

Development of a Co-Disposal Protocol for the Neutralization and Amelioration of Acid Mine Drainage with Fly Ash

Damini Surender¹ and Leslie Petrik²

¹ESKOM–Resources and Strategy, Lower Germiston Road, Rosherville, Private Bag 40175, Cleveland, 2022, South Africa; ²University of Western Cape, South African Institute of Advanced Materials Chemistry (SAIAMC), Faculty of Science, Private Bag X17, Bellville 7535, South Africa.

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ABSTRACT

The primarily coal based production of electricity in South Africa results in approximately 20 Mt of highly alkaline, aluminosilicate fly ash (FA) being produced per annum.¹

Acid mine drainage (AMD) associated with coal mining is produced by pyrite oxidation resulting in highly acidic waters with elevated sulfate, certain heavy metals and total dissolved solids (TDS) levels. AMD leaching into groundwater has a deleterious impact on the environment.

In this study, the potential of co-disposing AMD with fly ash was investigated at laboratory and pilot plant scale. The primary goals were development of a co-disposal protocol aimed at neutralization of AMD and reduction of heavy metal content. The co-disposal process was initially tested at laboratory scale based on the following parameters: ash neutralization potential, final desired pH and the heavy metal removal. Batch processes were conducted at laboratory and pilot scale by direct mixing of the fly ash with AMD at pre-determined FA:AMD ratios. Depending on the FA:AMD ratio, neutral and alkaline pH levels were achieved. Reduced heavy metal and sulfate concentrations with a corresponding decrease in conductivity were observed post co-disposal. The successful co-disposal of AMD with fly ash provides a technology suitable for neutralization and amelioration of AMD.

INTRODUCTION

ESKOM is the largest producer of electricity in South Africa, supplying 95 % of the South African electricity needs and approximately 50 % of that consumed by the African continent. Electricity generation in South Africa is largely dependent on coal combustion rendering coal mining and combustion as well as fly ash (FA) handling and disposal a necessity. The primarily coal based production of electricity in South Africa

results in excess of 20 Mt of highly alkaline, aluminosilicate fly ash being produced per annum.¹ A small percentage of fly ash is utilized by the cement industry and the remainder is disposed in landfills or ash dams.

Acid mine drainage (AMD) associated with coal mining is produced when pyrite (FeS_2) is oxidized upon exposure to air and water resulting in highly acidic waters with elevated sulfate, certain heavy metals and total dissolved solids (TDS) levels. The presence of acidophilic bacteria further influences pyrite oxidation. AMD leaching into groundwater has a deleterious impact on the environment. Legislation requires that this water be collected and neutralized prior to discharge. Current AMD treatment practice at Navigation colliery in South Africa replaces lime with limestone in the High Density Sludge (HDS) process.² The limestone purchased for this particular application is a by-product of the paper industry in powdered form. Neutralization of AMD and safe disposal of the resulting sludge has major financial implications.

Recent work which exploits the alkaline nature of fly ash has demonstrated the potential to neutralise acid mine drainage by co-disposing ESKOM fly ash or aqueous extracts of the fly ash with AMD and subsequently reduce heavy metal concentrations by precipitation.^{3,4} The co-disposal of fly ash with AMD may thus feasibly be used as a process to neutralize and ameliorate mine water.

Possible benefits associated with the co-disposal process include pollution abatement, neutralization of hazardous waste streams and recovery of water.

Thus, the objective of this study was to investigate the potential of utilizing fly ash for AMD treatment with a view for full-scale site implementation.

EXPERIMENTAL

The project plan consisted of 4 phases, namely:

- Phase 1: Identify suitable fly ash and AMD for treatment.
- Phase 2: Conduct laboratory tests and co-disposal process optimization.
- Phase 3: Design, construct and commission pilot scale co-disposal unit.
- Phase 4: Pilot scale testing and process optimization.

Phase 1: Identify suitable fly ash and AMD for treatment

The chemistry and mineralogy of fly ash is governed by a number of factors including the composition of the parent coal, combustion conditions, and type of emission control. Thus, not all fly ashes would be appropriate for neutralization. Based on the success of previous laboratory scale neutralization studies⁴, fly ash originating from a power plant in the Highveld region was selected for this study. Chemical analysis of the fly ash was performed by x-ray fluorescence (XRF) spectrometry.

