assessment of the mine site's ABA is obtained. Using techniques such as these researchers such as Skousen *et al.*, 2002 report a success rate of over 95% at over 50 mine sites in the Appalachian opencast collieries.

Table 27. Combined results for the entire mine using the PDEP spreadsheet methodology.

OVERBURDEN ANALYSIS - MINE SITE ACID-BASE ACCOUNT SUMMARY						
OPERATOR IGS			COUNTY			
PERMIT NO.			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				
MPA = SULFUR X 31.25:		WITHOUT ALKALINE ADDITION		
		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:		MPA	NP	NET NP
		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		

Table 28. Example of data input with calculated parameters.

OVERBURDEN ANALYSIS SPREAD SHEET						CARBONOLITH	CARB	2580	ALK ADD (TONS/AC CaCO3)		0				
OPERATOR	IGS	COUNTY				CLAY	CLAY	3450	LATITUDE						
PERMIT NO.	1	TOWNS OPT				COAL	COAL	1800	LONGITUDE						
DRILL HOLE	OB11					LIMESTONE	LMSN	3670	COAL SEAMS:						
						OTHER	OTHR	3670	STATE PLANE ZONE						
THRESHOLD	AP	NP				SANDSTONE	SNDS	3670	FEET (NORTH/SOUTH)						
VALUES	1	10				SHALE	SHLE	3700	FEET (EAST/WEST)						
						SILTSTONE	SLSN	3750	SURFACE ELEV.(FT.)						
						SOIL	SOIL	2000							
						TILL	TILL	3600	MPA, NP -TH = With Thresholds						
TOTAL DEPTH	238.73	TOP	ACREAGE	169.83	BOTTOM	169.83									
BOTTOM	THICKNESS	ROCK	AP	FIZZ	NP	ACREAGE	UNIT WT.	FRACTION	TONS	TONS	TONS	TONS	NET NP	NET NP	TONS OF
DEPTH (FT)	FEET	TYPE		RATING			TONS/AC-FT	SPOILED	MPA -TH	MPA	NP -TH	NP	TONS -TH	TONS	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	

Main Menu		OVERBURDEN ANALYSIS - MINE SITE ACID-BASE ACCOUNT SUMMARY				
Mine	Mine X					
DRILL HOLE	BOTTOM Area	TOTAL TONS AP using %S X 31.25	TOTAL TONS NP	TOTAL TONS NET NP	TOTAL TONS OB	NPR
Core1	250	9857308	2452496	-7404811	341879310	0.25
Core 2	300	2884587	3592070	707483	295632584	1.25
Core3	500	9470672	12534398	3063726	853891008	1.32
Core4	600	12643360	10039327	-2604033	1010393080	0.79
Core5	700	9265013	6530908	-2734105	966226304	0.70
Core6	800	0	0	0	0	0.00
Core7	900	0	0	0	0	0.00
Core8	1000	0	0	0	0	0.00
Core9	500	0	0	0	0	0.00
Core10	200	0	0	0	0	0.00
Totals	5750.00	44120940	35149200	-8971740	3468022287	0.80
ACID BASE ACCOUNTING SUMMARY PARAMETERS						
MPA = SULFUR X 31.25:		TOTAL TONS:		AP	NP	NET NP
OPEN SYSTEM				44120940	35149200	-8971740
ABA PARAMETERS (TONS/THOUSAND):				12.72	10.14	-2.59
DER RATIO (NP/MPA):				0.80		
				DEFICIENCY		
MPA = SULFUR X 62.5:		TOTAL TONS:		AP	NP	NET NP
CLOSED SYSTEM				88241880	35149200	-53092681
ABA PARAMETERS (TONS/THOUSAND):				25.44	10.14	-15.31
DER RATIO (NP/MPA):				0.40		
				DEFICIENCY		

Figure 136: Overall volumetric/mass calculation for the area.

8.1.3.1.1 THRESHOLD VALUES built into ABACUS

The concept of threshold values is important for ABA interpretation. Threshold values for AP and NP are defined through experience in a particular area, and cognisance of ABA concepts and limitations. Below the threshold values, 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% respectively. Samples that do not meet these criteria are assigned a value of zero and in essence are treated as chemically inert (Perry, 1998).

Very low values are thus disregarded, so that only the layers actively acidifying or neutralising are considered. Figure 137 gives an illustration of this concept for Core Borehole 7 at Optimum Colliery (Section 9.2). Thresholds were set at a conservative 5 kg/t CaCO_3 for AP and 10 kg/t 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 Figure 137), it can be seen that for the area of influence for this borehole the net volumetric balance under open system conditions shows an excess of 698 t of NP per acre. However, when the thresholds are considered, it can be seen that there is a deficit of 75 t 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				Without Thresholds @ 31.25			
MPA (Total Tons)	384049	Tons/1000 tons	7	MPA (Total Tons)	390418	Tons/1000 tons	8
NP (Total Tons)	375047	Tons/1000 tons	7	NP (Total Tons)	474299	Tons/1000 tons	9
Net Tons NP	-9002	Tons/1000 tons	0	Net Tons NP	83881	Tons/1000 tons	2
NP/MPA Ratio	1			NP/MPA Ratio	1		
Available NP (Tons per acre)	75 DEFICIENT			Available NP (Tons per acre)	698 EXCESS		
NP Available to achieve 0.6% NNP (Tons per acre)	2649 DEFICIENT			NP Available to achieve 1.2% NNP (Tons per acre)	4450 DEFICIENT		

Figure 137: Illustration of the use of thresholds.

Over time, as a larger database of ABA values, and subsequent auditing of field results, become available, specific values for such threshold values will be obtained. This will further serve to increase the success of ABA in coalmine water quality prediction and leading to assessments being done with a higher degree of confidence.

8.1.4 Instructions to ABACUS

A user's guide is provided in part 3 of the appendices to this thesis. Furthermore, the instructions in ABACUS contain macro-driven buttons which will lead users to the correct use of the system.

8.2 DEVELOPMENT OF AN EMPIRICAL GEOCHEMICAL MODEL FOR UNDERGROUND COMPARTMENTS IN SOUTH AFRICAN COLLIERIES

8.2.1 Background

A major deficiency in the currently available prediction tools is the lack of a useable tool to predict water quality evolution within South African collieries.

Two approaches to this problem are possible:

- Kinetic geochemical models.
- Empirical geochemical models.

The differences in terms of current data requirements and availability in South Africa are given by the Table 29 and (from Usher *et al.*, 2003):

Table 29. Requirements for kinetic geochemical models.

Parameter	Importance	Accuracy required	Current Accuracy	How to improve current
Mining plans				
Current	*****	*****	****	?
Future	*****		***	
Water Quality Monitoring	*****	****	***	More regular, more precise
In situ parameters (T, EC, pH)	****	****	**	More regular, more precise
Reaction rates	*****	*****	****	Can not
Reactive Surface Areas	*****	****	*	?
Precise flow paths	****	****	**	?
Mineralogy	****	****	**	More sampling
Stage Curves	****	*****	****	
Gas fluxes and partial pressures	****	***	*	Measurements+ models
Control on solution/precip	****	****	****	No Need

Table 30. Requirements for empirical geochemical models.

Parameter	Importance	Accuracy required	Current Accuracy	How to improve current
Mining plans				
Current	*****	****	****	
Future		**	***	
Water Quality Monitoring	*****	****	***	More regular, more precise
In situ parameters (T, EC, pH)	***	**	**	More regular, more precise
Salt generation rates	*****	***	*	Accurate, regular monitoring
Mineralogy	***	***	**	More sampling
Water Inflows	*****	*****	***	Recharge, aquifer parameters
Stage Curves	****	***	***	
Controls on solution/precip	*****	****	****	

From the tables above it is clear that the input requirements for kinetic modelling are generally not measured or available in South Africa. On the other hand, empirical models can be applied, since the necessary data are available; appropriate interpretation thereof is, however, required.

8.2.2 Development of an empirical model for underground coal compartments in the Highveld Coalfield

Based on the preceding discussion, it can be seen that a tool utilising the concept of an empirical sulphate production rate can be developed. Such a tool would need to have the following functionality:

- Incorporate the empirical sulphate prediction rate as driver for water quality predictions.
- Take the geometry of the mining compartment into account.
- Consider the mining method.
- Build appropriate neutralisation considerations into the model.
- Link acid production/neutralisation to data such as Acid-Base Accounting.
- Be able to consider several sources of water including the water currently in the compartment, recharge water through roof drip, fracture flow, and pumpage in and out of the compartment, in a mass balance approach.
- Provide logical constraints on water quality, by taking major drivers on quality into account.
- Be interactive so that users can understand the influence of each parameter.
- From all this be able to provide a qualitative guide to water management options to be employed by a mine.

The effect of each of these considerations and the incorporation thereof into an empirical prediction tool will be discussed in Sections 8.2.3 to 8.3.11.

To take all these effects into account, an empirical model was developed. The model has been named BUGLE, based on the approach used, namely a "Bayesian Underground Coal Mine Geochemical Evaluator" (See Figure 138). The Bayesian approach implies that empirical data are combined with logical constraints within a site-specific context, to predict the system's response.

It must be stressed at the outset that several of the parameters required for calibrating such an empirical model have not been measured at collieries up to the present. To compensate for this, well-constrained approximations based on available knowledge and data, fundamental reactions, and experience have been used as input to the model. For this reason the word Bayesian is included in the title, since Bayesian approaches attempt to do exactly this (Van Tonder, Personal Communication, 2003). Bayesian estimation techniques rely on the observed behaviour of system and inclusion of factors likely to influence this behaviour (Hoel and Jessen, 1971). In Bayesian estimation the likelihood of an event can be

estimated taking explicit consideration of certain contextual features. In the context of predicting water quality changes in an underground coal compartment, taking the observed water qualities into account and deriving relationships or causes from these, together with measured parameters such as ABA can be used in such an approach.

As time progresses and the appropriate measurements are made and data collected, all the factors within such a model will become more accurate and a wider applicability within the South African Coalfields will be achieved.

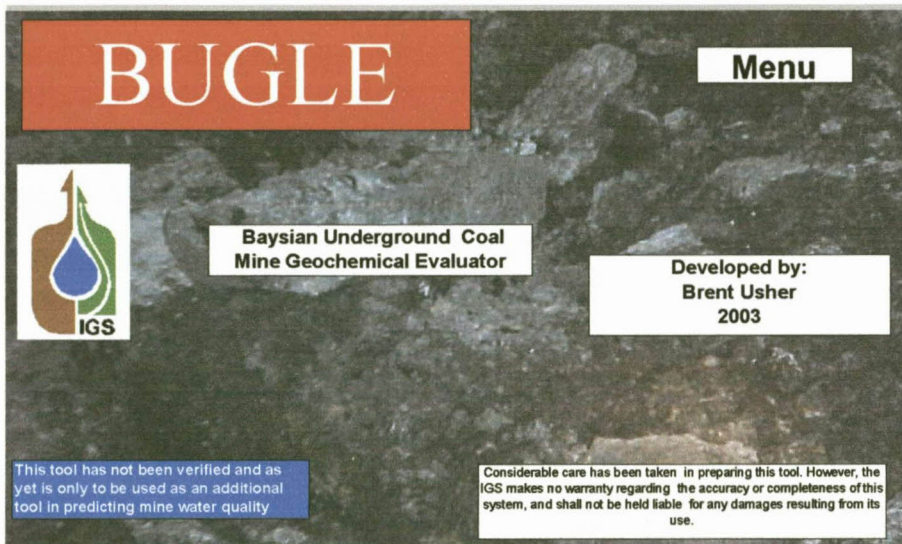


Figure 138: BUGLE title screen.

8.2.3 Empirical rates in South African coal mines

8.2.3.1 Opencast Collieries

Hodgson and Krantz (1998) report an empirical sulphate generation rate of between 5 and 10 kg/ha/day for opencast collieries. Van Tonder *et al.* (2003) explore this phenomenon further, and incorporate the possibility of gypsum precipitation into the generation rate (See Section 2.9).

8.2.3.2 Underground collieries

No consistent application or determination of an empirical sulphate generation rate was available for direct application. As part of a Coaltech 2020 investigation into the Witbank Coalfield, Hough (2002) and Usher *et al.* (2002) investigated probable sulphate generation rates.

8.2.3.2.1 Transvaal Navigational Colliery

The Transvaal Navigational Colliery's underground workings have been used to predict the production rates of sulphate generation at Block C, Block F and Welstand Block. The production rates are estimated by considering underground voids in different stages of fill-up. The volumes in the underground voids are determined with sulphate increases over

time, and from these values a production rate is calculated for sulphate generation. The method therefore provides a way to extrapolate future chemistry in the area.

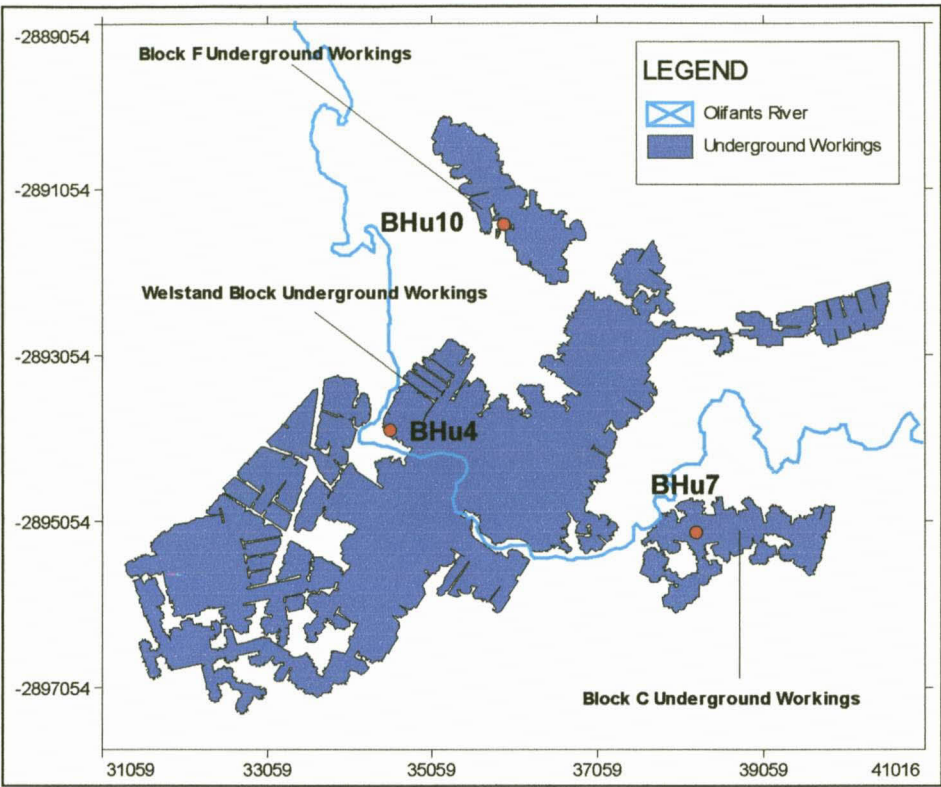


Figure 139: TNC's underground workings used to calculate the Sulphate Production Rate. Also indicated are the positions of the monitoring boreholes (after Hough, 2003).

Welstand Underground Block: Welstand Underground Block is about 95% flooded. Two dates with sulphate concentrations and water levels were selected to calculate the sulphate increase and water volume increase in underground workings (see Figure 139). The sulphate increase over the 750-day period is 101 mg/L, while the water level has increased by 0.94 m, and the increase in volume in the underground void was 3.73×10^8 litres. The Sulphate Production Rate calculated with these data was 0.343 kg/ha/d.

Table 31. Table of values used in the Welstand Block reaction rate calculations.

Borehole-BHu4	Sulphate Concentrations (mg/L)	Water Levels (mamsl)	Volume in Void (L)
Point 1 (Day-1)	967	1520.99	2.51E+10
Point 2 (Day-720)	1068	1521.93	2.55E+10
Difference in Values	101	0.94	3.73E+08

Block C Underground Workings: Block C is approximately 90% flooded. Using the same methodology, the Sulphate Production Rate calculated with these data was 0.422 kg/ha/d.

Table 32. Table of values used in the Block C underground reaction rate calculations.

Borehole-BHu4	Sulphate Concentrations (mg/L)	Water Levels (mamsl)	Volume in Void (L)

Point 2 (Day-990)	578	1532.633	2.38E+06
Difference in Values	6.4	13.375	8.01E+04

Block F Underground Workings: Block F is about 84% flooded. Calculating a sulphate generation rate through a mass balance approach yields a value of 0.532 kg/ha/d SO₄.

Table 33. Table of values used in the Block F underground reaction rate calculations.

Borehole-BHu4	Sulphate Concentrations (mg/L)	Water Levels (mamsl)	Volume inVoid (L)
Point 1 (Day-0)	973	1533.493	2.04E+06
Point 2 (Day-730)	980	1534.197	2.08E+06
Difference in Values	7	0.704	4.32E+04

To refine the above-calculated values more data over the South African Coalfields are needed; these are currently unavailable. It is recommended that more of these values (reaction rate values and percentage underground filled over time) be generated. With more reaction rate values the trend function will be obtained more accurately.

The reaction rate points were plotted on a graph and a trend line fitted to the data points by means of a second-order polynomial function of the form:

$y = -1.2727 (x)^2 - 0.0091 (X) + 1.4452$, where X = the % of the void which is full.

The values above are in line with values reported by Vermeulen (2003), who obtained an initial sulphate generation rate of 1.4 kg/ha/day in a bord-and-pillar compartment, which rapidly fell as the level of flooding increased. Vermeulen (2003) obtains rates in the order of 2 kg/ha/day for relatively unflooded mines which decrease to values of around 0.4 to 0.5 kg SO₄/ha/day when the mines reach the stage of 90% to 95 % full.

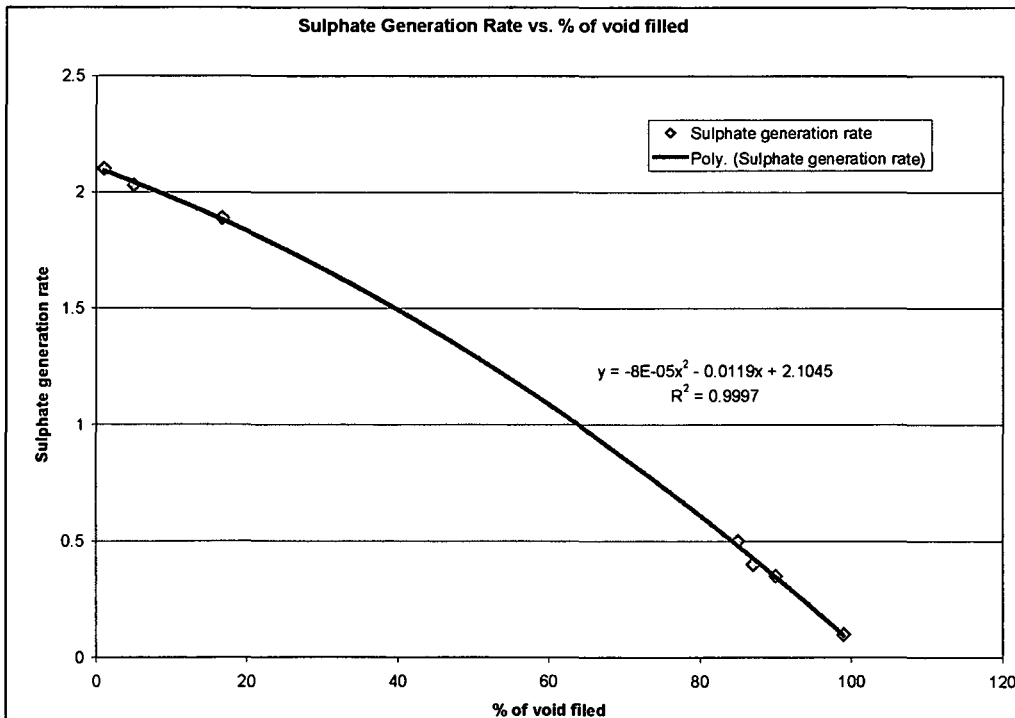
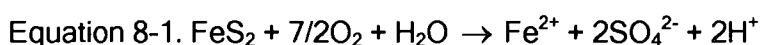


Figure 140: Graph of the calculated reaction rate points, trend line and function.

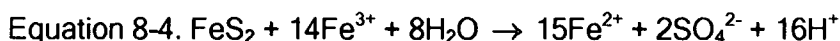
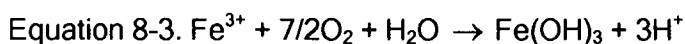
Overall, based on observations at 5 collieries, the following function provides a good estimate of sulphate production (in kg/SO₄/ha/day):

$$y = -8E-05x^2 - 0.012x + 2.15$$

It can be concluded from the calculations above that the reaction rate decreases as the underground void fills up with groundwater. The reason for this is that, as the void fills up with groundwater, the oxygen is cut off from the reaction surface, as can be seen in Equation 8-1 and Equation 8-2. Oxygen is a necessary oxidant, and if it is limited the AMD process will be inhibited. The first increment of water-level rise is very important, because the mining floor and rubble around the pillars will be inundated first, depriving a large part of the reaction surface of oxygen (Evangelou, 1995).



Oxygen diffusion to pyritic material is greatly reduced upon inundation, because the diffusion coefficient of O₂ through the covering water is only 1/10 000 of that through the atmosphere. Hence, the rate of O₂-consuming reactions becomes low and rate-limiting, and bacterial oxidation of pyrite becomes slow or nil (Evangelou, 1995).



In support of this, Castro and Moore (2000) show how inundation reduces the pyrite oxidation and sulphate generation in a pit lake.

The mass balance approximation is a method that needs further research to refine the sulphate generation rates. This method can be used to predict future scenarios. When the sulphate generation rate for opencast pits (5 -10 kg/ha/d) of Hodgson and Krantz (1998) is compared to the determined generation rate (0.1 - 1.5 kg/ha/d) for underground areas, it is clear that the sulphate generation rate for the underground workings is an order smaller. This is due to the much smaller reaction surface in the underground workings when compared to that of an opencast pit. It must also be noted that although the sulphate generation rate might be lower than that of the opencast, the sulphate concentration in underground areas could be higher, due to less dilution as a result of lower water ingress.

8.2.4 Determining a site-specific sulphate generation rate

The discussion above outlines the type of approach that needs to be followed to find a site-specific rate that can be used. The type of data to be collected over a period of time, as part of routine monitoring, would include:

- Concentrations of major anions and cations.
- Water level within the compartment.

- Determination of the degree of inundation in the compartment.
- Proportion of different types of mining.
- Water volume pumped from the compartment.
- Water volume and water quality pumped into the compartment.

From this a better site-specific empiric rate can be determined for application to future prediction.

8.2.5 Mining method and compartment dimension

The underground workings can consist of various layouts and configurations. These configurations are a function of mine plan and mining method, and can broadly be classified under bord-and-pillar and total extraction methods. Adits, shaft entrances, haulages to active sections and ventilation channels can all be considered as part of a bord-and-pillar section.

The different layouts of the mines are expected to have different effects on the quality of underground water. The extent to which these configurations affect the quality of underground water must be determined according to the different mining phases, the current status of the compartment, and the way in which water is managed within the compartment.

8.2.5.1 Mining Methods and its impact on groundwater

The coal-seam roof collapse caused by total extraction mining significantly alters the geohydrological properties of the rocks and soils overlying the workings. For shallow mines (<200 - 300m) the collapse usually propagates through to the surface and establishes a direct connection between shallow groundwater aquifers and the underlying workings. Although the specific technique used for total extraction does not significantly influence the extent of the impact on the groundwater regime, it is worth noting that two basic methods are usually employed:

Bord-and-pillar development (Figure 141) is often followed by pillar extraction using coal-cutting machines in the process called stooping (Figure 142). Longwall mining using mechanised methods in selected areas. Coal is removed in "panels". These panels are rectangular blocks of the coal seam that are mined as a single unit. Panels are typically 120 m to 200 m wide and approximately 1000 m long.

The common characteristic of these mining methods is that the removal of the coal seam results in the caving of the overlying strata into the mined void. This disruption of the overlying rock-mass has a significant effect on the geohydrology. For this reason, the relationship between mining-induced subsidence and groundwater flow has been studied in many investigations and research programmes.

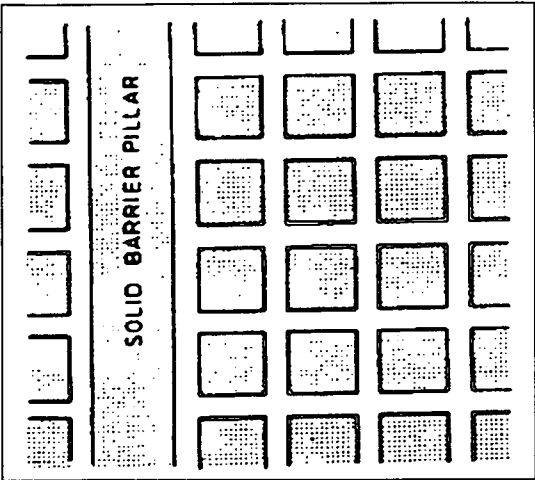


Figure 141: Example of bord-and-pillar mining in a modern underground colliery.

In longwall mining two sets of roads are developed by means of bord-and-pillar mining at right angles to the longwall face, which is generally about 200 m wide. One of the roads is used for the conveyor. The longwall mining pre-developed coal pillars (about 50 m wide) are extracted by means of continuous miners, shuttle cars and self-advancing hydraulic supports.

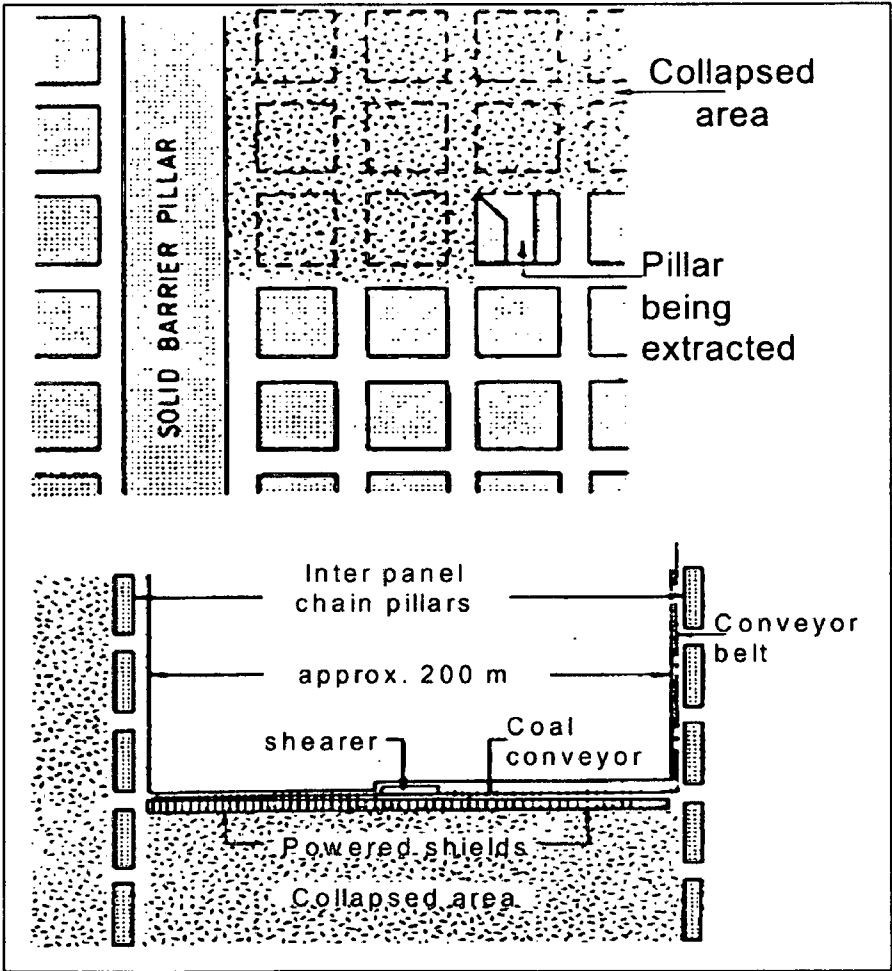


Figure 142: A. Pillar extraction, B - Longwall mining (Bezuidenhout and Sutherland, 2002).

8.2.5.2 Causes and effects of mining methods

8.2.5.2.1 Bord-and-Pillar mining

Recharge into bord-and-pillar compartments is generally lower when compared to high extraction compartments, due to the roof being kept intact through support by the pillars. This results in slower fill rates, allowing the build-up of oxidation products on reactive coal particle surfaces during the filling period. Pyrite oxidation is kinetically driven, and although it decreases over time if no flushing takes place, it can generate significant amounts of oxidation products.

Fracturing of the coal pillar and the roof sediments, results in an increased reactive surface area. This can significantly increase the mass of acidity produced by AMD processes (Bezuidenhout and Sutherland, 2002).

The created compartments can be turned into compartment dams, which will allow for the inundation of compartment reactive surfaces as well as make storage space available for water management/reticulation purposes.

8.2.5.2.2 High Extraction mining

Recharge into high extraction compartments is generally higher when compared to bord-and-pillar compartments, due to the fracturing of the overlying geology during goafing. This allows for higher recharge rates and hence faster filling rates, reducing the time for oxidation products to build up.

Where goafing results in higher rainfall recharge, the alkalinity mobilised in the overlying geology can contribute to the overall NP of the high extraction compartment (Bezuidenhout and Sutherland, 2002).

Neutralisation Potential (NP) associated with overlying rocks is introduced in the compartment due to goafing. This NP can significantly contribute to the alkalinity already present in the coal, as well as that associated with the recharge water.

Conversely, due to the presence of marine sedimentary rocks in the roof, a higher pyrite content is expected, which will in turn become active once goafing results in the exposure of fresh pyrite surfaces to oxygen.

High extraction compartments can be sealed off and rapidly filled with water to reduce the potential rate of pyrite oxidation to insignificant levels. During filling, the NP associated with roof material will become available for neutralisation of the water acidity in the compartment.

8.2.5.2.3 Subsidence Due to High Extraction Mining

Three processes occur in subsidence as recognised by Ropski and Lama (1973):

As the coal seam that supports the overlying rock mass is removed, the immediate roof of the seam fails and collapses, forming rubble fill (goaf). The caved rock breaks up into blocks varying in size from a few centimetres to several metres. These blocks rotate and pile up, partially filling the mined void. A stage will be reached when the mine workings are filled due to bulking of the rubble (Wagner *et al.*, 1989).

As the coal mining face advances, higher-lying beds fail, settle and compress the caved layer. The stress in this "secondary caving zone" depends on the degree of compression of the goafed material. Typically, an extensive network of horizontal and vertical cracks develops, although the degree of displacement is not such that the beds lose their relative positions.

Strata overlying the secondary caving zone bend and sag under their own weight, and compress the goaf. As a result, the strata part along bedding planes. Continuity of the beds is maintained although some fractures develop from the stress of bending and sagging. Sagging results in zones of tension and compression in the rock strata, and the development of cracks (Figure 143).

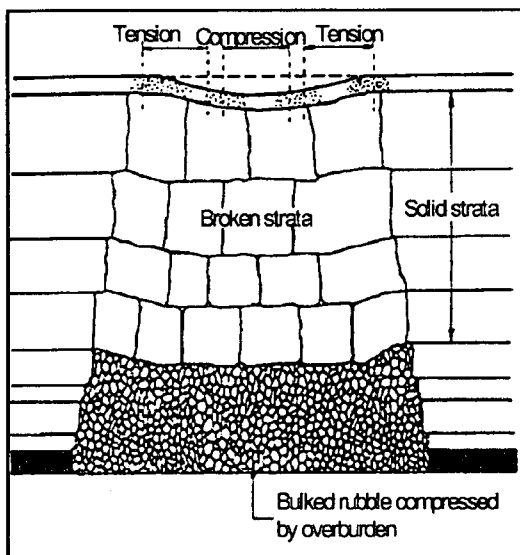


Figure 143: Schematic cross section of a subsided high extracted panel (Ropski, 1973).

