Utilization of South African Fly Ash to Treat Acid Coal Mine Drainage, and Production of High Quality Zeolites from the Residual Solids

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INTRODUCTION

A South African national perspective of mining related water research needs published by the Water Research Commission stated that the mining industry has a huge potential to impact negatively on the environment and that adequate measures to address this problem are not available.[1] Sources of water related pollution originate from underground and open cast mining, metallurgical plants, mining infrastructure and mine residue deposits and spoil heaps. For instance, upon infiltration by rainwater, spoil heaps leach highly acidic acid mine drainage to ground waters as a result of pyrite oxidation that forms sulphuric acid, which in turn mobilizes toxic metal species. South African (SA) coal mining creates huge volumes of sulphate-rich, pollutant-laden acid mine drainage (AMD). SA law requires costly treatment before AMD discharge. This source of AMD typically has a pH of about 2 and a TDS in the order of 4000-5000 mg/l. Coal mining in South Africa is estimated to produce 200 Ml of AMD per day in the Pretoria-Witwatersrand-Vereeniging (PWV) area alone. It is also estimated that 54% of the rainfall in the Witbank catchment area in SA is recirculated through mine residue deposits. This results in a highly polluted annual seepage flow of over 700 000 m^3 draining into the Loskop Reservoir. [2]

AMD results when under natural conditions certain coal seams are mined and the sulphide minerals are exposed to air and water. Pyrite (FeS_2), one of the sulphide minerals always found with coal, is oxidized to form sulphuric acid (H_2SO_4). The production of AMD depends on the rate of pyrite oxidation, the presence of acidophilic bacteria and the influence of carbonate minerals in the host rock. The H_2SO_4 in turn mobilizes toxic metal species by dissolution. AMD is characterized by: a pH as low as 2 (or even lower), Total Dissolved Solids (TDS) in the order of 4 000-5 000 mg/l (or considerably higher), high Fe content, high Al and Mn concentrations, and a high sulphate (SO_4) content. [3]

The treatment of AMD is currently done by natural means (i.e. AMD streams that pass through alkaline bedrock minerals which posses neutralization capacity), or by active treatment (whereby chemicals are added to the AMD) and passive treatment where AMD is passed through constructed wetlands.[4] The most commonly used chemicals for treating AMD are lime, limestone, CaO, $Ca(OH)_2$, $CaCO_3$, $NaOH$, NH_3 and Na_2CO_3.[5] These systems require the installation of a plant with agitated reactors, precipitators, clarifiers and thickeners. The costs also involve reagents, operation, maintenance and disposal of the resulting metal laden sludge.[6]

South Africa is largely dependent on the combustion of coal for power generation. This produces a number of by-products the major one being fly ash (FA). When low grade brown coal of the kind South Africa exploits is burned by coal powered utilities such as Eskom, the approximately 25% inorganic residue (FA) remains as waste. The FA is normally collected by air controlling devices (bag filters, electrostatic precipitators, etc.) and is dumped as a waste material. Electricity generation in South Africa produces >20Mt/annum of fly ash (FA) for which there is little large-scale application within SA (typically 5% is utilized), the remainder being disposed in FA dams or heaps.[7] This presents a huge disposal problem. For logistical reasons, coal-fired power stations are sited near to the coalmines that supply them.

Chemical compositions reveal that all natural elements can be found in fly ash (FA). The major elements in fly ash are Fe, Al and Si together with significant amounts of Ca, K, Na and Ti. The most common minerals that constitute fly ash include quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), hematite (Fe_2O_3), magnetite (Fe_3O_4) and a small portion of unburned carbon. In addition to these minerals anhydrite ($CaSO_4$), lime (CaO) and periclase (MgO) are also included. The free alkalinity imparted by CaO (approx. 7 wt%) and the fact that FA has a very high surface area and small particle size makes South Africa FA a good neutralization agent. [8] An analysis of fly ash material has shown that many toxic elements are present.[9, 10] Minerals such as sulphides, sulphates, carbonates, phosphates, silicates and clay minerals enrich the inorganic component of coal with elements such as Si, Fe, S, P. The balance is O, N, Cl, S, P, and elements such as Al, Zn, Pb, Cu, Cd, Sb, Hg Ni, Y, V, Th, Ge, Ce and U.

These toxic elements remaining in fly ash arise from rock weathering into coal basins or from trace element enrichment of humus formed from the original vegetable matter. Fly ash is pumped in slurry-form to ash heaps after carbon extraction and hardens to a rock like consistency over time. This makes surface ash heaps a poor option and there is no secondary use large enough to reduce the quantity of ash effectively. The slurry make-up water as well as rainfall, leaches out toxic metals, anions and cations from the ash heap. This caustic (pH>12) leachate contains high concentrations of hydroxides, carbonates and sulphates and precipitates minerals such as iron oxides and sulphates.[8-10] Groundwater and soils are contaminated and large areas of precipitates mar the environment around ash heaps, which are also the source of corrosive airborne particles.

Chemical, physical and mineralogical properties associated with SA fly ashes have been extensively studied. [8, 9, 11-13] Pilot studies indicated that co-disposal of AMD with aqueous extracts of Eskom fly ash simultaneously neutralizes these two highly corrosive waste streams.[14] Precipitation of alumino-silicates and iron compounds occurred at a pH of 10. Direct mixing of various ratios of simulated AMD and Eskom fly ash to a predetermined pH in the co-disposal process enhanced the formation of gypsum and soil components. These secondary aluminosilicate and/or aluminocalcium sulphate (ettringitic) or ferrihydrite precipitates have the capacity for mutual beneficiation of water quality in co-disposed AMD and fly ash.[15] Such materials when precipitated may also be of value in low-cost attenuation of toxic metallic waste streams. The neutralized process water contains only residual sulphate and low concentrations of ionic species [16,17] that may be recovered by zeolitic adsorbents or electrodialysis reversal (EDR) systems using a variety of high capacity ion exchange materials. [18-21]

Benefits of the co-disposal process may thus include pollution abatement, neutralization of hazardous waste streams and recovery of water, as well as preparation of high capacity adsorbents. This paper will focus briefly on some of the results obtained from laboratory experiments that have investigated the following variables (including chemical analyses): Different types and ratios of FA:AMD; Reaction time; Degree of release of soluble species from fly ash; Comparison of FA with different 'liming agents' (i.e. ash, limestone, lime); Synthetic AMD solutions (SAMD) and solutions with different Fe^{2+}/Fe^{3+} ratios; AMD neutralisation reactions using standard reagents (e.g. $Ca(OH)_2$ solution and SAMD constituents; Co-disposal of circumneutral AMD vs. low pH AMD with ash or leachate; Preparation of zeolites from co-disposal residues.

The Witbank Highveld coal-mining region in South Africa has been chosen as the study area for this project. This is a suitable area as numerous AMD discharges and large coal-fired power stations are present. The study considered four actual sources of AMD as well as simulated AMD, and three sources of FA. FA from Duvha, Matla and Arnot power stations and AMD from the acidic sources at Brugspruit, Navigation, Bank and Arnot collieries and the circumneutral drainage also found at Arnot opencast colliery are being used as source materials in the project.

EXPERIMENTAL

The different sources of fly ash (FA) or fly ash leachate (FAL) were reacted together in different ratios and for different times with the various acid mine drainage (AMD) samples drawn from the contaminated sites. These experiments investigated which FA:AMD ratios would result in the neutralisation of AMD by the FA, and at which ratio the optimum removal of sulphates and toxic elements would be achieved, and also produce the post co-disposal process water with the lowest electrical conductivity (EC). Initial bench scale experiments were followed by pilot scale experiments where a set volume of AMD was stirred continuously and a known mass of FA was added. For instance, in the 5:1 ratio of AMD to FA, 2800g of FA was added to 14 000 ml of AMD.

A number of experiments were conducted to investigate the differences between treating Navigation AMD with lime, limestone and FA. These were done to investigate the relative effectiveness of ash as a liming agent (i.e. mass required to neutralise a volume of AMD) and to monitor the EC change. In each experiment a set volume of AMD (e.g. 100 ml) was stirred continuously with an overhead stirrer and a known mass of solid reagent was added.

In addition, synthetic mine waters (SAMD) and leachates were used to investigate specific variables. The type and concentration of the extractant, the solid-to-solution ratio, the duration and temperature, and the intensity of agitation all influence the constituents that are extracted from FA. The degree of of soluble species release from fly ash was determined by preparation of FA leachate (FAL) by stirring equal masses of either Arnot or Matla FA and deionised water in an open beaker for 24 hours. FAL was also prepared by enclosing the slurry in 300 ml plastic containers, filled to approximately 90 percent capacity in order to minimise contact with air but still allow for sufficient agitation. These containers were mounted on a reciprocating shaker for 24 hours and the filtrate was vacuum-filtered through a Büchner funnel and stored in a 1L volumetric flask. Samples of FAL were also drawn in the field from dams on ash dumps and analysed for their elemental composition.

A number of co-disposal experiments using FAL and different SAMD waters were undertaken, and analysis and characterization of the synthetic precipitates formed was undertaken. This was done in order to identify the various precipitates probable (that may be forming upon the ash particles) during co-disposal. When using FA instead of FAL as ameliorant, the characteristic, highly crystalline signals of the major components in ash (mullite and quartz) make XRD identification of the minor, quasi-amorphous co-precipitated mineral phases difficult, whereas when using FAL as ameliorant, only the soluble species leached from the ash are present. In general soluble Ca species were the major alkaline constituent of FAL.

In addition, experiments investigating neutralisation reactions using standard reagents (e.g. $Ca(OH)_2$ solution and SAMD constituents (e.g. ferric chloride, etc.) have been done. The amounts used corresponded to the concentration of the major ions (iron and aluminium) present in AMD in the Blesbokspruit catchment according to a study of the biogeochemistry of acid mine drainage from a disused mine colliery near Witbank.[13] The composition of the SAMD prepared for the titration experiments was Al^{3+} = 12.7 mmol/l, Fe^{3+} = 7.3 mmol/l, Fe^{2+} =3.6 mmol/l, Ca^{2+} = 5.2 mmol/l and SO_4^{2-} = 40.8 mmol/l. The SAMD was prepared with freshly distilled water flushed with nitrogen gas. The reagents, $Al_2(SO_4)_3$, $CaSO_4$ and $FeSO_4$ were dissolved in approximately 750 ml of distilled water in a 1l volumetric flask. Prior to the addition of ferric sulphate, 2 ml/l of 1M H_2SO_4 was added to ensure a pH of less than 3, in order to prevent the immediate precipitation of ferric hydroxide. The solution was then made up to a volume of 1l. The precipitate products were prepared using different Fe:Al molar ratios of 2.5, 0.8 and 7.3 where the Al concentration was 4.4, 13.3 and 1.5 mmol/l, respectively and the Fe concentrations remained the same as stated above.

