Use of Fly Ash to Treat Acid Mine Drainage Before Use in Backfill Operations

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Abstract

Large quantities of fly ash (FA) are generated annually in South Africa and some of it is used in backfill operations. However, this waste can also be used to treat acid mine drainage (AMD,) another waste stream commonly found in the minerals industry. Particle size distribution (PSD) of FA plays an important role in the AMD treatment quality and viscosity of the residual solids that can be used directly for backfill purposes. In this study, we have investigated the behaviour of two types of FA in treating AMD as well as the rheology of the resulting paste. Small-scale studies were first carried out in the laboratory where the rheology was determined using a rheometer as well as larger-scale pipe tests. Chemistry studies indicated that the higher fines fraction enhances the treatment of AMD by reducing the time taken to reduce the pH to a minimum of 7. However, it was found with the two different types of FA tested, increasing the coarse fraction results in higher viscosity than when the fines fraction is increased. Similar behaviour was found in previous studies but the viscosity increase was attributed to changes in pH. However, this study shows that there may be some truth in the controversial effect of coarse particles on the rheology of suspensions.

1   Introduction

FA is a coal combustion by-product from power stations. It is highly alkaline in nature and is an environmental hazard related to energy generation which has received much attention of late. Only 5% of the FA that is produced in South Africa is gainfully utilised, and the rest is dumped in ash dams and landfills (Eskom, 2001). Poor management of FA causes various environmental problems such as loss of usable land, as well as detrimental effects on plants and soil, air pollution and aesthetics (Carlson and Adriano, 1993). There is mounting pressure on power stations to manage their FA in an effective manner that is beneficial to the environment. FA from South African power stations has been used successfully to treat/neutralise AMD (Gitari et al., 2006). AMD is a consequence of the oxidation of sulfide bearing minerals which are exposed to the environment, mainly by mining and smelting activities. AMD is highly acidic (pH 2-4) and carries a high load of heavy metals and sulphates with it (Razo et al., 2004). The insoluble solid residues (SR) that were obtained as a result of the reaction between FA and AMD proved suitable as a backfill material to stabilise mining activities (Petrik et al., 2006a).

The particle size distribution (PSD) of a particular FA varies with time, depending on the coal burning conditions in the power stations. Such variability in the PSD of FA could influence its capability to neutralise AMD and sequester toxic metals. Moreover, it could also influence the rheological properties of the resultant SR paste. Rheological investigation of SR will elucidate certain critical parameters such as optimum solids to liquid ratio, yield stress, hydraulic gradient, etc. to transport SR to the backfill site. Understanding the rheology of SR is critical to the design and optimisation of the hydraulic transportation system.

Neutralisation experiments were carried out using standard FA and FA altered with respect to its fine and coarse particle content, to understand the effect of PSD on the neutralisation kinetics. The SR recovered after these experiments were investigated for their rheological behaviour and also to understand the influence of the PSD of FA on the rheology of SR, and the results are presented and discussed in this paper.

2   Effect of particle size distribution on the neutralisation capacity of FA

The FA from Arnot power station in South Africa was used for this study. This standard sample of fly ash was altered to increase the volume of fines (>25 μm) and coarse (75-150 μm) fraction before the neutralisation. PSD analysis showed that the FA particle size distribution was < 25 μm (38%), 25-75 μm (42%) and 75-150 μm (14%). The percentage of fine and coarse particles (in the context of this study) could influence the neutralisation capacity of FA. Therefore, the original FA was compared with samples that were prepared by fine or coarse particle addition to double the < 25 μm or the 75-150 μm fractions. AMD from Landau mine was reacted with un-altered (original) FA and two altered FAs that were doubled with respect to the mass % of their fine and coarse fractions. The above FA (both the standard and enriched samples) was reacted with AMD at a ratio of 1:3. The pH and electrical conductivity of each reaction was monitored every half hour until the mixture reached a pH of 7 or greater. The original AMD and process waters recovered from different reactions were analysed for metal and sulphate concentrations using Inductive Couples Plasma Mass Spectrometer (ICP-MS) and Ion Chromatography (IC) respectively. The original FA, two altered FA and solid residues recovered from the reactions were examined for major oxides using x-ray fluorescence (XRF).