Large quantities (by mass) of fly ash were collected from the electrostatic precipitator (ESP). The fly ash samples were homogenized and sealed in airtight bags to avoid air

ingress. The rationale for this practice was to prevent calcite formation, which occurs when the fly ash reacts with CO₂ from the atmosphere. This would ensure consistency in the mineralogy of fly ash for the duration of the study.

The AMD generated from South African coal-mines may have pH values as low as 2, are rich in sulfate, iron and aluminum, and the TDS ranges between 4000-5000 mg/l. A colliery, also based in the Highveld region, generates approximately 10 000 m³ AMD per annum. The AMD has a low pH, high TDS levels and high iron and sulfate content. Further, this colliery is within close proximity to power stations with easy access routes. Thus AMD samples from the Highveld colliery was thus selected for co-disposal studies with suitable fly ash in the same vicinity. Acidity, pH, electrical conductivity (EC) and chemical analysis of the AMD was done prior to conducting co-disposal tests.

AMD samples were collected in high-density polyethylene (HDPE) bottles and stored under refrigeration (4 °C) so as not to lose their integrity.

Phase 2: Conduct laboratory tests and co-disposal process optimization.

Beaker tests were conducted to determine the mass of fly ash required to neutralize the AMD. Various quantities of fly ash were added to 500 ml AMD at pre-determined FA:AMD ratios. The following FA:AMD ratios were studied: 1:1, 1:2, 1:3, 1:5, 1:10 and 1:20. Fixed volumes of fresh AMD samples were added to the beakers and stirred with overhead stirrers at 250 rpm/min for approximately 15 minutes to allow the AMD to achieve ambient conditions. The fly ash was weighed and gradually added to AMD with continuous stirring. The pH and conductivity of each mixture was measured at regular time intervals. By controlling the pH endpoint of the co-disposal reaction, neutralized water with reduced metal content could be obtained. The solid and liquid phases were separated by filtration upon reaching a stable pH. The liquid phase was then analyzed by Inductively Coupled Plasma Spectroscopy (ICP) and ion chromatography (IC).

Upon optimization of the co-disposal process at laboratory scale, pilot scale testing and optimization was conducted.

Phase 4: Pilot scale testing and process optimization

The pilot scale studies were conducted in a similar manner as the laboratory scale studies except much larger volumes of AMD and fly ash were utilised.

RESULTS AND DISCUSSION

Phase 1: Identify suitable fly ash and AMD for treatment

The results of the XRF analysis are presented in Table 1.

Table 1: Chemical composition of fly ash

Component	Fly Ash
Total Alkalinity	10 000 mg/l
Silicon (as SiO ₂)	50.9 %
Aluminum (as Al ₂ O ₃)	26.5 %
Iron (as Fe ₂ O ₃)	5.20 %
Titanium (as TiO ₂)	1.40 %
Calcium (as CaO)	6.90 %
Magnesium (as MgO)	2.70 %
Sodium (as Na ₂ O)	0.01 %
Manganese (as MnO)	0.05 %
Phosphorous (as P ₂ O ₅)	0.33 %
Potassium (as K ₂ O)	0.40 %
Sulphur (as SO ₃)	0.06 %

Fly ash consists predominantly of quartz (SiO₂) and varying amounts of hematite (Fe₂O₃), magnetite (Fe₃O₄), mullite (Al₆Si₂O₁₃) and lime. The essential ingredient for effective AMD neutralization is CaO, which is present in significant quantities in the Arnot fly ash. Upon hydrolysis, CaO transforms into carbonates, forming the buffering constituents.⁵ The alkalinity of Arnot fly ash was determined by titration with standardized nitric acid (HNO₃) to a end point pH of 4.5.⁶ The alkalinity imparted by the fly ash was 10 000 mg/l CaCO₃. The free alkalinity imparted by CaO and small particle size with increased surface area makes this fly ash a good neutralizing agent.

Results of the AMD analysis are presented in Table 2. This particular AMD has very low pH, high acidity and corresponding elevated sulfate concentrations. The extreme nature of the AMD would require an effective neutralizing agent.

Table 2: Chemical composition of AMD

Component	AMD
Acidity	15060 mg CaCO ₃ /L
pH	2.60
Conductivity (mS/cm)	7.52
Sulfate (mg/l) SO ₄ ²⁻	1380
Iron (mg/l) Fe	5000
Aluminum (mg/l) Al	200

Phase 2: Conduct laboratory tests and co-disposal process optimization.