The degree of subsidence is dependent on the strength of the overlying strata. Palchik (2002) indicates that in the weak rock, a ratio of 4.1-11.25 exists between the height of the caved zone and the height of the underground coal workings, whereas in strong rocks this ratio is 1.63-4.

8.2.5.3 Incorporating mining method/geometry into BUGLE.

To consider all the influences that the mining method and geometry have on water make and quality, the following data input is required in BUGLE:

- Size of the compartment (ha).
- Area of bord-and-pillar (ha).
- Area of total extraction (ha).
- Mining height.
- Extraction ratio for bord-and-pillar mining.
- Total volume of the compartment.

The areas are required since the empirical rates are expressed as a function of area, and the empiric generation rates differ as a function of mining. In total extraction areas, the size fraction of the collapsed areas is such that the reactive surface area is significantly higher than in a bord-and-pillar area. The degree of collapse is also important, as is the nature of the overlying collapsing material. The mining height is used to determine the likely collapse ratio. In the Highveld Coalfield this has been determined to be in the order of between 1.5 and 2 (Van der Merwe *et al.* (2001), Canbulat *et al.* (2002)).

The total volume of the compartment can be determined through stage curve approaches. A stage curve is a plot of the available storage in a compartment against elevation. Such a plot allows one to determine the storage at any particular water level within the compartment (Figure 144). Construction of a stage curve requires information of mining floor contours, mining heights and an appropriate S-value. In bord-and-pillar mining the extraction ratio is a good estimate of the S, while in total extraction the mining height and relationships of total collapse are used. In the Highveld Coalfield values of 0.2 are used in total extraction areas (Walker *et al.* (2002), Hodgson (2003)).

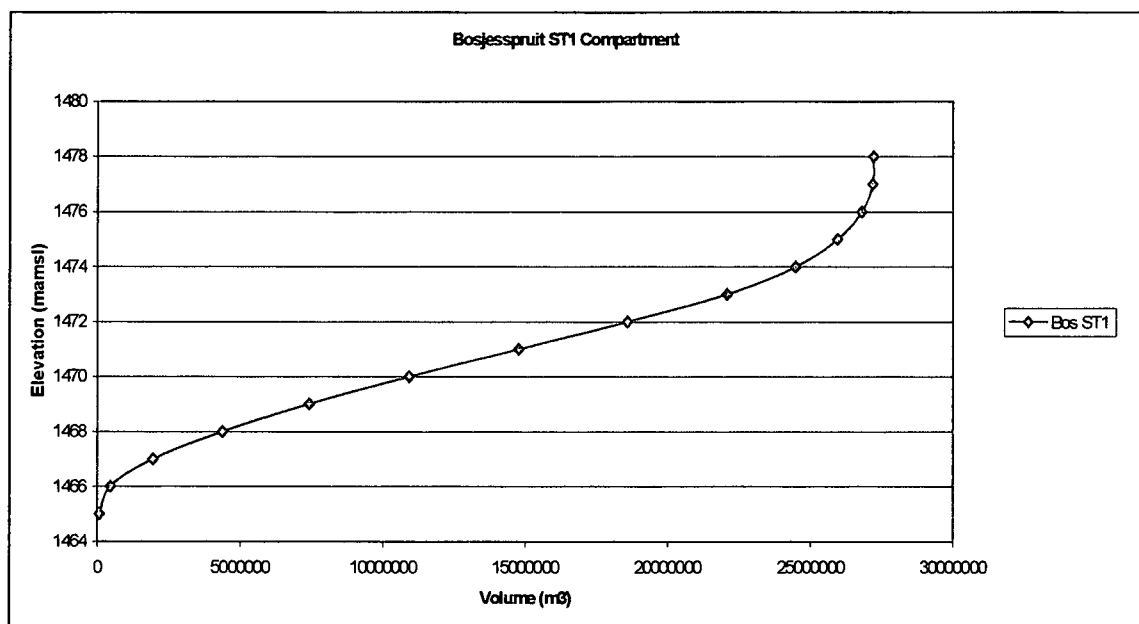


Figure 144: Stage curve for Compartment ST1 showing the position of the decant point as well as the volume of water at that specific point in the pit.

Based on the mining geometry-related information provided, BUGLE will calculate the following:

- Estimated total reactive mass in the compartment.
- Sulphate reaction rate.

BUGLE also uses this information to calculate reactive surface areas, influx into the compartment and various other parameters, which will be dealt with in the sections that follow.

The overall sulphate generation is thus a function of the relative proportion of mining types, with some the influence of ABA parameters also built into this empiric rate.

The mass determination extrapolates the area of each mining type, the mining height and extraction ratio to determine the total mass that can react. By combination with for example ABA, the mass of acid producers and neutralisers can be determined.

8.2.5.4 Determining the overall Acid-Base Balance

Employing the same approach as for the total mass determination, the mass of AP and NP can be determined. For this, ABA data are required. BUGLE allows the input of seven ABA values for a compartment; three representing the coal seam and four the overlying lithology. From research currently underway (Usher, 2003) as part of a Water Research Commission study, it has been found that although the coal seam is fairly homogenous, some variation exists (Refer to Section 9.6). Thus values for the upper, middle and lower third of the seam can be included. The four values for the overburden allow the reacting portions of the collapsing sediments to be included in the assessment for the TE areas. Shown on Figure 145 is the input requirement in BUGLE:

Acid Base Accounting Data		Thickness(m)	NP(kg/t CaCO ₃)	AP(kg/t CaCO ₃)
7	Fourth roof unit			
6	Third roof unit	3.6	15.50	10.18
5	Second roof unit	2.1	15.05	14.49
4	First roof unit	2	17.60	24.70
3	Upper third of coal seam	0.833	40.45	14.63
2	Middle third of coal seam	0.833	57.91	13.05
1	Lowest third of coal seam	0.833	57.48	21.06

Figure 145: Input of ABA data in BUGLE.

Based on this input, the total amount of NP and AP, and the ratio of NP: AP for the entire compartment can be determined. These totals are then also used for calculations based on the empirical reaction rates to determine the depletion of NP and AP over time. The core assumption for these latter calculations is that all the AP is derived from pyrite, and the NP from calcite. The former is generally true in South African coalmines, but the latter needs verification. For this, typical Ca/Mg ratios in static tests, kinetic tests and field observations are useful. It has been found that dolomite forms an important part of the NP, and corrections for this must be made.

Calcite neutralisation reaction (calcite dissolution by sulphuric acid):



Dolomite neutralisation reaction (dolomite dissolution by sulphuric acid):



Thus for every mol of calcite half a mol of dolomite would provide the equivalent neutralisation. In terms of mass relationships this equates to:

$2^*(\text{Mr}_{\text{dolomite}}/\text{Mr}_{\text{calcite}}) = 2^*(100 \text{ g.mol}^{-1}/184\text{g.mol}^{-1})$. This gives an equivalence of 1.0867. In other words, one gram of dolomite has the equivalent NP of 1.0867 g of calcite. If the relationship of calcite: dolomite can be derived from mineralogical

determinations or other tests, the dolomite fraction can therefore also be determined using BUGLE.

From Figure 146 and Figure 147 it is clear that both calcite and dolomite occur within the coal seam. A ratio of 2:1 would indicate equal quantities of calcite and dolomite while 1:1 would indicate pure dolomite, assuming that Ca and Mg only originate from these two minerals. As a starting point therefore it would seem that there are several samples containing more calcite than dolomite and that a 3:1 split would be a fair assumption to work on a mine complex basis.

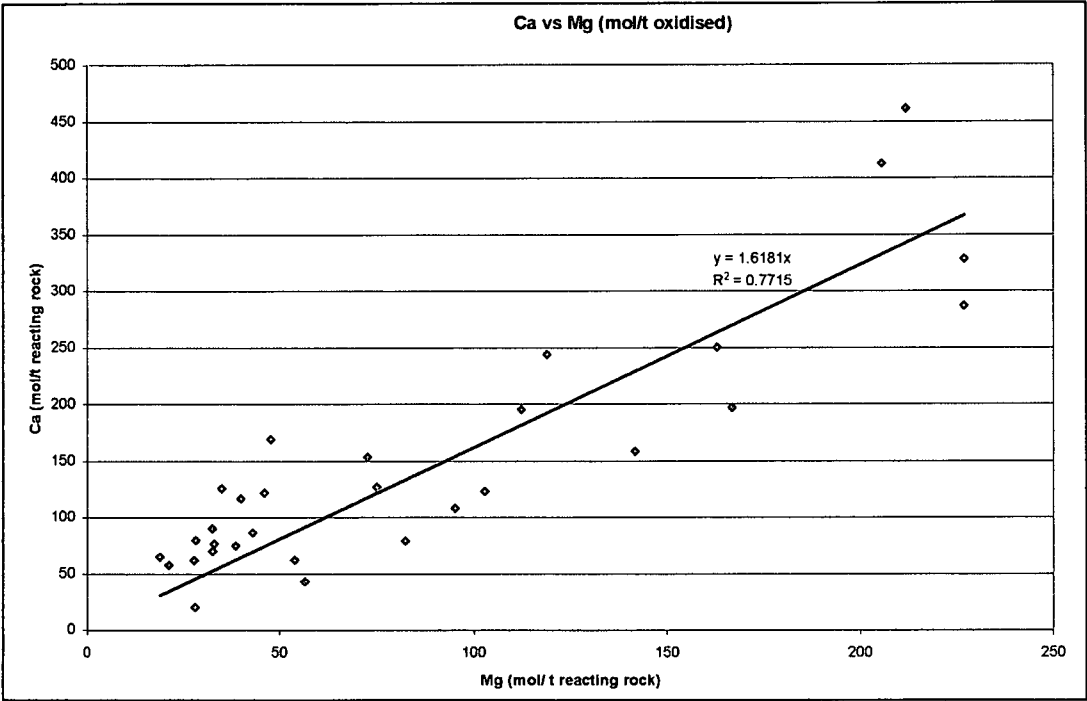


Figure 146: Relative amounts of Ca and Mg released under complete oxidation at Brandspruit S7.

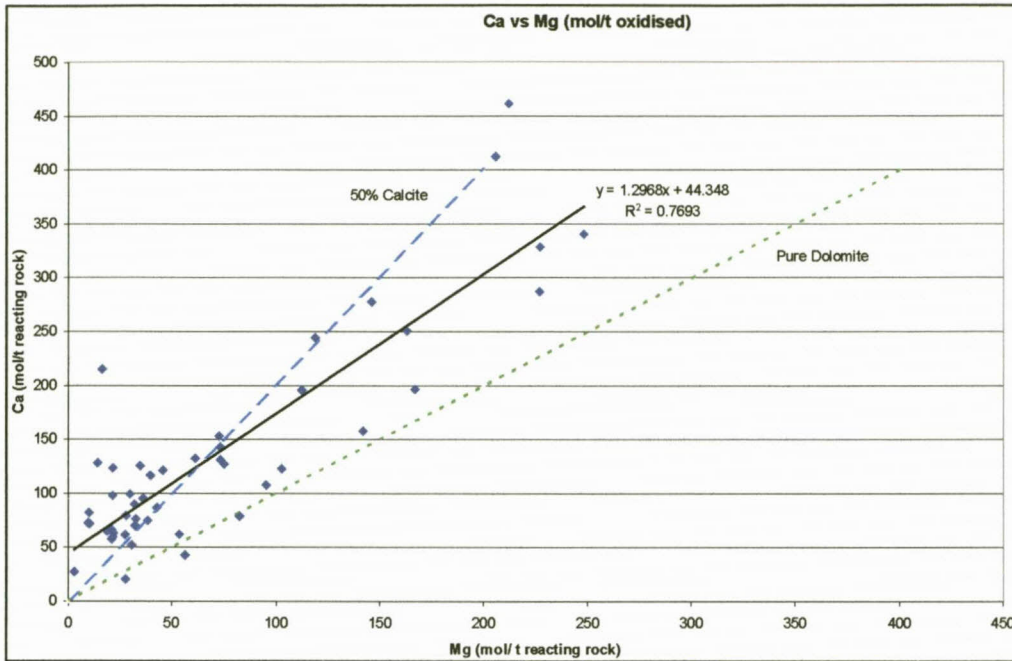


Figure 147: Ca vs. Mg ratio for 50 samples taken at three mines in the Sasol Complex.

Using the ratio determined previously, the mass contribution of each specie can be determined.

The reactions in a system where gas transfer occurs freely, are as follows:

$\text{FeS}_2 + 2\text{CaCO}_3 + 3,75\text{O}_2 + 1,5\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + 2\text{SO}_4^{2-} + 2\text{Ca}^{2+} + 2\text{CO}_2$ (carbon dioxide exsolves into the atmosphere) or equivalently:



and for dolomite:



or equivalently:



If then we have a calcite/dolomite ration of 2:1, for every 3 moles of pyrite that oxidises, 6 SO_4^{2-} , 5 Ca^{2+} and 1 Mg^{2+} ions would be produced. In the same way at a ratio of 3:1, for every 8 SO_4^{2-} , 7 Ca^{2+} and 1 Mg^{2+} ions would be produced. This allows a semi-quantitative estimation of the amount of Ca and Mg produced with sulphate release to be calculated (Figure 148).

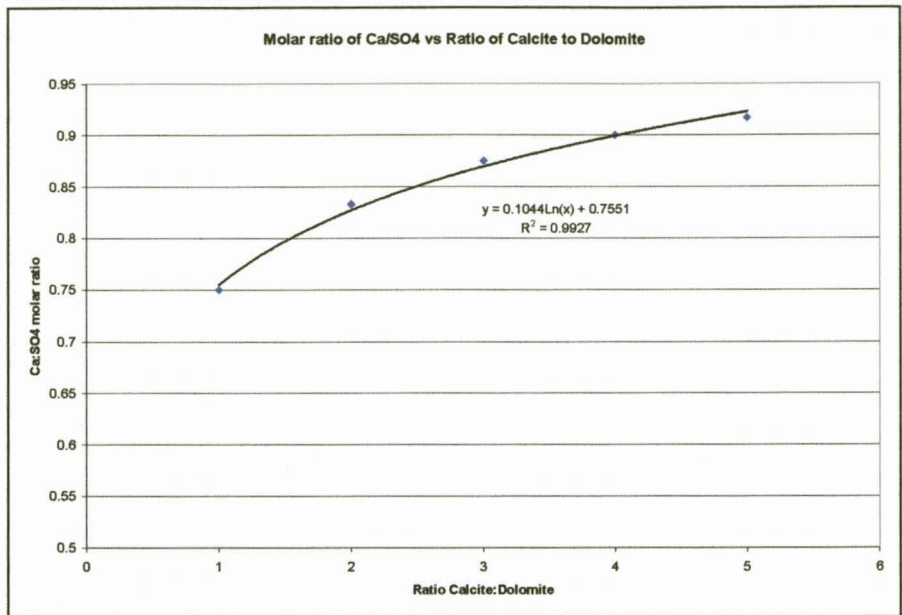


Figure 148: Determination of the molar reaction ratio as a function of calcite and dolomite.

Using SO₄ generation rate as master variable necessitates the determination of the other rates of solubilisation/release relative to sulphate. Using the ABA data available for the mines in the area, sixty samples could be evaluated to see what is released under complete oxidation. The most important question relates to calcium and magnesium as surrogates for calcite and dolomite reaction.

Figure 149 shows the molar ratio of calcium and magnesium released by hydrogen peroxide oxidation in a static test. From this figure, a rate of release in the order of 1:1 is suggested, and has been built into BUGLE as the default ratio. Users can vary this ratio, based on the observations in laboratory tests or from field data. An input option for this is included in BUGLE.

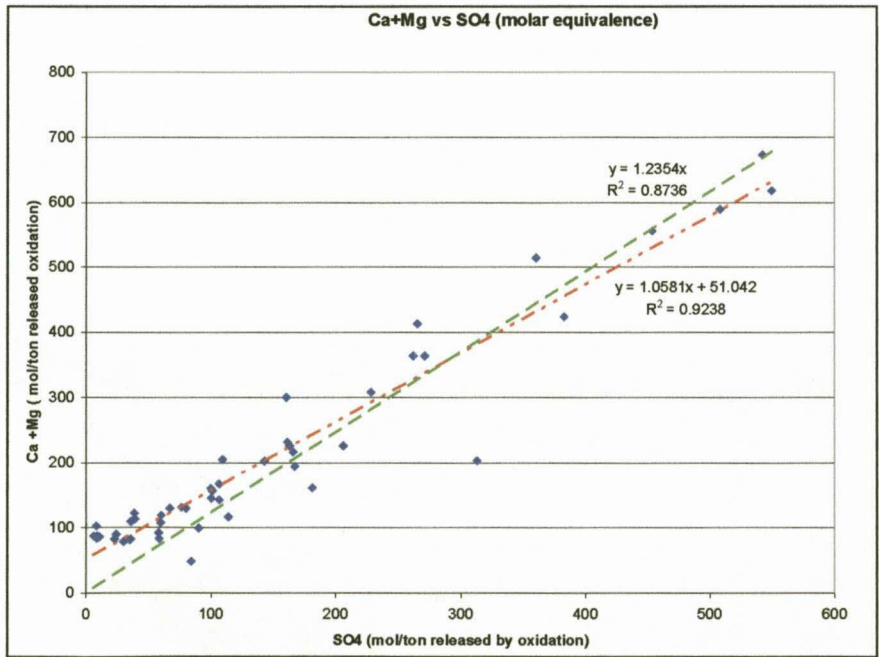


Figure 149: Molar ratio of Ca+Mg released by complete oxidation against SO₄ produced.

The high sodium values observed in the Highveld Coalfield mines, cannot be explained from a mineralogical point of view. Earlier discussions on cation-exchange do not fully explain the complete dominance of sodium as cation. To allow for this from an empirical point of view, two major sources of sodium are included. The first, and most important source is the high sodium recharge water encountered as roof drips, and where fissures are intersected in the underground mines (Section 2.3.2.2). The second source allowed for, arises from the process of pillar scaling that occurs in underground collieries. To this end, recent research undertaken by Canbulat *et al.* (2002) was used. Their research was focussed on predicting pillar failure and subsidence in the different coal mining areas. As part of this they considered the relationship between mining height and pillar scaling in different coalfields. A figure related to this is shown below (Figure 150):

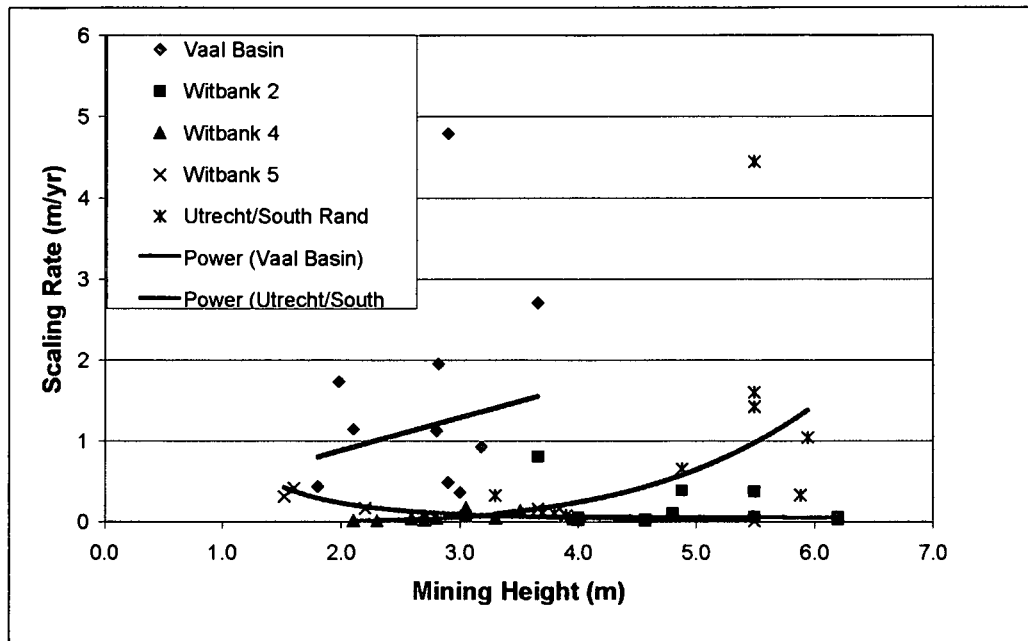


Figure 150: Relationships between mining height and scaling rate for the different mining areas (Canbulat *et al.*, 2002).

From this figure a relationship between mining height and pillar scaling for the Highveld Coalfield could be derived. The authors go on to caution that this figure over-estimates pillar scaling due to factors such as geometric constraints. The research also yields a very important finding in terms of the decrease of scaling with time. The scaling rate is therefore not constant but decreases exponentially. This is very important in terms of rebounding water tables and the release of primary or precipitated minerals from scaled material. Far more material will be scaled in the shorter term (20- 30 years based on the time scales used by Canbulat *et al.*, (2002)).



Figure 151: Two views of typical rubble encountered on the coal floor.

Over time the rate of addition from scaling material will decrease. Stabilisation or decreasing observed reaction rates is thus not only a geochemical process, but is also related to the physical constraints on pillar scaling. The scaled material accumulating on the coal floor also represents one of the greatest unknowns in terms of accurate source terms in a fundamental kinetic geochemical model. Section 6.4 describes an attempt to characterise the floor rubble at Brandspruit's S7 compartment.

Once the amount of scaling has been determined based on the mining height and geometry, an attempt to relate this to sodium content is needed. Static test data are used to accomplish this. Two types of solubilisation tests are done- of the sample in water and on the hydrogen peroxide oxidised supernatant. By using these data (which can also be determined in units of kg/t), maximum release rates (See Figure 152) can be determined and related to the amount of pillar scaled in each time step. A major constraint is that these values provide upper limits. In reality only a fraction of the scaled material will release material such as sodium, due to the scaling mechanism releasing material in primarily very large size fractions. The interstitial water released in each time step is therefore a fraction of the total amount present. In BUGLE the user can define this fraction to obtain a better fit with observed values.

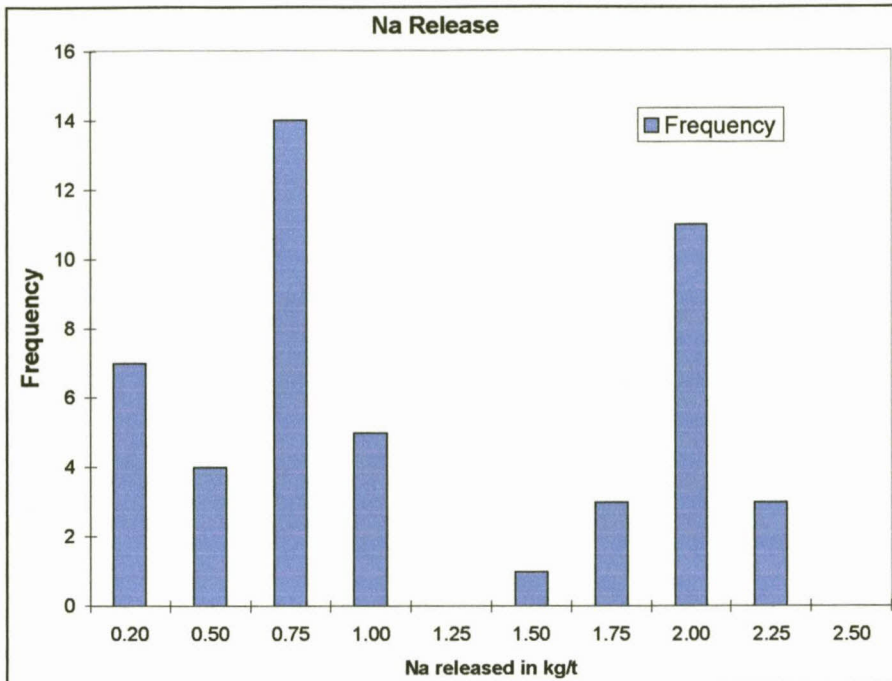


Figure 152: Histogram of sodium release.

8.3 OBSERVED DRIVERS ON WATER QUALITY

To ensure that appropriate mineralogical considerations are taken into account, the currently available monitoring data for the underground compartments in the Highveld Coalfield were considered.

Two hundred complete analyses from over the entire area could be used to determine the drivers on water quality.

These samples were analysed for important mineral phases using the geochemical modelling program PHREEQC (Parkhurst and Appelo, 2002).

8.3.1 Equilibrium Models of Reaction

Most of these reaction types are reversible and can be expressed by the following relationship:



Le Chatelier's principle applies. Any change will force the reaction in the direction that minimises the change.

8.3.2 Mass Action, Equilibrium Constants and Concentration

The law of mass action states that the rate of a chemical reaction is proportional to the concentration of the reacting substances.



$$\text{Rate} \propto [A][B]^2$$

or $\text{Rate} = k[A][B]^2$

For reversible reactions:



Forward rate = $k_1 [A]^a[B]^b$

Backward rate = $k_2 [C]^c[D]^d$

At equilibrium the forward rate = backward rate

Thus $k_1[A]^a[B]^b = k_2[C]^c[D]^d$

And $K = \frac{k_1}{k_2} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{\text{Products}}{\text{Reactants}}$

Thus the concentrations of the reactants at equilibrium can be expressed in terms of the equilibrium constant K.

8.3.3 Solubility Product

The solubility product constant, K_{sp} is defined:

$$K_{sp} = \frac{\text{Products}}{\text{Reactants}} = \frac{\text{Products}}{1} \quad (1 \text{ since the reactants are solid})$$

K_{sp} is a constant at equilibrium.

The product of the measured concentration of ions in a non-saturated or equilibrium solution is called the ion product. This is usually referred to as the Ion Activity Product (IAP) if the values have been converted to activity.

If the ion product is = K_{sp} , the solution is saturated.

If the ion product is < K_{sp} , all the ions are in solution.

If the ion product is > K_{sp} , precipitation occurs.

In a similar approach the saturation index has been defined.

$$SI = \log \frac{IAP}{K_{sp}}$$

Where IAP = Ion activity product $[A]^a[B]^b$ calculated from the measured concentrations.

K_{sp} = The solubility product of the solid species $[A_xB_y]$. Obtained from theoretical values, read from tables or calculated from the thermodynamic data.

If: $SI < 0$ The groundwater is undersaturated in $[A_xB_y]$ and dissolution will occur.

$SI = 0$ The water is in equilibrium with the mineral.

$SI > 0$ The water is supersaturated with the solid components and precipitation should result.

8.3.4 Correction for Non-Ideal Behaviour

In an ideal solution, each ion behaves independently of the others. As the concentration of a solution increases, the ions interact with each other and their behaviour departs from ideality. The activity is a measure of the effective concentration of a solution. If activity is used as the concentration, thermodynamic data can be applied as if the solution were ideal, even if this is not the case. Activity is always less than or equal to the measured molal concentration.

The activity coefficient (γ) can be used to convert molar concentrations to activity. It is

$$\text{defined as } \gamma = \frac{a}{m} = \frac{[\text{activity}]}{(\text{concentration})}$$

γ is always less than or equal to 1.

The deviation from ideal behaviour is related to the square of the valence:

$$\text{Nonideality of a solution} = \sum m_i z_i^2$$

To estimate the effect of concentration on the behaviour of ions in solution, the term

$$\text{Ionic Strength (I) has been defined. } \gamma = \frac{a}{m} = \frac{[\text{activity}]}{(\text{concentration})}$$

Where m_i is the concentration (molality) of the i th species and z_i is the ionic charge of the i th species. Both concentration and ionic charge affect the degree of non-ideal behaviour.

For more accurate work, activity must be determined. Empirical equations to do this have been proposed by Davies for concentrated solutions ($I < 0.5$).

Davies Equation

$$\log \gamma = -Az_i^2 \left(\frac{\sqrt{I}}{1 + Ba_i \sqrt{I}} \right) + b_i I$$

Where A and B are temperature-dependent constants and a and b are constants depending on the ion size.

The relationship of γ with increasing ionic strength, for a number of different ions, is shown in Figure 153.

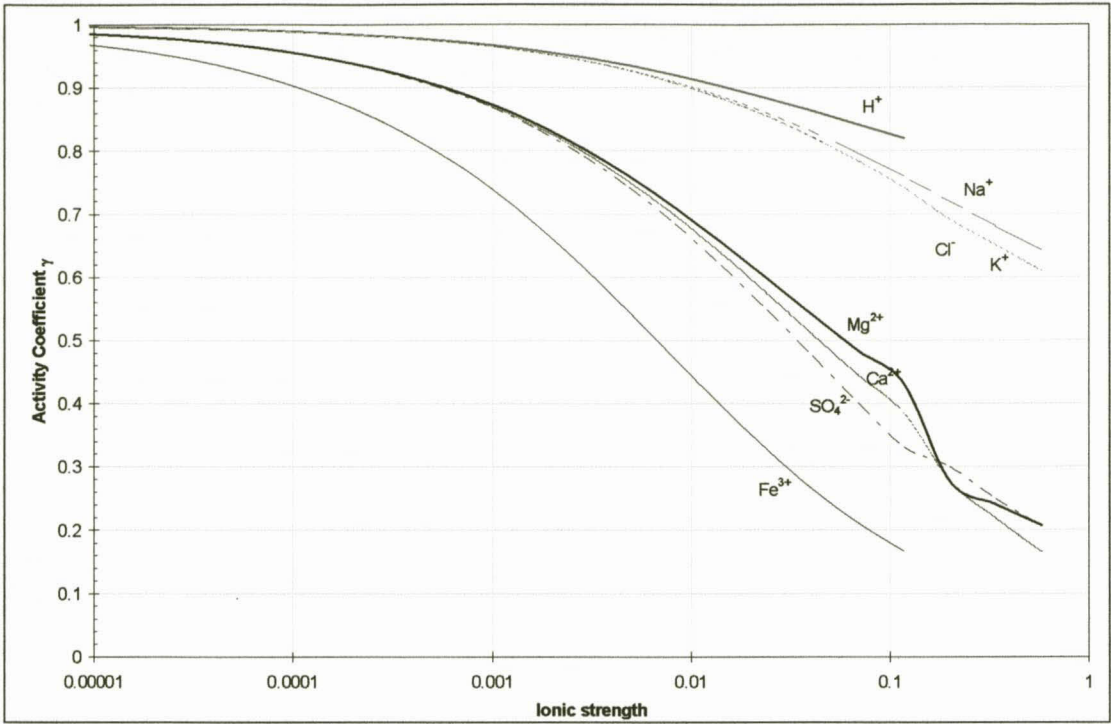


Figure 153: Activity coefficients as a function of Ionic Strength.

8.3.5 Saturation state of Highveld Coalfield water

Using these approaches, the SI of the different waters can be evaluated. The output from these PHREEQC simulations is given on the figures below (Figure 154 to Figure 157):

The first figure plots the saturation state of the expected controlling mineral phases as a function of pH.