The various titrations were carried out using a PHM 290 pH-Stat controller and an ABU 901 Autoburette (Radiometer). The pH stat controller delivered titrant at a rate of 3ml/min and the pH and EC were logged at 15-second intervals throughout the reaction. The alkalinity measurements were performed using a 702 SM Titrino Metrohm titrator.

By controlling the pH endpoint of the co-disposal reactions, circum-neutral co-disposal solid residues could be obtained and used for the preparation of high capacity ion exchange adsorbents such as zeolites. In addition to neutralisation experiments and analysis of the resultant waters, analysis of residual ashes and precipitates (mostly sludges of insoluble metal hydroxides formed by oxidation, pH adjustment and flocculation/coagulation) was undertaken.

Moreover, preparation of high capacity adsorbents was attempted using the fly ash sampled as feedstock for Si and Al, or leached ash or residual solids after the co-disposal reaction. The zeolite synthesis outlined by Rayalu *et al* [22] favours the formation of faujasite if the $[SiO_2]/[Al_2O_3]$ ratio is higher than 1.5 in FA and FA-related precipitates and the procedure outlined in their work was used to transform the solids to zeolite materials.

Characterization
Analysis of waters, leachate and precipitates was initially performed using pH, alkalinity studies, and electrical conductivity (EC). The major anions Cl^-, F^-, Br^-, NO_3^{2-} and SO_4^{2-} were analysed by ion chromatography using a Dionex DX-120 ion chromatograph with an Ion Pac® AS14A column and AG14-4 mm guard column. The eluent was Na_2CO_3 and $NaHCO_3$. Samples for ion chromatography (IC) were diluted to less than 100uS/cm using milli-Q water depending on the EC of each sample. The samples were filtered through 0.45um Millipore filter membrane before dilution. The samples were stored in a refrigerator before the analyses were carried out.

The filtered supernatants were analysed for the major cations Na^+, K^+, Ca^{2+}, Mg^{2+} and total Fe by atomic absorption spectrometry using a Varian Spectra AA-250 plus. The supernatant samples were also analysed for Al^{3+} and Si^{4+} by inductively coupled plasma-atomic emission spectroscopy using a Varian Liberty Series 2 sequential ICP spectrometer. The calibration standards were prepared in a concentrated gypsum solution to minimise salt concentration effects. Dilutions were made to less than 100us/cm depending on the original EC of each sample. The dilutions were made using milli-Q water.

Structure was characterized by use of X-Ray Diffraction performed using Cu kµ radiation (I=1.542Å) in a Phillips P W1050/37 goniometer controlled by PW 3710 electronics. The samples were scanned over a range of 3-50 in steps of 1 °2θ per second. The precipitates were carefully washed with distilled water to prevent the crystallization of some soluble salts on the surface as the presence of salt crystals could interfere with the x-ray diffraction pattern.

The surface area of the precipitates was determined through the Brunauer-Emmett-Teller method (Brunauer, 1943) of analysis using a Micromeritics Accelerated Surface Area and Porosimetry (ASAP) 2010 system.

The surface charge of the products was determined using a similar approach to that described by Hunter. [23] The ion association model PHREEQC [24] was used to calculate ion activities and saturation indices of mineral solids based on the pH and solution concentrations of major ions in supernatants that were analysed after titration completion.

Cation Exchange Capacity (CEC) was determined as follows. Approximately 5.0 g of the zeolite sample was weighed out and placed in a 100 ml polyethylene bottle. A 25 ml ammonium acetate solution was added and the mixture shaken for 1 hour. The supernatant was filtered directly into a 100 ml volumetric flask through filter paper, and care was taken not to pour any sample into the filter funnel. The extract was then made up to 100 ml with deionised water and the concentration of exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) determined by ICP-MS analysis

RESULTS

Elemental composition of the FA leachate (FAL)
Elemental composition was determined of the FAL formed by stirring equal masses of either Arnot or Matla FA and deionised water in an open beaker for 24 hours. The results of the analyses show that some species in the FAL are highly mobilized under these conditions. These include the concentrations of Ca, Na, K, Fe, Cr, Sr and Ba. The high alkalinity of the leachate could thus be attributed to the high concentrations of Ca, Na and K present in the respective leachates. Furthermore, the Ca, Fe, Se and Hg concentrations of the two leachates were fairly similar. The concentrations of B, Mo and Zn are higher in the Arnot FAL, compared to that of the Matla FAL. Other trace and major metal species, such as Cu, Ni. Mn, Sb, Cs, Hg, Pb, U and Cd, exhibit less mobility.

Investigation into use of different liming agents (lime, limestone, Arnot FA) with Navigation AMD
A number of experiments were conducted to investigate the differences between treating Navigation AMD with lime, limestone and fly ash. These were done to investigate the relative effectiveness of ash as a liming agent (i.e. mass required to neutralise a volume of AMD) and to monitor the EC change. In each experiment a set volume of AMD (e.g. 100 ml) was stirred continuously with an overhead stirrer and a known mass of solid reagent was added. Figure 1 shows data for a series of experiments where different AMD:limestone ratios were used. The limestone was that currently being used in the CSIR pilot liming plant at Navigation. In general an increase in the dose of limestone (i.e. a decrease in the AMD:limestone ratio) leads to an increase in both pH and EC. The pH maximum seen in any of these experiments was just over 7, consistent with the literature on limestone AMD treatment. The pH in most

cases was at a maximum at around the 3 hour stage, but the majority of the pH change had occurred in the first 20 minutes.
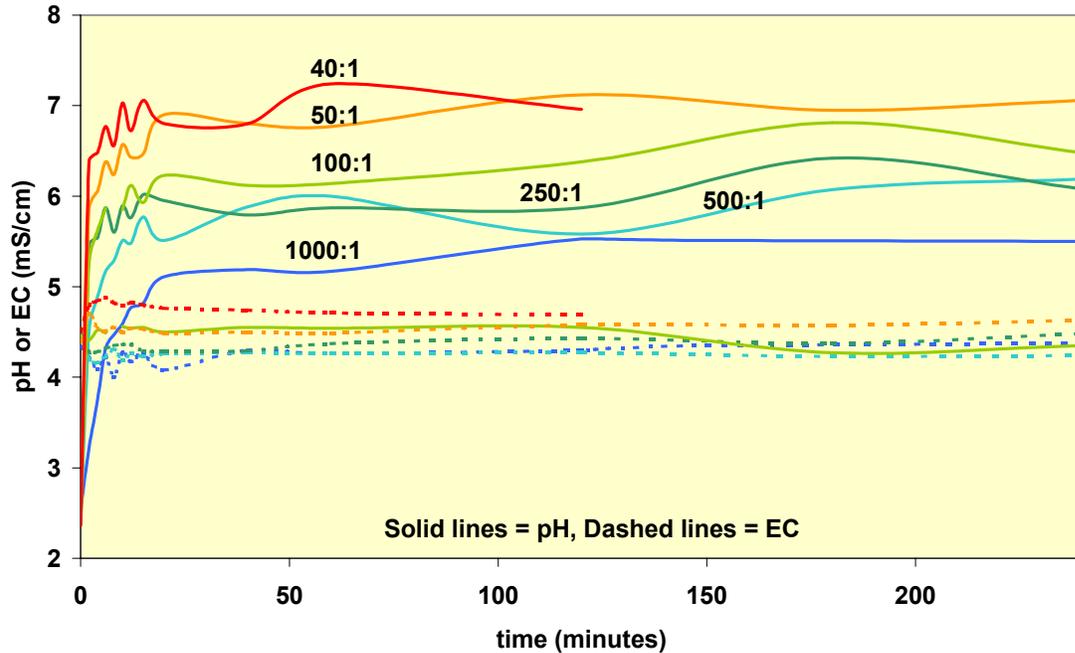

Figure 1. EC and pH curves for experiments in which different Navigation AMD:limestone ratios were used (ratios given on chart) in co-disposal reactions.
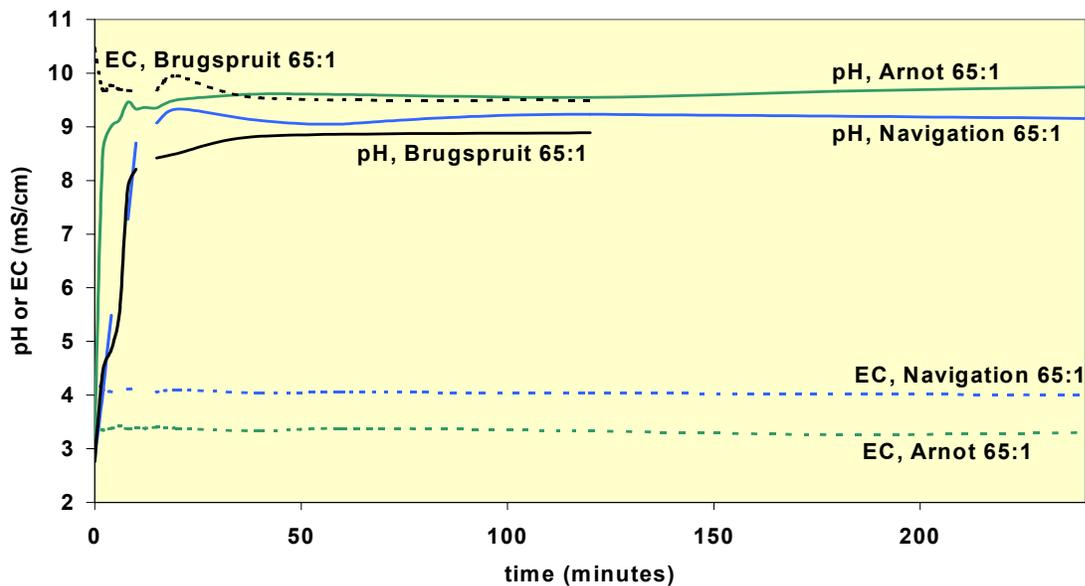

Figure 2. EC and pH curves for experiments in which different AMD sources (set volume) were co-disposed with Arnot fly ash.

Figure 2 shows data from a number of experiments in which different AMDs (set volume) were co-disposed with Arnot fly ash. Again the ratios given in the figure refer to

the AMD:solid ratios. The striking difference in the resulting EC of each solution is attributable to the different start AMDs. In all cases the EC remains fairly constant throughout the experiment, with a slight decrease with time. The pH of each solution was observed to increase with time, with the majority of the change occurring in the first 20 minutes as was seen for limestone (Figure 1).