2.1   Particle size distribution of FA

Figure 1 shows the particle size distribution obtained using a Malvern 2000 particle sizer and the results are tabulated in Table 1 showing the percentage of fine and coarse particles in each of the FA mixtures prepared. The density of the FA particles was 2200 kg/m^3. The samples are described in terms of the volume percentage of fines as shown in Figure 1.
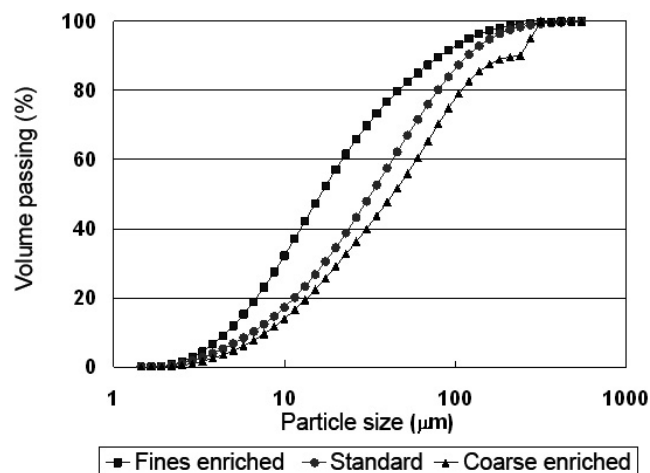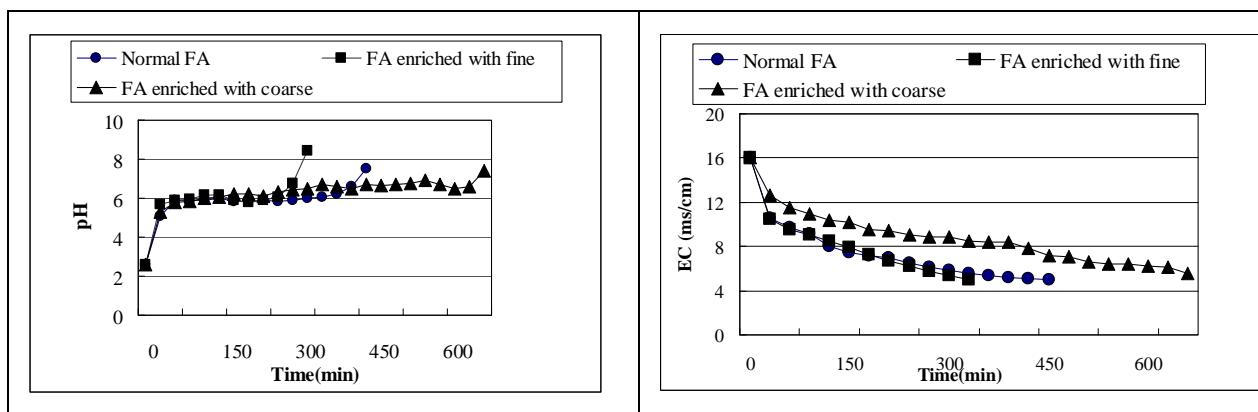

Figure 1   Volume % particle size distribution plot of standard and modified ash

Table 1   Percentage of fine and coarse particles in different FA

FA	% Fines	% Coarse
Normal	38	14
FA enriched with fines	76	5.4
FA enriched with coarse	32	28

2.2   Effect of particle size distribution on electrical conductivity and pH

Figure 2 gives a clear indication of pH and electrical conductivity (EC) trends of different neutralisation reactions. Although no significant difference is observed in the EC values between the three reactions, it is quite apparent that the time of reaction to reach alkaline pH was the fastest when using FA enriched with fines, followed by the reactions that used normal FA and coarse FA.

Figure 2   pH and EC trends of different neutralisation reactions that used different FA

2.3   ICP-MS and XRF results

Table 2 shows the XRF analysis of the unaltered Arnot FA; altered Arnot FA enriched with respect to fine or coarse particles and solid residues recovered from the different neutralisation reactions that used the above mentioned FA. Although the differences are generally low, it is evident from the above table that the mass percentage of most of the major oxides such as Al_2O_3, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO and TiO_2 is more in the FA that is enriched with fine particles when compared to the normal FA and FA enriched with coarse particles. The enrichment of Fe in all the solid residues indicates their efficiency to remove iron from the AMD. It can also be noticed that minor amounts of major oxides such as SiO_2, Al_2O_3 and CaO were also utilised during the neutralisation reactions. The results also indicate that the main mechanisms that control the removal of metals from AMD are ion adsorption, precipitation and co-precipitation. Similar conclusions were made by Komnitas et al., 2004 while cleaning acidic leachates using FA barriers. Table 3 gives a clear picture of the efficiency of each FA to remove toxic elements from AMD. Figure 6 graphically represents and compares the efficiency of different FA to remove toxic elements and sulphate from AMD.