The laboratory scale co-disposal trials were initially conducted at FA:AMD ratios ranging from 1:1 to 1:10. The pH and EC trends with fly ash addition are depicted in Figure 1.

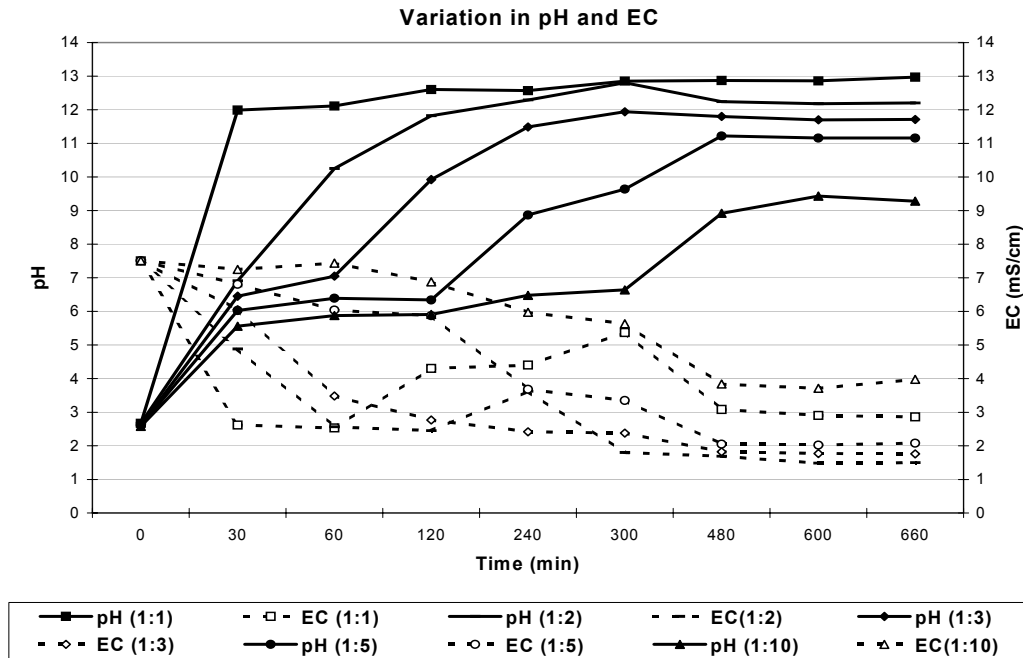


Figure 1: Co-disposal of Landau AMD with Arnot fly ash

The most rapid change in pH occurred within the first 30 minutes of the reaction and thereafter a gradual increase was observed until equilibrium was reached. FA:AMD ratio 1:1 display a rapid increase in pH from 2.67 to 12.97. The pH increased steadily for all ratios with a corresponding decrease in conductivity.

A distinct plateau was observed between pH 5 and 7 for ratios 1:3 and lower due to the buffering capacity of the AMD. This was more prominent at the lower ratios, which contained smaller masses of fly ash.

A noticeably rise in EC occurred around 300 minutes as the gradient of pH curves decreased. Thereafter, the EC continued to decrease possibly due to the dissolution of the fly ash glassy phase, which imparts additional alkalinity and buffering capacity to the solution.

The 1:1 ratio resulted in a thick slurry, which was difficult to stir and filter. Due to the large mass of ash consumed, consistency of this mixture, extremely rapid and uncontrollable pH increase, the 1:1 ratio was considered not to be a viable ratio for co-disposal.

The 1:3 ratio steadily increased to neutrality within an hour and eventually stabilized at a pH of 11.67.

The post co-disposal waters were filtered through a Whatman no. 41 filter paper for ICP analysis and through a 0.45 µm Millipore filter for IC analysis.

The reduction in iron, aluminum and sulphate is graphically depicted in figures 2-4. Landau AMD refers to the bulk solution prior to co-disposal. By raising the pH, certain metals are expected to precipitate out of solution thereby reducing the metal content in the final solution.