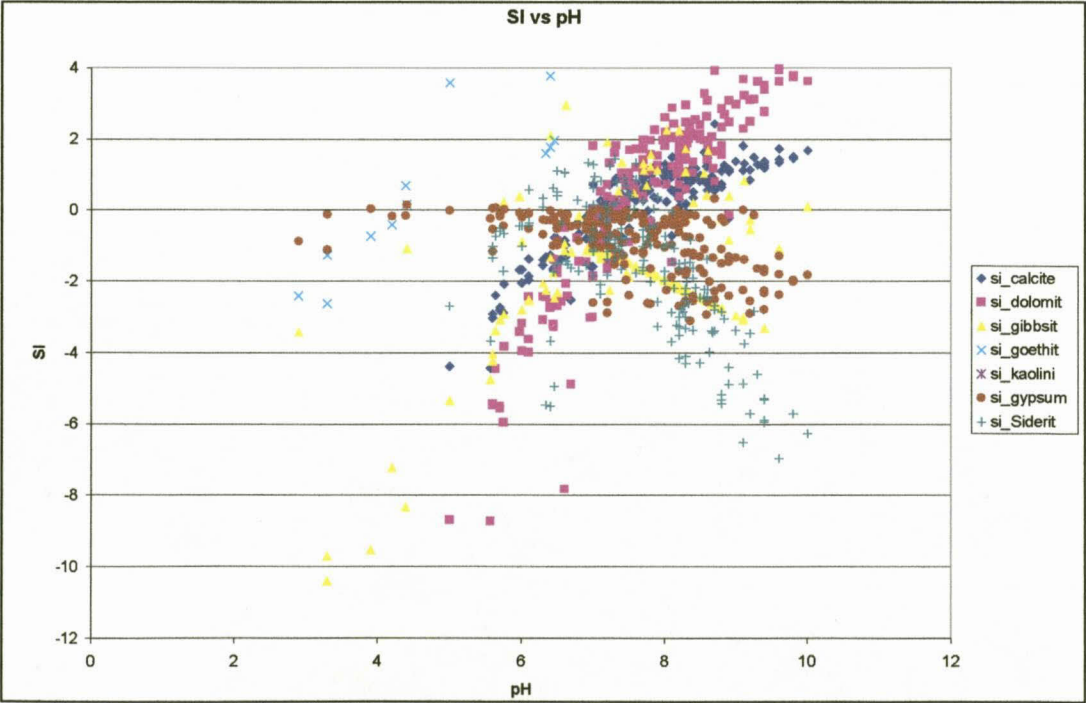


Figure 154: Saturation of different minerals as a function of pH.

The approach used above uses the concept of a Saturation Index (SI) to classify the saturation state of each of the 200 samples.

From the figure above the following phases can be seen to be important in terms of pH control on the observed water quality:

- The carbonates, calcite and dolomite.
- Possibly the alumino-silicates, kaolinite and gibbsite, but at low rates and at lower pH's (See Sections 2.7.3 and 7.2.5).
- Gypsum is often seen nearing saturation (i.e. SI=0).

Also of significance is that siderite does not appear to be acting as a temporary buffer, and can therefore be disregarded in terms of an empirical model.

It is also interesting to note that calcite and dolomite are consistently oversaturated at pH-values above 7.3. The apparent oversaturation with calcite is common in natural aqueous systems and is often attributed to slow precipitation kinetics (Herman and Lorah, 1988; Inskeep and Bloom, 1986; Suarez, 1983).

This is a very important observation, and following this is that, as the pH increases, the relative degree of apparent supersaturation also increases. In terms of using a conventional thermodynamic model such as Minteq or PHREEQC, this has important implications. In these models, the assumption is usually that waters should approach equilibrium. By using such an approach the "oversaturated" calcite and dolomite would be forced to precipitate out of solution, which would radically alter the solution's composition. These programs can, however, deal with any assumed state of saturation, and thus the problem can be overcome. In the development of an empirical model, this does need to be considered, and since the calcite and dolomite are closely matched in terms of observed saturation, calcite is used as the controlling phase for Ca and the inorganic carbonates. This decrease is probably related to the increase in solubility of $\text{CO}_2(\text{g})$ in water with increase in pH. The degree of oversaturation decreases with increasing pH (Eary, 1999). To more accurately reflect the observed chemistry, a pH-dependent function, based on the observations, has been included to deal with calcite saturation. This is based on Figure 155:

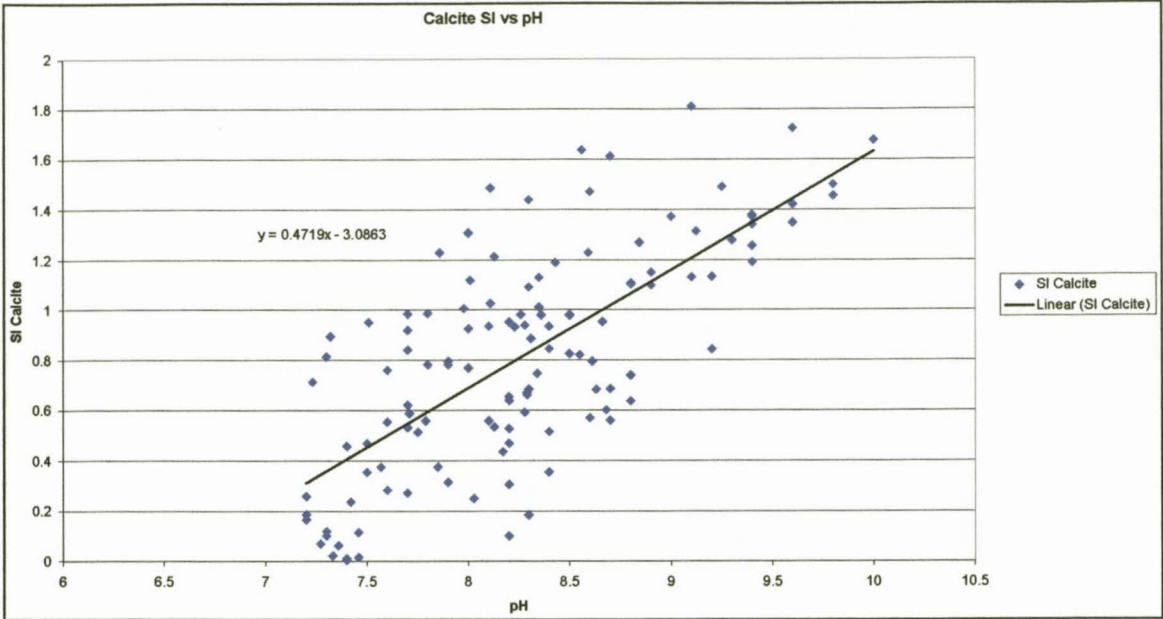


Figure 155: Calcite SI as a function of pH.

By including this function, a more realistic indication of the true behaviours of the system can be obtained, than would usually be achievable in a conventional model.

8.3.6 Calcite, Dolomite and Gypsum

Previously the liberation of Ca and Mg was considered based on static test results. Inspection of the 200 samples for the underground compartments shows that the system behaves in a very similar mode in the field (Figure 156).

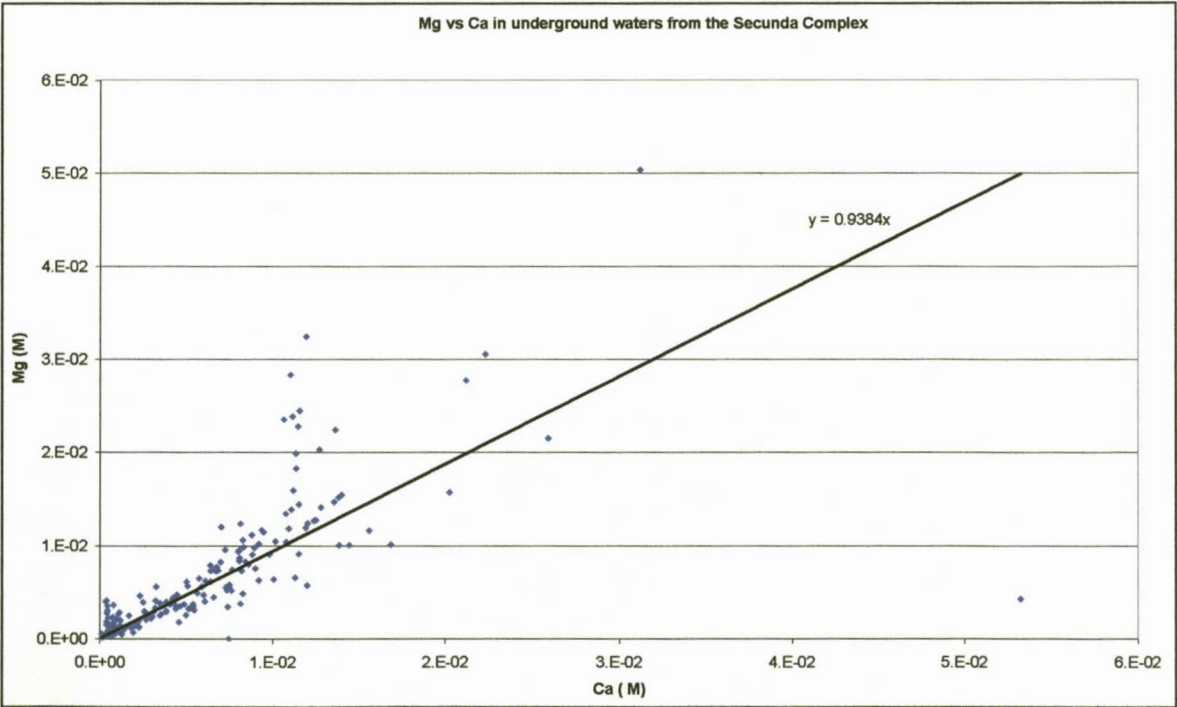


Figure 156: Relationship between Mg and Ca in underground samples.

The previous assumptions of calcite and dolomite ratios appear to be valid, although some enrichment of Mg relative to Ca is observed. The reason for this appears to be associated with gypsum precipitation, which removes some of the calcium from solution, and the fact that dolomite is used as stone dust underground. Figure 157 shows that gypsum saturation is a very important process in these underground compartments, and can also serve as a constraint on the eventual sulphate concentration observed in the field.

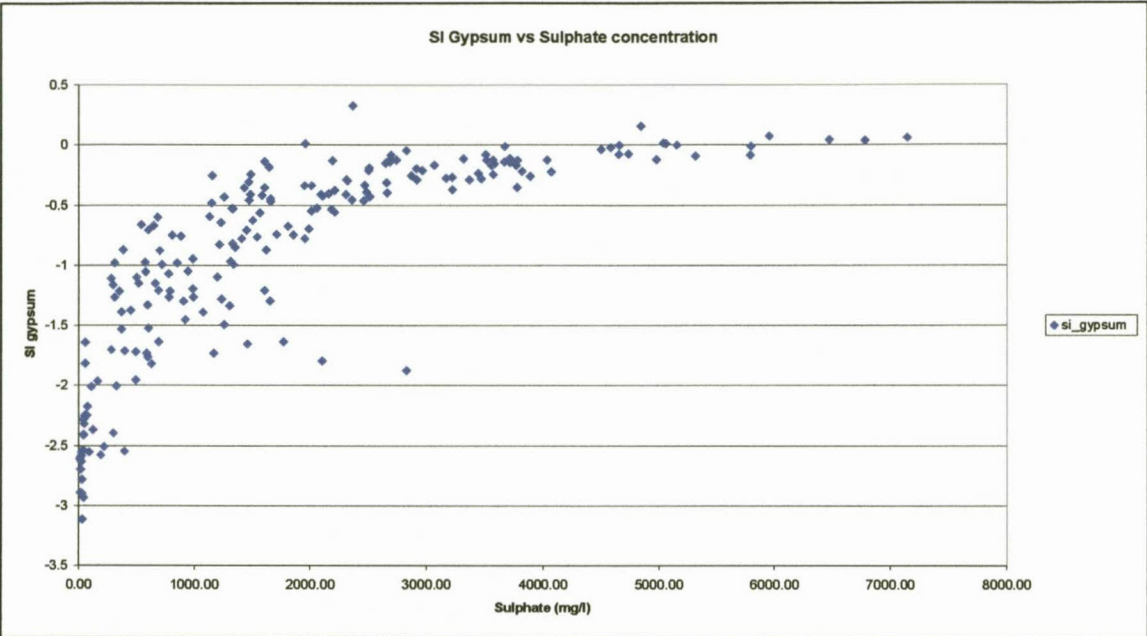


Figure 157: Gypsum saturation as a function of sulphate concentration.

Some of these higher sulphate values need to be considered with circumspection, since the ionic balances of the analyses exceed the 10% guideline often used as a guide. Nonetheless the principle of gypsum saturation needs incorporation into any empirical model, and has therefore been included in BUGLE. Figure 158 below shows some examples of gypsum precipitates observed in the underground compartments in the Highveld Coalfield.

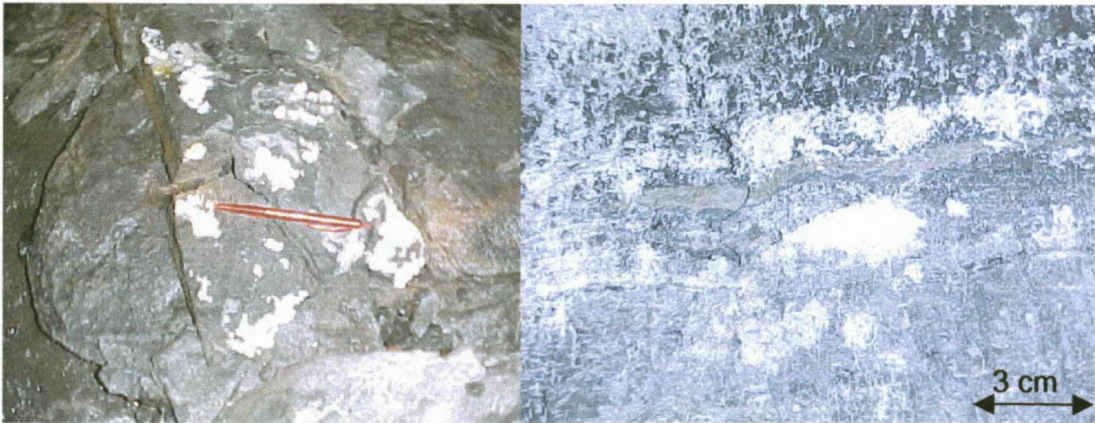


Figure 158: Examples of typical precipitates observed in underground workings.

This principle can be illustrated by the exclusion of gypsum precipitation in other empirical models. One example is the decant spreadsheet model developed by Van

Tonder (2001). This model utilises the expected recharge into rehabilitated spoils dumps at between 15% and 20%, but allows recharge as low as 2% to be assigned. The program also uses the empirical sulphate generated, reported by Hodgson and Krantz (1998) to be between 5 and 10 kg/ha/day. With these sulphate generation rates sulphate concentrations of up to 30000 mg/L can be predicted. Since these values have not yet been encountered in South African opencast collieries, some constraining factor needs inclusion. The concept of gypsum saturation was therefore included by Van Tonder and Usher (2002). By assigning expected calcium values based on observations, mineralogy or ABA, a more realistic indication of expected sulphate values can be obtained.

The Mg enrichment relative to Ca is also an important observation in real systems. Hough (2003), Usher *et al.* (2002) and Vermeulen, (2003), investigating reactions within the TNC workings, found that after flooding the mines in 2000, the water quality in the workings showed an enrichment in Mg and SO_4 . PHREEQC was used to determine the reason for this enrichment. As a preliminary step the water was evaluated to determine the saturation state relative to gypsum. It was found that gypsum saturation was generally approached in these enriched waters. Different scenarios where investigation with the aid of PHREEQC. Eventually the most likely explanation found was that before flooding, the AMD acidity had been neutralised by more dolomitic carbonates. These simulations are included in Appendix 3.

This process can be simulated by allowing sulphuric acid to react incrementally with an excess of dolomite. By simulating this, the following was obtained (Figure 159 and Figure 160):

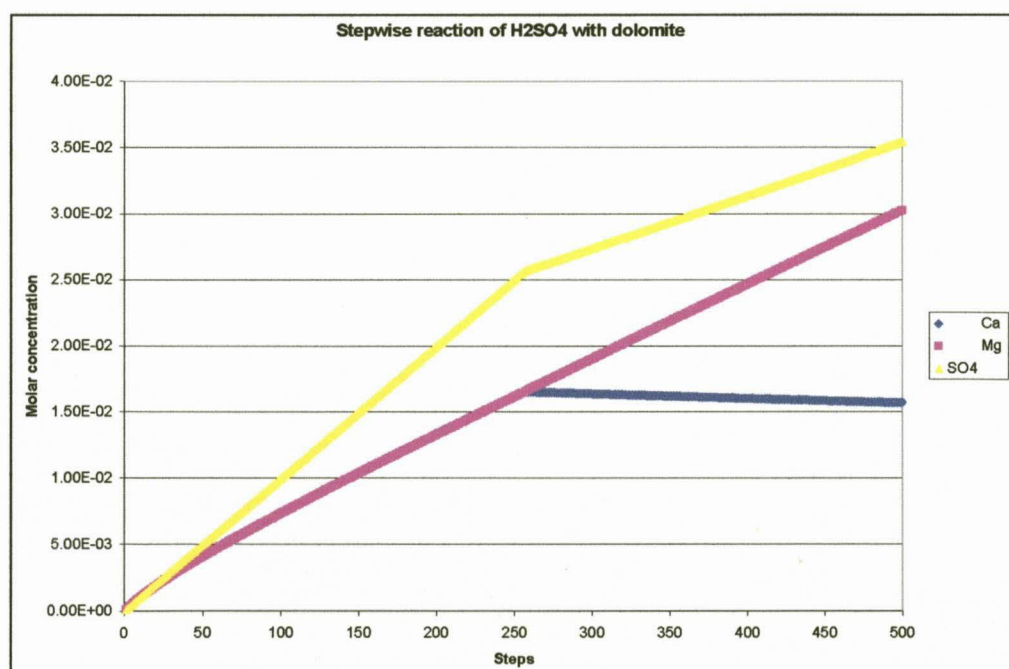


Figure 159: Effect of reacting sulphuric acid with dolomite on molar concentrations.

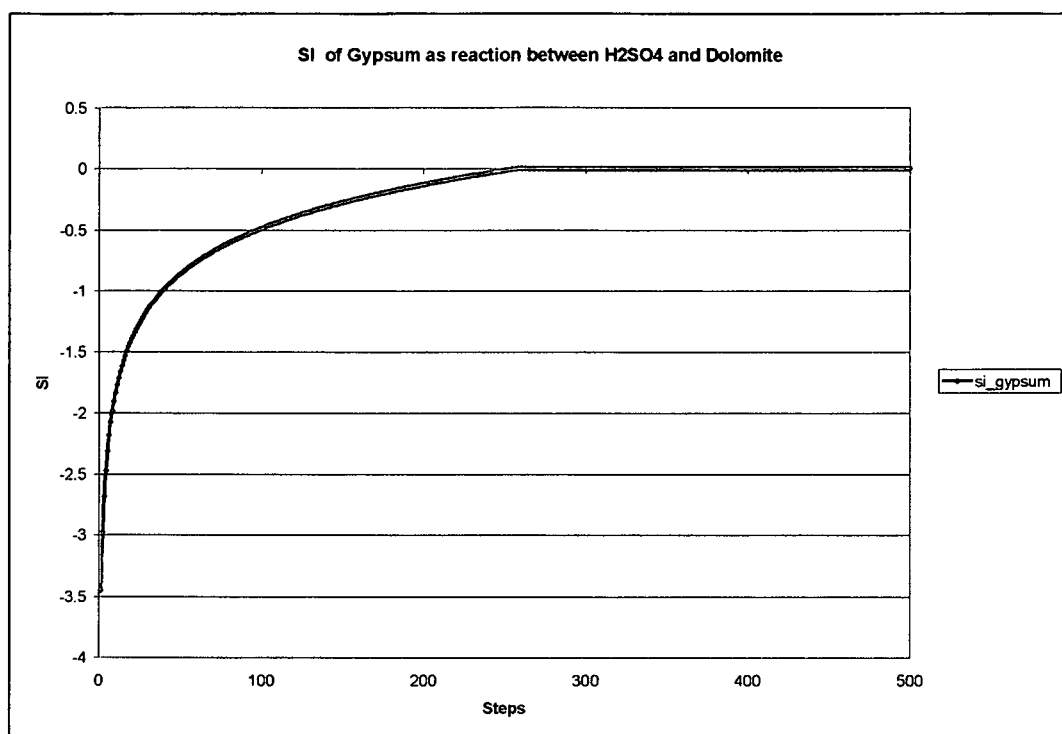


Figure 160: Gypsum saturation from reaction of AMD with dolomite.

BUGLE therefore considers two major limiting processes, calcite and gypsum saturation. To do this, based on the previous discussion, BUGLE needs to consider the non-ideality of the solution. This by following the following steps:

1. Determine the ionic strength.
2. Calculate the activity co-efficient using the Davies equation (which is valid to ionic strengths of up to 0.5, which equates to TDS values in the order of 20 000 mg/L).
3. Calculate the activities of Ca^{2+} , SO_4^{2-} and HCO_3^{2-} .
4. Determine CO_3^{2-} activity by using carbonate equilibria and pH, assuming a fixed partial pressure of CO_2 so that there is no build-up of CO_2 acidity (open system conditions).
5. Use K_{sp} values of calcite and gypsum to determine SI.
6. Use the derived calcite SI vs. pH relationship for pH above 7.3.

If either of these phases exceeds saturation by more than an acceptable margin (allowing for inaccuracies due to assumptions) BUGLE provides the user with a warning. The user can then run an equilibration routine to equilibrate the water with the over-saturated phase. This equilibration uses the thermodynamic information and a forward Newton iteration method built into Excel's Solver.

Since BUGLE is an empirical model to provide insight into how the system would react, speciation and complexation reactions are ignored to expedite the calculations. A routine is available within BUGLE to consider these interactions, but the concepts

of allowing apparent supersaturation can then not be accommodated. Iterative replacement via a forward Newton method as performed by EXCEL's Solver again needs to be implemented. This is the same type of solving process employed by models such as PHREEQC; the intention of BUGLE is, however, not to be able to compete with packages such as PHREEQC, but to minimise the calculations through justifiable assumptions and correction factors.

8.3.7 Using the EDCM approach to calculate iron concentrations

8.3.7.1 Introduction

Post-mining drainage chemistry depends strongly on geochemical and hydrologic processes that occur during the operational years. Where routine operational monitoring data are abundant, the dominant processes can often be evaluated with no additional, special studies. Thus, post-mining drainage chemistry can be predicted with confidence based on the operational data. This is referred to as empirical drainage-chemistry modeling (EDCM) (Morin and Hutt, 2001).

The EDCM approach determines the annual mean and the short term variations using simple scatter-plots and simple statistical procedures available in any spreadsheet software. The EDCM approach is an inexpensive, and relatively easily understood tool for summarizing and predicting aqueous concentrations at mine sites.

The following steps must be used when making use of the EDCM approach:

- Compile all available monitoring data for an entire minesite or coalfield in this case or one or more of its components.
- Concentrations must be plotted against independent, or 'master', geochemical parameters which are typically pH and sulphate at sulphate-bearing minesites. If there are geochemical equilibrium controls, then there will be noticeable correlation.
- A best-fit line can be drawn through the correlation using least-linear fitting, and this line often represents the annual average concentration at a particular value of the master parameter.

8.3.8 Application to iron

Over 2000 iron analyses from colliery waters in the Witbank and Highveld Coalfields were used to obtain the EDCM for iron. Figure 161 represents all the available iron data vs available pH values. From the graph it can be seen that there are two noticeable changes in the iron graph of iron at a pH between 2 and 4.5 as well as between 5 and 9. Two separate graphs were then plotted to illustrate the two above-mentioned trends.

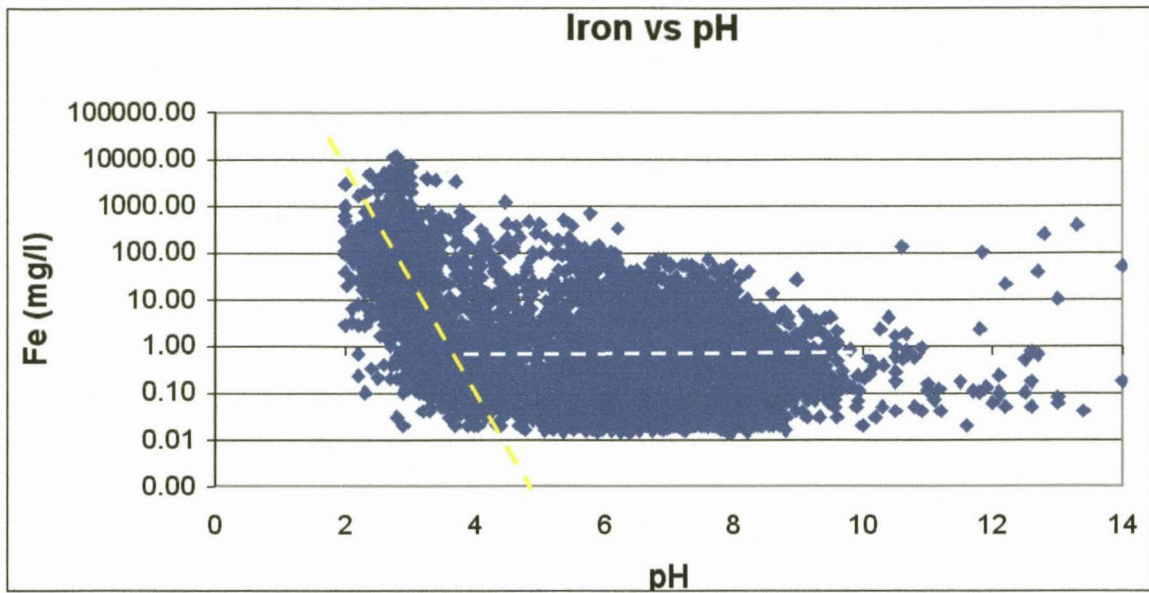


Figure 161: Iron vs pH- all available data.

From Figure 161, it can be seen that two trends of iron concentrations are evident; these are a nearly straight line with little pH dependence down to a pH of approximately 3.6 and a sharp increase in iron concentrations as pH drops below this value. For the sake of convenient inclusion in the empirical model, a pH-value of 4.5 was deemed to represent the pH where increase in iron is manifested. Theoretically a sharp increase in iron should also be seen at a pH of approximately 3.5 due to the conversion of ferric to ferrous iron (See Figure 6). From the ion-solubilisation data obtained from ABA, this increase is often seen (Hodgson, 2003). In the field pH and redox conditions will determine if, and at what pH, this conversion occurs.

The reasons for these trends merit further interpretation and the solubility fields of different iron species are useful in this instance. The figure below from Hem, 1967 is informative. It shows the relative stability fields of the ferric and ferrous iron species and the expected solid phases associated with them. Of particular importance is the fact that at different total iron concentrations these stability fields vary and the Eh conditions where these phases are stable. It can be seen that at lower iron concentrations of around 10^{-5} mol/L which equates to roughly 1 mg/l of dissolved iron the boundary between the solid phase iron hydroxide and the aqueous species is at higher pH values.

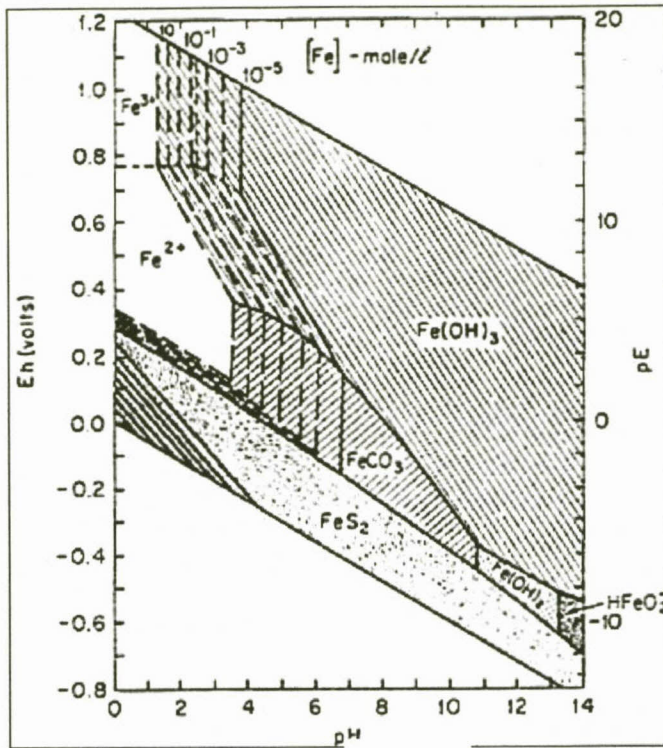


Figure 162: Stability fields for main solid phases and aqueous species of iron in water as a function of pH and Eh, 25°C and 1 atm pressure. Dashed lines represent solubility of iron for total bicarbonate of 10^{-2} M.

The true field conditions in South African collieries also needs consideration. In the figures below, down-the-hole multi parameter logging results using a YSI probe are displayed. The data shown is from two blocks, Welstand and Block F at Transvaal Navigational Colliery. There are several analogous examples from other mines, which indicate similar data, but these are chosen to illustrate expected conditions.

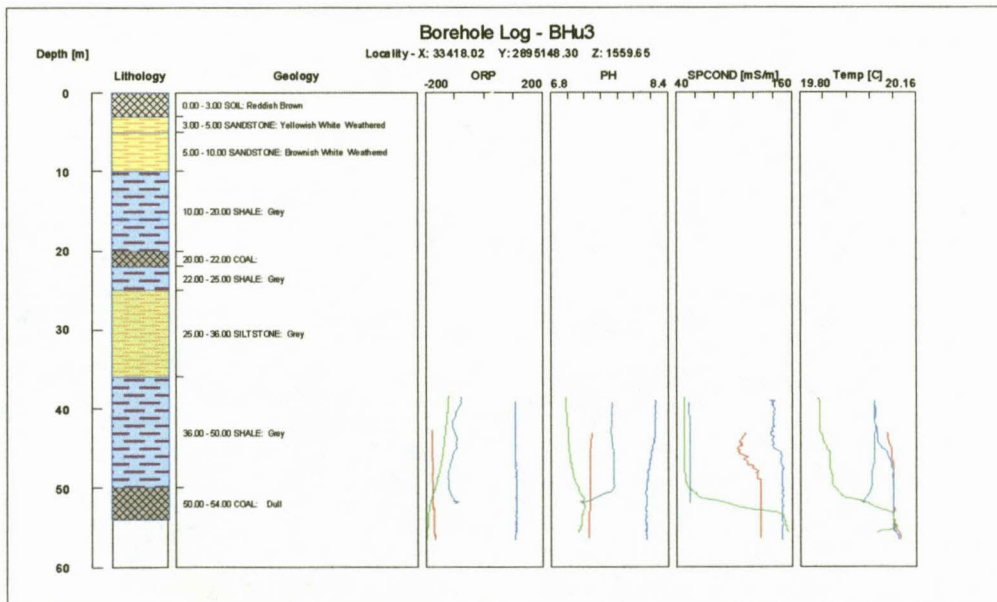


Figure 163: Depth related parameters from TNC's Welstand block (different coloured lines are at different times over a three year period)

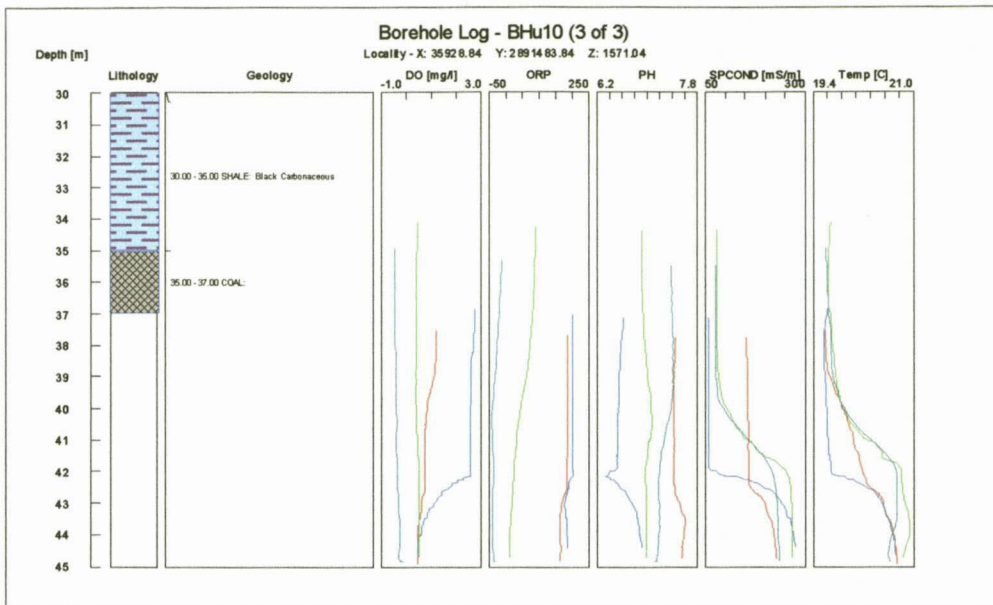


Figure 164: Depth related parameters from TNC's Block F (different coloured lines are at different times over a three year period)

On these figures it is important to note the ORP values (reported in mV) for the different blocks, and also the variation over time. It is clear from these figures that the conditions in many underground mine waters are not excessively oxidising and that Eh values of below 0.5V are common. By comparison to Figure 162, it is clear that aqueous Fe^{2+} will be stable to pH values in excess of 4 and where iron concentrations are low or in more reducing conditions as high as pH 5.