Figure 3 shows data for Navigation AMD neutralisation experiments using Arnot ash, lime or limestone (the last two being obtained from the Navigation liming plant). The EC and pH curves are very similar in form for each solid reagent used. In each case the major pH change occurs within the first 20 minutes of the experiment and then there are some minor changes during the remainder of the experiments. The EC curves are also very similar, with the lowest EC recorded for the experiment using Arnot ash and highest for limestone.
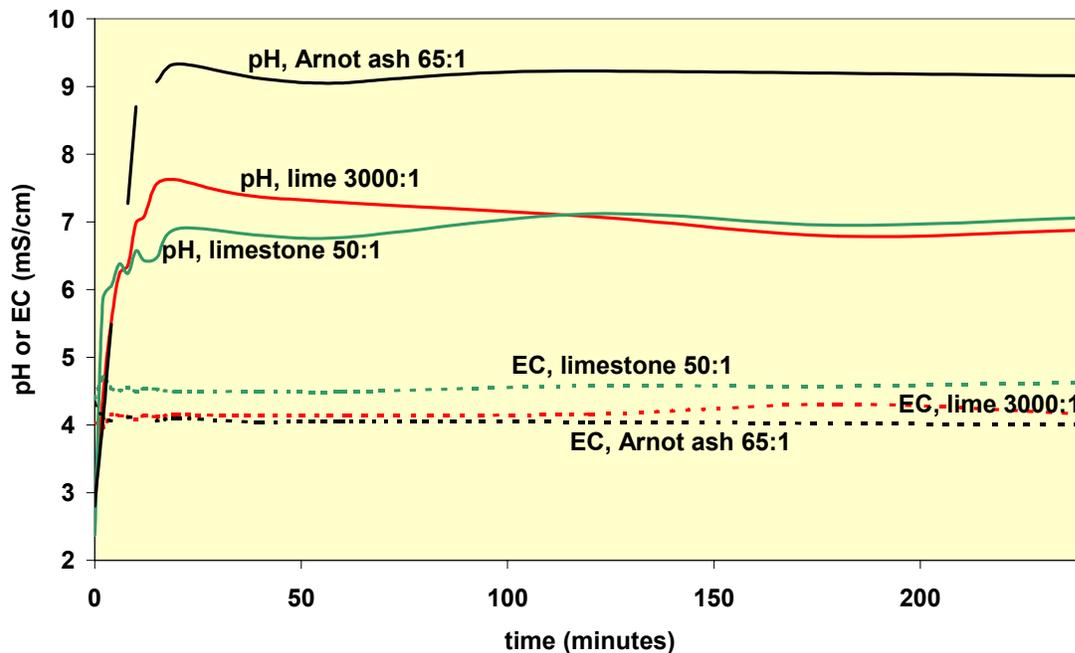

Figure 3. EC and pH curves comparing the liming capability of Arnot ash with lime and limestone from Navigation liming plant on Navigation AMD.

These experiments provide good evidence that fly ash is a suitable liming agent in the treatment of AMD. They indicate in some cases that fly ash will produce a liquid with a lower EC than that found for neutralisation with lime or limestone. All solid reagents used resulted in a slight decrease in EC with time. Rapid pH adjustment occurs in all experiments, the first 15-20 minutes of each experiment seeing the most striking pH change. The mass of Arnot fly ash required to cause neutralisation is greater than that required of lime. However, less ash was required than limestone, which is currently becoming the favoured industrial liming agent in preference to lime. Most significantly,

the pH could be controlled to any level, dependent upon the ratio of ash used, and was not limited to a maximum of about pH 7 as in the case of limestone.

Co-disposal of circumneutral Arnot AMD with Arnot leachate or ash
Co-disposal experiments were undertaken using circumneutral AMD from Arnot and either Arnot FA or Arnot FAL. These were done to compare the pH and EC trends during the reactions between the ash and leachate and with those seen for acidic AMD samples neutralised with leachate. These reactions are important because a significant number of coal mine waters are circumneutral and if co-disposal is successful for these waters as well as highly acidic ones it will have much wider application.

Figure 4 shows data for the two experiments described above. In each case a fixed volume of Arnot circumneutral pH AMD (200 ml for leachate experiment, 250 ml for ash) were agitated with an overhead stirrer and small masses or volumes of reagent added and the reaction allowed to stabilise for 5 minutes before pH and EC readings were taken. Considerable difference is seen in both pH and EC measurements for the two experiments. The leachate EC readings are consistently lower at comparative pH values. Evident in both cases is that EC decreases throughout the reaction.
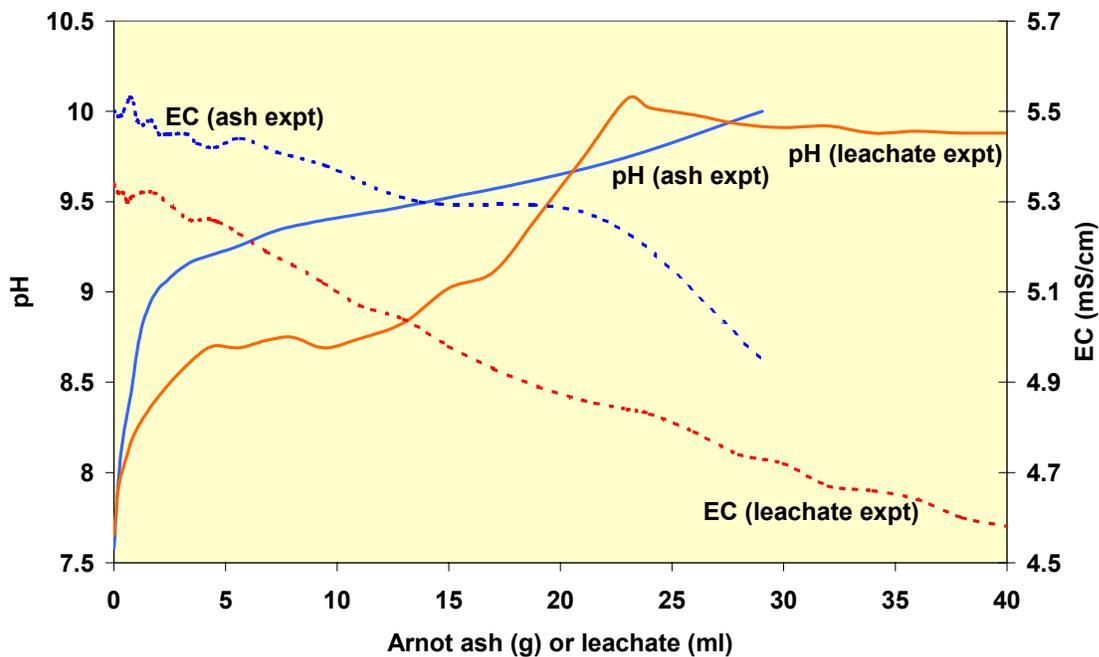

Figure 4. EC and pH curves for Arnot circumneutral pH AMD co-disposed with Arnot ash or Arnot ash leachate.

The pH curves are strikingly different, with a maximum reached at about pH 10 for the leachate experiment and then a decrease in pH with additional leachate. It is probably the reaction of CO_2 from the atmosphere forming calcite with the $Ca(OH)_2$ in the leachate that is affecting the pH. In the case of the ash experiment, readings ceased before this pH was reached but it seems unlikely that CO_2 would have had such a profound effect on pH in this situation as leachates made in open vessels from ash and

water have pHs in excess of 12. The precipitate formed from the reaction of AMD and leachate was creamy white, and was small in mass.

It is encouraging that considerable residual acidity is present in these circumneutral waters. The continued reduction in EC values also indicates that the co-disposal of these high sulphate waters with either FA or FAL is a viable proposition to reduce contaminant levels.

Synthetic AMD or H₂SO₄ and Ca(OH)₂ or Arnot leachate

Figure 5 shows the results of a number of experiments in which SAMD or sulphuric acid was reacted with a near saturated Ca(OH)₂ solution or Arnot ash leachate. The pH curve for the sulphuric acid reaction is that of a simple neutralisation reaction. The SAMD pH curves are broadly similar to natural AMD samples, with plateaux seen where a particular metal is precipitated as the hydroxide or oxyhydroxide. Comparison of the volumes of base required for neutralisation indicates that the ash leachate is a more concentrated base than the Ca(OH)₂ solution, implying that ash leachate may be a more potent treatment for AMD than lime. The EC curves shown in Figure 5 indicate that the dissolved load of the product water decreases throughout the experiments.
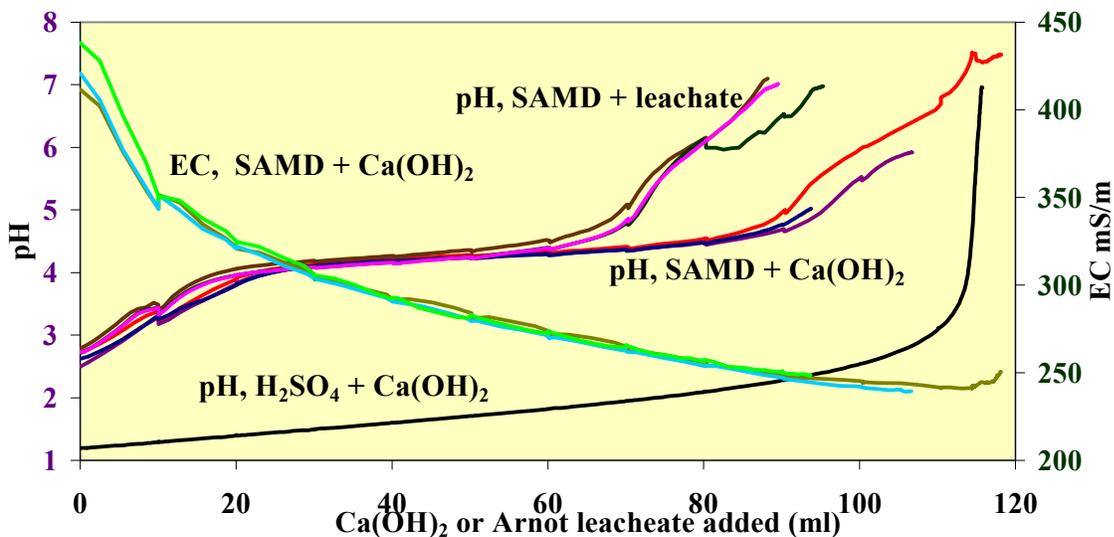

Figure 5. EC and pH curves for reactions carried out with pH stat equipment. Reagents used indicated on the chart.