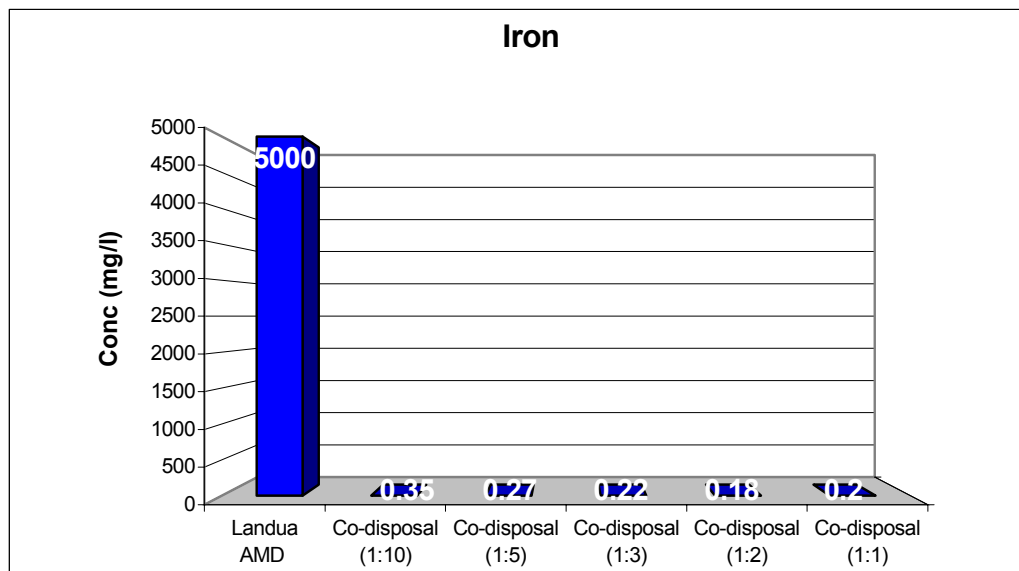
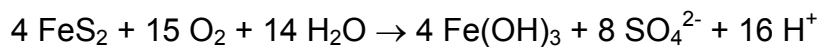


Figure 2: Reduction of Iron – post co-disposal

The formation of AMD can be explained by the following reaction:



Since pH also affects the oxidation of Fe^{2+} and Fe^{3+} , by raising the pH to > 5.5 , the ferrous iron is oxidized to ferric hydroxide, which then precipitates out of solution.² Aeration enhances the oxidation the process. This was confirmed by a reddish-brown precipitate, which accumulated at the surface.

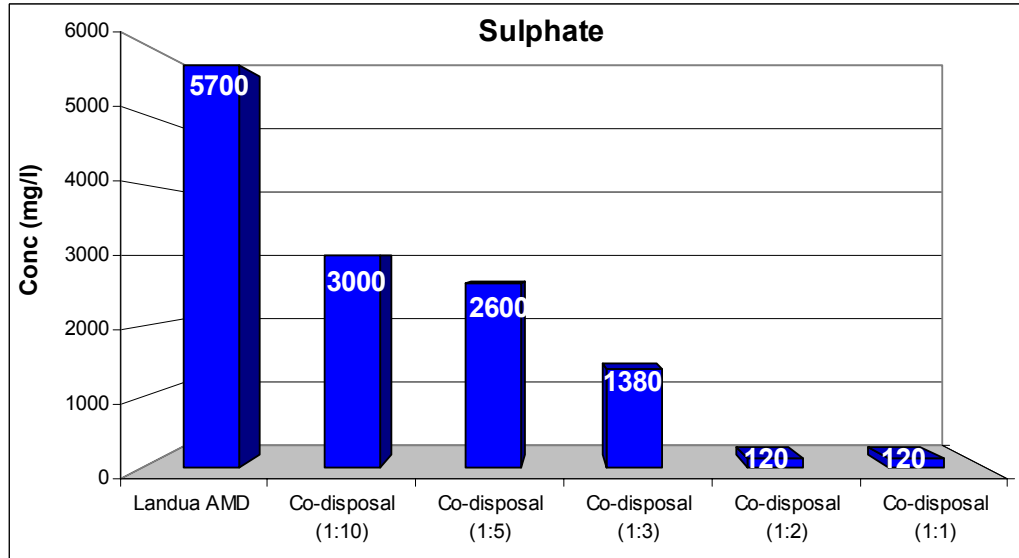


Figure 3: Reduction of Sulphate – post co-disposal

The reduction of sulfate concentrations could be attributed to the precipitation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) at low pH, ettringite ($\text{Ca}_6\text{Al}_2\text{O}_6(\text{SO}_4)_3 \cdot 32\text{H}_2\text{O}$) at high pH, and other metal sulfate species at intermediate pH (Maree and O'Brien).

