

The Use of Fly Ash for the Control and Treatment of Acid Mine Drainage

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Summary

This report details the results of laboratory scale column tests to determine the feasibility of utilising fly ash to treat and direct acid mine drainage (AMD). The AMD emanates from most open cast coal mines, when sulphide bearing rock is exposed to the atmosphere. The oxidation of these pyritic elements and the subsequent contact with water, either from rain or underground sources, forms an effluent with a pH often below 2, TDS in the order of 4000 – 5000 mg/L and high sulphates. As this effluent flows through the surrounding strata the heavy metals are leached.

Eskom produces approximately 22 million tons of fly ash annually. For the most part this ash is dumped on ash dumps which have to be rehabilitated. The highly acidic nature of ash is well known as is its buffering nature. Research has been undertaken to determine whether fly ash, placed *in-situ* in the mine spoils, would be effective as a treatment and later a controlling barrier to the AMD.

Introduction

Acid Mine Drainage (AMD) or Acid Rock Drainage (ARD) is one of the largest environmental problems facing the mining industry today. AMD is produced as a result of the oxidation of sulphide rich mine tailings and the subsequent contact with water to produce sulphuric acid. The most common sulphate is Fe₂SO₄ (Pyrite). This reaction is usually catalysed by bacteria and proceeds to the following general equation (ENPAR Technologies, 1999).



The one consistent point in the literature is the role of bacteria in the oxidative process (White, 2000). Nordstrom and Southam (1997) have listed 22 species, which are known to be associated with mine waters. The most common of these is *Thiobacillus ferrooxidans* (O'Brien, 2000). This bacterium metabolises inorganic compounds, including sulphides (White, 2000). *T. ferrooxidans* is classified as an acidophilic lithotroph, an acid tolerant microorganism that gains energy from the oxidation of inorganic compounds (Nordstrom and Southam, 1997). It is thus through their natural behavior that these microorganisms catalyse the AMD producing reactions (White, 2000).

The metal load of the leachate varies dependent of the surrounding strata. In some cases the rock may have a buffering effect and the resultant effluent is neutral (O'Brien, 2000). Generally, however, the leachate has a very low pH of approximately 2 or lower and a total dissolved solids of 4000-5000mg/L. In addition, the sulphate concentrations are normally in the thousands of mg/L (Gericke *et al*, 2001).

It is estimated that approximately 54% of rainfall in the Witbank catchment percolates through the mine spoils. This relates to 700 000m³ of polluted water flowing into the Loskop Dam (Bullock and Bell, 1997).

Various methods have been considered to treat this water, ranging from lime neutralisation (Gericke *et al*, 2001) to electrochemical protection (Pulles *et al*, 1996). These forms of treatment are costly and require constant management (Anon, 2000). The water produced after these treatments can only be utilised for irrigation and this only if the heavy metals have been removed sufficiently (Gericke *et al*, 2001).

The 100 million tons of low grade coal burnt in Eskom power stations annually produces approximately 22 million tons of inorganic fly ash (Willis, 1999). This waste creates huge disposal problems and at present is heaped on ash dumps except for a small percentage that is used in the building industry (Reynolds, 1999).

Eskom power stations are generally built near to the colliery supplying the coal and the two waste streams are in close proximity. Fly ash has been used historically as a supplement to backfill to reduce AMD (Proposed ASTM guide, 1999).

Materials and methods

Acid Mine Drainage samples were obtained from a Mpumalanga Mine. The mine collects the toe seep from the coal spoils and treats it with a lime based neutralization. The AMD has a low pH and high sulphates.

Fly ash, was obtained from various power stations. Initially the choice of ash was based on the particle size. It was believed that a coarse ash would allow the AMD to percolate though relatively easily, treating the water, by increasing the pH, converting the sulphates to ettringite or gypsum and subsequently precipitating many of the metals out of solution.

If a finer ash, with high alkalinity was used the precipitants would quickly fill any void spaces and effectively dam the AMD system.