Synthetic AMD components and Ca(OH)₂ in air

Figure 6 shows data for a number of reactions involving both SAMD and its components reacted with the Ca(OH)₂ solution used above. Each component (i.e. $FeCl_3$, $FeSO_4$, $Al_2(SO_4)_3$) shows considerably different behaviour in terms of both EC and pH when titrated with Ca(OH)₂. An important observation is the buffering zone at pH 4-4.5 for the SAMD. This plateau is mirrored in the pH curve for the $Al_2(SO_4)_3$, strongly supporting the proposition that Al compounds precipitate at this stage of the reaction in the SAMD.
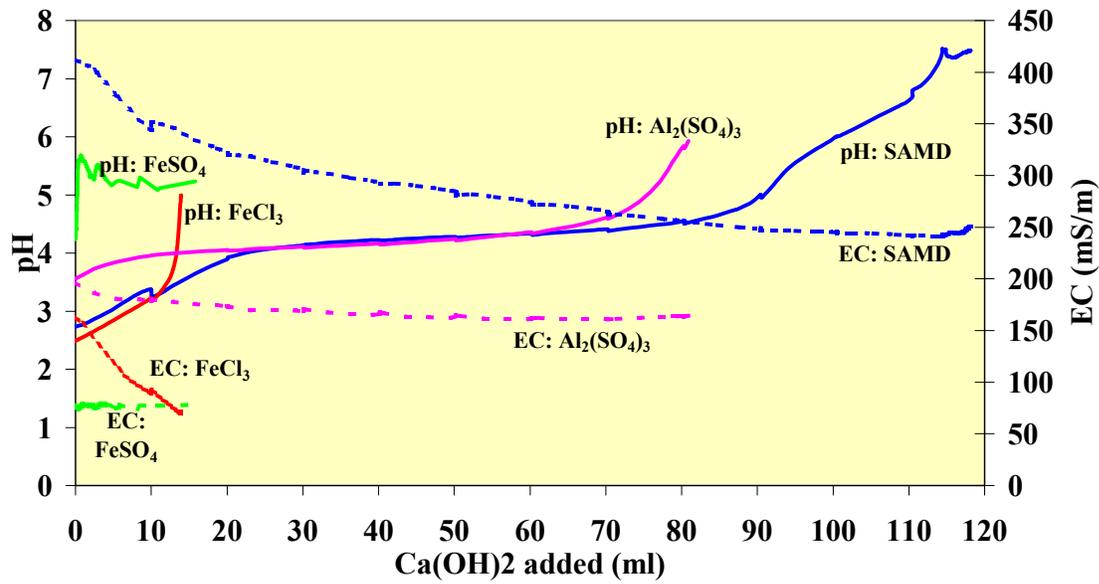
Figure 6. EC and pH curves for experiments undertaken using pH stat equipment.

Solutions used are as indicated on chart, neutralised with a near saturated $Ca(OH)_2$ solution. Experiments were undertaken in a compressed air environment (provided by pump). The results of these experiments indicate that reactions with SAMD and its components in a controlled environment provide valuable data to help in the interpretation of experiments involving real AMD. These experiments also allowed the reaction kinetics to be explored.

Synthetic AMD and different bases, CO_2 present
Figure 7 shows data for a number of experiments in which SAMD was reacted with different bases in the presence of CO_2. Again, the characteristic pH curves observed for natural AMD with different bases are seen. However, what is noticed is that the highest pH seen in these reactions is less than 6.5. This is attributable to the slow reaction rates in these experiments allowing the CO_2 present to react with the bases and buffer the solutions. The SAMD pH reaction curve seen in Figure 6 reaches a much higher value (> 7.5) than its counterpart shown in Figure 7. The EC curves for these reactions look relatively unaffected by the presence of CO_2.

Co-disposal of ferrous, ferric and ferrous/ferric mixed solution with Arnot leachate
Experiments were carried out in open beakers to assess the role of the oxidation state of iron on co-disposal reactions. Investigation of this parameter is important as mine waters show considerable variation in ferrous:ferric ratios, and pre-treatment (e.g. oxygenation) may be an important consideration for optimising co-disposal reactions. Figure 8 shows EC and pH curves for three experiments using 50 mg/l ferrous or ferric iron (as sulphates) and 25 mg/l of both ferrous and ferric iron (again added as sulphates). The start pH of each solution was normalised using dilute sulphuric acid. Each reaction was undertaken in an open beaker with continuous agitation with an
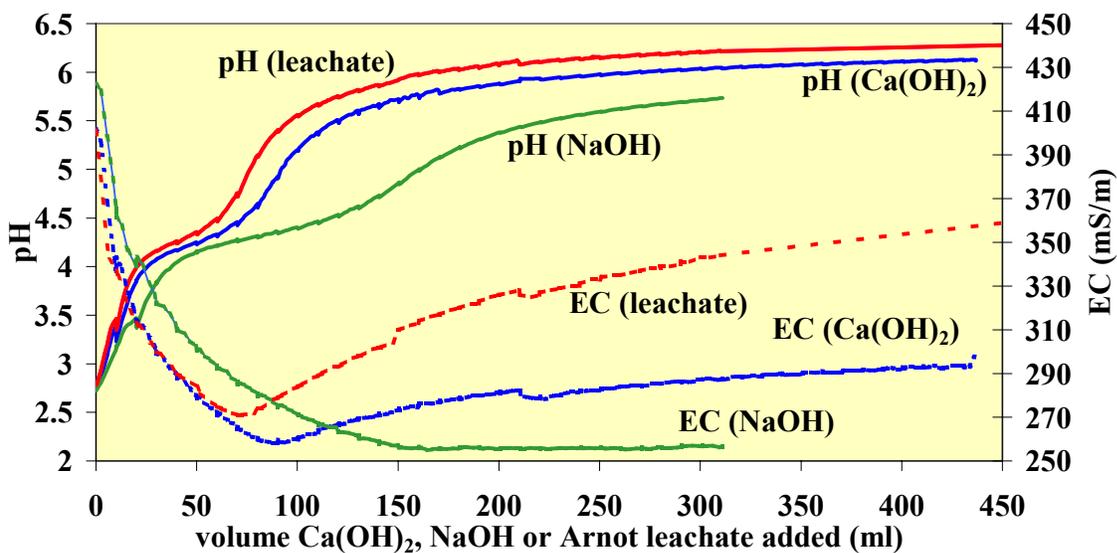
Figure 7. EC and pH curves for reactions undertaken using pH stat equipment. Reactions were done with SAMD and either Arnot ash leacheate, NaOH or Ca(OH)$_2$ (indicated on chart).
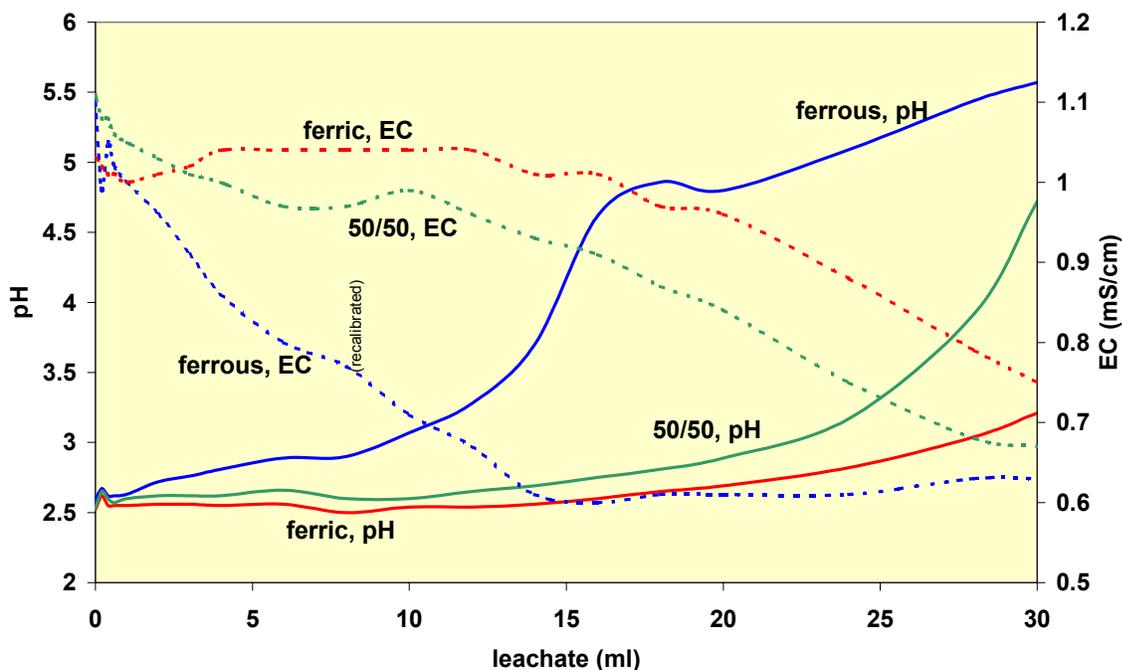

Figure 8. EC and pH curves for 50 mg/l total iron solutions (either ferrous, ferric or 50/50 mixture) neutralised with Arnot ash leachate. Iron added as sulphates.

overhead stirrer. Reactions were done with SAMD and either Arnot ash leacheate, NaOH or Ca(OH)$_2$ (indicated on chart). Reactions were undertaken in a CO$_2$ environment. Small aliquots of Arnot ash leachate were added and the reaction allowed to proceed for five minutes before readings were taken. In addition to pH and EC readings a number of subsamples were analysed for their total and ferrous iron content

by colorimetry. The pH curves vary considerably, that for the mixed solution being intermediate between the two pure solutions. The EC curves also largely follow this trend. The ferric solution buffered the pH, which was still very low at the end of the experiment. However, a thick precipitate was thrown and no iron was detected in solution above pH 3. No ferrous iron was detected in any of the subsamples taken. The ferrous solution did not lose much iron from solution until around pH 5 and above. Some oxidation did occur due to the agitation and aeration and the colour of the precipitate indicated that some of this was of ferric compounds. Above pH 5, considerable precipitation of iron occurred. The mixed solution again behaved in an intermediate manner, throwing some precipitate throughout the reaction. Colorimetry indicated that the majority of the iron lost from solution was in the ferric form with a much higher proportion of ferrous iron left in solution at the end of the experiment.

These reactions compliment those shown in Figure 6 and again indicate that the oxidation state of iron in co-disposal reactions will strongly influence the reaction kinetics and the mineralogy of the precipitates formed.

Synthesis and characterisation of sesquioxidic precipitates formed by the reaction of acid mine drainage with fly ash leachate
The objectives of this experiment were to compare FA to other common neutralising reagents, examine the solution chemistry to determine the effectiveness of FA in removing metals and other salts, synthesise the ochres formed by the neutralisation of AMD and investigate their composition, mineralogy and surface characteristics. This was performed in order to examine the reactions that occur during the co-disposal of FAL and synthetic acid mine drainage (SAMD) and examine the precipitates that result from the neutralisation reaction.