Bearing these facts in mind, two best-fit lines were plotted on the graph representing data between a pH of 2 and 3.8 namely a log and an exponential fit. The following information was gained from the best fit lines.

Best fit Log: If $\text{pH} < 3.8$, $\text{Log}(\text{Fe vs pH}) = -665.12\text{Ln}(x) + 910.11$

Best fit Exponential: If $\text{pH} < 3.8$, $\text{Expon}(\text{Fe vs pH}) = 73026e^{-2.8206x}$,

While at pH values above 3.8 the best-fit line $y = 0.8587e^{-0.137x}$ can be obtained. This latter line is particularly uncertain, since from the data set the iron values at each of the pH values above 5 vary over three orders of magnitude. Further refinement of the approximations, taking approaches such as those used by Younger, 1999, and thermodynamic solubility constraints will be required, for which specific onsite conditions such as redox conditions are necessary as input.

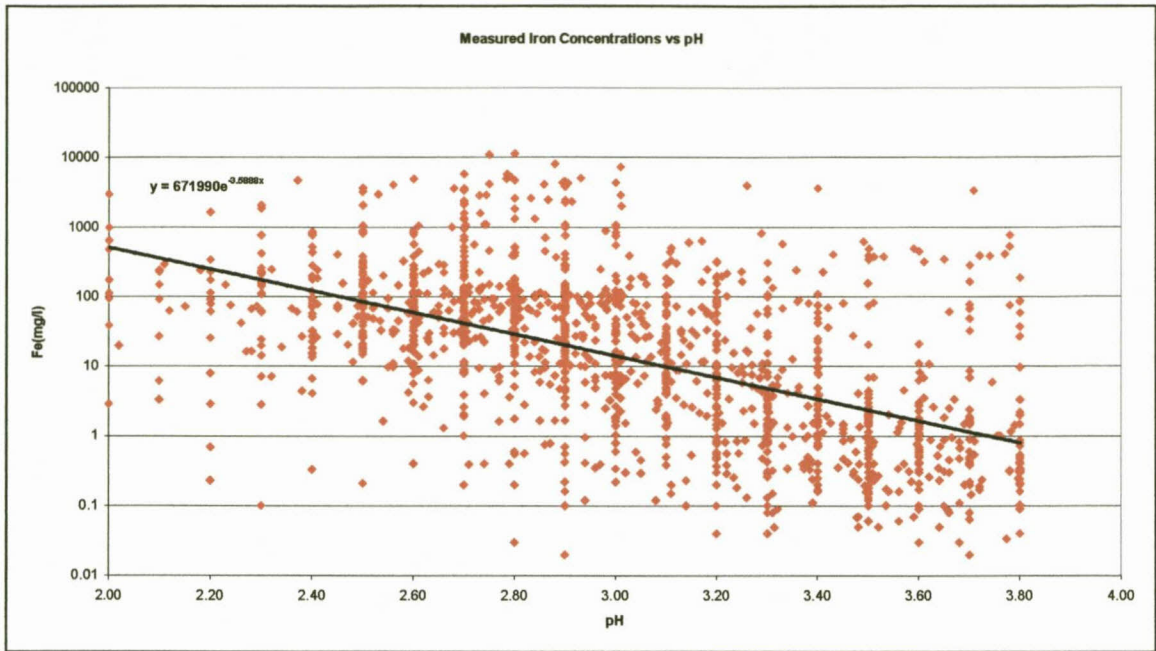


Figure 165: Iron vs pH-trend between 2 and 4.5.

Figure 166 shows the expected behaviour of iron over the lower pH range. This data correlates well to figures provided by other authors such as Birkland, 1984, who provides this overview of solubility influences of pH on iron and aluminium.

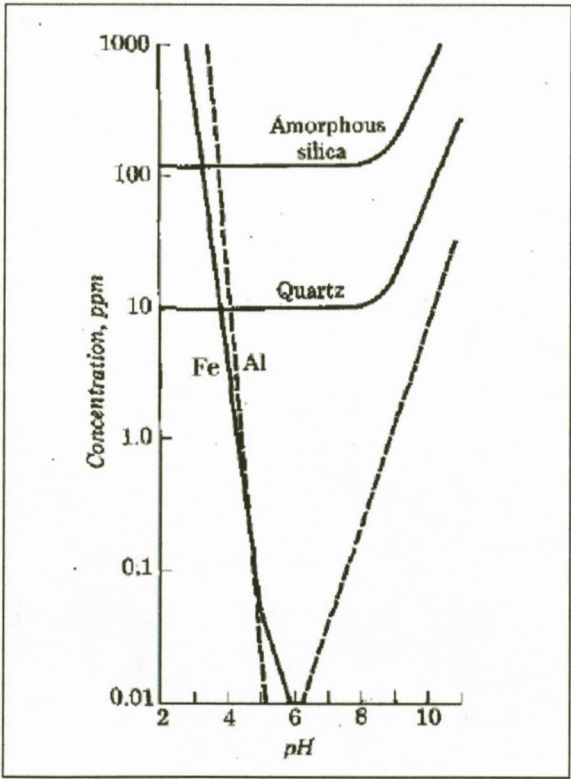


Figure 166: Relationship between pH and common elements solubility. (From Birkland, 1984)

Figure 166, is well supported by the PHREEQC simulations of pH solubility as indicated below. Here the total aqueous iron is obtained by acidification and using the most soluble solid phase (amorphous $\text{Fe}(\text{OH})_3$) as equilibrium phase. This shows a marked similarity to the observed trend.

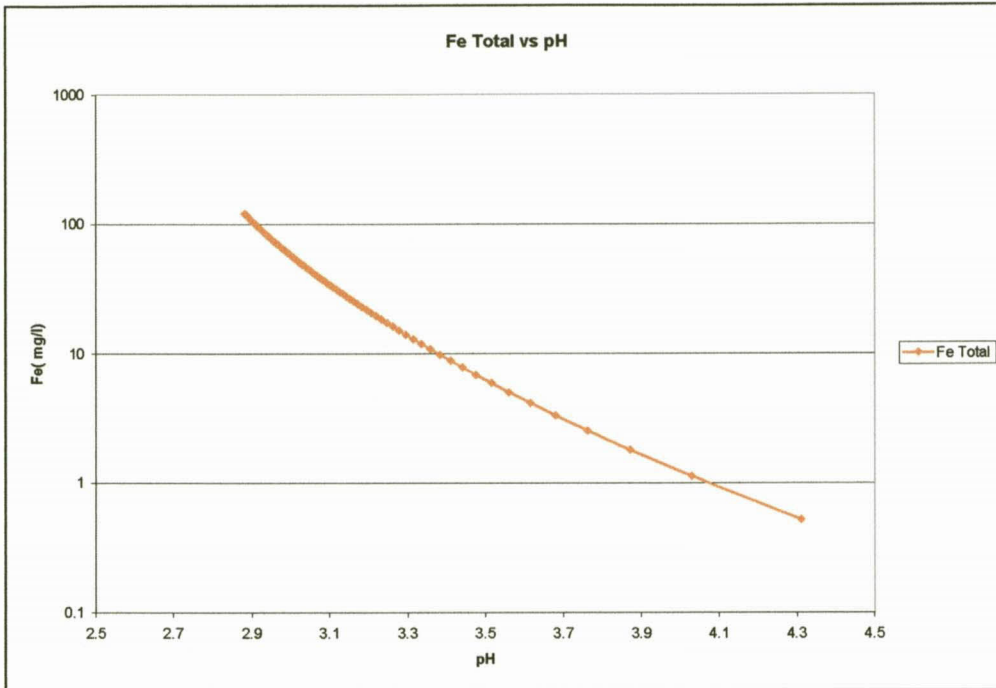


Figure 167: PHREEQC determined iron solubility

Using this approach therefore allows iron to be constrained to observed pH values, since at the higher pH values, iron is constrained by the conditions rather than the total amount produced. In BUGLE the equations above and an electro-neutrality function are included to accommodate iron.

8.3.9 Validation of BUGLE

The background and approach to BUGLE are discussed in the preceding sections. This section will concentrate on showing the workings of the model, and on using other geochemical models such as PHREEQC as comparison.

8.3.9.1 Mass balance and reaction products

The first objective of BUGLE is to ensure that it can accommodate several sources of water of differing quality, and the products of the acid generation, neutralisation and natural release.

In order to do this, a simplified compartment is considered, where simulations have been run for 5 years, in 5 time steps. The compartment dimensions are an area of 1 ha with a mining height of 4 m, as is often used in the Highveld Coal mines. The extraction ratio is set at 50%, which is close to the average bord-and pillar extraction achieved by the SASOL mines. To simplify the calculations, a flat horizontal plane is assigned to the floor, which allows a straightforward determination of storage. Based on the dimensions provided, the total storage in the compartment would be 20 000 m^3 , disregarding the small contribution of storage in the pillar rocks. It is assumed

that the compartment is initially 10% flooded, i.e. at the beginning, the compartment contains 2 000 m³ of water.

For the sake of clarity, only one influent source of water is considered, namely a sodium bicarbonate recharging water. The initial water qualities are as follows:

Table 34: Initial water qualities

Water Source	Water in compartment	Groundwater/Recharge water quality
	mg/L where appropriate	mg/L where appropriate
pH	7.42	8.2
Ca	20	5
Cl	24	48
F	0.63	3
Fe	0.07	0.01
K	1.4	1
Total Alkalinity as CaCO ₃	120	520
Mg	10.5	1
Mn	0.005	0
Na	24	285
Si	45	0
SO ₄	20	5

BUGLE allows two approaches for recharge volumes, namely assigning from other calculations, e.g. a calibrated water balance or a calculation based on the type of mining and local knowledge of local conditions. Recharge estimates for bord-and-pillar mining range from 1% to 8%, with 2% as the default value. By employing scroll bars, the user can define the recharge based on site-specific conditions. In this simulation, the lowest value of 1% was used. This equates to a recharge of approximately 70 m³ per year. In terms of a mixing ratio this equates to a ratio of 0.966: 0.034 for the first year, which decreases to 0.971: 0.029 for year five.

Based on the previous discussion, at 10% flooding, the sulphate generation rate for only bord-and-pillar mining is approximately 1.27 kg/day. For this simulation a calcite: dolomite ratio of 1: 1 is assumed. Based on the earlier discussion, this reflects as 0.4 kg Ca and 0.0778 kg/day Mg. The sodium release rate from the pillars in the time step, based on static test results, pillar scaling and a calibration factor of 0.1, is calculated to be 0.151 kg/day. The influxing water represents the major source of sodium.

These values all need conversion into molar quantities for input into PHREEQC, with the conversion made to constrain the water volume to a 1 kg solution (as used by PHREEQC). Thus for year 1, the values need to be divided by 2.07×10^6 . Thus in PHREEQC for a 1-year period, 0.22425 mol of sulphate must be added to the overall solution.

These calculations were done in BUGLE and PHREEQC for a five-year period. The results are displayed below (Figure 168):

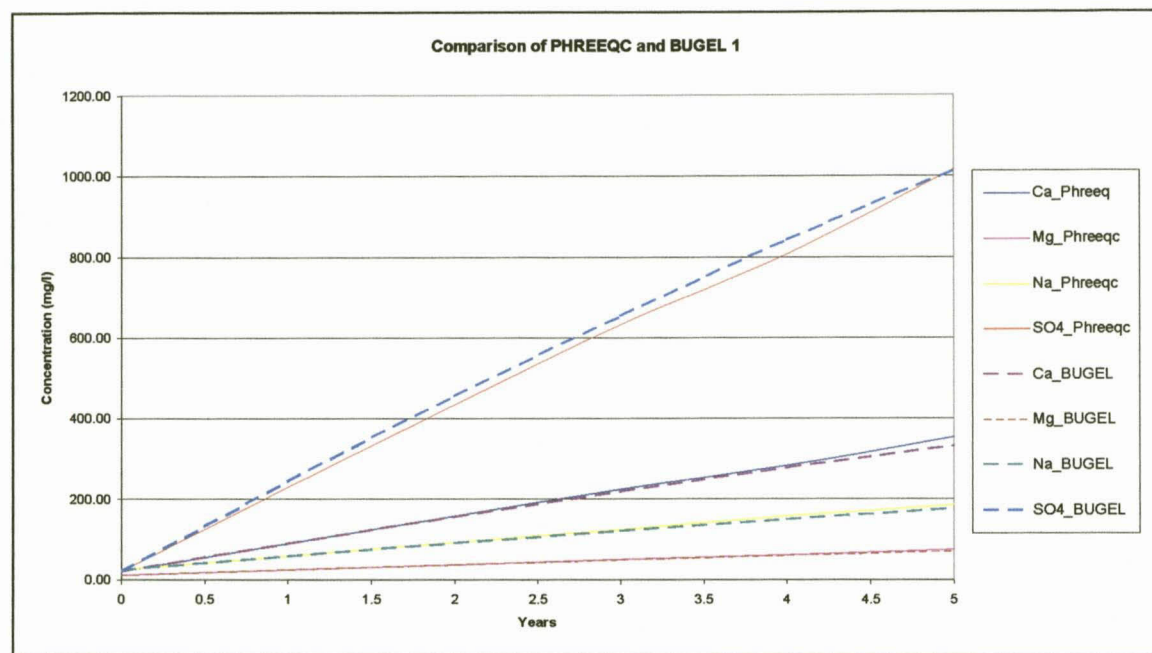


Figure 168: Comparison between PHREEQC and BUGLE for mixing and reaction over 5 years.

From the figure above it can be seen that BUGLE compares very well to PHREEQC in terms of handling the mixing of the solutions and the added reaction products. The mass balance functionality of BUGLE is thus adequate, and can be considered to give answers as expected. BUGLE's calculated recharge allows easy integration of geohydrological and geochemical considerations to determine the response of any particular system.

8.3.10 Calculating pH response

One of the most challenging aspects in the construction of an empirical model is the correct calculation of pH response. In many programs of this sort, pH is used as a charge balance equaliser, and where the whole range of possible complexation and speciation reactions are considered, such an approach can have merit if used with caution. In a model such as BUGLE, this approach would be fraught with danger, and no attempt to balance charge with pH has been made. Instead several assumptions (which will be explained) are used. These include:

- The system is an open system; this allows a fixed partial pressure of CO_2 to be used to constrain the alkalinity and the pH.

- That pH is fairly stable, while there is an excess of neutralising potential in the form of calcite and dolomite.
- That pH drops rapidly once the NP has been depleted.
- Alkalinity associated with recharge water is depleted before carbonate minerals are consumed.

In terms of solving this within an empirical model, the following approach was used:

1. Based on the SO_4 generation rates, determine the acidity that would be produced.
2. Determine the total acid consumption by the recharge water within the time step.
3. Use the correlation ratios; define the amount of Ca and Mg released to neutralise the remaining acidity via the release of bicarbonate.

Since the pH is held fairly constant and the total dissolved inorganic carbon content is constrained by the fixed P_{CO_2} , the bicarbonate concentration can be calculated.

In BUGLE therefore, when the user selects the P_{CO_2} , an assumed range of pH is used to constrain the system.

The effect of adding sulphuric acid to a pure water/calcite system at a fixed P_{CO_2} is shown in Figure 169 (as determined by PHREEQC):

In this system calcite acts as the equilibrium phase with 10 mmol initially available, while gypsum is also set as an equilibrium phase with 0 mmol initially. The partial pressure of carbon dioxide is assigned as $\text{Log } P_{\text{CO}_2} = -2$.

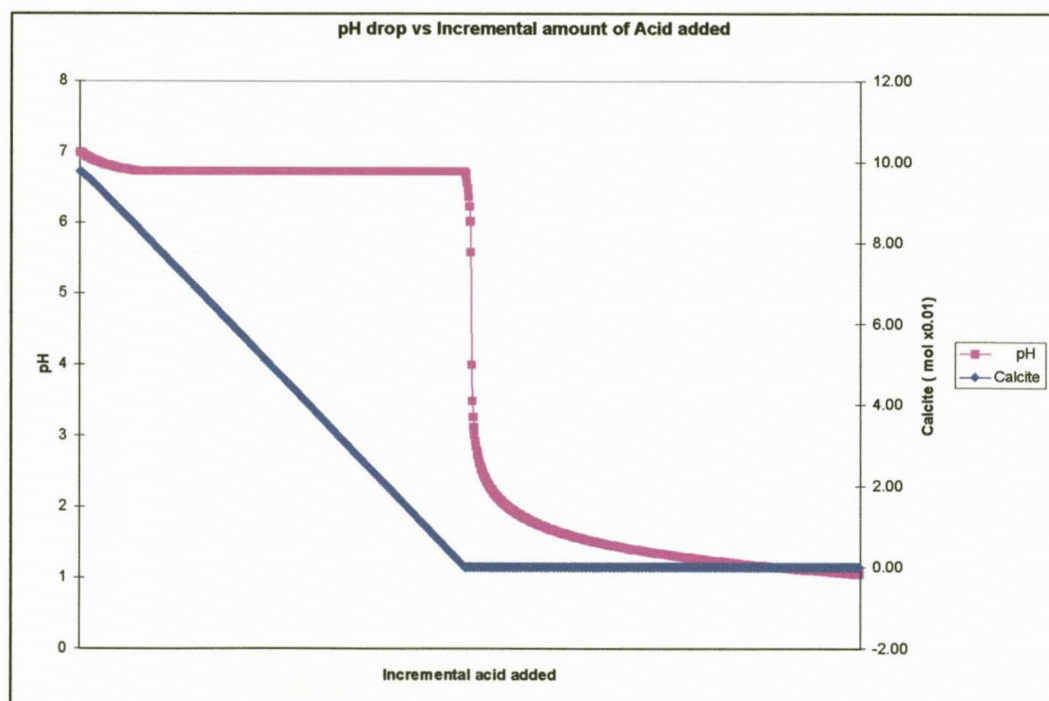


Figure 169: pH drop vs. amount of acid added at fixed P_{CO_2} .

From this it is clear that the pH remains fairly constant until the calcite is depleted, after which there is a rapid drop in pH. Inspection of the calcium and bicarbonate concentrations reveals an interesting trend, in that the calcium greatly exceeds the bicarbonate as the reaction proceeds (see Figure 170). This is in contrast to what is observed in the field in the Highveld Coalfield mines, since the real systems are dynamic with recharge water being constantly added. The calcium stabilises due to gypsum solubility constraints.

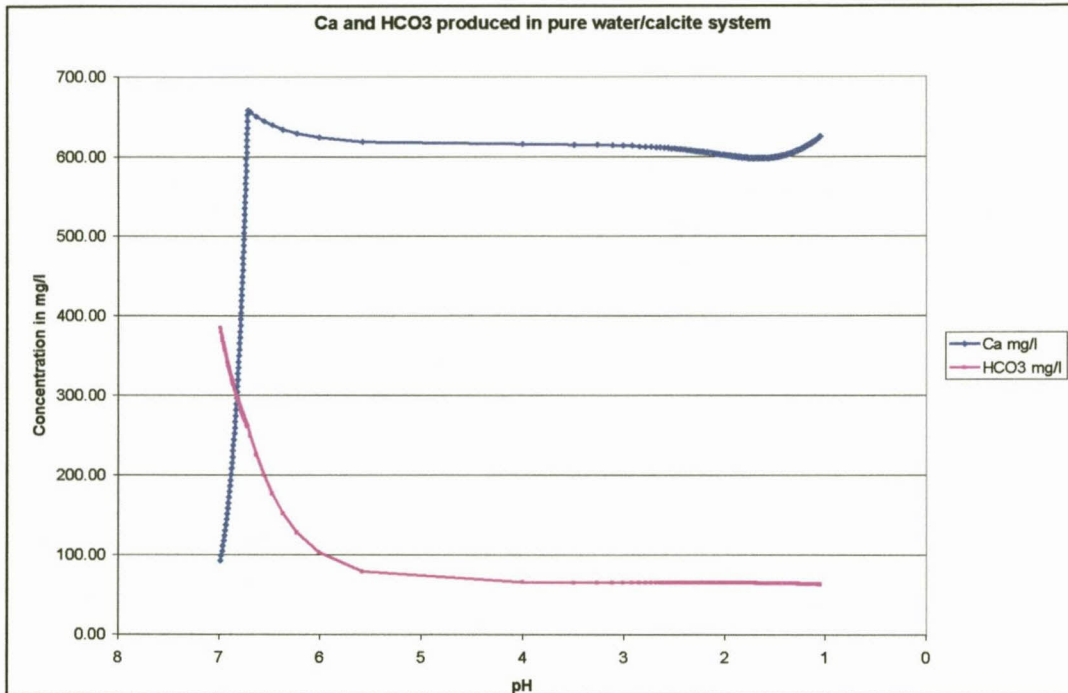


Figure 170: *Ca and HCO₃ concentrations as reaction proceeds.*

Using a pure water/calcite system to predict the system's response will obviously lead to erroneous assumptions in the empirical model.

To deduce the manner in which the system would react in reality, a simulation using Bosjesspruit Colliery roof drip water was used (Figure 171).

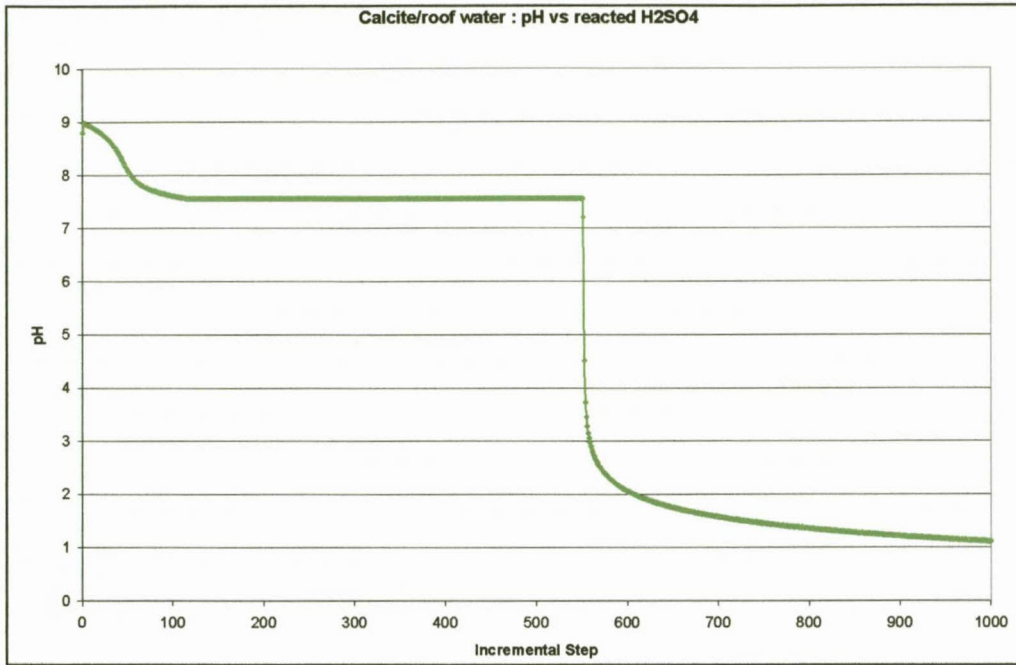


Figure 171: pH response of roof water/calcite system at constant P_{CO_2} .

Once again the calcite maintains a constant pH until it is depleted. This confirms the assumption that as long as calcite is present, the pH will remain fairly constant. This is possible at a constant P_{CO_2} ; however, the first portion of the pH-drop is interesting (Figure 172).

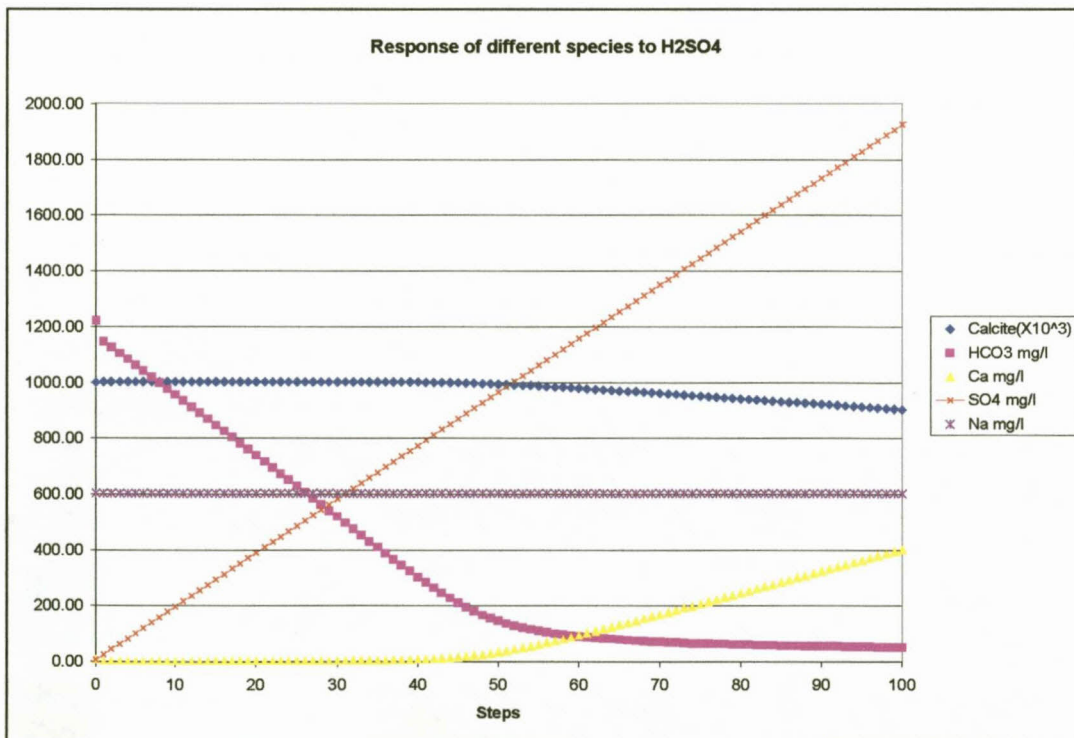


Figure 172: First portion of the reaction.

From Figure 172 it is clear that before step 45, no calcite reaction has taken place. This confirms another of the assumptions viz. that the recharge water's alkalinity first has to be consumed before the carbonate minerals are placed under stress by acidification.

The concentrations portrayed in the above figure also provide a vital understanding of the expected system response. Depending on where along the early part of the reaction path the system is when sampled, completely different ion ratios will be obtained. In the early part of the reaction path the system is a typical Na-HCO₃ water showing enrichment in sulphate relative to bicarbonate (Figure 173). The sodium content remains constant with the water becoming progressively more calcic as the reaction proceeds. In the longer term as the reaction continues, sulphate and calcium will be constrained by gypsum precipitation for as long as calcium is released by calcite buffering. When this ceases the system rapidly acidifies and the sulphate concentrations rapidly rise since no more gypsum can be produced to remove sulphate from solution.

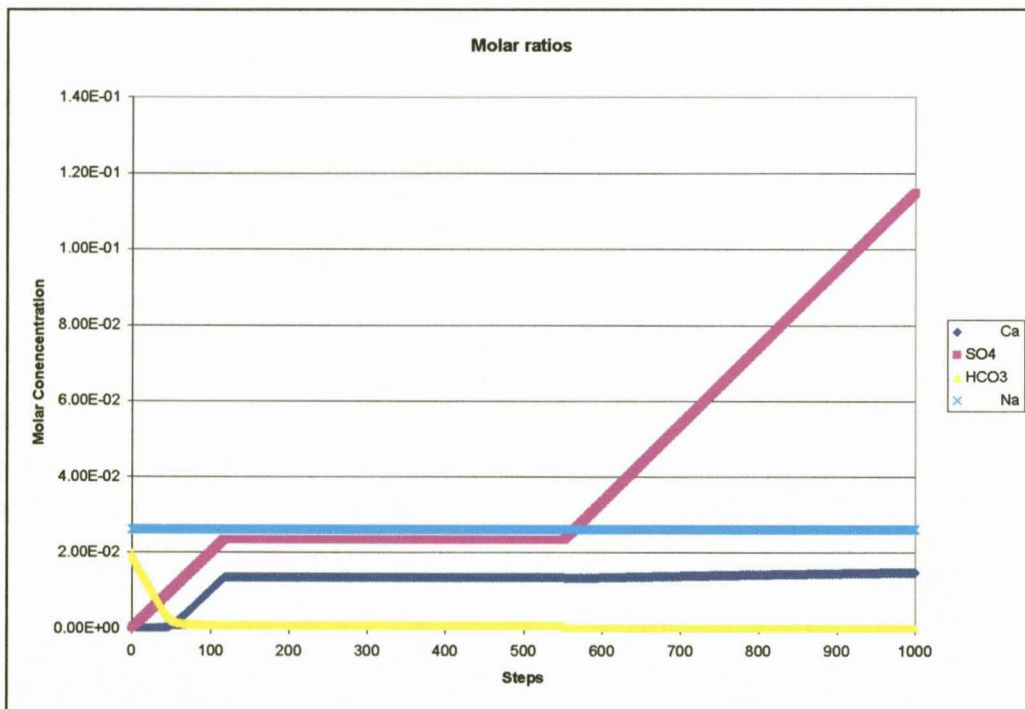


Figure 173: Molar concentrations throughout the reaction path.

The buffering effect of the recharge water is marginally pronounced when added in steps rather than in a single step. The reason for this is that, as the recharge is added, bicarbonate is added. This shifts the equilibria and results in very slightly less calcite being required to maintain neutral conditions (Figure 174).

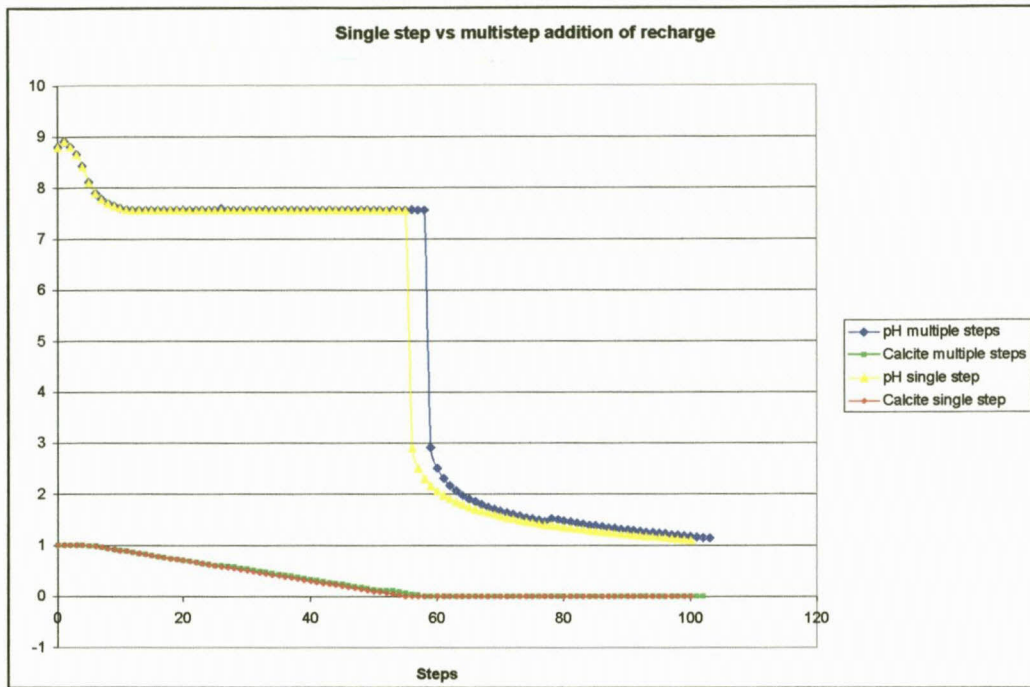


Figure 174: Difference between single step and multiple recharge addition.