Once the two extremes in terms of particle size had been examined a third ash was tested. This one was chosen due to its believed low CaO content, which theoretically should have given a poorer neutralizing activity. Subsequent analysis of this ash has shown a higher level of alkalinity than the initial two ashes, although a smaller particle size than the fine ash. For the purposes of the paper they will be referred to as ash A (coarse), B (Initial fine) and C (low CaO)

For all the different ashes the protocol was the same. The fly ash was packed into columns of various lengths and settled by means of an orbital shaker. The weight of the column before and after filling was noted to ensure that the test duplicates were exactly the same.

The AMD was gravity feed through all columns simultaneously. In this way a constant head was maintained.

As the water passed out of the ash column, it was collected and analysed for pH, conductivity, sulphates and heavy metals. The analyses were initially conducted daily for two weeks, spreading out to once a week and once every two weeks thereafter.

Once the pH had dropped sufficiently the flow through the columns was stopped and the ash removed. The ash was then sampled from the top, middle and bottom of the extracted column. These samples were analysed by XRF, XRD, IR, Raman and SEM.

Results and conclusions

Table 1 shows the parameters of the initial AMD and Fly ash.

Table 1 Parameters of the AMD and various ashes.

Parameter	Value		
	A	B	C
AMD			
pH	2.88	2.88	2.7
Sulphate (mg/L)	3654	4015	7926
Conductivity (μ S/cm)	0.47	9.7	38.10
Al (mg/L)	33.5	272	470
B (mg/L)	0.06	0.701	<0.03
Ba (mg/L)	0.01	0.172	<0.03
Be (mg/L)	<0.005	<0.005	0.07
Cd (mg/L)	0.04	<0.005	2.0
Co (mg/L)	0.54	<0.005	0.9
Cr (mg/L)	<0.005	1.279	1.0
Cu (mg/L)	0.05	0.532	<0.03
Fe (mg/L)	122	3900	8169
Mn (mg/L)	43	34.97	106
Ni (mg/L)	0.68	0.5	2.0

Pb (mg/L)	0.03	0.039	0.2
Sr (mg/L)	0.71	<0.005	<0.005
Zn (mg/L)	2.8	6.34	16.0
Fly ash Coarse			
pH	11.34	11.50	11.20
Conductivity ($\mu\text{S}/\text{cm}$)	676	0.68	3.88
Alkalinity (mg/L)	150.0	428.4	582.2
Particle size (μm)	114.5	30.95	17.75
Surface area (m^2/g)	0.315	1.000	2.325

The columns were sealed before the AMD was passed into them, in order to withstand the water pressure of the head of water, as the AMD did not pass directly through the ash.

The AMD broke through the 0.25 and 0.5m column of the A ash tests on day 2, while the 1.0m and 1.5m columns broke through on days 3 and 5 respectively. It passed through the 0.25m and 0.5m B ash columns on day 1 and 4 respectively and through the 1.0 and 1.5m columns on day 15. This may be due to the particle size. All the C ash columns allowed AMD passage after day 2.

The various sets of columns were allowed to run until the pH of the leachates fell below 8 or the columns blocked. The 1.5m, A ash columns ran for 273 days, while the B ash columns of the same length blocked after 46 days. The C ash was allowed to run for 151 days.

From the onset of the AMD addition iron deposition was noted on the surface of the ash

The results obtained indicated that the pH of the leachate AMD passing the ash columns was raised to greater than 12. This indicates the buffering ability of all of the fly ashes. The A ash leachate pH began to decrease after day four, with the duplicate columns exhibiting similar trends. The B ash columns maintained their pH above 12 for the duration of the test (46 days). The C ash tests maintained the pH above 12 for 34 days, after which the shorter column pHs dropped sharply. The 1.0 and 1.5m column pHs began to drop after 151 days.