Potentiometric titration was employed to investigate the reaction of SAMD with FAL. Precipitates, prepared from these titrations at various pH values and Fe:Al ratios, were characterised according to composition, mineralogy and surface properties. Upscale potentiometric titrations of SAMD show buffer zones at pH values of 3.5, 4, 6 and 10 corresponding to Fe(III) precipitation, Al precipitation, Fe(II) hydrolysis and oxidation, and Al redissolution, respectively, while downscale potentiometric titrations with SAMD show buffer zones at pH values 12 – 11, 9 and 4.5, which correspond to Fe oxidation and precipitation, Al precipitation and Al re-dissolution, respectively. High concentrations of Al precipitated from the SAMD inhibited the crystallinity of the product and resulted in a large quantity of SO_4 being removed from solution, which suggests that an aluminium sulphate phase was precipitating, but was not sufficiently crystalline and could thus not be identified by XRD. Titrations performed upscale by adding FAL to AMD showed near-complete metal and substantial SO_4 removal from solution. The characterisation of reaction solids revealed that the precipitates consist of poorly crystalline, highly Al-substituted goethite and ferrihydrite with large amounts of SO_4 included in the structure. Poorly crystalline bayerite appears at a high pH and high Al concentration, and calcite is present in precipitates made by adding SAMD to FAL. High surface charges of between 330 $cmol_c$/kg positive and 550 $cmol_c$/kg negative charge

and potentially large specific surface areas of up to 236 m^2/g suggest a strong potential for the precipitates to function as low-grade adsorbents in wastewater treatment.

The titration curves are generally characterized by four distinct regions: At high pH values (> 12,7) the solutions are in equilibrium with ($Ca(OH)_2$). Between pH 12 and 10.3 ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}. 26H_2O$) precipitates and acts as a weak pH buffer. Below pH 10.3 ettringite dissolves incongruently to form gypsum and amorphous $Al(OH)_3$. Gypsum was identified by XRD to pH values of 5.6, although thermodynamic modeling indicates that the solution is in equilibrium with gypsum to pH value of 4.1. The presence of amorphous $Al(OH)_3$ could not be confirmed directly, but is inferred from the modeling of the solution chemistry. Very little buffering is observed between pH values of 10.3 and 4.5 where the solution composition is controlled by gypsum and amorphous $Al(OH)_3$. Between pH values of 4.5 and 4.1 the system exhibits a very strong buffering capacity, which is considered to be the result of the dissolution of the amorphous $Al(OH)_3$.

The kinetics of the neutralization reaction were investigated by monitoring the pH and electrical conductivity (EC) of three fly ash: AMD mixtures (1:5, 1:10. 1:20) over a period of 72 hrs. The kinetics of the neutralization reaction are initially very rapid, with the pH increasing from 2.5 to 4 within 5 minutes for all fly ash: AMD ratios. This rapid neutralization reaction is considered to be the result of the free lime present in the fly ash (approx 7wt%). The reaction rates decrease as equilibrium is approached. For both fly ash samples the pH had stabilized within 24 hrs. Those experiments whose equilibrium pH was below pH 10 maintained a constant EC from the time the pH stabilized until the experiment was terminated. Where the equilibrium pH was higher than 10 the EC continued to decrease and had not stabilized when the experiments were ended. This slow decrease in the EC is considered to be due to the slower kinetics of ettringite precipitation as equilibrium is approached. These secondary aluminosilicate and/or aluminocalcium sulphate (ettringitic) or ferrihydrite precipitates may have the capacity for improving water quality in co-disposed AMD and fly ash. Such by-products may also be of value as adsorbents for low-cost removal of toxic metals in wastestreams

Co-disposal with different ratios of AMD and FA
Beaker tests were carried out (designed to mimic the industry process of neutralizing AMD) to determine the change in pH and EC with time when different ratios of AMD and FA were added. In these experiments a set volume of AMD was stirred continuously by means of an overhead stirrer and a known mass of FA was added. The samples were stirred for 4 hours. The pH and EC were recorded every 10 minutes until 30 minutes and thereafter every 30 minutes. The product was then filtered through a Whatman No.1 filter paper. The water samples were filtered through a 0.2 μm membranes before multi-element analysis using ICP-MS for cation concentrations and IC for anion concentrations. These experiments were conducted to see how the initial pH and EC changed when different volumes of Navigation AMD and different masses of Arnot FA were added together over a time period.
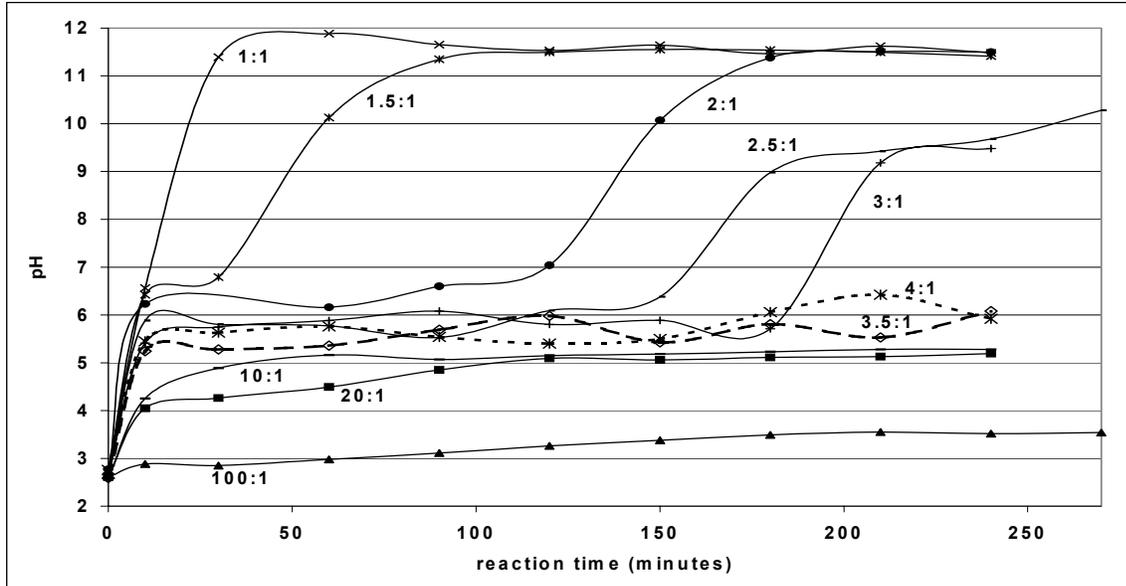
Figure 8. pH measurements of Navigation AMD neutralized with Arnot fly ash at different volume AMD to mass fly ash ratios. AMD:fly ash ratios given on chart (e.g. 10:1).

Figure 8 shows data for pH reading for different volumes of Navigation AMD neutralized with different masses of Arnot FA. Each line represents an experiment of different AMD: fly ash ratio. For example in the 2:1 ratio 400g fly ash was added to 800ml of AMD. These pH data show consistent trends from lower to higher ratios. For the higher ratio (100:1, 80:1, 30:1 and 10:1) the fly ash added does not have the capacity to change the pH of the AMD from pH 4 up to pH 6.5. However, below this ratio there is enough alkalinity in the fly ash to push the reaction to higher pH. For the 1.5:1 ratio there is a rise for the first 10 minutes (from pH 2.61 to 6.42) then a small plateau is seen for the next 20 minutes to pH 6.79, followed by a steady rise (to pH 11.35) and no significant change over the rest of the experiment. The 2:1 and 3:1 followed the same pattern but for them it took longer for the second rise. For the 3:1 ratio it takes about 3 hours before the second rise, from pH 5.75 to pH 9.18 occurs. For the 1:1 ratio there is sufficient alkalinity in the reaction, and no plateaus visible, to overcome this phenomenon.

There appears to be a considerable buffering capacity, with processes such as Al or Fe precipitation taking place, for these waters for the pH range from 4 to 6.5, whereafter the fly ash may be releasing more alkalinity via processes such as dissolution of the glassy phase.

Figure 9 displays EC readings for different AMD:fly ash ratios with time. The graphs show EC trends for the different AMD: fly ash ratios used. High ratios (100:1, 80:1, 30:1 and 10:1) have little impact on the EC of the AMD. This may be as a result of too low a ratio of fly ash being added and that contaminant or soluble species that may be released from the fly ash into the AMD was minimal. However for lower (1.5:1 and 1:1) ratios, a much steeper decrease in EC to the minimum is seen followed by a slight increase in some cases. The variation in EC is probably indicating rapid neutralization of

the AMD (decrease in EC), followed by some release of soluble species from the fly ash. The intermediate ratios (4:1, 3:1 and 2:1) reveal a steady decline over the period of the experiments.
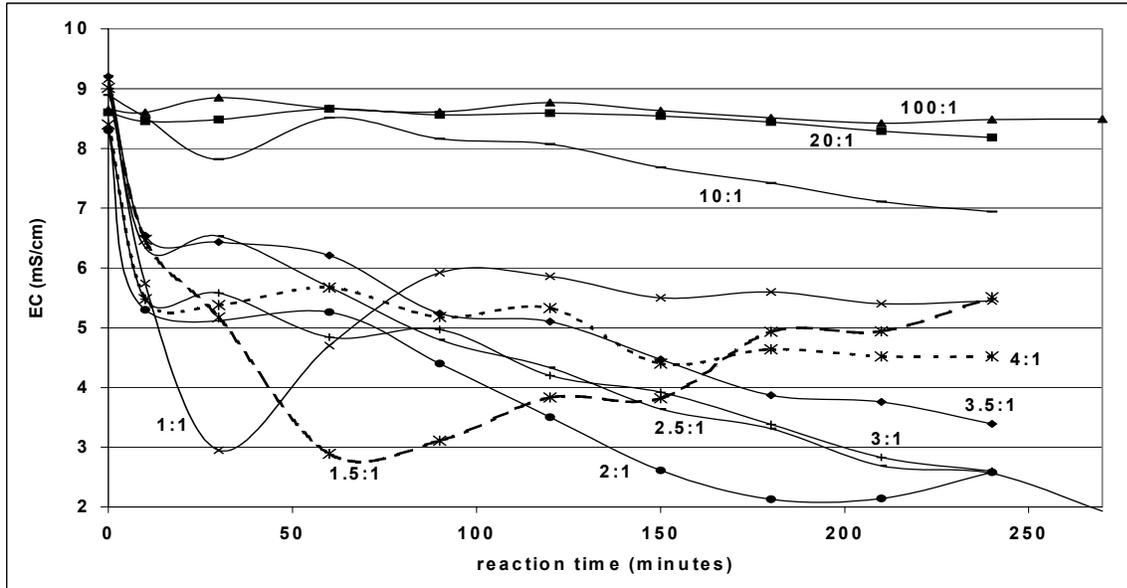