8.3.11 Effect on production rates with mining methods

The type of mining method is also expected to play a role in salt-generation rates. In total extraction areas, the collapse of the overburden will cause a far greater reaction surface. Furthermore, the effects of the roof lithologies become more pronounced, thus depending on the ABA nature of these lithologies, different conditions of reaction can be expected. The rate and nature of recharge are also different to that in a bord-and-pillar area. Research by workers in this field such as Hodgson (2001) and Vermeulen (2003), indicate that in most of these situations, an initial high rate of influx will be experienced after collapse. The quality of this initial influx is expected to resemble that of the roof water previously discussed. As time progresses, the amount of water will decrease and stabilise, and stable recharge rates of at least 6% increasing to values up to the early teens or higher, where fractures run into the weathered aquifer, can occur. Where subsidence induced fracturing occurs, rapid recharge to the deeper-lying high extraction areas lead to increased influx. As this occurs, the quality of the recharge is expected to change to a more dilute Ca-HCO_3 water.

The only data currently available for the overlying layers, come from two core boreholes drilled adjacent to Brandspruit's S7 compartment. Based somewhat

tenuously on these data, the deduction is that the pyrite content is very similar, albeit slightly lower than for the coal, while the neutralising potential is far lower and only just equal to the acid potential. Based on this, the increased rock: water ratios as described below, and with the increased surface area, the sulphate production rate is expected to be somewhat higher when compared to the bord-and-pillar mining.

The same simulation as previously, with a 1 ha high extraction area, is therefore expected to yield significantly different results. The first change that can be observed is that the overall Neutralising Potential Ratio (NP: AP) changes from 3.4:1 to 1.41: 1. The storage value remains the same, with the storage merely redistributed further up in the lithological column. The core assumption is that surface subsidence has occurred to the order of half the mining height (Hodgson, 2002), resulting in a conservation of the total amount of storage. The total mass of material that can react also increases from 0.03M t to 0.12M t. This is as a result of the decrease of porosity from 0.5 to 0.2, and also the change in rock density from 1.5 g/cm³, which is the average for South African coals (Nel, Personal Communication, 2002) to 2.6 g/cm³ used for sandstones and shales, based on quartz specific gravity of 2.7 g/cm³. The water: rock ratio also changes from roughly a maximum of 1:1 to a maximum of 1:3.

Again starting with 10% flooding, BUGLE gives the following salt generation rates (Table 35):

Table 35. Initial salt generation rates calculated by BUGLE for high extraction mining.

3.282	kg/day SO ₄
1.033	kg/day Ca
0.151	kg/day Na
0.201	kg/day Mg

These rates are significantly higher for the first year than for bord-and-pillar. For the first year all the influx is again assumed to be typical roof waters as discussed earlier. Based on the arguments above from the second year onwards, the incoming recharge is regarded as being derived from a fresh rapid recharge and roof water, mixed in a ratio of 3:1. This results in a water with the following composition recharging from year 2:

Ca	Cl	F	Fe	K	MALK	Mg	Mn	Na	pH	SO ₄
7	15	0.7	0	0.17	123.5	2.1	0	72	7.2	2

A recharge percentage of 11% is assigned to the high extraction area, based on figures determined by Hodgson *et al.* (2001) and Hodgson (2003). One important effect of this is that the degree of flooding of the compartment has changed significantly from 10% when the simulation was started, to 33% after 5 years. This impacts on the rates as follows (Table 36):

Table 36. Salt generation rates calculated by BUGLE after a year of influx.

2.412	kg/day SO ₄
0.759	kg/day Ca
0.151	kg/day Na
0.148	kg/day Mg

These values, apart from Na, which is defined as constant source term, have dropped significantly from year 1, due to the increased inundation of the reactive minerals.

The results of this simulation yield extremely interesting observations (Figure 175).

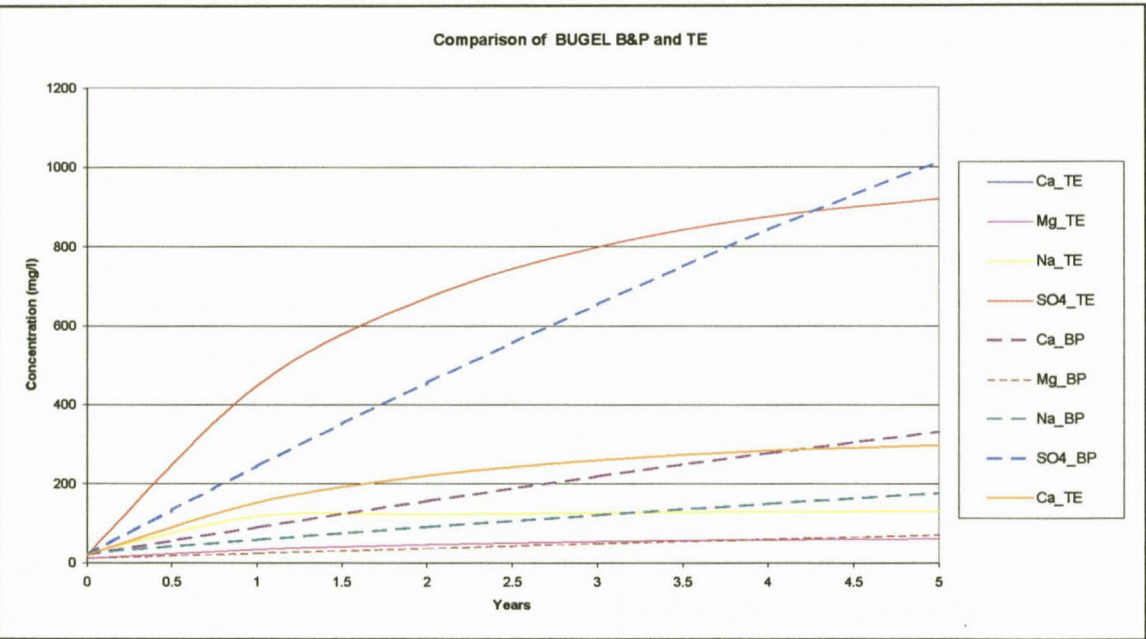


Figure 175: Comparison of 1 Ha compartments bord-and-pillar vs. high extraction.

It is clear that in the TE compartment, the water quality initially deteriorates at a far higher rate than in the bord-and-pillar compartment. An example would be the sulphate value, which is almost double in the TE compartment after a year and 50% greater after two years. This is expected due to the high rate of reaction and the relatively small amount of water. However, as time progresses, two factors, namely the high level of dilution due to the high recharge and the associated rapid inundation of the reactive minerals, result in the concentrations being equal after approximately four years.

This comparison is based on extremes. Lowering the TE recharge and increasing the bord-and-pillar recharge to more realistic values will provide a better assessment of the longer-term behaviour. The importance of the geohydrological aspects can

therefore not be overemphasized. One of the key deficiencies identified by recent research (Usher *et al.*, 2003) in the Witbank and Highveld Coalfields, is the lack of regular water-level measurement simultaneously with water qualities. Until this is done on a large scale in South African collieries, the understanding of the interactions will remain based on assumptions, which may not be universally applicable.

Figure 176 describes a contrasting situation, where the higher reaction rates result in higher concentrations; with the dilution and inundation still not significant enough for lower concentrations than in bord-and-pillar mining.

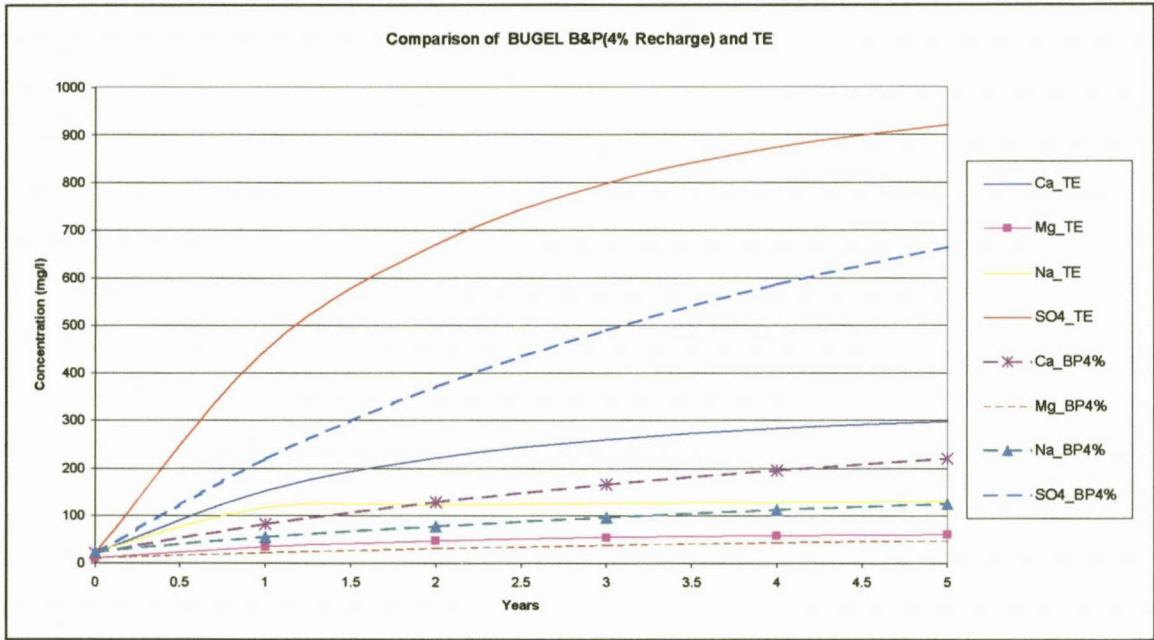


Figure 176: Comparison of bord-and-pillar (with 4% recharge) and high extraction mining.

These fairly simple simulations, which are site-specific, already illustrate the usefulness of an empirical model such as BUGLE. As situations become more complex, a tool such as BUGLE can provide a valuable understanding that may not be intuitively quantifiable.

8.4 LIMITATIONS OF BUGLE

As with any empirical approach there are several important limitations that should be highlighted:

- The model is only as good as the available data. Thus far complete datasets are the exception rather than the rule within the South African Coalfields.
- Some expertise is required from the user. Several of the parameters have to be estimated, and while good estimates are given, some experience of local conditions is required.

- The use of Solver is not always ideal- occasionally values are obtained which are not expected or a solution is not found. This usually corrects itself in the next time step.
- Ms-Excel's Solver cannot accommodate a variable function to solve to, thus a fixed SI value for calcite needs to be used. Again this usually only results in incorrect results for a single time step.
- The answers that are obtained will not correlate precisely to a program such as PHREEQC, since precise speciation is not included. In most cases this should not cause excessive deviation from observed water quality.

Thus far the system has not been applied at enough "real" systems. Testing at further field sites will highlight further deficiencies, which need to be addressed.

8.5 ADVANTAGES OF BUGLE

- As the relevant data is gathered and processed, the level of accuracy in any mining area should improve.
- The predictions should improve as better understanding of the correlation between on-site ABA and observed concentrations is obtained.
- BUGLE can independently include the water balance components so that any assessment can be done in BUGLE as a standalone item.
- The impacts of changes in mining or management strategy on compartment scale can be very quickly and easily evaluated.
- The inclusion of onsite controls such as observed supersaturation of carbonate minerals makes the prediction of water quality more realistic than can easily be obtained commonly used geochemical modelling codes.
- BUGLE can be used for on-site training so that responsible persons at the mine site can understand the key processes and the relative importance of each data type in a monitoring program.
- Incorporation of the relative level of flooding on the geochemical response of the system expedites the inclusion of observed inhibition of pyrite oxidation under submerged conditions.

8.6 CONCLUSIONS

Through the application of well-constrained assumptions and observed water chemistries, a realistic prediction tool for underground water quality evolution has been created. BUGLE has sufficient functionality to address the key reactions, but eliminates unnecessary complications. It is felt that as the data sets grow and BUGLE is applied at more sites, the degree of confidence in its predictions will increase. The evaluation of alternative management options in BUGLE, allows rapid decision-making, based on expected future water quality. Currently, BUGLE has only been

applied to the mines in the Secunda area. The implementation thereof in terms of site-specific application is currently underway. As the system is tested in other areas, site-specific modifications will be made and more robust reaction schemes, which will be able to deal with the variability across the South African Coalfields, are envisaged.

9 APPLICATION OF PREDICTION TECHNIQUES

9.1 THE COMPARISON OF FIELD OBSERVATIONS TO PREDICTION TECHNIQUES

An important consideration is the integration and comparison between values observed in the field and those obtained from applied prediction tools. In this section several mine sites will be used for comparison.

The techniques discussed in Chapters 4 to 8 have been applied in different combinations at several collieries. This section will highlight the techniques used at each site, and any pertinent observations made as a result. The full case studies are in Appendix 4 of this thesis; if the reader requires the background to any of the case studies, these can be found there.

9.2 OPTIMUM COLLIERY

Optimum Colliery is used to illustrate the use of static test data, monitoring data and groundwater flow modelling to determine the long-term water quality. Since it utilises several of the techniques, it is presented more completely; the other case studies have utilised similar approaches, with additional techniques applied where necessary.

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.

To determine the long-term influence of the opencast mining, 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 *et al.* (IGS, 1999). Their conclusions are used as input in this investigation to quantify the nature of the hydrochemical regime.

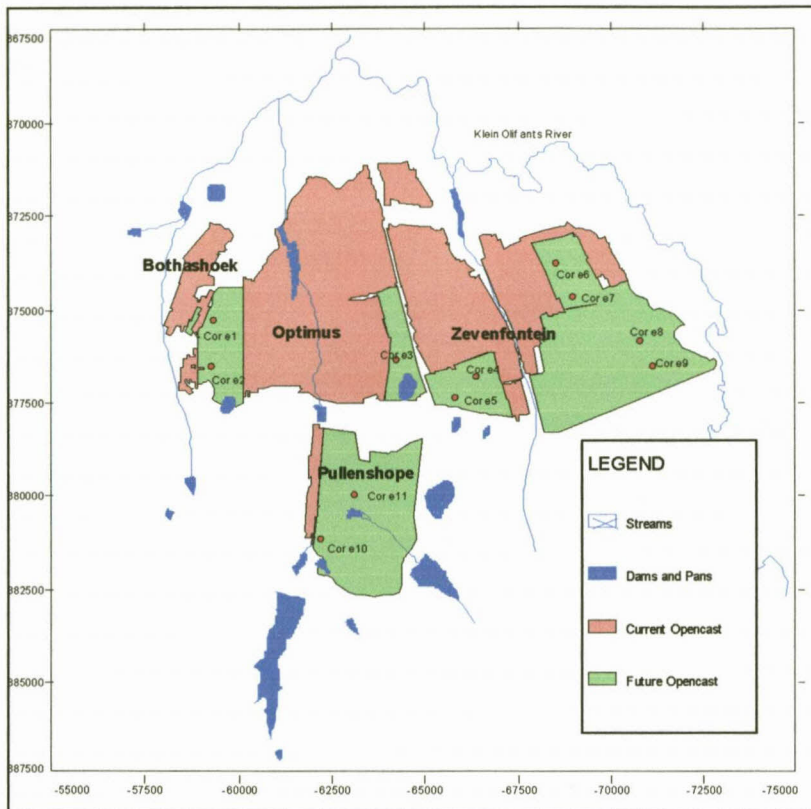


Figure 177: Plan showing current and future Optimus Opencast sections and core boreholes

The techniques used at Optimus include:

- Acid-Base Accounting (ABA) on rock and coal samples (89 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.
- 15 trenches were also dug in the spoils, in two areas, with vastly different conditions. These results have been discussed fully in Section 6.3.
- Chemical profiling of water within available monitoring boreholes.
- Calculating concentrations of constituents that will be present during and after mining.
- Equilibrium modelling using PHREEQC to identify constraints on water quality.
- Calculating salt balances for current and post-closure scenarios.

9.2.2 Acid-Base Accounting (ABA)

9.2.2.1 pH-LEVELS

11 cored boreholes were drilled by Optimum Colliery, in areas still to be mined. Geological logs of these boreholes are included in Appendix 4. 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 pH is expected. Figure 178 and Figure 179 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 4.

The following is a translation of the codes used in Figure 178 and Figure 179:

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.

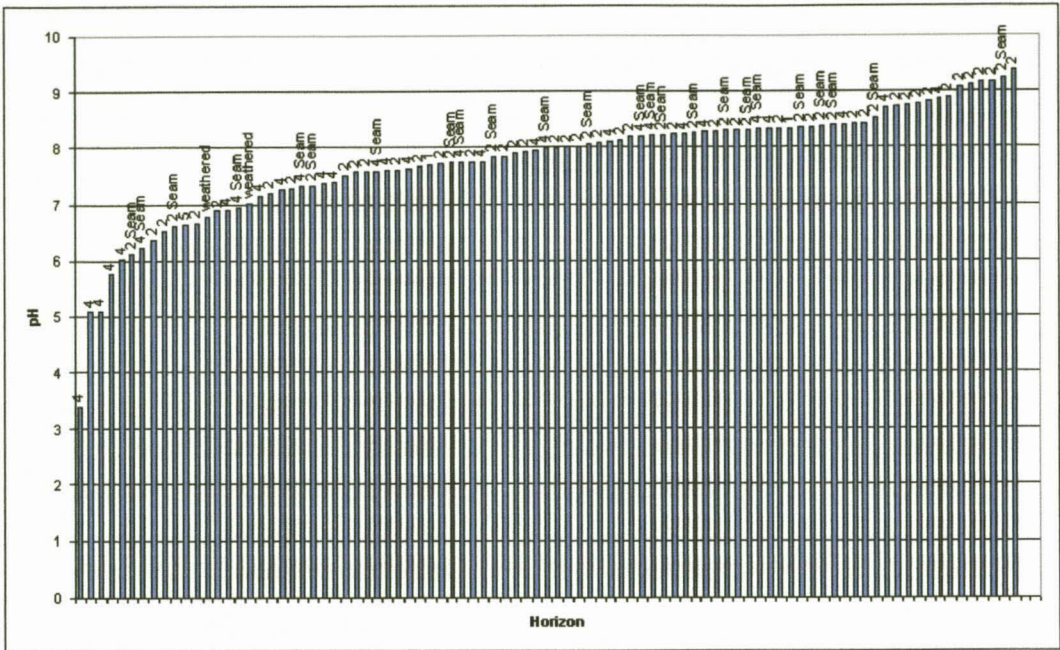


Figure 178: Natural pH vs. horizon.

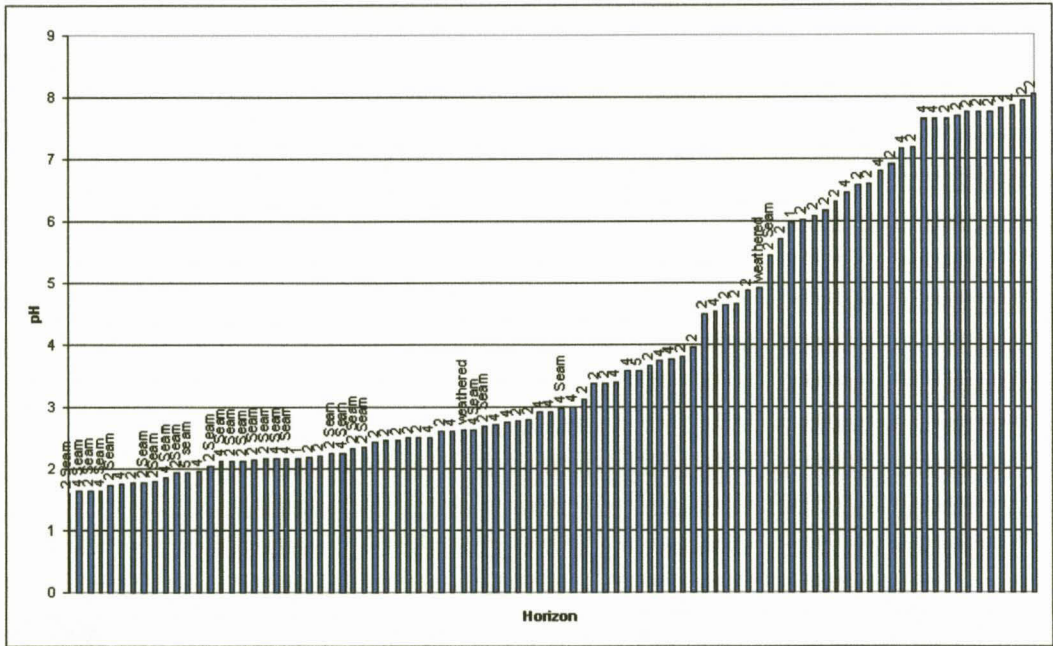


Figure 179: Oxidised pH vs. horizon.

Conclusions from the natural pH-levels (Figure 178) are:

- Over 80% 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.
- 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, much of this has been preserved due to the paucity 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 179 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 179) 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

Static testing was done according to the methodologies outlined in Chapter 4.

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 180 to Figure 182.

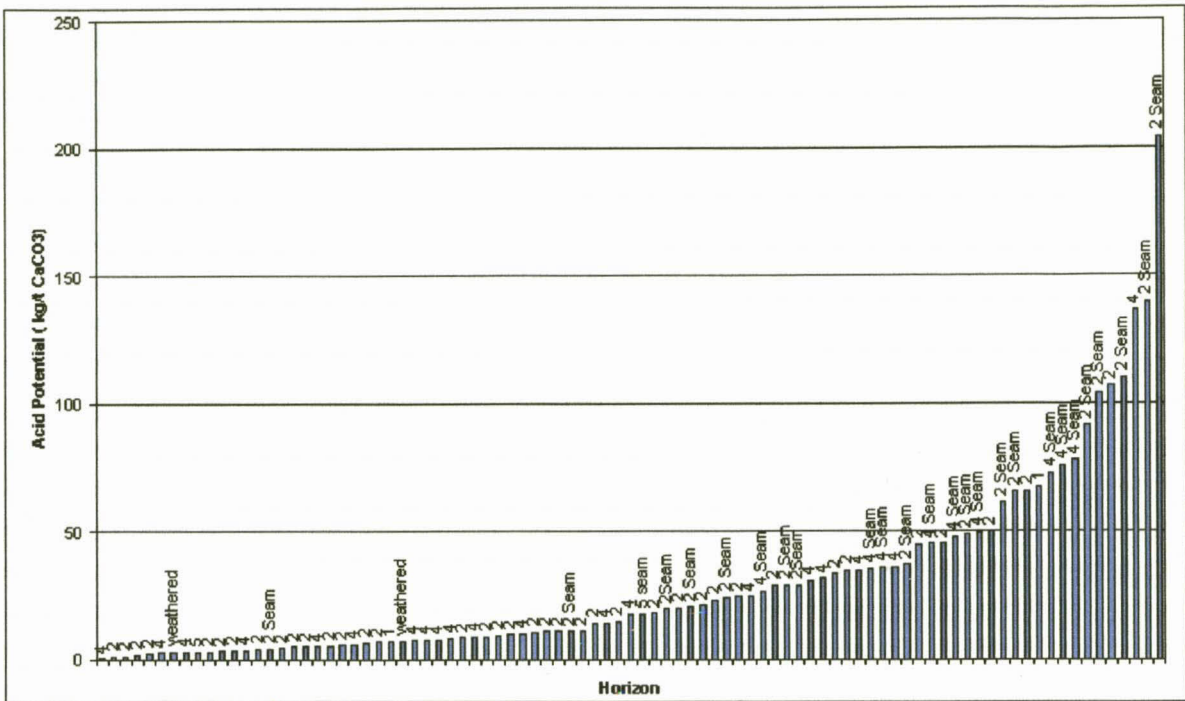


Figure 180: Acid Potential by horizon.

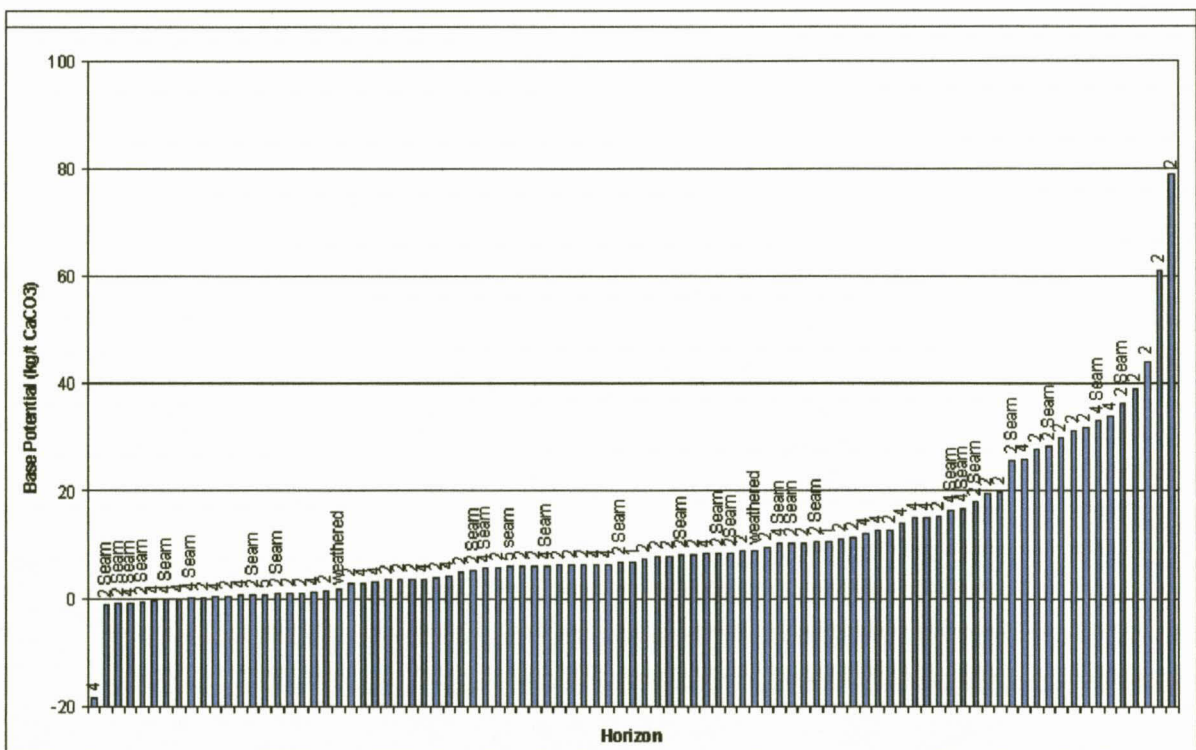


Figure 181: Base Potential by horizon.

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 182).
- 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 182). 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 open and closed conditions. Under closed conditions, the acid potential is doubled 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 (Hodgson and Krantz, 1998)
- 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 183. 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.

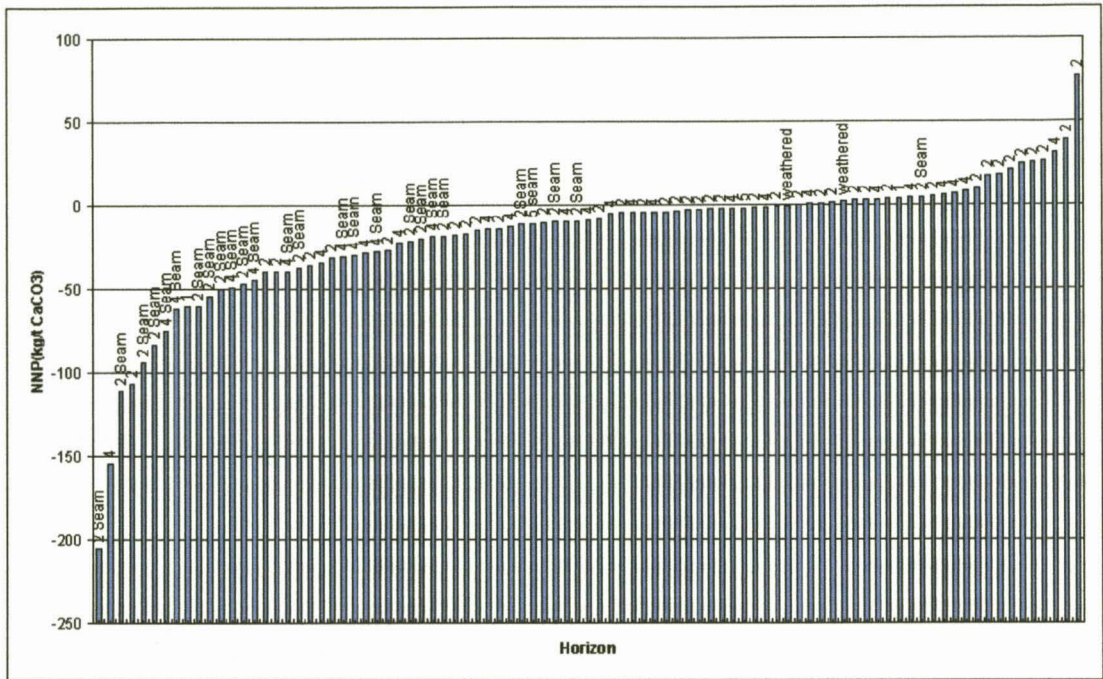


Figure 182: NNP by Horizon .

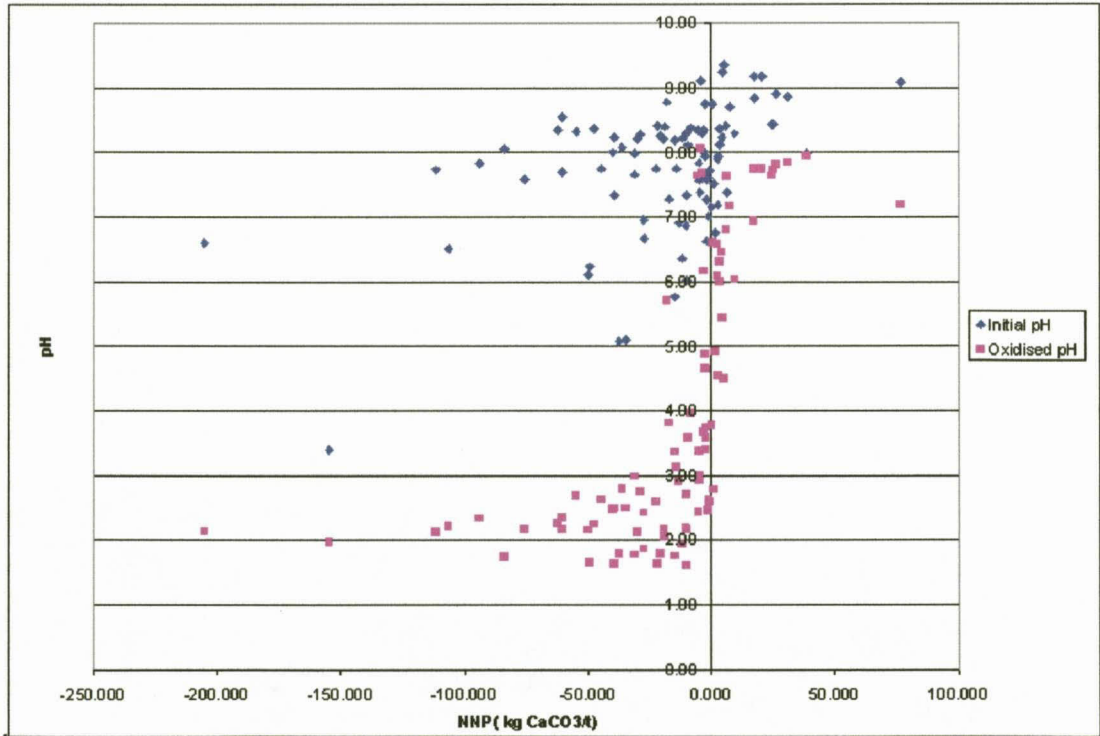


Figure 183: Initial and Oxidised pH vs. Closed NNP.