The conductivity (EC) of the A ash effluent decreased from 5-3mS/cm², after 14 days, and remained constant thereafter for 151 days. An initial spike to over 7mS/cm² was noted on day 4. The B ash effluent EC increased 10-12mS/cm² gradually over the first 6 days, whereafter it decreased to below 8mS/cm², for the short columns and below 2mS/cm² for the long columns, over a period of 46 days. The EC of the C ash leachate decreased rapidly from 40mS/cm² to 12mS/cm² on day 2 and thereafter continued to slowly decrease over 151 days to below 5mS/cm².

The initial sulphate concentrations of all the test leachates dropped from 3600, 4000 and 8 000mg/L in the A, B and C ashes respectively. This reduction was quicker the longer the column.

The A ash column leachates all reached their lowest concentrations after 14 days, followed by a gradual increase which was quicker the shorter the columns. All the column leachates appeared to stabilize at a sulphate concentration of approximately 2000mg/L.

The B ash leachate's sulphate concentrations dropped in below 500 mg/L immediately. They remained at this concentration for the duration of the test (46 days). The C ash tests indicated an immediate reduction of sulphate concentrations on day 2, to below 500mg/L from 18 000mg/L. These concentrations were maintained until day 60 for the shortest columns. The long columns showed a slight increase after 136 days.

In general the heavy metals concentrations decreased. Beryllium, Cadmium, Cobalt, Lead and Nickel concentrations were all low and decreased to undetectable levels.

The aluminium concentrations dropped from 33.5 to <1.0mg/L, 272 to <5mg/l and 470 to <0.06mg/L for the A, B and C ashes respectively. This lowered concentration was maintained for the entire duration of the various tests.

The Barium concentrations, for the coarse ash, were fairly stable (approx 0.01mg/l) with the exception of a peak (34mg/L) in concentration noted on day 14. Thereafter the concentrations returned to their initial levels. In the fine ash the concentrations were highly erratic and no conclusive conclusions could be drawn. In the low CaO ash however, the initial concentration (0.03mg/L) was maintained for 5 days after which the concentrations fluctuated wildly before stabilizing after day 55 to approximately 20mg/L and then slowly returning to the original concentrations.

The Boron concentrations for the various tests followed no trend. In the A ash the concentration trends upward, to a maximum of 26mg/L from an initial concentration of 0.06mg/L. The B ash trended upward followed by a slight decrease. In the case of the C ash the concentrations were erratic for the first 51 days after which the concentrations stabilized around 0.2mg/L. These unstable results may be due to the fact that the Boron is initially fused to the fly ash particle during the combustion process, forming borates, which are not detected as Boron. Once the pH is increased the borates are solubilised and the Boron is released.

The Chromium concentrations in all the tests show an initial spike in concentration, followed by a decrease to below detectable limits after 15, 15 and 6 days respectively for the A, B and C ashes.

Copper concentrations in the A ash tests indicate an initial increase (0.05- 14mg/L) followed by an immediate reduction to below 0.25mg/L for the duration of the test. In contrast the B ash tests showed an initial decrease followed by slight increase and the C ash tests were totally erratic until day 51 when they began to stabilize below 0.1mg/L.

Iron concentrations decrease from 122 to 0.01 mg/L; 3900 to <3mg/L and 8169 to <0.005mg/L for the A, B and C ashes respectively. This may be attributed to the formation of Hematite on the top of the columns.

The Manganese results in A, B and C ashes show an immediate decrease in the concentrations from 43, 35 and 106mg/L to below the detection limit of 0.005mg/L.

The Zinc concentrations for all the tests decreased. The A ashes decreased from 2.8, 6.3 and 16mg/L to <0.1mg/L. The time taken for this decrease was different for each test. The A tests took 20 days to reach the low levels, while ashes B and C took 15 and 2 days respectively.

Once the pH of the columns fell below 8.0 the flow was stopped and samples taken from the top, middle and bottom of the column. The various samples of the extracted ash column were submitted for XRF, XRD and Electron Microscopic analysis to determine the change in mineralogy.