Figure 9. EC measurements of Navigation AMD neutralized with Arnot fly ash at different volume AMD to fly ash ratios. AMD:fly ash ratios given on chart (e.g 10:1)
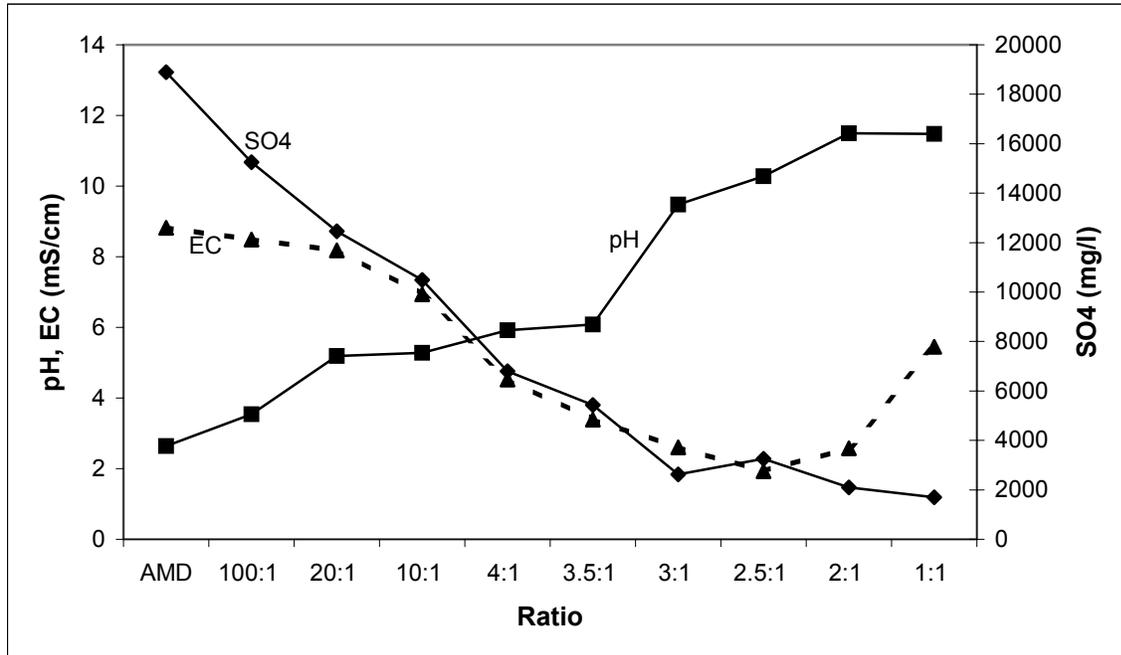

Figure 10. Variation in sulphate concentrations in water samples produced from Navigation AMD and Arnot fly ash, AMD:fly ash ratios given along x-axis in decreasing ratio, A signifies Arnot fly ash used. AMD = start AMD.

The different sulphate concentrations for different AMD:fly ash ratio product water samples are shown in Figure 10. A sharp decrease in sulphate concentration from the start AMD is seen almost across the entire AMD:fly ash ratio, with a small increase over 3:1 to 2.5:1 ratio. The sulphate concentration decreases from almost 19000 mg/l in the start AMD to almost 1700 mg/l in the 1:1 ratio. Sulphate is seen to decrease even when the EC started to rise again in the lower ratio samples. Sulphate concentrations were found to be controlled by the precipitation of gypsum ($CaSO_4 \cdot 2(H_2O)$) at low pH, ettringite ($Ca_6Al_2O_6(SO_4)_3 \cdot 32H_2O$) at high pH, and other metal sulphate species at intermediate pH.[2, 8]
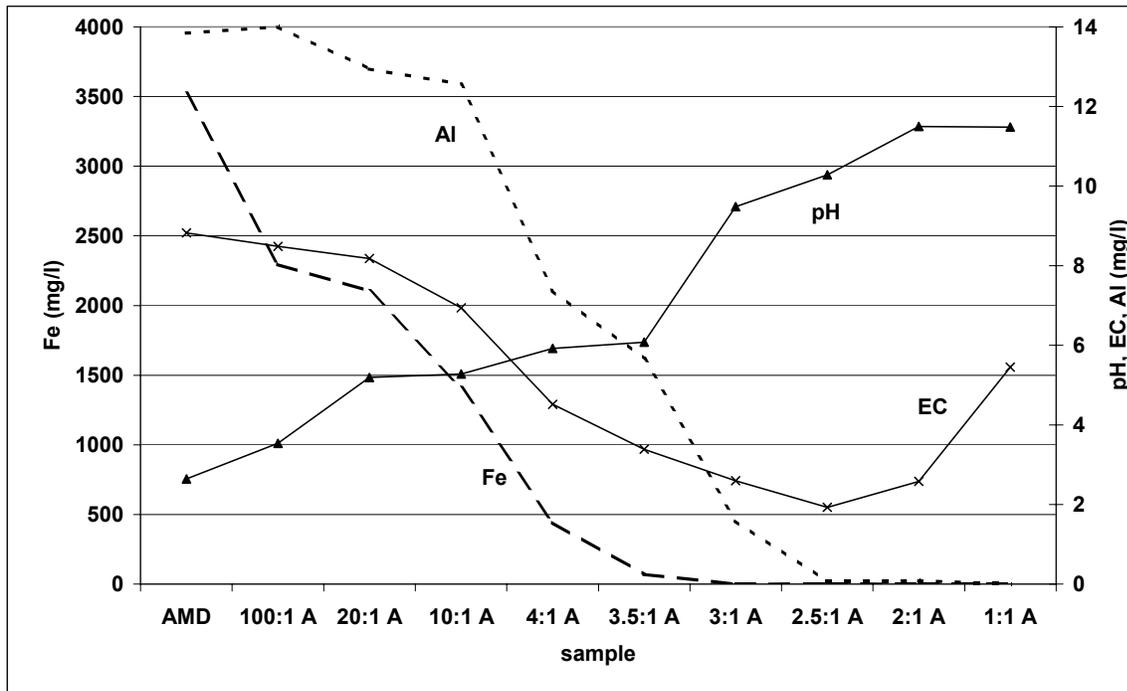

Figure 11. Variation in Fe and Al concentrations in water samples produced from Navigation AMD and Arnot fly ash, AMD:fly ash ratios given along x-axis, A signifies Arnot fly ash used. AMD = start AMD.

Iron and Aluminum concentrations for the different ratio AMD:fly ash product water samples are displayed in Figure 11. A sharp decrease in Fe concentration is seen from the start AMD (approximately 3 500 mg/l) to ratio 3.5:1 (almost 70 mg/l), followed by a steady decrease to below detection limits for the rest of the lower ratios. Fe could precipitate out of solution as hydroxides or oxyhydroxides.[4] The Al concentration showed a steady decrease for the higher ratios (100:1, 20:1 and 10:1), followed by a sharp decrease from the 10:1 to the 2.5:1 ratio. The Al concentration then continued to below detection limits for the rest of the lower ratios.

No significant variation in concentration was seen (Figure 12) for most of the common cations Na, K and NH_4. A gradual increase in Ca concentration was detected across

most of the AMD:fly ash ratios with a decrease to the 1:1 ratio. This is directly as a result of the removal of sulphate up to a point where the product water is saturated with $CaSO_4 \cdot 2(H_2O)$ (gypsum). [2] The Mg concentration increases steadily in the higher ratios with a sharp decease in the lower ratios. The lower EC range shows a 59% Mg removal. Also, significantly, although considerably more ash was added at the lower ratios than at the higher ratios, little release of soluble species from the fly ash can be observed, even though the EC increases. This is further confirmation that at high pH the FA glassy phase dissolution could be contributing to EC values and contributing to additional alkalinity and buffering capacity.
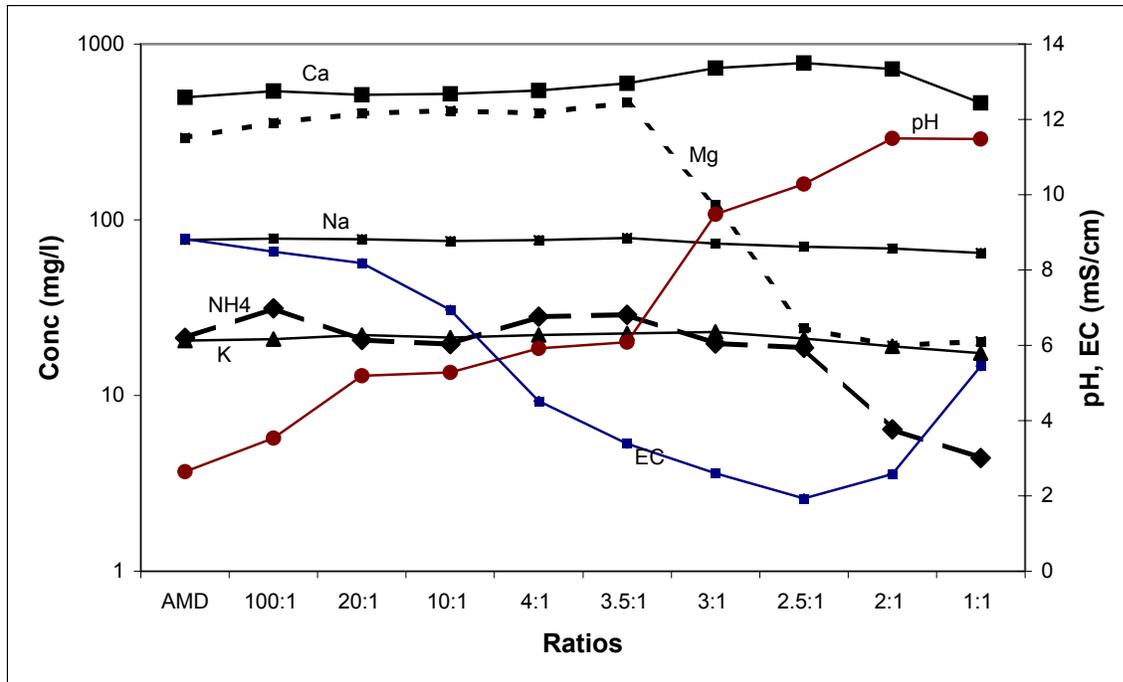

Figure 12. The variation in K^+, Na^+, NH_4^+, Ca^{2+} and Mg^{2+} concentrations of Navigation AMD neutralized with Arnot fly ash over ratios of different volume AMD to mass fly ash ratio.