An additional graph to demonstrate the likelihood of long-term acidification is shown in Figure 184. 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.

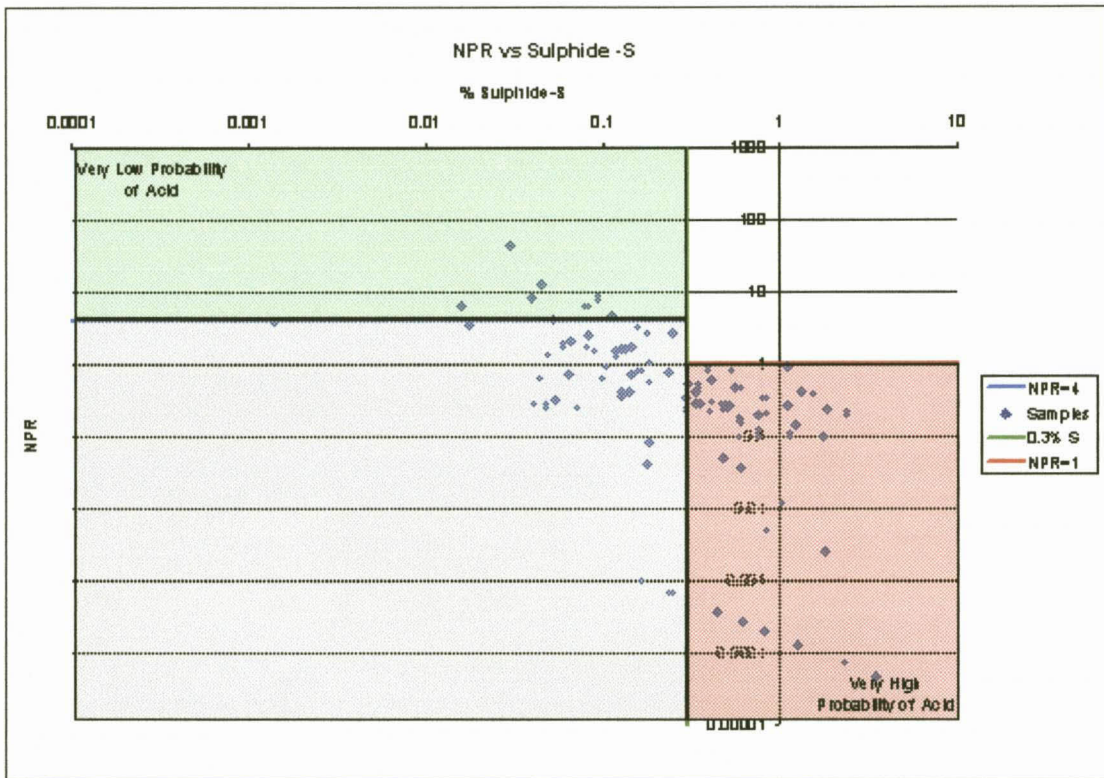


Figure 184: Acid-generating probability of the spoil.

The next step in Acid-Base Accounting is to relate the laboratory measurements to the field situation. Table 37 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 185. 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 CaCO_3 . In the context of the mine, however, removal of the coal will not change the end situation because acidification will still take place.

Table 37. 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

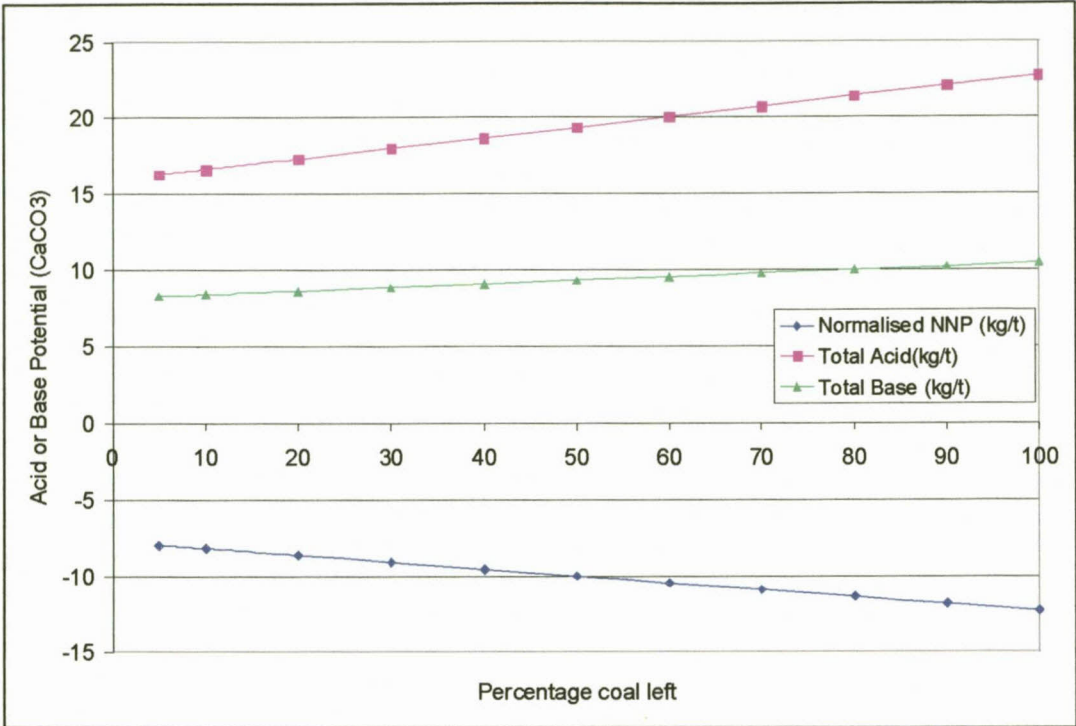


Figure 185: Acid, base and NNP in the spoil as they relate to various percentages of coal extracted.

The probability of spoil acidification can also be calculated. The results are presented in Figure 186.

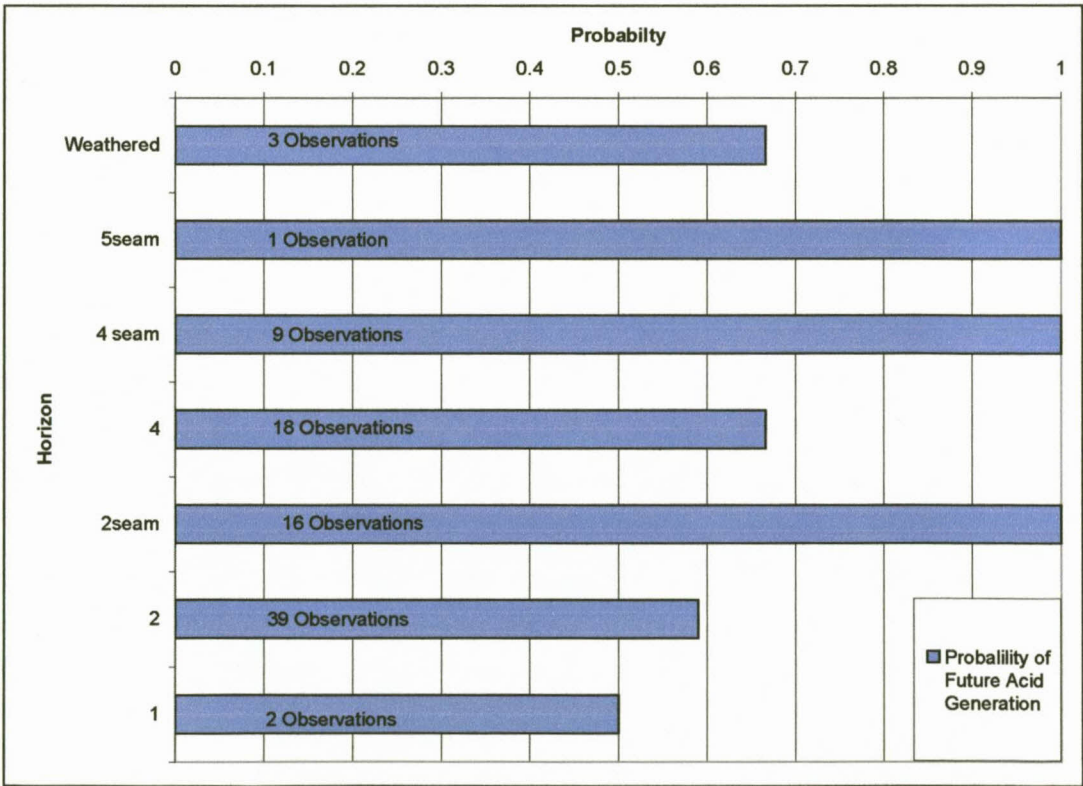


Figure 186: Probability of acidification of the spoil for the various lithologies.

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 spoil, 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 Using ABACUS to calculate the ABA for the entire mine

As a comparison to the preceding section, the values for each area were again determined, using the ABACUS tool. The results, given in Table 38, 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 (Hodgson and Krantz, 1998).

Table 38. Evaluation of NNP by area.

	DRILL HOLE	Area No.	BOTTOM ACREAGE	TONS MPA	TOTAL TONS NP	TOTAL TONS NET NP	TOTAL TONS OB
Area Totals	OB1	1	245.0	3153476.0	587039.2	-2566436.9	99128798.9
	OB2	1	87.5	152130.4	375248.7	223118.3	42446174.0
			332.5	3305606.4	962287.9	-2343318.6	141574972.8
Area Totals	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
Area Totals	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
			451.3	1660930.0	2150028.0	489098.0	213393503.9
Area Totals	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 39 and Table 40 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.

Table 39. Area 2 overall evaluation.

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 CaCO ₃ REQUIRED (1:1):	2809	<u>EXCESS</u>	
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 CaCO ₃ REQUIRED (1:1):	1746	<u>DEFICIENCY</u>	

Table 40. Area 3 West 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 CaCO ₃ REQUIRED (1:1):	1084	<u>EXCESS</u>	
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 CaCO ₃ REQUIRED (1:1):	2597	<u>DEFICIENCY</u>	

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 187 to Figure 190. 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.

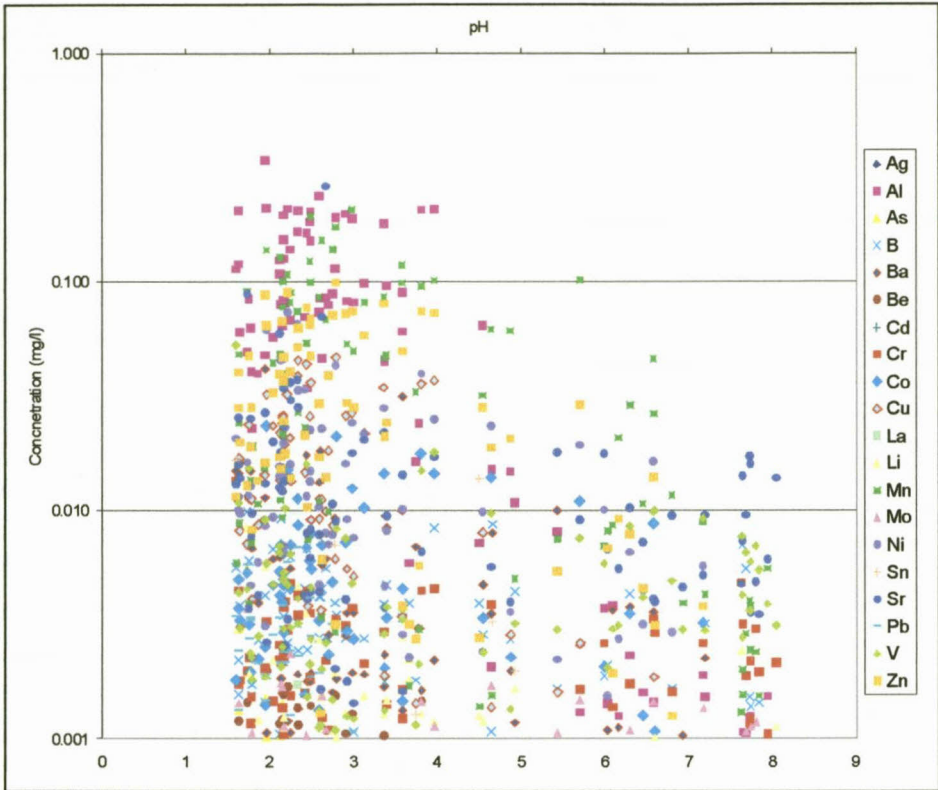


Figure 187: Concentration of macro-elements after oxidation, showing the likely composition of leachate, depending on pH.

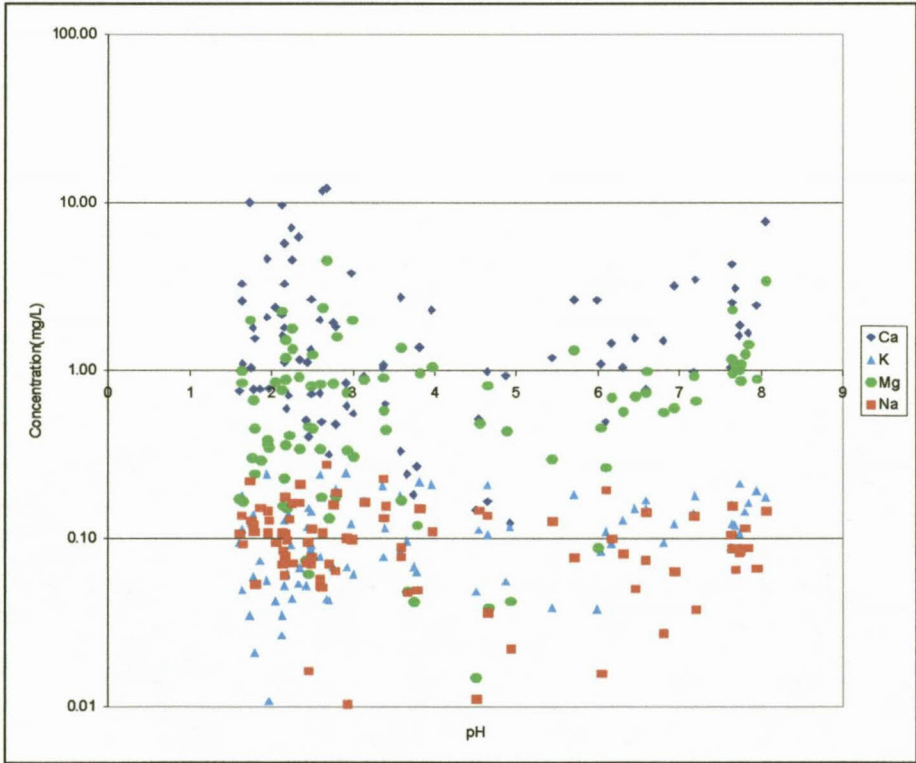


Figure 188: Concentration of micro-elements after oxidation, showing the likely composition of leachate, depending on pH.

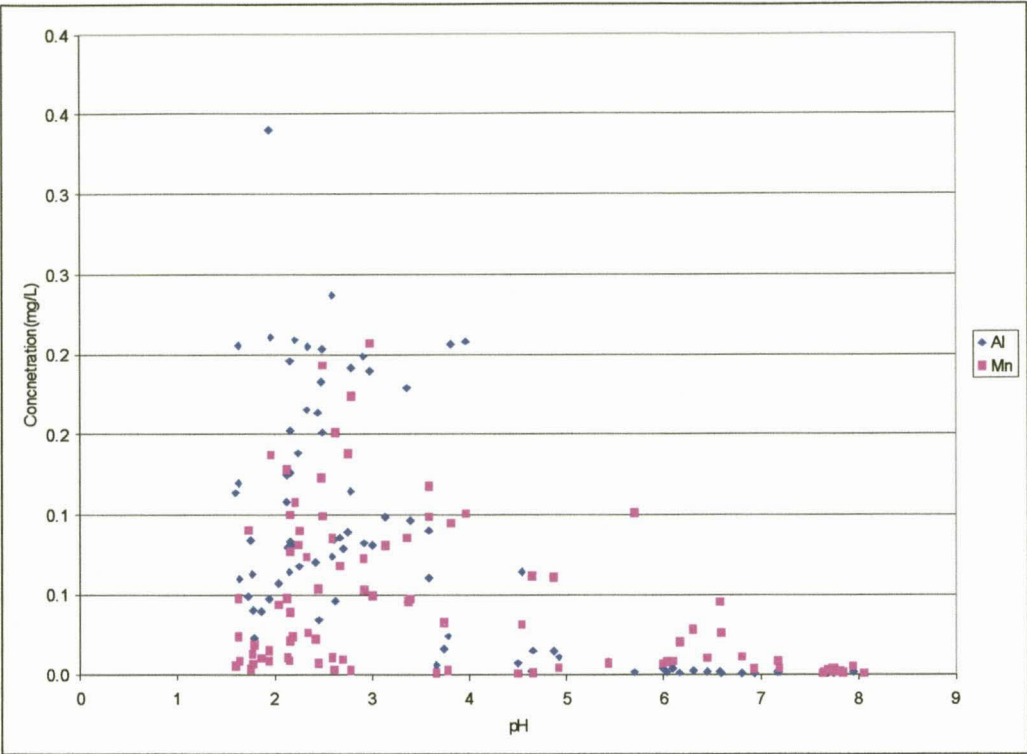


Figure 189: Concentration of Al and Mn after oxidation, showing the likely composition of leachate, depending on pH.

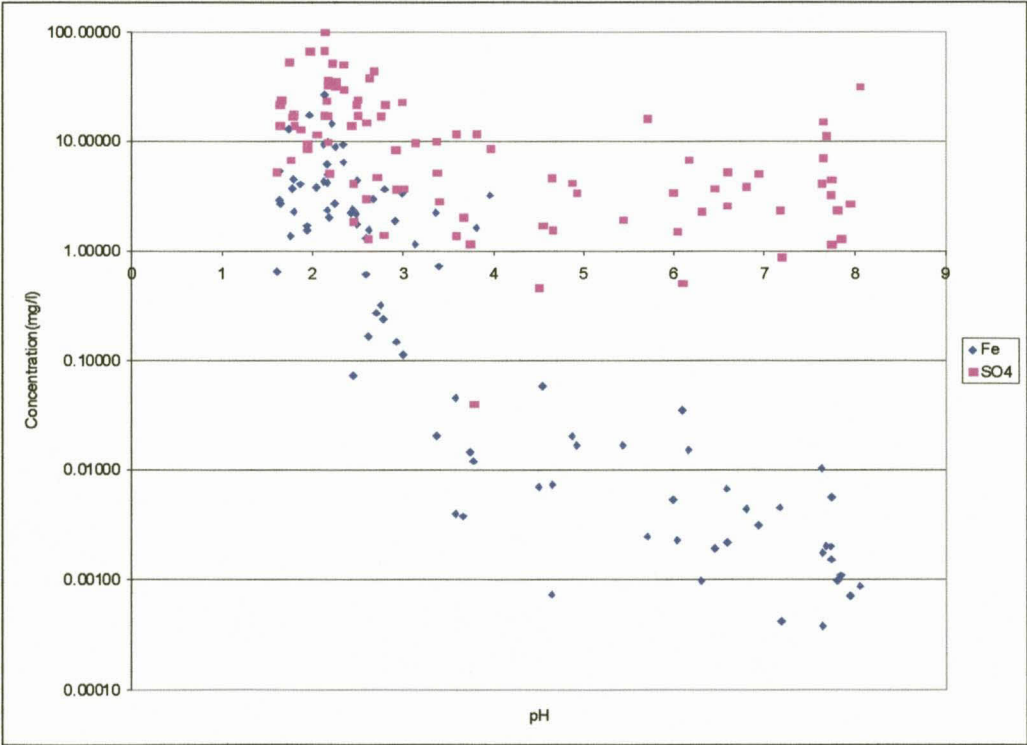


Figure 190: Concentration of Fe and SO₄ after oxidation, showing the likely composition of leachate, depending on pH.

9.2.3 Current Mine Water Quality

9.2.3.1 WATER QUALITY THROUGH SAMPLING

Water sampling positions for this case study are shown in Figure 191. The analytical results are presented in Appendix 4. Samples P1 - P11 are surface water samples. This sampling was to supplement and test the validity of information from Acid-Base Accounting.

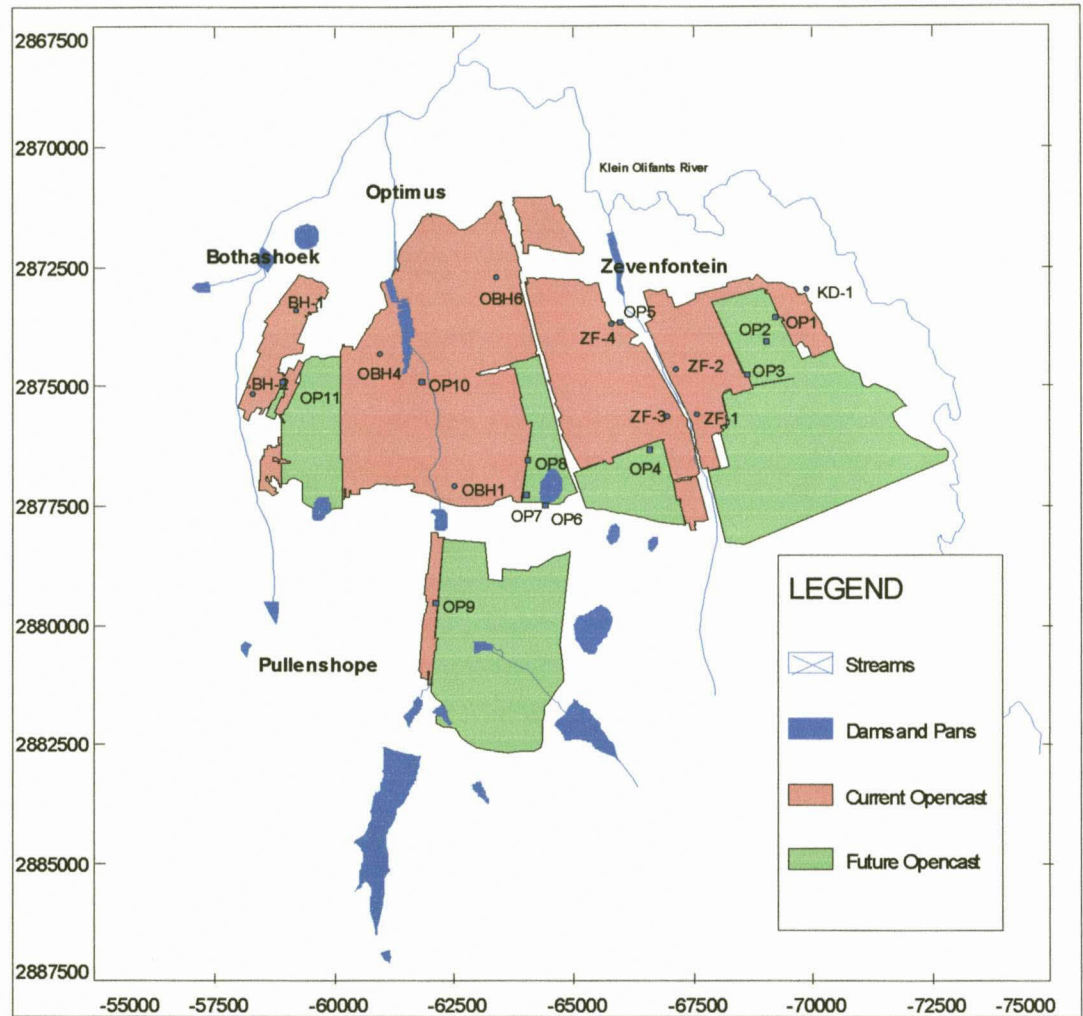


Figure 191: Localities of water samples for chemical analyses.

The following conclusions are drawn from chemical analyses of the water samples:

- Only one borehole, and a single surface water sample are acidic. 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 drilled into unmined sediments. Its composition is not unusual for the lower Ecca sediments (Cogho *et al.*, 1992). 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.

9.2.3.2 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 (Figure 192). 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 4.

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 those of calcium/magnesium carbonate (pH 8.0 - 6.5); siderite (pH 5.5); clay minerals (illite and kaolinite, 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. 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 redox 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.

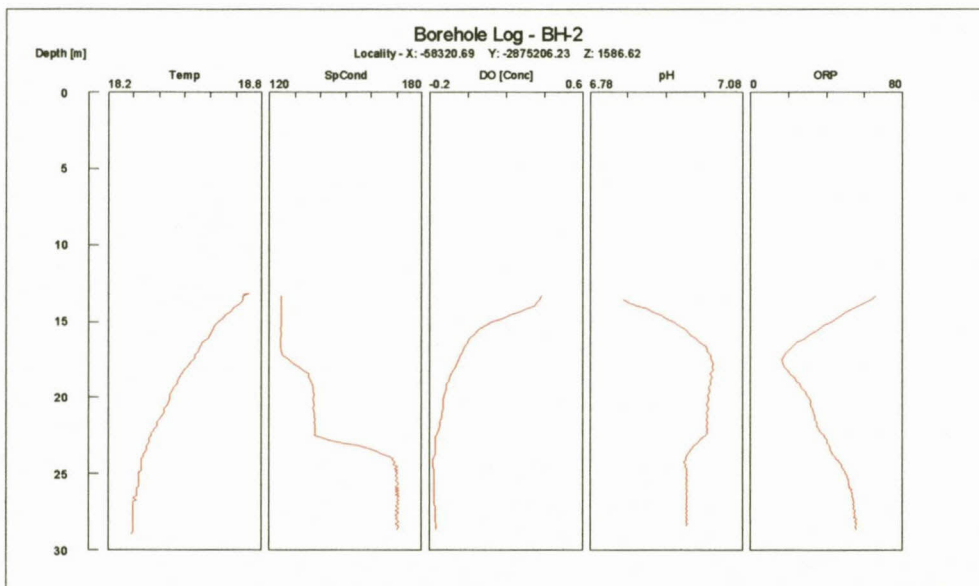


Figure 192: An example of the hydrochemical logs of spoil water at Optimum.

9.2.3.3 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 193).

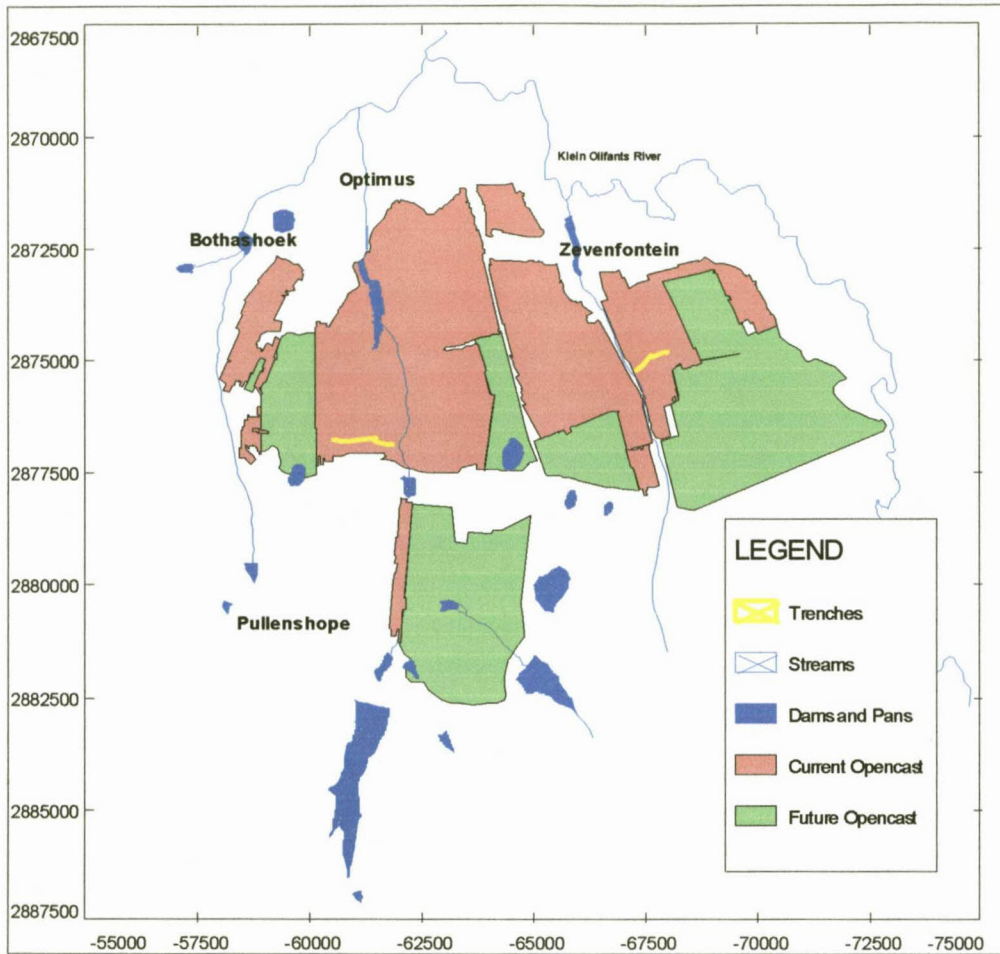


Figure 193: Localities of inspection pits at Area 2 and Area 3.

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 6.3, relating to field methods in the ABATE strategy.

9.2.4 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 41).

Table 41. Expected post rehabilitation decant volumes [m³/day].

PIT	AREA	MINIMUM VOL.	AVERAGE VOL.	MAXIMUM VOL.
	[HA]	[M³/DAY]	[M³/DAY]	[M³/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, were determined. The Stage curve for Area 2 pit, up to its decanting level is shown in Figure 194. Surface contours and floor contours are shown in Figure 195 and Figure 196, respectively. The degree to which the floor of the pits will be flooded is shown in Figure 197.

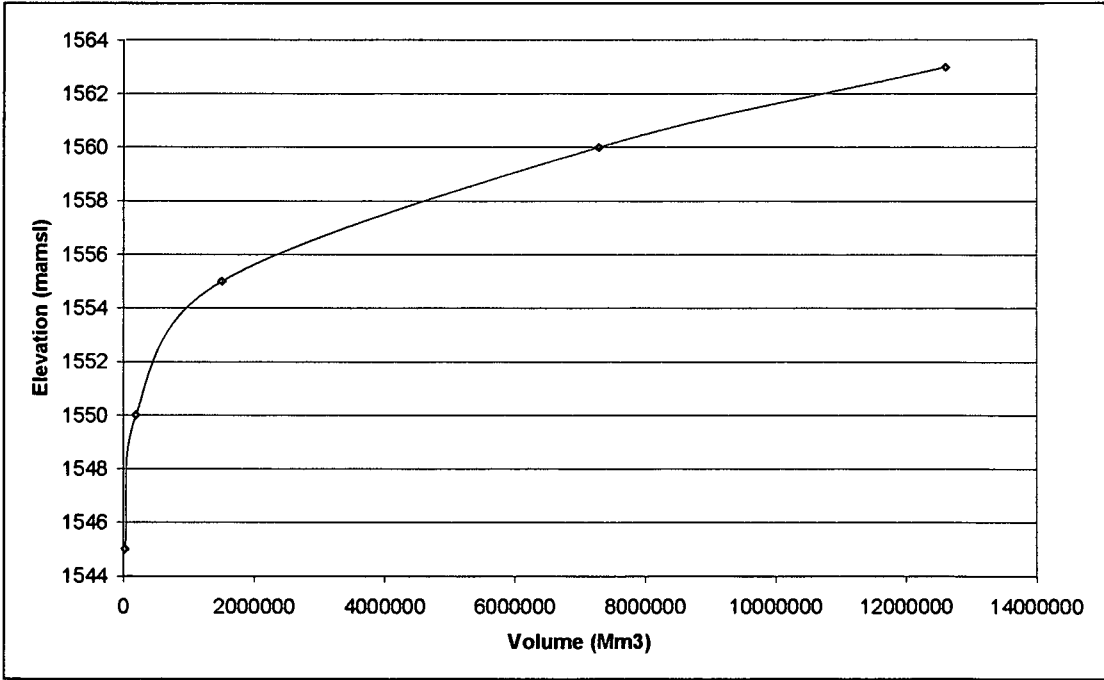


Figure 194: Stage curve for Area 2 pit, up to its decanting level.