The results of the XRF and XRD analyses on the ash samples are shown in Table 2 and 3.

The XRD analyses showed that gypsum (CaSO_4) is being formed at the top of the columns. This may be due to the presence of the sulphuric acid at the top of the column. The H_2SO_4 reacts with the Ca and forms Gypsum.

The XRF analysis showed very slight differences of the columns to the original fly ash. The only marked variation is that of Ca which was high in the fly ash but lower in the column. In addition the Ca concentration increased down the column. This may be due to the formation of gypsum at the top of the column. Not conducted on C ash.

Table 2 XRD analysis of the ash columns (Percentages shown where available).

Sample	A	B	C
Fly ash	Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) Quartz (SiO_2)	Mullite Quartz	Mullite Quartz
A0.25 Top	Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) Hematite (Fe_2O_3) Mullite Quartz	Gypsum 41 Mullite 29 Quartz 17 Amorphous 13	Quartz Mullite Aluminium oxide Gypsum Hematite
B0.25 Top	Gypsum Hematite Mullite Quartz	Gypsum 44 Mullite 29 Quartz 16 Amorphous 11	Quartz Mullite Gypsum Hematite
A0.25 Middle	Gypsum Hematite Mullite Quartz	Mullite 34 Gypsum 33 Quartz 21 Amorphous 12	Quartz Mullite Bassanite
B0.25 Middle	Gypsum Hematite Mullite	Mullite 34 Gypsum 33 Quartz 22	Quartz Mullite

	Quartz	Amorphous 14	
A0.25 Bottom	Gypsum Hematite Mullite Quartz	Mullite 45 Quartz 25 Amorphous 18 Gypsum 12	Quartz Mullite Calcium sulphate hydrate
B0.25 Bottom	Gypsum Hematite Mullite Quartz	Mullite 46 Gypsum 23 Quartz 18 Amorphous 13	Quartz Mullite Corundum
A0.5 Top	Gypsum Hematite Mullite Quartz	Gypsum 36 Mullite 32 Quartz 18 Amorphous 14	Quartz Mullite Gypsum Hematite
B0.5 Top	Gypsum Hematite Mullite Quartz	Mullite 52 Quartz 27 Amorphous 17 Calcite 4	Quartz Mullite Gypsum Maghemite Aluminium Oxide
A0.5 Middle	Gypsum Hematite Mullite Quartz	Mullite 47 Quartz 27 Amorphous 16 Gypsum 7 Calcite 3	Quartz Mullite Bassanite Aluminium oxide
B0.5 Middle	Gypsum Hematite Mullite Quartz	Mullite 52 Quartz 27 Amorphous 17 Calcite 4	Quartz Mullite Silicon oxide Corundum
A0.5 Bottom	Gypsum Hematite Mullite Quartz	Mullite 52 Quartz 27 Amorphous 17 Calcite 4	Quartz Mullite Gypsum Calcium aluminium oxide
B0.5 Bottom	Gypsum Hematite Mullite Quartz	Mullite 52 Quartz 23 Amorphous 21 Calcite 4	Quartz Mullite Gypsum Corundum
Sample	A	B	C
A1.0 Top	Gypsum Hematite Mullite Quartz	Mullite 35 Gypsum 31 Quartz 18 Amorphous 16	Quartz Mullite Gypsum
B1.0 Top	Gypsum Hematite Mullite Quartz	Mullite 52 Quartz 23 Amorphous 21 Calcite 4	Quartz Mullite Gypsum Calcium aluminium oxide
A1.0 Middle	Gypsum Hematite Mullite Quartz	Mullite 45 Quartz 31 Amorphous 19 Calcite 5	Quartz Mullite Gypsum Corundum
B1.0 Middle	Gypsum Hematite	Mullite 48 Quartz 25	Quartz Mullite