A dramatic decrease for most of the common anions (Figure 13) was detected. An increase in concentration of F and NO_3 were seen from the start AMD to 100:1, with a decrease in the lower ratios (including the lower EC range) but with an increase of NO_3 at the lowest range, which may be a further reason for the increase in EC generally observed at the lowest ratio applied. The Cl concentration decreased over most AMD:fly ash ratios. The lower EC samples (i.e. ratios 4:1 to 3:1) shows a Cl removal of between 74 to 87%. The PO_4^{3-} concentrations were generally low throughout all ratios.

A dramatic decrease for most of the heavy elements (Figure 14) was detected. However, Figure 15 shows the graphs of the variation of B, Mo, Se and As concentration of Navigation AMD neutralized with Arnot fly ash water samples. An increase in concentration was seen for these particular elements. Boron release is well known for fly ash leaching studies. Mo was released into solution at low AMD:fly ash ratios and might be a result of the coal grinding mills.
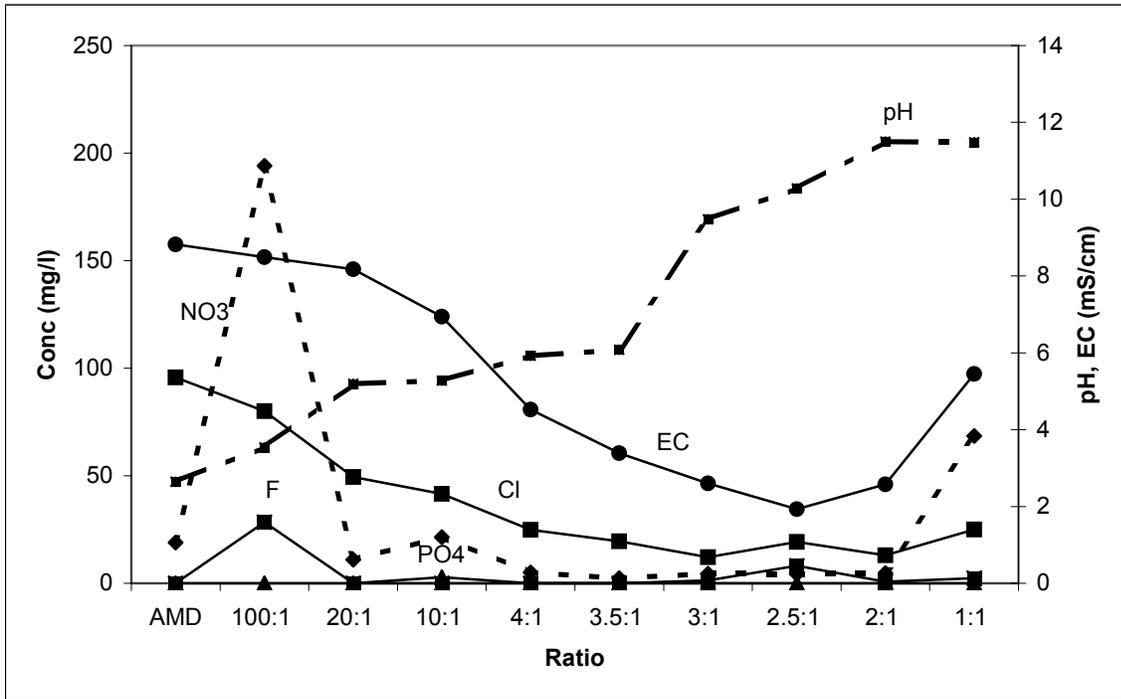
Figure 13. The variation in F^-, Cl^-, NO_3^- and PO_4^{3-} concentrations of Navigation AMD neutralized with Arnot fly ash over ratios of different volume AMD to mass fly ash ratio.
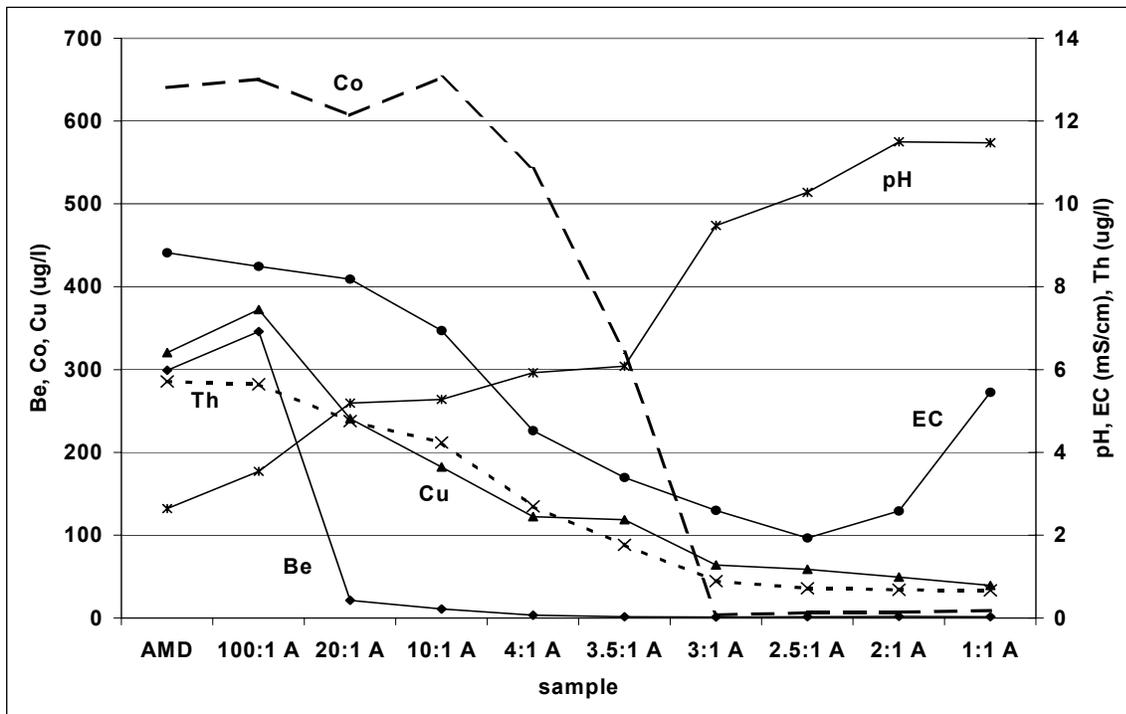

Figure 14. Variation in Be, Cu, Co, Th in post process water. Details as before.
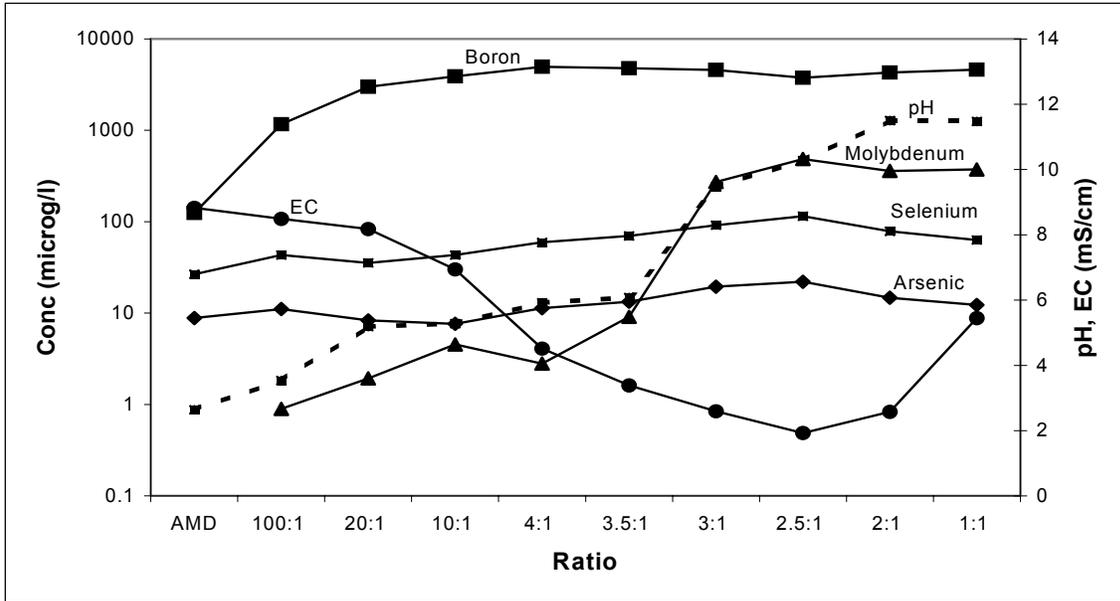
.
Figure 15. The variation in B, Mo, As and Se concentrations of Navigation AMD neutralized with Arnot fly ash over ratios of different volume AMD to mass fly ash ratio.
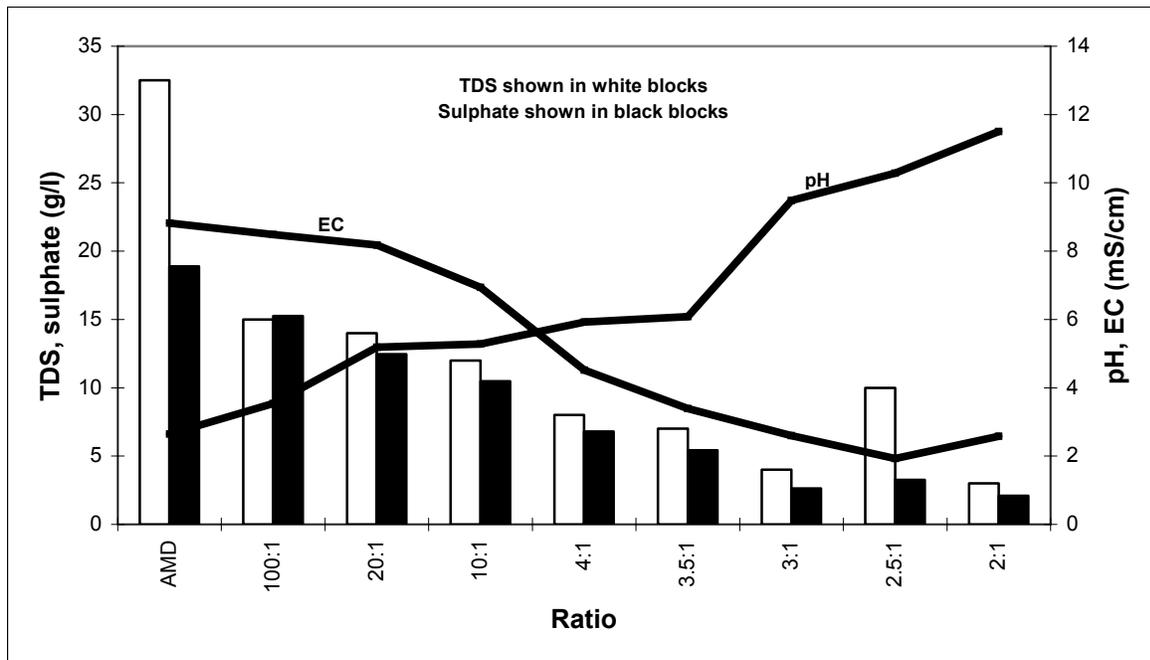

Figure 16. The variation in sulphate and Total Dissolved Solid (TDS) concentrations of Navigation AMD neutralized with Arnot fly ash over ratios of different volume AMD to mass fly ash ratio.