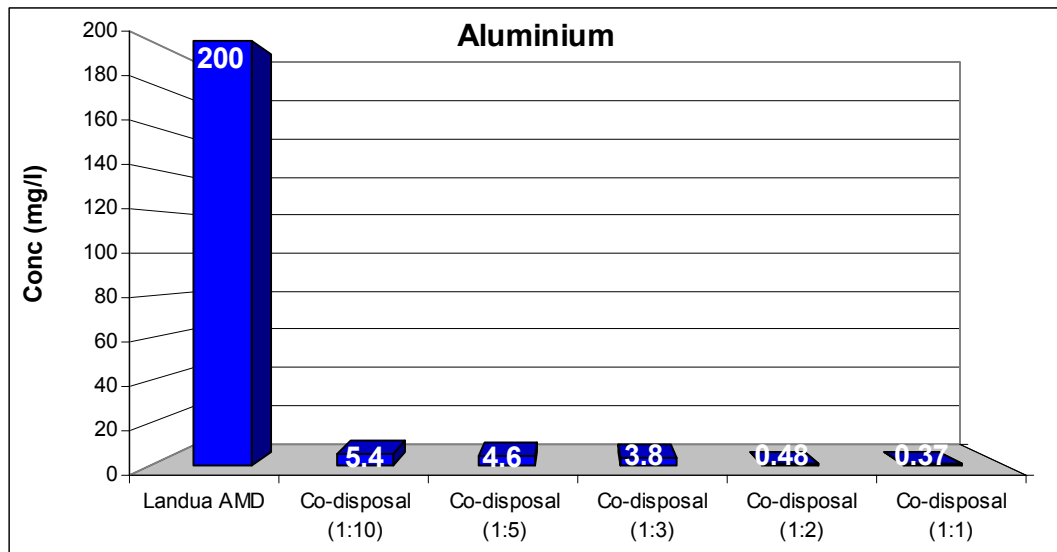


Figure 4: Reduction of Aluminium – post co-disposal

Aluminum hydroxide precipitates above pH 5.2 resulting in reduced concentrations of aluminum in the final solution.

A significant reduction for iron, sulphate and aluminum concentration was noted at all FA:AMD ratios. Almost complete removal (99%) of iron and aluminum, and 96 % reduction in sulfate was achieved by co-disposing the AMD with fly ash.

The laboratory study was extended to include a 1:20 FA:AMD ratio.

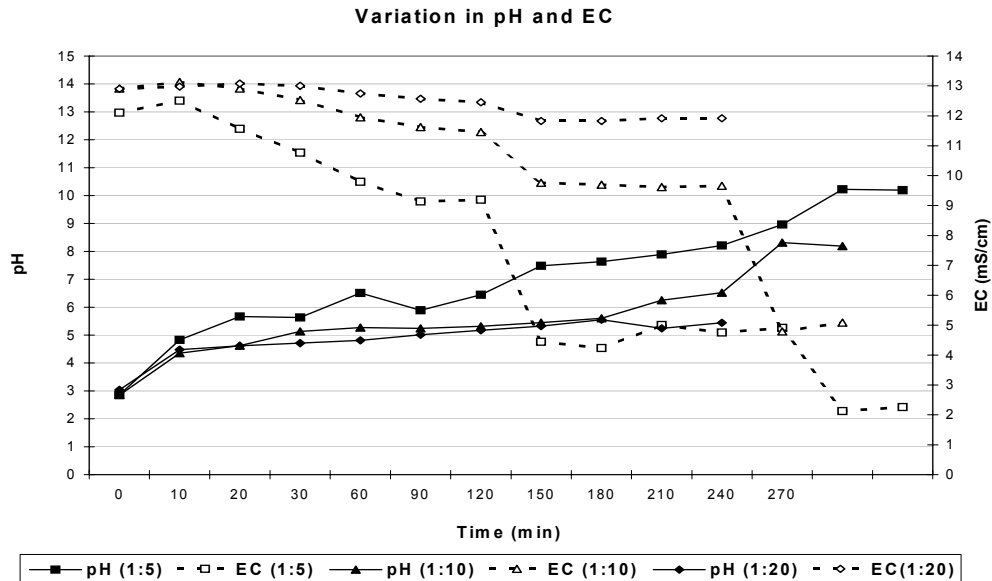


Figure 5: Co-disposal of Landau AMD with Arnot fly ash

The 1:20 FA:AMD co-disposal study was stopped after 4 hours as there was no significant change in pH and conductivity. The 1:5 and 1:10 ratios demonstrated a gradual increase to a neutral pH with a corresponding decrease in conductivity as in the previous study.