	Mullite Quartz	Amorphous 15 Gypsum 8 Calcite 4	Gypsum Corundum
A1.0 Bottom	Gypsum Hematite Mullite Quartz	Mullite 55 Quartz 23 Amorphous 17 Calcite 5	Quartz Mullite
B1.0 Bottom	Gypsum Hematite Mullite Quartz	Mullite 46 Quartz 24 Amorphous 19 Gypsum 7 Calcite 4	Quartz Mullite Gypsum Aluminium oxide
A1.5 Top	Gypsum Hematite Mullite Quartz	Mullite 37 Gypsum 34 Quartz 16 Amorphous 13	Quartz Mullite Gypsum
B1.5 Top	Gypsum Hematite Mullite Quartz	Gypsum 36 Mullite 33 Quartz 17 Amorphous 14	Quartz Mullite Gypsum Aluminium oxide
A1.5 Middle	Gypsum Hematite Mullite Quartz	Mullite 53 Quartz 23 Amorphous 20 Calcite 4	Quartz Mullite Gypsum Corundum
B1.5 Middle	Gypsum Hematite Mullite Quartz	Mullite 51 Quartz 27 Amorphous 18 Calcite 4	Quartz Mullite Bassanite
A1.5 Bottom	Gypsum Hematite Mullite Quartz	Mullite 49 Quartz 21 Amorphous 17 Gypsum 8 Calcite 5	Quartz Mullite Gypsum Corundum
B1.5 Bottom	Gypsum Hematite Mullite Quartz	Mullite 48 Quartz 22 Amorphous 19 Gypsum 8 Calcite 3	Quartz Mullite Weustite

Table 3 XRF analysis of the ash columns.

As h	Column	Position	Combustible material	SiO ₂	AlO ₃	FeO ₃	TiO ₂	P ₂ O ₅	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	MnO
A	Fly ash		0.5	55.3	33.1	3.5	1.7	0.43	4.7	1.5	0.01	0.5	0.5	0.04
	0.25a	Top	3.3	54.8	33.5	3.7	1.7	0.41	3.1	1.2	0.01	0.5	0.5	0.07
		Middle	2.7	52.4	31.6	3.3	1.6	0.41	3.6	2.1	0.01	0.5	1.3	0.05
		Bottom	3.0	53.5	32.4	3.4	1.6	0.45	4.5	1.9	0.01	0.5	1.6	0.05
	0.25b	Top	3.2	51.9	32.4	3.5	1.5	0.42	3.1	1.3	0.01	0.5	1.0	0.07
		Middle	5.6	50.5	31.4	3.3	1.5	0.43	3.6	2.1	0.01	0.5	1.3	0.05
		Bottom	5.6	51.2	31.7	3.2	1.5	0.44	4.4	1.7	0.01	0.5	1.5	0.05
	0.5a	Top	3.2	47.5	33.5	3.1	1.4	0.44	3.3	1.7	0.01	0.5	1.6	0.09
		Middle	3.4	49.4	32.4	3.1	1.5	0.44	3.6	2.2	0.01	0.5	1.5	0.08
		Bottom	3.7	48.6	32.1	3.1	1.5	0.41	3.5	2.1	0.01	0.4	1.3	0.09
	0.5b	Top	6.6	46.3	31.4	2.9	1.4	0.42	3.3	1.9	0.01	0.4	1.5	0.12
		Middle	5.1	48.3	31.9	3.0	1.5	0.43	3.7	2.0	0.01	0.5	1.5	0.06
		Bottom	5.8	47.0	32.0	3.0	1.4	0.42	3.5	2.2	0.01	0.5	1.3	0.08
	1.0a	Top	3.3	48.3	32.8	3.2	1.5	0.44	3.4	2.0	0.01	0.4	1.5	0.08
		Middle	4.8	47.8	32.0	3.0	1.4	0.43	4.1	1.8	0.01	0.5	1.3	0.04
		Bottom	2.6	48.9	33.2	3.2	1.5	0.42	4.3	1.5	0.01	0.5	0.8	0.04
	1.0b	Top	3.6	49.0	32.4	3.1	1.5	0.45	3.8	2.1	0.01	0.5	1.9	0.09
		Middle	3.0	48.3	33.2	3.1	1.5	0.43	3.5	2.3	0.01	0.5	1.3	0.09
		Bottom	3.5	49.4	34.1	3.1	1.5	0.45	4.4	1.8	0.01	0.3	1.4	0.04
	1.5a	Top	2.9	49.9	32.5	3.1	1.5	0.44	3.6	1.9	0.01	0.5	1.5	0.10
		Middle	3.6	49.0	31.8	3.1	1.5	0.41	3.7	1.9	0.01	0.5	1.0	0.07
		Bottom	4.8	48.6	31.4	3.0	1.5	0.42	4.0	1.7	0.01	0.4	1.1	0.05
	1.5b	Top	2.6	49.8	32.6	3.1	1.5	0.44	3.5	1.9	0.01	0.5	1.6	0.11
		Middle	4.4	48.7	31.9	3.0	1.5	0.42	4.2	1.7	0.01	0.5	1.2	0.04
		Bottom	5.3	50.9	31.6	3.1	1.6	0.42	4.2	1.6	0.01	0.6	1.1	0.05
B	0.25a	Top	10.4	36.94	29.75	3.69	1.32	1.28	9.98	0.67	0.89	0.84	14.64	NA
		Middle	5.2	38.21	25.98	10.07	1.27	1.69	8.88	2.04	1.14	0.89	9.83	NA
		Bottom	4.8	41.98	28.48	3.10	1.84	1.37	12.27	3.20	0.91	1.05	5.80	NA