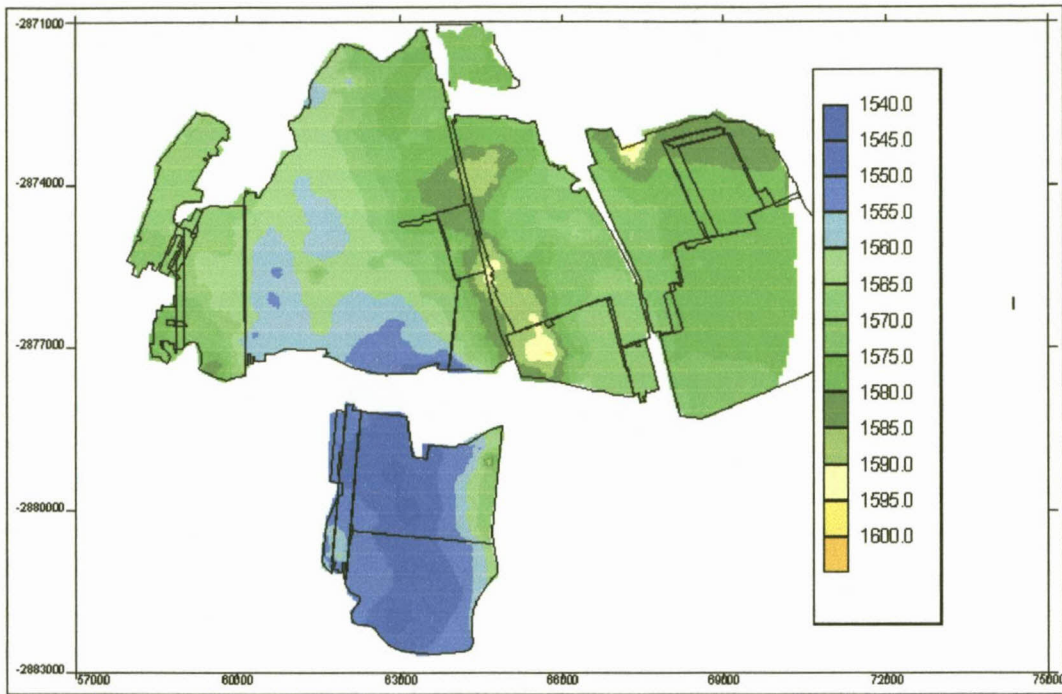


Figure 195: Coal floor contours (mamsl) in the pit areas.

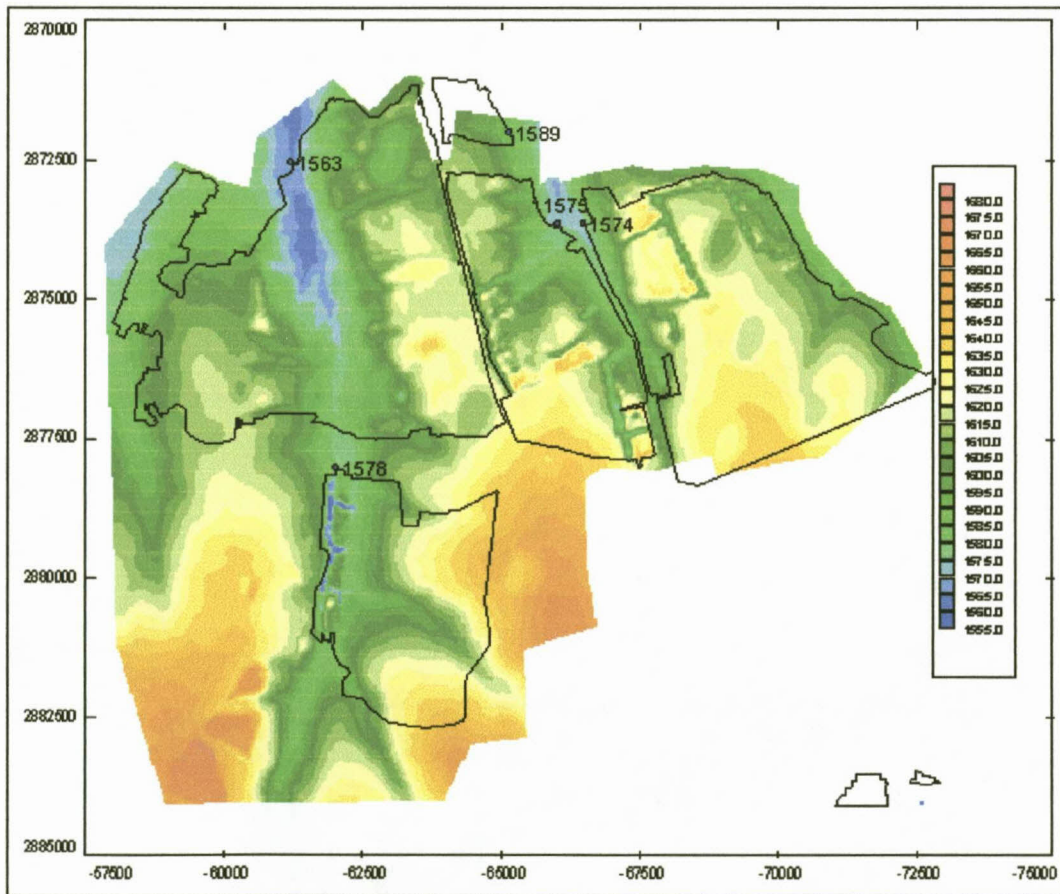


Figure 196: Current surface contours (mamsl).

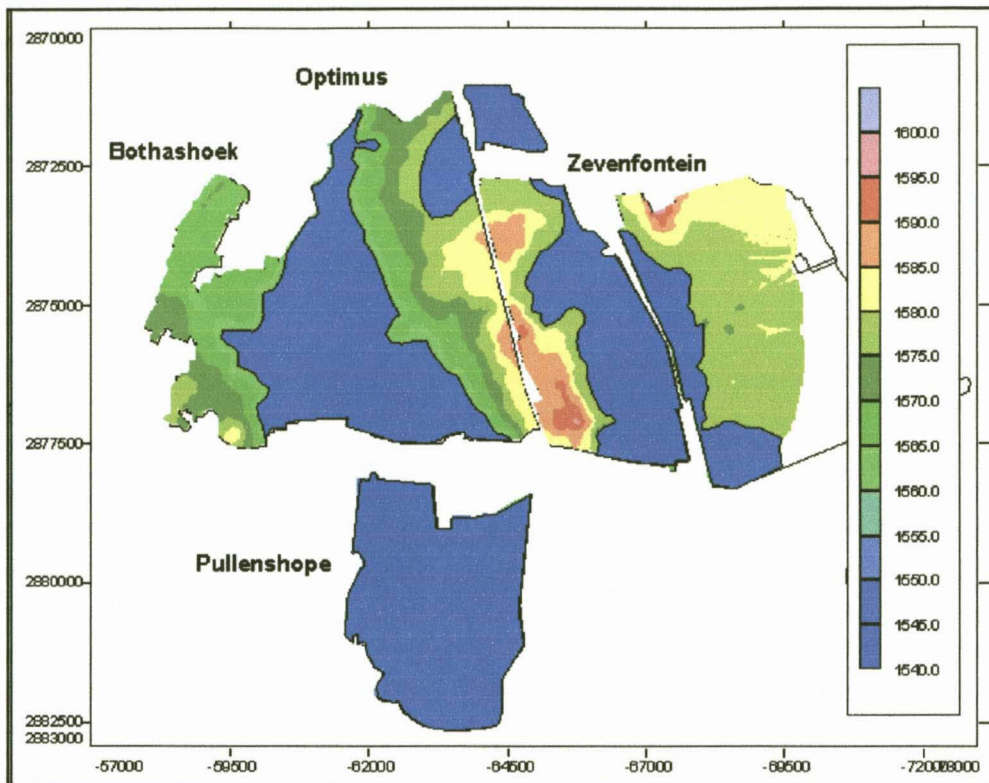


Figure 197: Coal floor contours (mamsl) and future water accumulations in the pits at their various decanting levels.

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 *et al.* (1999) 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.

9.2.5 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 commences when mining starts. 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 42, 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 42 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 42). 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 Figure 187 to Figure 189).

Table 42. 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
SO ₄ 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

9.2.6 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 neutralisation 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 Colliery.

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 acidification of the spoil water at Optimum Colliery is probable.

It is felt that this case study provides an excellent example of the combined use of several prediction techniques to arrive at an indication of likely water quality evolution.

9.3 COLLIERY 2

Colliery 2 also lies in the Witbank Coalfield. The same techniques were used, with the addition of detailed mineralogy and consequent generalised geochemical modelling. Of prime interest here is the correlation between the results and the post-investigation resultant water quality.

9.3.1 Geochemical Modelling

To obtain a generalised indication of what could occur on-site, use was made of geochemical modelling. PHREEQC was again used to speciate the water and determine saturation indices. This indicated that at this colliery gypsum saturation acts as a control on the maximum sulphate concentrations and that calcite and dolomite are the principle buffering agents as far as pH is concerned. Eary *et al.* (2003) use a similar approach of ABA, saturation considerations and simplified modelling to characterise a coalmine's hydrochemistry.

Geochemist's Workbench (Bethke, 1996) was used to obtain a profile of the expected water quality of time. The data that were used in this simulation is derived from the

average acid and base potentials for the ABA-boreholes and extensive mineralogy done on the 73 core borehole samples (Figure 198 and Figure 199). From this detailed mineralogy the principle minerals are characterized as quartz, kaolinite, illite and montmorillonite, with lesser quantities of K-feldspar, calcite, dolomite, pyrite and Ca-plagioclase minerals. The data that were used in this simulation is derived from the average acid and base potentials for the ABA-boreholes and detailed mineralogy done on these samples. The detailed X-ray Diffraction and X-ray Florescence results are included in Appendix 4 .The values that were used are: Acid: 2.8% pyrite; Base: 2% dolomite; Clay (kaolinite with some illite) in excess, in the presence of oxygen and water. The results demonstrate the expected sequence of events, but detailed reactive surface area determinations were not done. Oxygen at full oxygen availability is only present on the outside of rocks in the spoil. Inside the rocks, they saturated with water and pyrite does not oxidise. For oxidation to take place inside a rock, the rock first has to disintegrate through weathering. This could take hundreds (thousands) of years, depending on specific circumstances. Based on these principles, the conclusion is that the outside of a spoil boulder (at excess acid potential and above the water table) could acidify within a matter of less than 10 years, while its inside would still be alkaline. Trenches dug into existing spoil in the spoils as part of this research, confirm this observation.

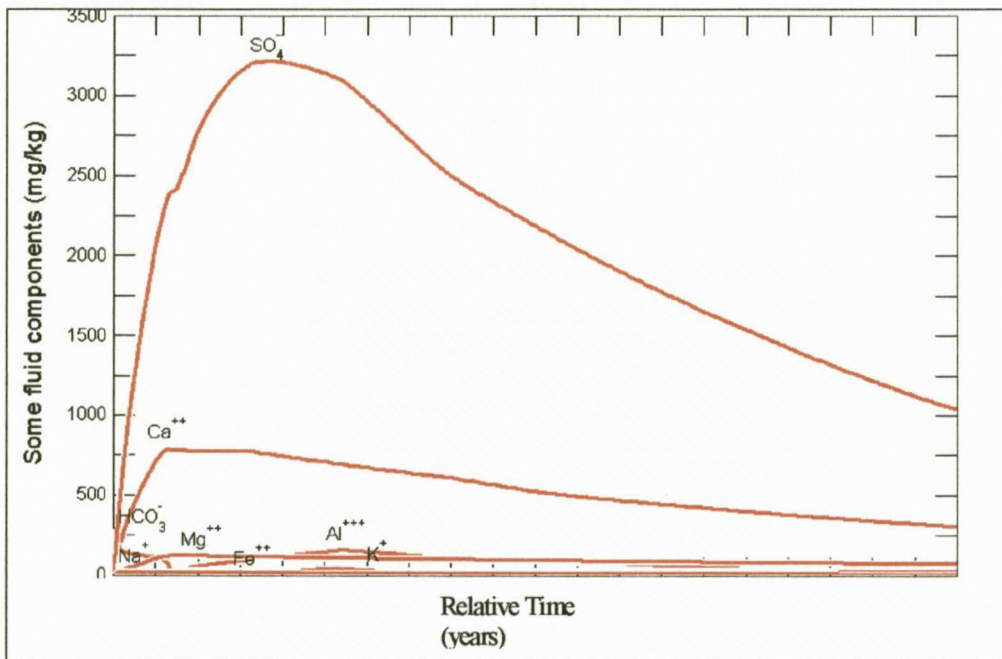


Figure 198: Expected concentration profile over time (using the average mineral assemblage determined by this study and a aquifer transmissivity of $0.5 \text{ m}^2/\text{day}$).

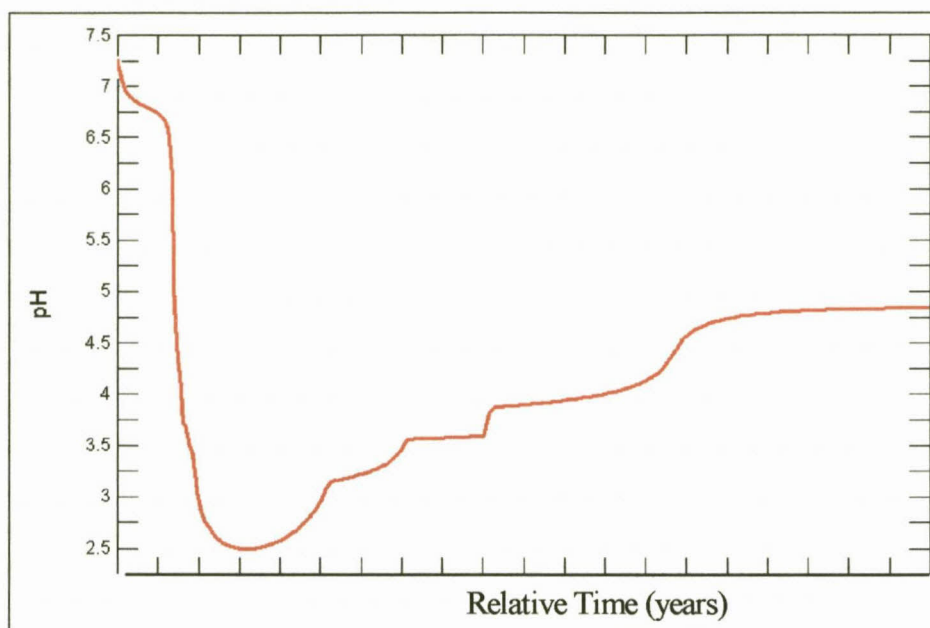


Figure 199: Expected pH profile over time.

Of interest is the fact that within 12 months of this study, excess mine water flowed out of a control area. The quality of this water was around 3 000 mg/L SO_4 at a pH of around 3.5. It is clear that using a properly constrained conceptual model in conjunction with other data can lead to more accurate predictions of water quality, even when key parameters have not been measured. An important caveat here is that the time graph is not specific; the profiles indicate the expected evolution but not the timing thereof.

9.4 USING NUMERICAL MODELS AND REACTIVE TRANSPORT MODELS TO PREDICT IMPACTS AT ZULULAND ANTHRACITE COLLIERY

Zululand Anthracite Colliery's case study is along the same lines as Colliery 2; the additional technique utilised here is simplified reactive transport modelling to illustrate probable attenuation of any acidic water which is generated.

Zululand Anthracite Colliery (ZAC), is a supplier of high-grade anthracite coal, which lies between Empangeni and Ulundi in Kwazulu Natal. Usher, van Tonder and Vermeulen, undertook a detailed groundwater quality and quantity study at Zululand Anthracite Colliery in 2002.

Of interest to this section is the use of simplified reactive transport modelling to assess the natural attenuation of a potential contaminant plume using concepts similar to those employed by Berger *et al.* (2000).

The approach followed included:

- Samples obtained from 13 core boreholes.
- ABA done on 121 samples.
- Mineralogy on several of these samples.

- On-site water quality determinations.
- Hydraulic testing through pumping and tracer tests.
- Groundwater flow modelling to determine water balances.
- Mass transport modelling to determine plume development.
- Geochemical equilibrium and simplified reactive models to determine possible water quality evolution.

9.4.1 Reactive Transport Model

In order to understand the way in which the plumes generated by the mass transport model would react hydrochemically, a simplified reactive transport model was constructed. The flow velocities and flow paths obtained from the numerical flow model in the preceding section were used as hydraulic input in the model, while expected average case acidic water obtained through the geochemical modelling was used as input for the source term of the model. The current groundwater chemistry obtained was used as additional input.

The reactive transport modelling was done using the transport capabilities in the PHREEQC modelling package. The flow path is assumed to be a one-dimensional column along which the mine water flows, thereby replacing the original groundwater. The flow path is divided into several sections or cells along which the chemical evolution can be traced. Zhu and Burden (2001) used a similar methodology to assess attenuation of a mine water plume.

In this case, a situation was taken where the flow length is approximately 160 m along its midpoint (refer to Appendix 4 to assess the two-dimensional plume development). Forty cells of equal length were used to delineate the flow path. The initial solution in each cell was assigned the groundwater chemistry in the area surrounding the Sheleza A area at ZAC, while the incoming fluid represents a typical mine chemistry. It was assumed that the mine water chemistry remained constant throughout the simulation. A dispersion coefficient was assigned to each cell in line with the values obtained from the tracer tests and used in the mass transport model. The reacting minerals in each cell, in this case, is only calcite, which due to the rate of transport is assumed to act in an equilibrium manner. A calcite value in line with the values of NP value obtained by ABA was used for the aquifer.

The following figures (Figure 200 and Figure 201) show the results of these simulations over time and along the flow path in typical breakthrough curves. It can be seen that the sulphate plume takes approximately 3600 days to move along the 160 m flow path, in line with the plume spread previously displayed. This is the period required for the mine water to reach the stream as indicated. Since the sulphate value is relatively low compared to the expected equilibrium value, the movement along the flow path does not significantly change the concentration. Dilution from mixing with water from above or adjacent to the flow path was not incorporated for sake of simplicity. If the mine water concentration was for example 4000 mg/L, it is expected that the concentration would decrease to the value of around 3000 mg/L or less due to gypsum precipitation.

The pH breakthrough curves are significantly different from the sulphate curves. It can be seen that in 3600 days, the acid front would only have migrated approximately 15 m from the mine, and that it takes approximately ten times as long for the acid front to reach the end point. This has significant implications in terms of the risks to the river system and aquatic reserve for the Mfuluzi River, since the neutral pH-values will limit the more harmful metals from reaching the river. More detailed work in this regard will decrease the current uncertainties, but if the compartment can be flooded completely and the effects of recharging water are taken into account, it is clear that the risk of highly acidic water reaching the river by moving through the sediments is not significant.

Simplified reactive transport modelling can be fruitfully used to understand the hydrochemical evolution of a plume from a mining area. No previously published reports on reactive transport modelling of plumes from underground compartments in South Africa could be obtained. It is felt that the answers obtained enhance the understanding of the system's response to such a plume, and should lead to more realistic assessment of the impacts.

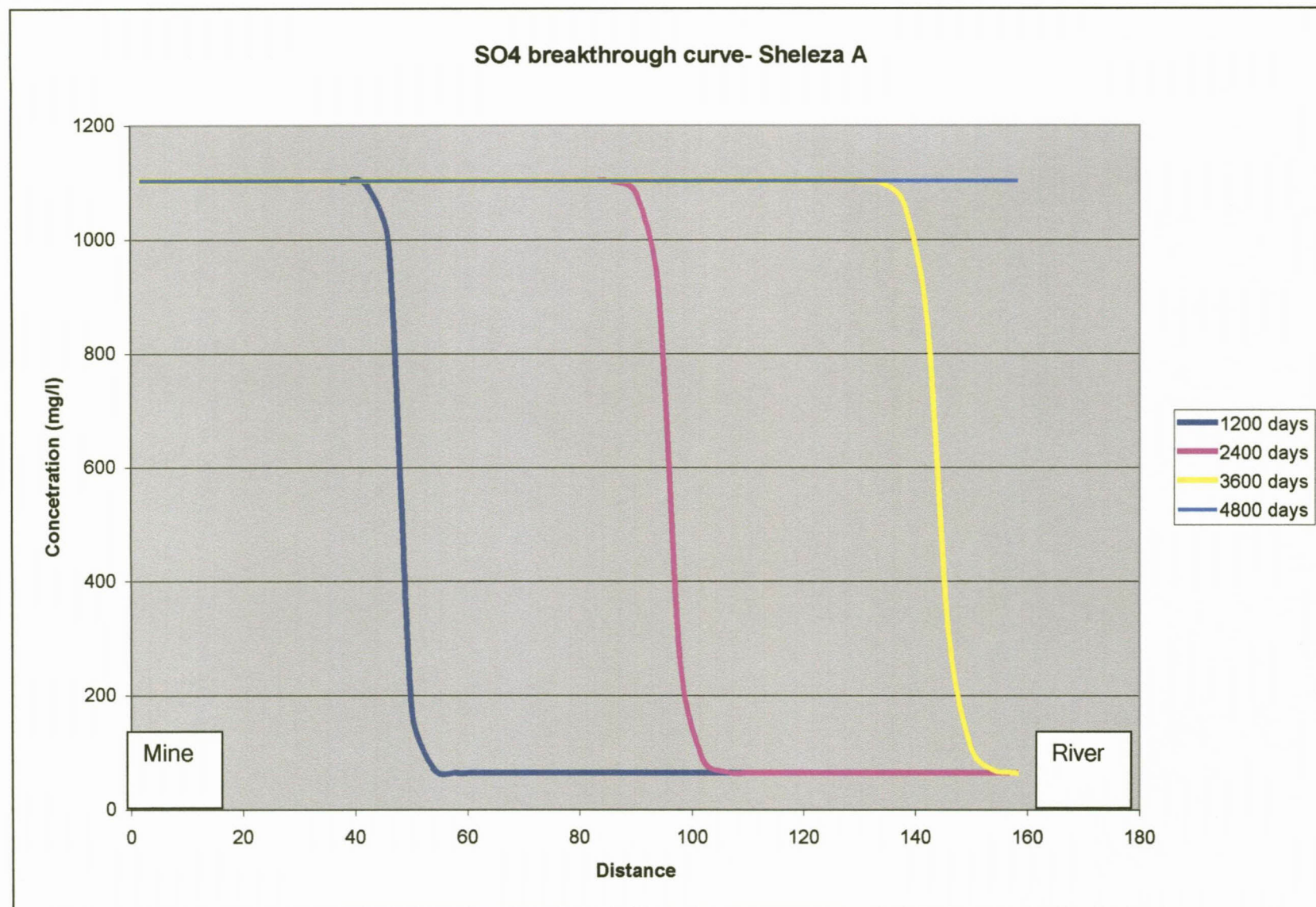


Figure 200: Sulphate breakthrough curve from reactive transport model.

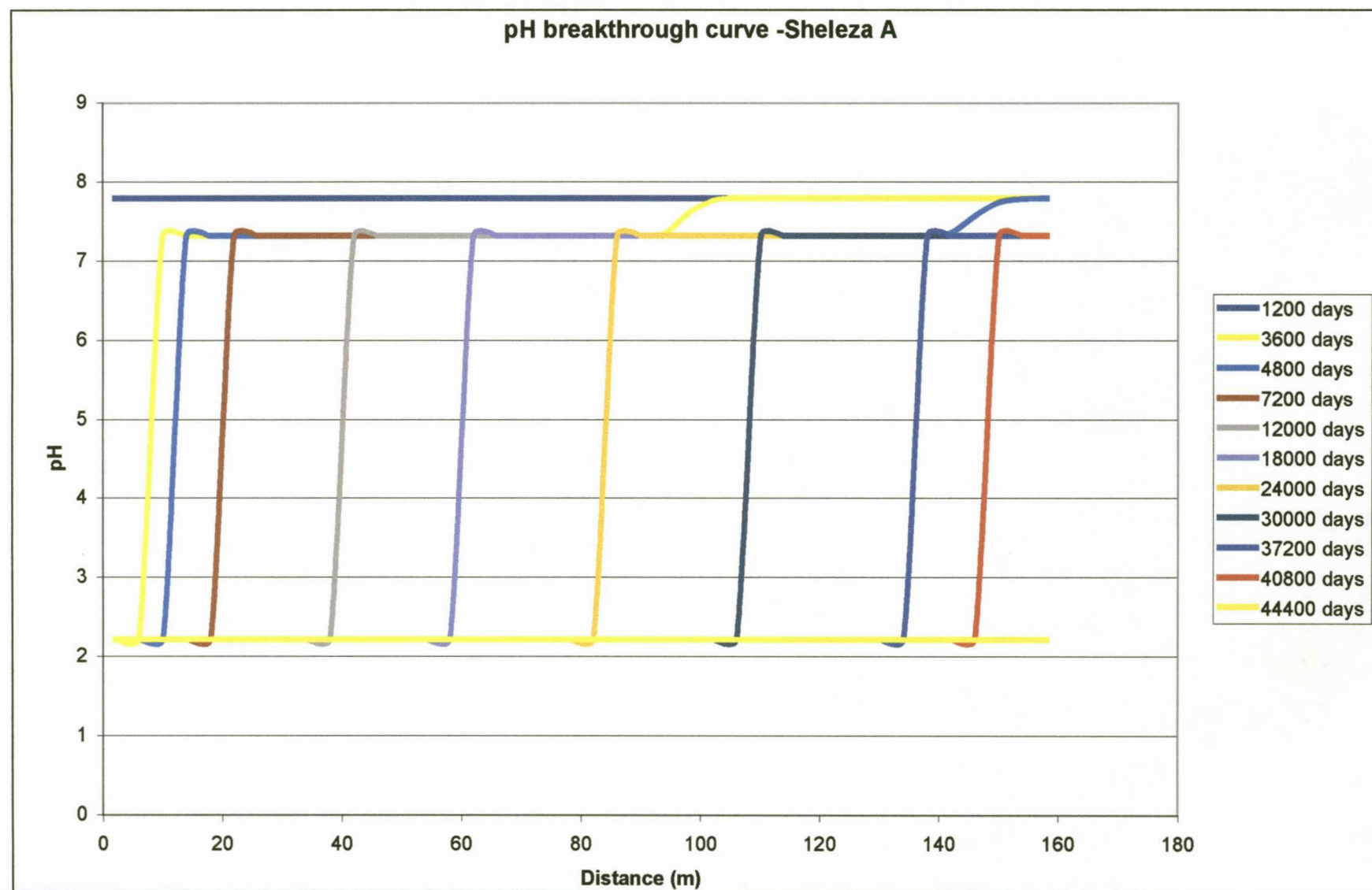


Figure 201: pH breakthrough curve.

9.5 ARTHUR TAYLOR COLLIERY

Arthur Taylor Colliery provides insight into the *in situ* condition of spoils and provides an excellent correlation through static testing, kinetic testing and field observations regarding observed acidic conditions.

The rehabilitated spoils area at Tavistock's Arthur Taylor Colliery (ATC) was 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).

Acid-Base Accounting has been done on several samples from Tavistock Colliery (Hodgson, 1999 and Hodgson, 2001). These results show a clear potential for acidification to occur.

The results of the ABA from two core bores in the spoils of interest are indicated in a more presentable manner as logs, with Figure 202 shown as an example. Using this type of diagram, the most problematic layers are easily identified. It is evident from these two cores that most of the lithological layers have a tendency to acidify. This then should be reflected in the spoil chemistry discussed in Section 9.5.1.

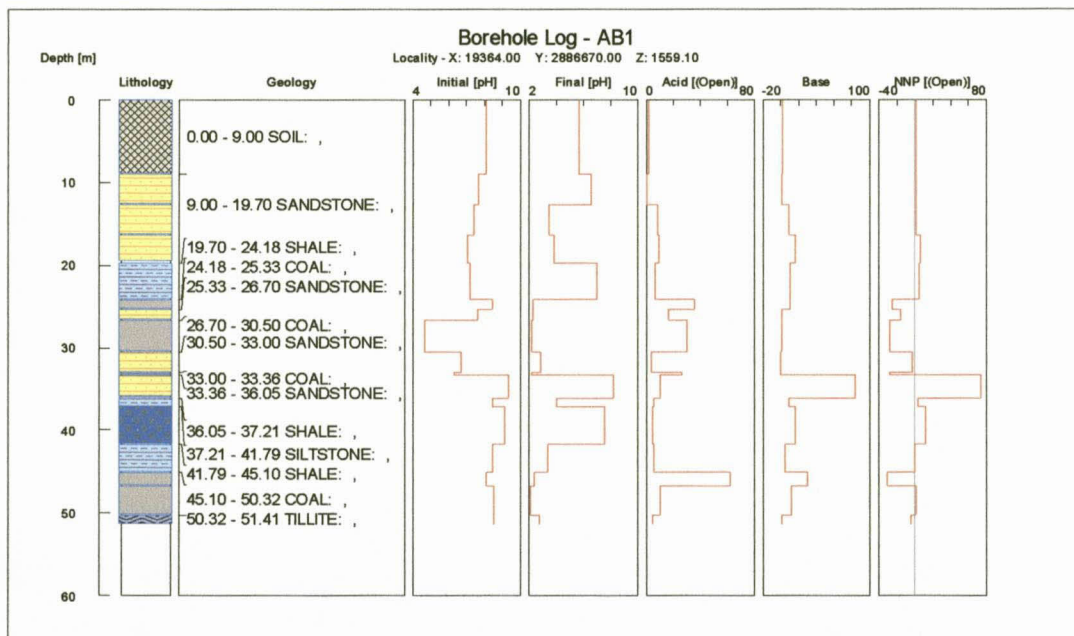


Figure 202: Acid-Base Accounting results with depth and compared to lithology for AB1.

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.

9.5.1 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 rehabilitated 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. These could 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 (Section 6.3), 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 consist 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 an average of 5.7 and ranging from 6.15 to 5.95 in Pit 2. Deionised water was used in all of the determinations, thus values 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, ranging from 4.5 to 3.5, were encountered in the lower portion, although this was very localised and varied considerably over distances of less than half a metre.