Based on the results obtained in the laboratory study, it was concluded that power plant fly ash could be an effective neutralizing agent for AMD, with proper agitation and effective aeration.

Phase 3: Design, construct and commission pilot scale co-disposal unit

Various mixer design configurations were considered during the design and construction phase. The following crucial parameters were taken into consideration:

- Efficient agitation and aeration,
- Slurry density and flocculation,
- Bulk solids separation and handling and
- Water recovery.

The pilot scale mixer consisted of a turbulator/aerator unit with a 250 L tank capacity. This turbulator/aerator ensures adequate agitation of the AMD/fly ash mixture with

aeration to enhance iron oxidation. The slight conical base of the tank allows for separation of the sludge from the liquid (figure 6).



Figure 6: Pilot scale mixer with 250 L tank capacity and turbulator/aeration unit.



Figure 7: Agitation achieved with pilot rig

The top view in figure 7 shows the extra baffle plates that were added to enhance mixing and prevent dead zones.

Phase 4: Pilot scale testing and process optimization.

Results of pilot scale co-disposal tests

Whilst laboratory scale co-disposal tests indicated that a 1:3 ratio was optimum for fly ash and AMD co-disposal, constant variations in the quality of the fly ash and AMD required verification and optimization of this ratio at pilot scale. Further, the pilot scale mixer was equipped with a variable speed drive mixer with aeration, which was expected to enhance mixing as compared to beaker trials and this was further expected to alter the ratio at pilot scale.

Fresh AMD and fly ash were sampled for the pilot scale co-disposal studies. 1:4, 1:5 and 1:6 FA:AMD ratios were tested at pilot scale. 200 L AMD was added to the tank and stirred until ambient conditions were achieved. The respective mass of fly ash added and mixed at 1500 rpm. Electrical conductivity (EC) and pH was monitored at regular time intervals with a portable Hanna pH/EC/TDS/Temp meter.

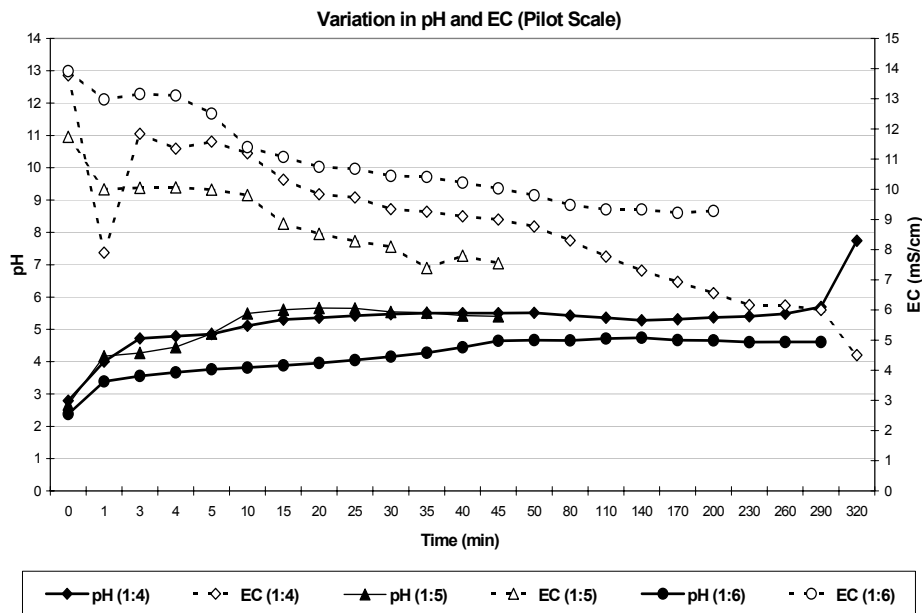


Figure 8: Co-disposal of Landau AMD with Arnot fly ash at a 3:1 ratio

As expected, the response in pH change was different in the pilot study as compared to the laboratory due to a number of possibilities. One major factor is the variation in quality of fly ash and AMD and others being the technical aspects of the mixer. The 1:4 ratio achieved a pH of 7 within 5 hours while the response of the 1:5 and 1:6 ratios were much slower. The 1:5 reaction was terminated at 45 minutes as the pH began to decrease and the 1:6 ratio stabilized at approximately 260 minutes. In addition to minimizing the mass of fly ash, sludge volume and transportation costs, the

design of the co-disposal process must be efficient enough to handle any variations in fly ash and/or AMD quality.