Conclusions

The use of fly ash to treat AMD has been proven effective with fly ash on Mpumalanga AMD. The sulphates and heavy metals are reduced and the pH increased.

References

- ANON, Proposed ASTM standard guide for the use of coal combustion products for surface mine reclamation, American Coal Ash Association, 1999.
- Bullock SET and Bell FG, Environmental Geology, 33
- ENPAR Technologies, Electrochemical Cover to Remediate Acid Mine Drainage, ENPAR Technologies Inc, 449 Laird Road, Unit 12, Guelph, Ontario, Canada, N1G4W1. 1999.
- Evangelou and Zhang
- GAI Consultants, Inc, Fly Ash structural fill handbook, Electric Power Research Institute, EPRI EZ-1281, Palo Alto, CA, Dec 1979.
- Gericke G, Petrik L and White R, Simultaneous Neutralisation of two harmful effluents, fly ash and acid mine drainage, for water beneficiation: A site specific case at Arnot Power Station, Eskom Resources and Strategy, Project Proposal.2002
- Nordstrom DK and Southam G, Geomicrobiology of sulphide mineral oxidation. In: BANFIELD, JF and NEALSON KH (Eds) Geomicrobiology: Interactions Between Microbes and Minerals. Mineralogical Society of America, Washington DC, 361-390, 1997.
- O'Brien RD, The Neutralisation of Acid Mine Drainage by Fly Ash. Unpublished MSc Thesis, University of Cape Town, RSA, 2000.
- Pulles W, Howie D, Otto D and Easton J, A manual on mine water treatment and management practices in South Africa. Appendix Volume 1: Literature Reviews. WRC Report No 527/1/96.
- Reynolds KA, SLASH Field Trials, Research Report RES/RR/99/00054, Eskom Technology Services International, 1999.
- Dr Richard Kruger, New Products Development Manager, Ash Resources, PO Box 3017, Randburg, 2194.
- White RA, Behaviour of the rare earth elements in ochreous mine drainage: a laboratory and field study. Unpublished PhD, University of Wales, Aberystwyth, UK, 2000.
- Willis J, Lectures given as part of the Environmental Geochemistry MSc course, Geological Sciences, University of Cape Town, 1999.