Sulphate and Total Dissolved Solids (TDS) concentrations for the different ratio AMD:fly ash water samples are displayed in Figure 16. In these experiments a set volume of

Navigation AMD was stirred continuously and a known mass of Arnot fly ash was added. Water samples were filtered through Whatman no. 1 filter papers and then through a 0.2μm Millipore filter before it was send for IC analyses. The TDS was measured by evaporating the filtrate to dryness in a weighed dish at $180^{o}C$. A sharp decrease in TDS and sulphate concentrations from the initial AMD to the 1:1 ratio, with a steady decrease across to ratio 3:1, followed by an increase again to the 2.5:1 ratio and a decrease to 2:1 ratio. The 100:1 ratio showed a slightly higher concentration for the sulphate than in the TDS concentration. It is possible that most of the metals deriving from the AMD could be mobilized as metal sulphates. The small increase in ratio 2.5:1 for both the sulphate and TDS could be that some ionic species went into solution, which may be Si species by dissolution of the glassy phase, as suggested. A sharp increase in alkalinity was seen across the ratios from 20:1 to 2:1 as expected with an increase in the amount of fly ash (CaO) added.

The preparation and characterization of ion exchange adsorbents, synthesized from the precipitates collected by co-disposal of FA and AMD.

The use and application of synthetic zeolites for ion exchange, adsorption and catalysis has shown enormous potential in industry. With an increasing demand for zeolite material, XRF analysis was used to determine whether the concentrations of Si and Al precursors in FA or codisposed residues, analysed with this technique, can serve as an indicator to determine whether the alkaline hydrothermal conversion of fly ash related material into zeolites can be successfully achieved.

This study involved co-disposal reactions wherein FA was reacted with AMD, firstly to raise the pH of the solution to near neutral, and secondly to collect the codisposed precipitates for zeolite synthesis. The Si and Al content of the FA residues/precipitates were utilized in the alkaline hydrothermal conversion of the FA compounds into zeolites.

The co-disposal precipitates were collected at a near neutral pH by using a FA:AMD ratio of 1:3.5 to 1.5. The reactants used were either Arnot or Matla FA co-disposed with one of Navigation or Brugspruit AMD. These co-disposal precipitates were then analysed by XRF for quantitative determination of SiO_2 and Al_2O_3. The $[SiO_2]/[Al_2O_3]$ ratio obtained in the precipitates range from 1.4 to 2.5. The $[SiO_2]/[Al_2O_3]$ ratio was used to predict whether the fly ash precipitates could successfully be converted to faujasite zeolitic material by the synthetic method of Rayalu et al.[22] If the $[SiO_2]/[Al_2O_3]$ ratio is higher than 1.5 in the fly ash precipitates, it favours the formation of faujasite.

The zeolite synthesis included an alkaline hydrothermal conversion of the co-disposal precipitates. In the zeolite synthesis method the FA precipitates were fused with sodium hydroxide in a 1:1.2 ratio at 600 ºC for about 1 – 2 hours. The fused product was then mixed thoroughly with distilled water and the slurry was subjected to aging for 8 hours and crystallization at 100 ºC for 24 hours. The solid product was recovered by filtration and washed thoroughly with deionised water until the filtrate had a pH of 10 to 11. The product was then dried at 70 ºC.

Mineralogical and physical analysis of the zeolitic material produced was performed by X-ray diffraction (XRD), Fourier Transformed Infrared Spectroscopy (FTIR) and nitrogen Brunauer-Emmett-Teller (N2 BET) surface analysis. Scanning Electron Microscopy (SEM) was used to determine the morphology of the zeolites, while Inductively Coupled Mass Spectroscopy (ICP-MS) and Cation Exchange Capacity (CEC) techniques were used for chemical characterisation.

Different factors were investigated during the synthesis of zeolite to ascertain their influence on the end product. The factors included the amount of water in the starting material, composition of fly ash related starting material and the FA:NaOH ratio used for fusing the starting material.

With the addition of different amounts of water to 1 g of the fused co-disposal precipitates, different or no zeolite products resulted. With the addition of 6 ml of deionised water to 1g of fused co-disposal sample material, faujasite and sodalite were produced as zeolite phases in the co-disposal samples with a $[SiO_2]/[Al_2O_3]$ ratio higher than 2.

The use of two different sources of FA, Arnot and Matla FA and different FA related starting materials were also investigated to assess the influence of FA quality on the zeolite phases produced. The starting material prepared from Arnot FA included fresh FA, water leached FA and HCl leached FA. In the case of Arnot FA, the untreated fresh FA produced faujasite as the zeolite phase, the water-leached FA produced zeolite A and the HCl leached FA produced sodalite or sodalite/faujasite mixtures as zeolite phases. In general Arnot FA was a successful feedstock whereas using Matla FA did not result in successful zeolite phases. This may be due to the fact that Matla ash was more enriched with heavy metals than Arnot ash as XRF analyses of the fresh ash showed.

A further variable investigated was the use of different FA:NaOH ratios during fusion of the starting material. In the synthesis steps outlined by Rayalu et al.[22] a FA:NaOH of 1:1.2 was used. This FA:NaOH ratio was varied to 1:1.1 and 1:1.5 to investigate the effect it had on the zeolite phase produced. In using the co-disposed residues as feedstock, with different FA:NaOH ratios, a ratio of 1:1.1 produced faujasite and sodalite as products, while a ratio of 1:1.5 produced only faujasite as zeolite product, compared to no zeolite product for a ratio of 1:1.2. A change in the FA:NaOH ratios of the water-leached FA had the following effect on the zeolite product formed. For both the ratios of 1:1.1 and 1:1.5 sodalite was produced as zeolitic material, compared to no zeolite product for a ratio of 1:1.2. For the acid (HCl) leached FA, a FA:NaOH ratio of 1:1.1 produced no zeolite phase, with the ratios of 1:1.5 and 1:1.2 producing the same zeolite phases of faujasite and sodalite.

The BET surface area and the pore volume of the synthesized zeolitic materials were determined for a range of starting material used. The values of the surface areas for the zeolitic material prepared from the co-disposal precipitates generated through co-disposal of Arnot FA and Navigation AMD ranged from 91 – 245 m²/g. The highest

surface area for zeolite products prepared from co-disposed residues was 245 m²/g which was obtained for a product containing faujasite and sodalite as zeolitic material, prepared at a FA:NaOH ratio of 1:1.2 and with additional water.

A high surface area of 515 m²/g was obtained for a sample prepared using fresh Arnot FA as starting material in the zeolite synthesis. This sample contained faujasite as zeolitic material and also had the highest pore volume of 0.45 cm^3/g. The results of the surface area for the water and HCl acid leached fly ash used in the zeolite synthesis range from 71 – 188 m²/g. The values for the pore volume range from 0.16 – 0.33 cm^3/g. These results show that the purity of the Si source is not necessarily conducive to high yields or pure phases of zeolite product, and that the additional Al supplied by the co-disposal precipitates may have a positive effect on the purity and yield of zeolite.

CONCLUSION
Pollution control of South African mining and coal powered utility waste streams has been shown to be possible by application of a process for removal of toxic ionic impurities from AMD by co-disposal with fly ash, which process permits neutralization of two hazardous waste streams and the preparation of high capacity ion exchange material, for treatment of secondary waste waters.

The alkalinity in FA (primarily present as CaO) has been utilized in this study to neutralize AMD. Direct mixing of various ratios of AMD and fly ash to a predetermined pH in the co-disposal process enhanced the formation of gypsum and soil components upon ash residues. Precipitation of alumino-silicates and metal hydroxides as well as iron compounds occurred at a pH of 10. The secondary aluminosilicate and/or aluminocalcium sulphate (ettringitic) or ferrihydrite precipitates have the capacity for mutual beneficiation of water quality in co-disposed AMD and fly ash. Such materials when precipitated may also be of value in low-cost attenuation of toxic metallic waste streams. It was shown that both ash or co-disposal residues could furthermore be used to prepare high capacity zeolitic adsorbents such as faujasite, sodalite and Zeolite A. The post process solid waste residues thus could be used for the large-scale production of high capacity ion exchange material in the form of granules useful for secondary effluent treatment.

Most significantly, the two waste products AMD and FA could be neutralized, and when reacted together, produced much cleaner water, broadly comparable to post process water derived from lime or limestone treated AMD. This newly developed co-disposal procedure worked best for treating high TDS AMD. Sulphate removal rates were in the region of 90%, Fe, Al and heavy metal removal was often total depending on the final pH, and EC was seen to drop to a minimum at pH ~10. Post process waters were significantly purified, with only relatively low concentration of some species of toxic elements remaining in solution (e.g. As, B, W and Mo) at high pH, normal for these elements. The neutralized process water thus contains only residual sulphate and low concentrations of ionic species that may be recovered by zeolitic adsorbents or EDR systems using a variety of high capacity ion exchange materials.

The solids remaining after co-disposal of FA and AMD were often suitable raw materials for the synthesis of zeolites via NaOH fusion. High quality, high yield, clean phase zeolites formed included zeolite Y (faujasite), zeolite A and sodalite produced by using fly ash or co-disposal residues as reactant source. These zeolites have widespread potential application in water treatment or as catalysts. N_2-BET analyses indicated that some faujasite samples had surface areas in excess of 500 m^2/g.

In this study it is shown that neutralization is possible of various sources of AMD, with high sulphate removal and recovery of water by co-disposal with several different sources of fly ash or fly ash leachate. This study also shows that it is possible to prepare high capacity adsorbents such as zeolites from the co-disposed solid residues. The prepared zeolites are applicable as adsorbents for further treatment of dilute process water and other waste streams. Hence neutralization of AMD waste streams with fly ash allows water purification by co-disposal of two hazardous wastes, without additional use of liming agents or standard water purification chemicals such as strong acids or bases, and simultaneously allows the preparation of high capacity adsorbents such as zeolites.

Co-disposal of coal mine derived AMD utilizing South African fly ash is thus a suitable method for the low cost treatment of acid coal mine drainage, resulting in cleaner water and high quality zeolite adsorbents by post process synthesis of solid process residues.

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