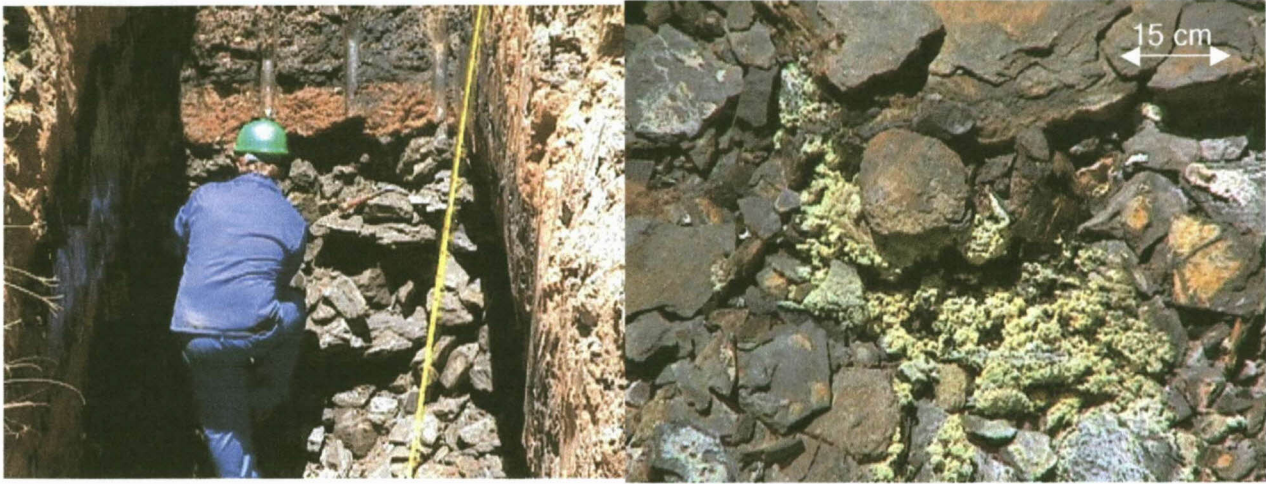


Figure 203: Sampling in spoils and secondary mineralisation observed in spoils.

9.5.2 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.

9.5.2.1 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 in Section 4.

9.5.2.2 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 Table 43 below.

Table 43. 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	SO ₄
	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	SO ₄
	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 CaCO ₃ 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 was successful and that secondary minerals such as jarosite 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 less than 0.2. This would imply that if this boulder were 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.

9.5.3 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 5.3, 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 5.3. Only one of the cells will therefore be used as an illustration here.

Figure 204 shows the pH-profile from this humidity cell over time.

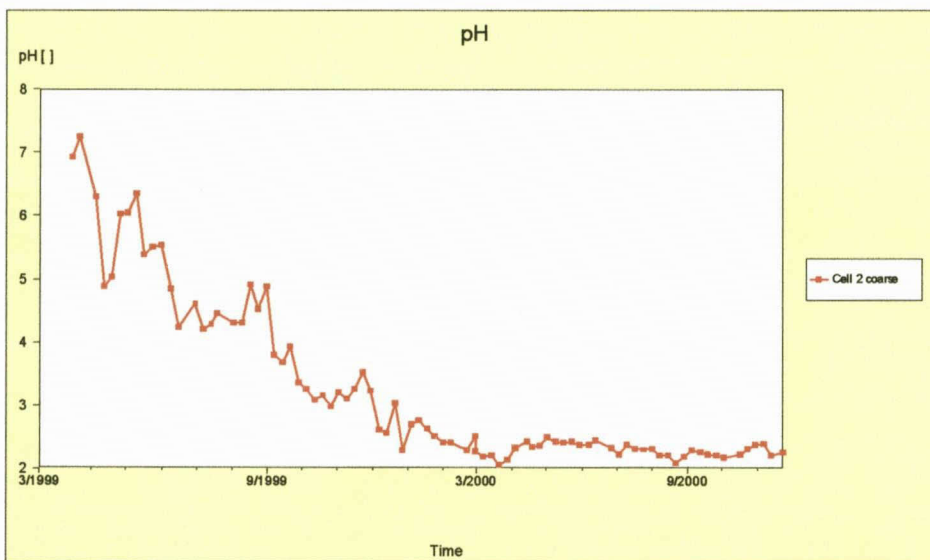


Figure 204: pH-profile from crushed spoil shale boulder in humidity cell test.

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 205) 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).

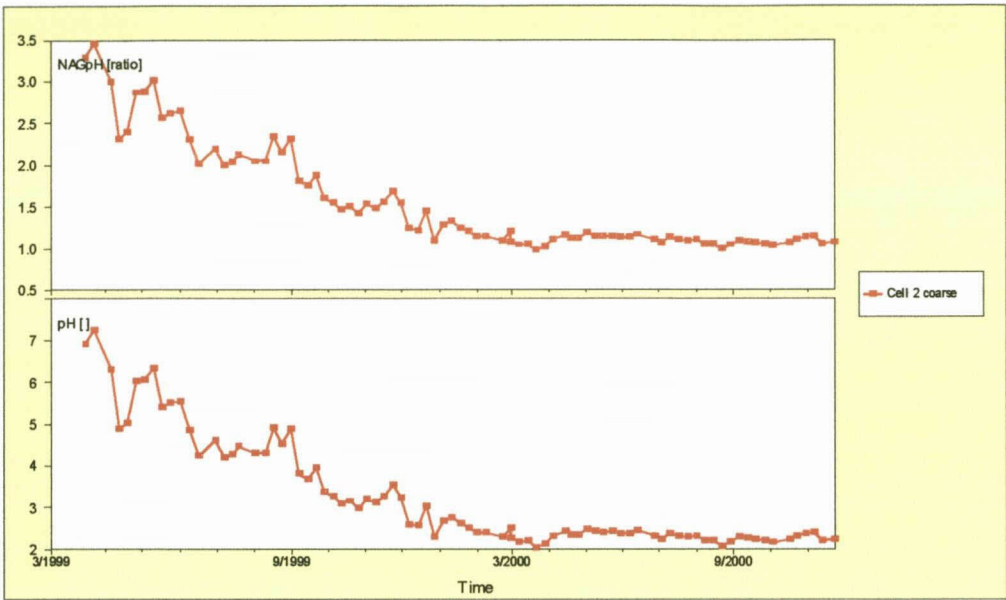


Figure 205: Comparison between the observed cell pH and the NAG pH from ABA.

Also of interest, is the correlation between the predicted neutralising potential and the pH-profile. Figure 206 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.

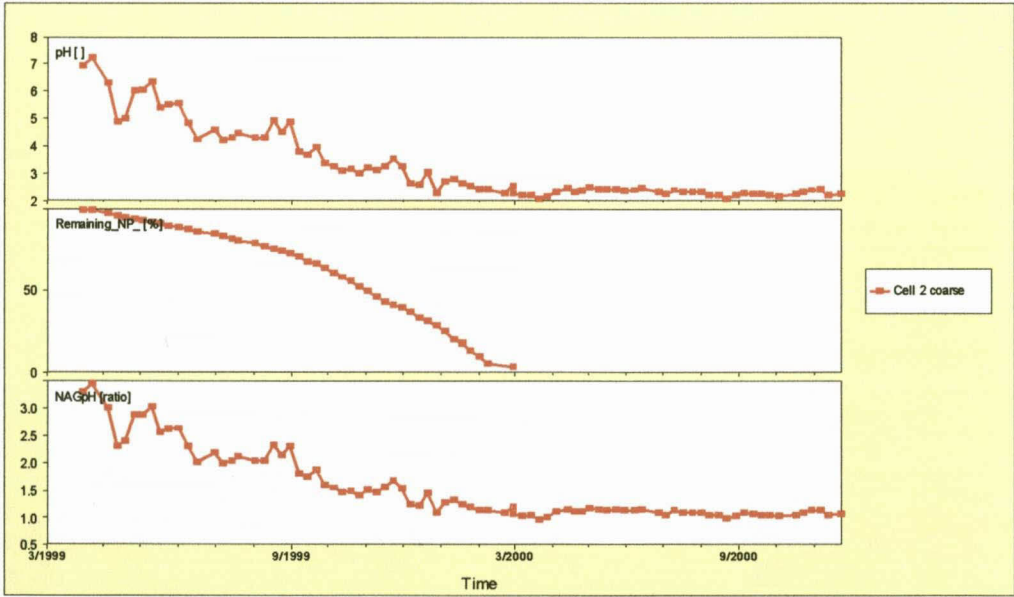


Figure 206: Comparison between theoretical remaining neutralising potential and observed pH.

The humidity cell results, ABA and field observations are therefore in excellent agreement as all point to the same conclusion for this case.

9.5.3.1 Observed water quality

The fact that most of the spoils will remain alkaline in the short term as indicated by the first two test pits, is also reflected in the current water quality of a monitoring borehole located in the spoils. Results from this borehole show that the water quality is thus far of a neutral to alkaline type with slightly elevated sulphate values. Long-term monitoring of this borehole will continue as an early warning of acidification.

9.5.3.2 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 (Figure 202). The testing conditions can best be described as pseudo-kinetic as it was a long-term modified NAG test performed on the boulder. The methodology was 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.

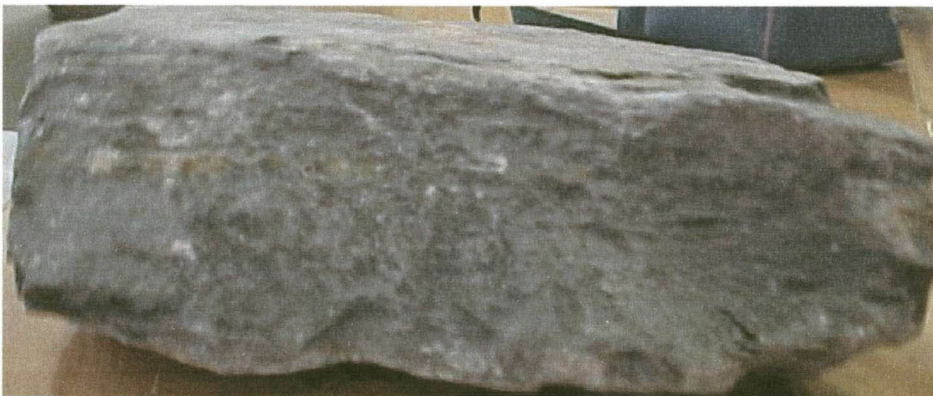


Figure 207: Side on view of boulder before test. (Vertical Extent approximately 10 cm)

In the figure (Figure 202) above some idea of the natural appearance of the boulder that was used can be obtained.

The pH-profile for this test is shown below (Figure 208). 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 it has begun.

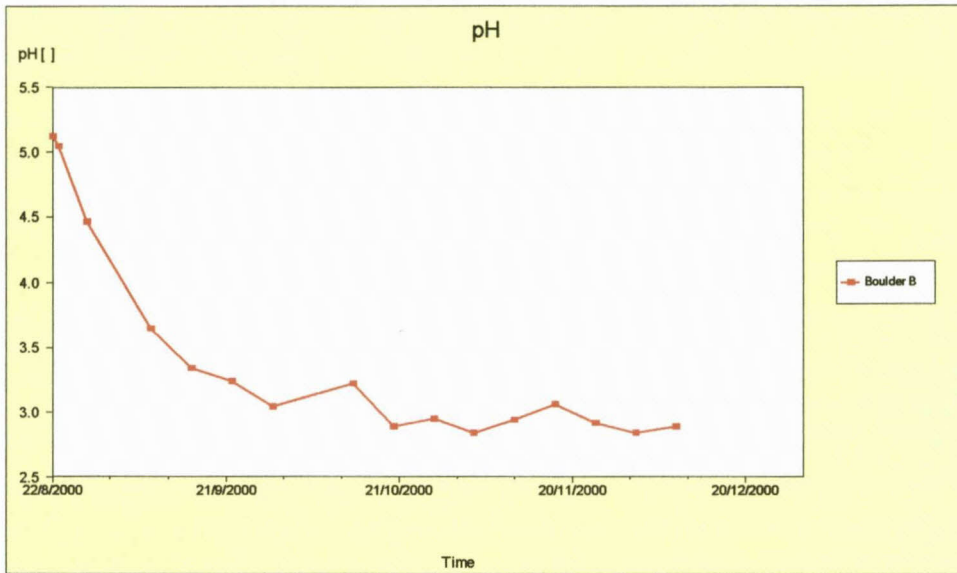


Figure 208: pH-profile of hydrogen peroxide test on shale boulder.

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, developed into major areas of weakness and over time the entire structure of the rock disintegrated

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 as reflected in the electrical conductivity (Figure 210).



Figure 209: Side view with a close-up showing development of cracks.

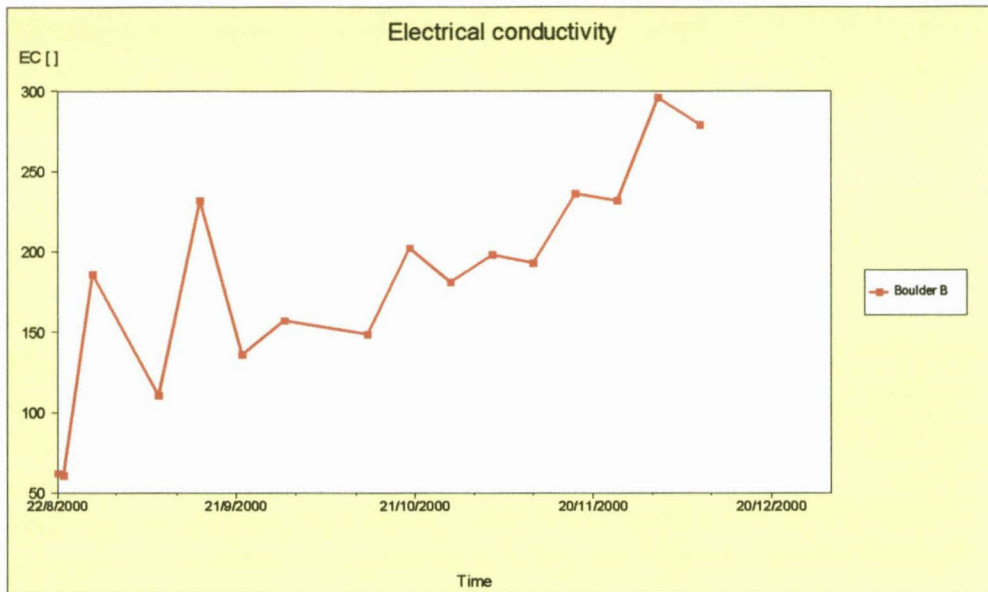


Figure 210: Increase in salinity over time due to increased surface area and acidification.

This evidence appears to support the notion of an 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.

9.6 ABA AND WATER QUALITY AT COMPARTMENT S7, BRANDSPRUIT COLLIERY

The Water Research Commission is sponsoring a project related to prediction at underground collieries. The IGS and Pulles, Howard and De Lange are undertaking the research.

The application of ABA interpretation at Brandspruit Colliery's S7 compartment illustrates how ABA can be used to determine which units are the most problematic as far as future acidification is concerned, the application of sample size estimates, the caveats behind such estimates, and the use of monitoring data, ABA and a proper conceptual model to determine expected hydrochemical evolution. Detail to this is provided in Appendix 4.

9.7 KRIEL

Kriel Colliery also deals with in situ spoil chemistry and illustrates the correlation between consistent net neutral predictions from ABA with on site conditions and water monitoring data.

Kriel Colliery has been investigated at various times to determine whether a potential for AMD exists (Hodgson and Krantz, 1998, Hodgson, 1998 and Hodgson, 2001). The findings of these investigations are that for the probability of acidification of the spoils is very low, based on the ABA results. The next step would thus be to find *in situ* values for the spoils.

9.7.1 Test Pits in the Spoils

Seven Test Pits were dug in the spoils in regions ranging from very recently deposited and rehabilitated spoils to older established rehabilitation areas.

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 (Figure 211). 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 9.2 and Section 6.

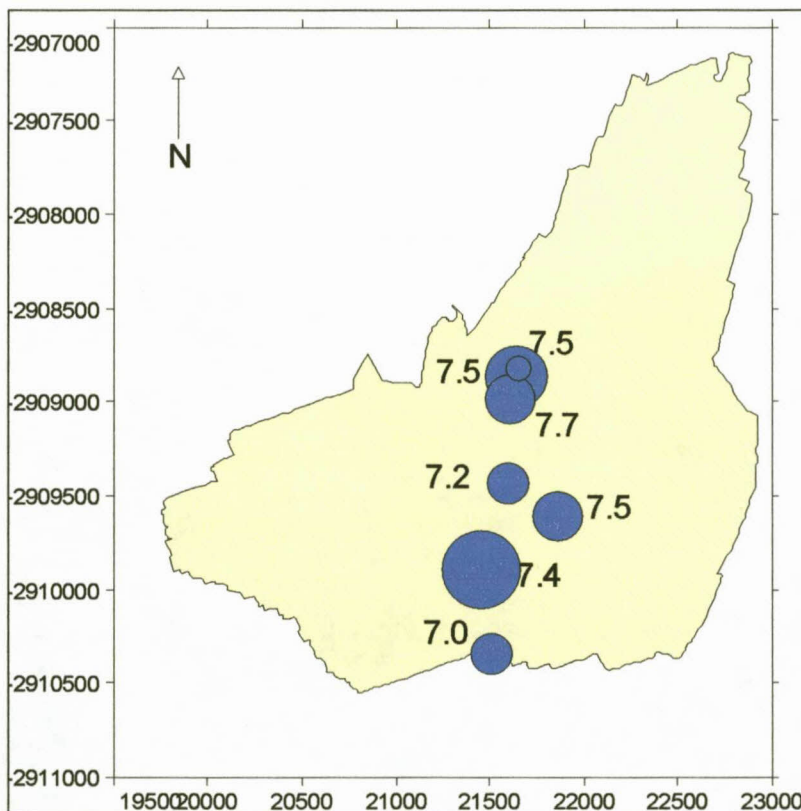


Figure 211: The measured paste pH-values.

The variation in the paste pH found, 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.

9.7.2 On-Site Water Quality Data

From the on-site water quality data, 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.

Figure 212 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.

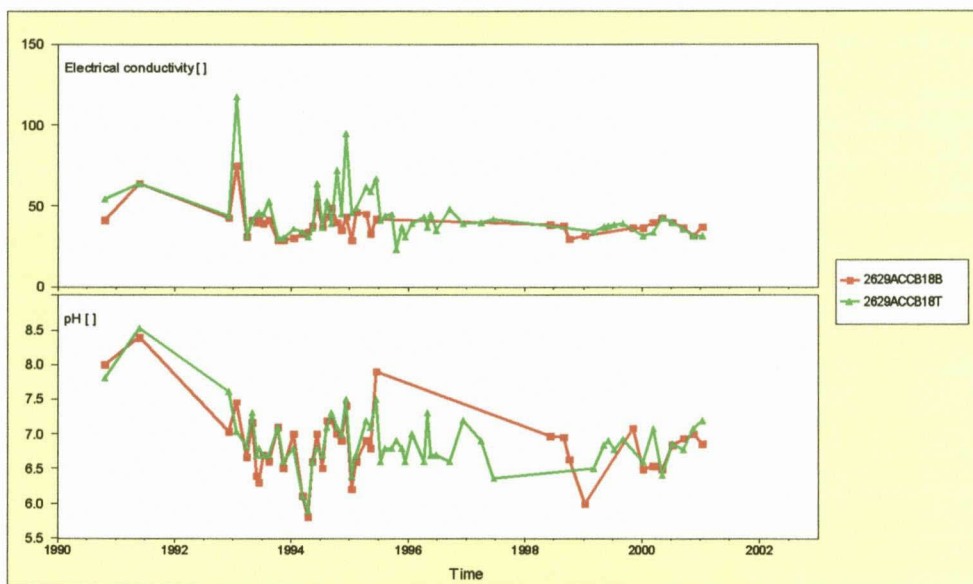


Figure 212: Variation in pH and EC over the last decade.

9.8 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 that can be used for publications. 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.

9.8.1 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 become acidic. The field values show the occurrence of this extreme acidity. The current field situation is thus an clear verification of the validity of ABA techniques in coal mining in South Africa.

9.8.2 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.

10 CONCLUSIONS

This thesis has investigated hydrogeochemical prediction techniques ranging from static methods to geochemical models, in the context of South African collieries. For each of the methods the advantages and drawbacks in different scenarios were highlighted, from theoretical considerations and in the practical implementation. Several case studies illustrated the conjunctive use of different methods, and the advantages these have in terms of the confidence of the answer.

Based on this the most important conclusion is that it is recommended that to predict the water quality evolution at South African collieries, all the components of the so-called prediction wheel be used.

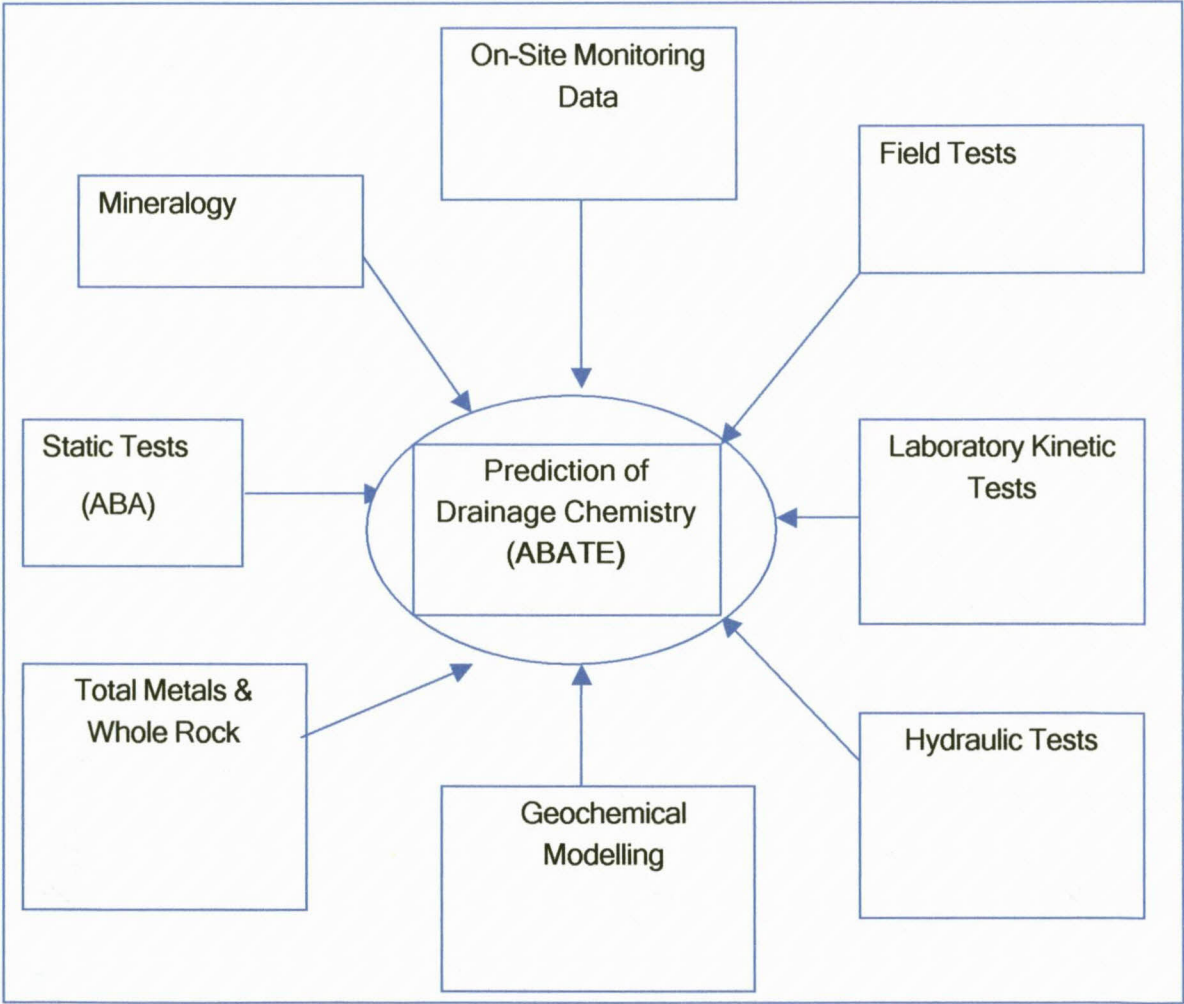


Figure 213: Review of ABATE Process.

It is also recommended that the methods be applied in an iterative and logical manner. A suggested flow path to follow would be as shown in Figure 209:

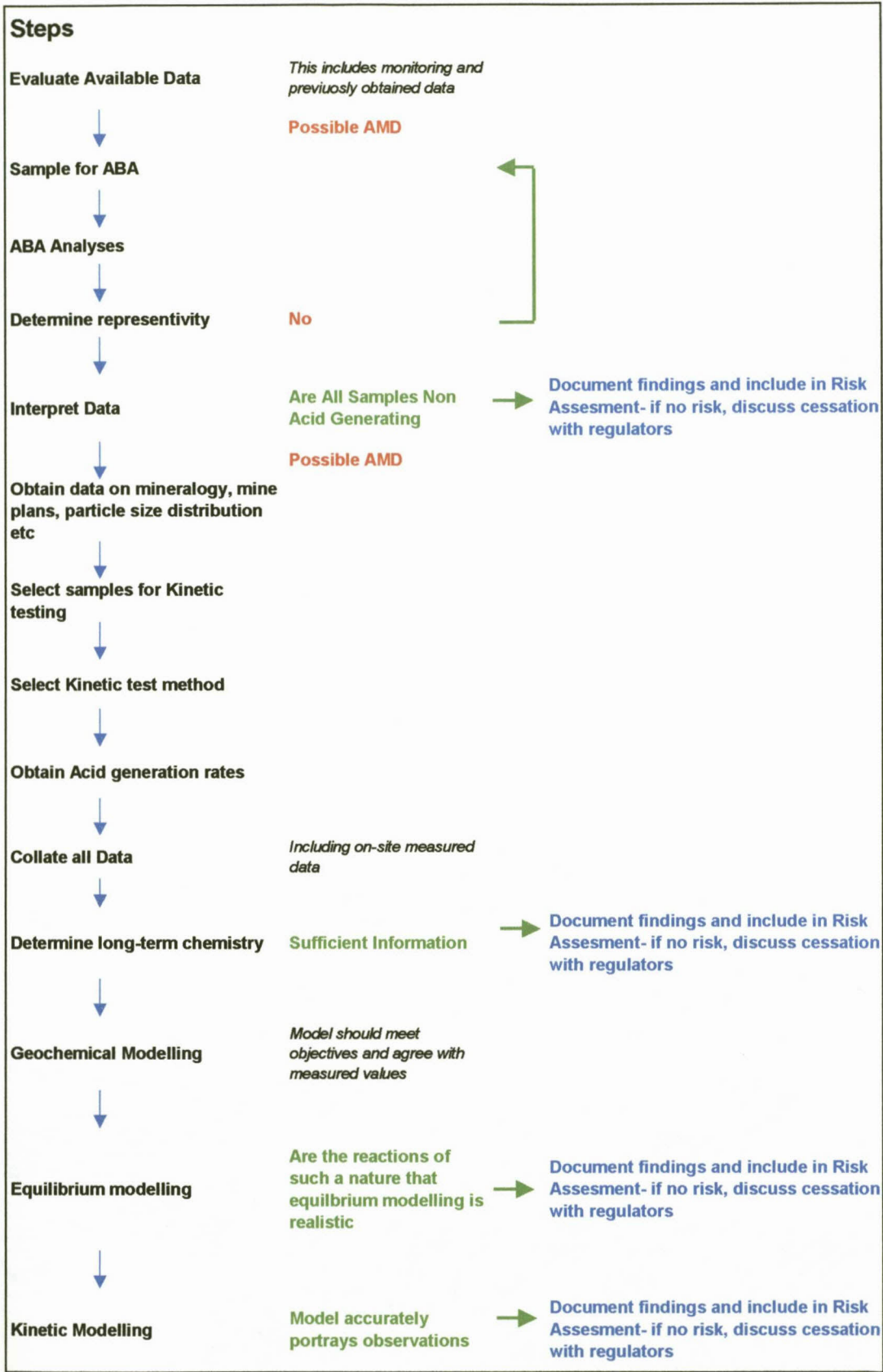


Figure 214: Suggested flow path for opencast spoil chemistry prediction.

The methods below are therefore selected for use in the ABATE strategy. A document of recommended methods from Usher *et al.* (2002) is included as Appendix 5, for the sake of completeness.

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.
 - For underground areas that core boreholes be used and channel sampling be done.
- Sampling of roof sediments is essential in areas where high extraction mining is done.
- *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, and 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.
- The modifications that have been made 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.
- Evaluation of over 500 lithologically sorted samples gives a clear indication of the relative contribution to the overall acid-base account on a coalfield scale.
- This indicates that generally the upper most sediments contribute very little due to active groundwater movement, that the coal seams usually have the greatest acid potentials and that the layers above the lower most coal seam can contribute most to neutral conditions due to the low pyrite content and unleached carbonates.

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/SO₄ 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 spoils and floor rubble, 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 have been provided in this document.

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.
- 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 enhancing the understanding of the manner in which a site is likely to react.
- Where ABA, mineralogy and detailed groundwater modelling are available, a well-constrained conceptual model can be developed, which allows the prediction of expected water quality evolution. In most cases, sufficient data on reactive surface areas and gas fluxes can not be obtained to accurately quantify temporal changes.
- Reactive transport modelling provides an additional tool, which can fruitfully be used in the overall quantification of a colliery's impact on the hydrogeological regime.

10.5 DEVELOPMENT OF INTERPRETATION TOOLS

Two unique tools were developed as part of this research, namely the ABACUS interpretation tool to provide an easy and standard method of interpreting static test data and the BUGLE empirical model to simulate water quality evolution in underground compartments.

- ABACUS provides a standardised tool for the interpretation of ABA data.
- Through the use of consistent units, criteria and interpretive diagrams, the confidence in the use of ABA should increase.
- Inclusion of volumetric assessments in ABACUS, will improve the interpretations and predictions based on ABA in South African Coalfields may over time approach the 96% success achieved in Pennsylvania. (Skousen *et al.*, 2002).
- The concept of a threshold value is included in ABACUS, and the identification of appropriate South African values will improve the assessments made.

The development of BUGLE has shown how understanding of observed water quality and static test interpretation can be fruitfully used to understand the way a compartment is likely to react over time.

- BUGLE includes empirical salt generation rates, allowances for different mining types, and fundamental thermodynamic principles to obtain realistic simulations of the situation.
- As the relevant data is gathered and processed, the level of accuracy in any mining area should improve and the predictions should improve as better understanding of the correlation between on-site ABA and observed concentrations is obtained.
- The inclusion of onsite controls such as observed supersaturation of carbonate minerals makes the prediction of water quality more realistic than can easily be obtained commonly used geochemical modelling codes.
- Incorporation of the relative level of flooding on the geochemical response of the system allows the observed inhibition of pyrite oxidation under submerged conditions to be taken into account.

10.6 CASE STUDIES

Six case studies showed the application of ABA to a field scale.

From the three collieries where test pits were dug in the spoils the following can be concluded:

- 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.

In terms of the case studies, integrating different components of the ABATE process, the following points are worth highlighting:

- 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 use of different volumetric methods, clearly illustrated the advantage of suing core bore holes to obtain samples, and provided a means to evaluate the mine as a whole to ascertain likely future acidification.
- At Colliery 2 the inclusion of mineralogical assessment and geochemical modelling based on all the other data collected, provided a better understanding of the expected water quality changes.
- The reactive transport modelling, done with a simplified conceptual model, used the numerical groundwater and mass transport modelling and results form ABA, mineralogy and geochemical models, to illustrate the attenuation of any generated acidity.
- The ATC comparisons illustrated an excellent correlation with ABA from core boreholes, *in situ* determinations, subsequent ABA and kinetic testing.
- The use of ABA and observed water qualities at an underground compartment in the Highveld Coalfield illustrated the use of ABA in identifying problematic lithological layers, and how this data can assist in understanding the expected chemistry in the compartment. It also illustrated the determination of appropriate sample numbers, the application of volumetric assessment on the overall ABA and the use of observed water quality data within a defined conceptual model to determine expected water quality changes.

- The Kriel Colliery case study is an example of a mine classified previously as an unlikely acid producer by ABA. *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.

10.7 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
5. Collection of detailed water level and quality data to improve salt generation rate estimates over the South African Coalfields.

10.8 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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