Table 3: Data obtained from co-disposal experiments.

% solids/L sample after co-disposal	17%
Solids : Water (after co-disposal)	1:4.7
settling rate (1:6)	4-5 min

The 1:4 FA:AMD ratio was sampled at various time intervals and analyzed by Inductively Coupled Plasma Spectroscopy (ICP).

Table 4: Results of post co-disposal water

	pH	Al (mg/l)	Fe (mg/l)	Mn (mg/l)	SO ₄ (mg/l)
Landau AMD	2.55	267	4800	328	4812
2 min	3.63	232	3002	-	3546
4	3.81	230	2870	-	3486
6	3.93	195	2821	-	3430
10	4.03	155	2736	-	3900
20	4.24	79	2709	-	3795
30	4.45	33	2658	-	3620
45	4.76	-	2194	-	3659
60	4.98	1.98	-	-	3600
100	5.49	1.47	-	-	3364
120	5.66	0.14	182	325	3264
% Removal		99.9 %	96.2 %	0.91 %	32.2 %

Certain results for Al, Fe and Mn have been rejected and not reported due to analytical error. Greater than 90 % of Al and Fe removal from the original AMD was achieved. There is not expected to be any Mn removal as Mn precipitates at pH values greater than eight.

The FA:AMD ratio of 1:4 was effective in neutralizing the AMD and removal of the major contaminants. The quality of post co-disposal water is such that it could be applied in other process applications while the sludge component could be pumped into underground mines to further treat AMD or prevent AMD formation.

During further pilot scale investigations, a deviation in expected results was experienced whereby, the pH did not increase to the desired pH levels (figure 9). Upon further investigation and analysis of the fly ash, it was noted that the fly ash contained a large percentage of unburned carbon. This was attributed to problems with the parent coal and combustion at the power plant.

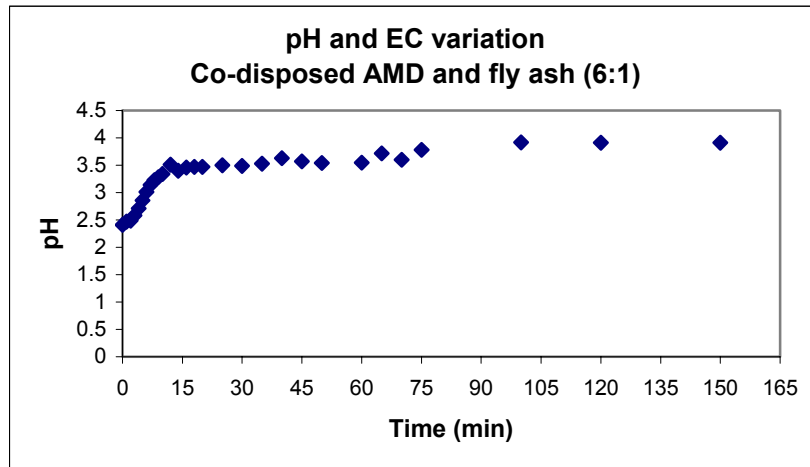


Figure 9: Co-disposal with high carbon ash

The percentage carbon in this fly ash sample was 6.6 %, which is in excess of the usual 3.2 %. This demonstrates that variations in the composition of fly ash can occur randomly, which may affect neutralization reactions. Variations in the quality of AMD with respect to pH and metal content have also been experienced. As such, the optimized co-disposal process may change with varying AMD quality and fly ash composition. Full chemical analysis of both fly ash and AMD must be conducted prior to co-disposal.

CONCLUSIONS

The use of fly ash for the neutralization and amelioration of AMD has been successfully implemented at both laboratory and pilot plant scale. Alkaline fly ash effectively neutralizes AMD and the increased pH allows for the removal of certain heavy metals by precipitation. This co-disposal protocol has been optimized at pilot scale, but due to the variation in chemical composition both of fly ash and AMD, large-scale treatment plants may require further optimization.

The co-disposal process may thus feasibly be applied in large-scale plants and allows for low cost water treatment. This process simultaneously addresses the potential environmental risks associated with fly ash disposal and AMD pollution.

ACKNOWLEDGMENTS

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