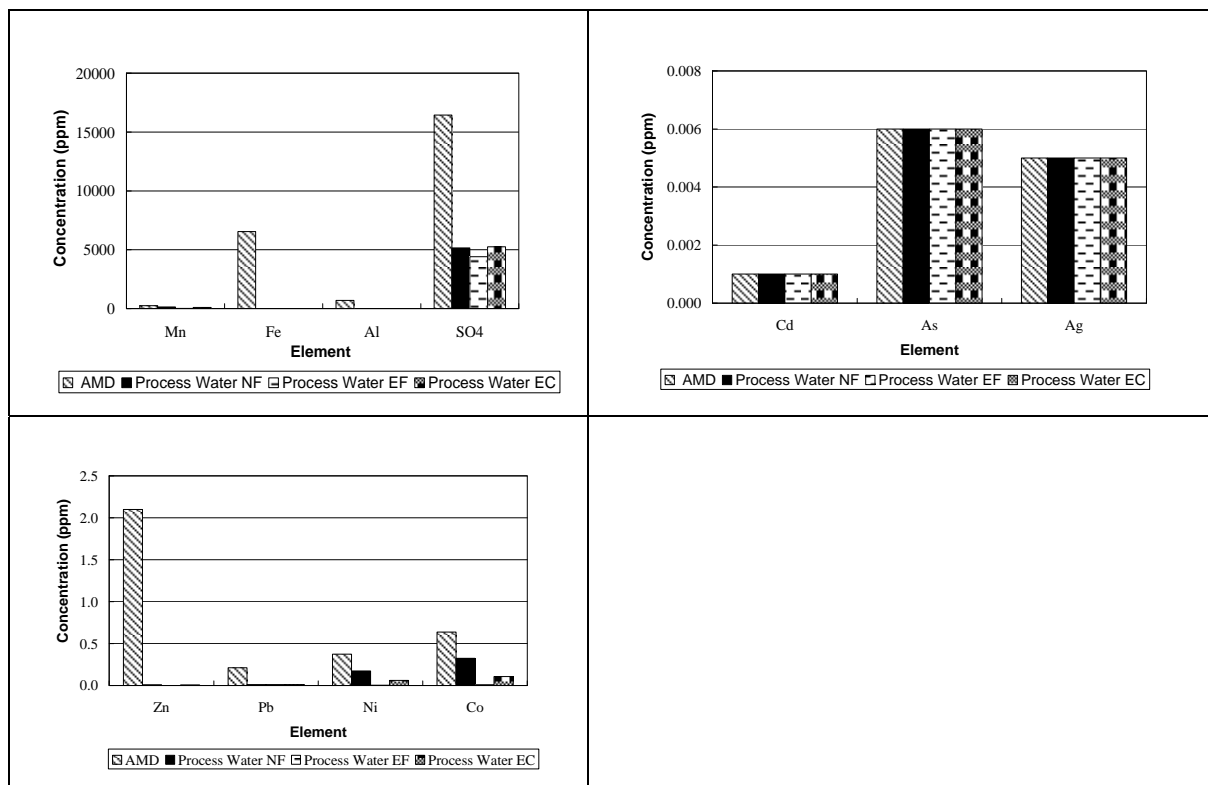**Table 2   XRF analysis for different FA and SR recovered from different reactions**

Oxide (w/w %)	Arnot FA	SR-Arnot FA	Arnot FA+EF	SR-EF	Arnot FA+EC	SR-EC
SiO_2	53.69	49.79	53.81	49.12	53.86	51.25
Al_2O_3	25.55	24.30	27.19	25.18	25.093	24.47
CaO	6.641	6.047	6.682	5.969	6.502	6.197
Cr_2O_3	0.053	0.048	0.063	0.061	0.046	0.045
Fe_2O_3	3.837	5.324	3.947	5.153	3.751	5.252
K_2O	0.587	0.559	0.615	0.555	0.603	0.565
MgO	2.600	2.201	2.668	2.421	2.565	2.271
MnO	0.055	0.11	0.050	0.13	0.057	0.11
NiO	0.010	0.0090	0.011	0.012	0.0080	0.0090
P_2O_5	0.302	0.274	0.360	0.328	0.280	0.281
TiO_2	1.610	1.468	1.742	1.547	1.577	1.506

SR-Arnot FA: Solid residues obtained from the reaction between un-altered FA and AMD; Arnot FA+EF: Altered Arnot FA enriched with fines; SR-EF: Solid residues obtained from the reaction between FA enriched with fines and AMD; Arnot FA+EC: Altered Arnot FA enriched with coarse; SR-EC: Solid residues obtained from the reaction between FA enriched with coarse and AMD.

Table 3   ICP analysis of raw AMD and process waters from different reactions (in mg/L)

Element	Landau AMD	Process water-NF	Process water-EF	Process water-EC
Zn	2.100	0.0080	0.0000	0.0070
Pb	0.21	<0.010	<0.010	<0.010
Ni	0.373	0.173	0.00200	0.0600
Mn	238.8	127.9	14.83	98.74
Fe	6540	0.5940	0.09200	0.1270
Co	0.637	0.324	0.008	0.106
Cd	0.001	0.001	0.001	0.001
As	0.006	0.006	0.006	0.006
Ag	0.005	0.005	0.005	0.005
Al	693	0.100	0.693	0.0310
SO_4^{2-}	16452	5158	4401	5244

- Process water-EF: Water recovered from the neutralisation Reaction with FA enriched with fines
- Process water-EC: Water recovered from the neutralisation Reaction with FA enriched with coarse
- Process water-NF: Water recovered from the neutralisation Reaction with unaltered FA

Figure 3   Toxic element removal efficiencies of different size fractions of FA

The reaction that used FA that was enriched with fines was more efficient in removing elements such as Ni, Mn, Fe and Co and sulphate concentrations from AMD than the FA enriched with coarse size fractions. This can be attributed to the higher surface area of fine particles which has a greater reactive surface. Interestingly, the reaction that used FA that was doubled with respect to the mass % of coarse particles achieved a better removal efficiency compared to the neutralisation reaction that used normal FA. This is

Figure 4   Effect of fines at a volume fraction $\phi = 0.41$
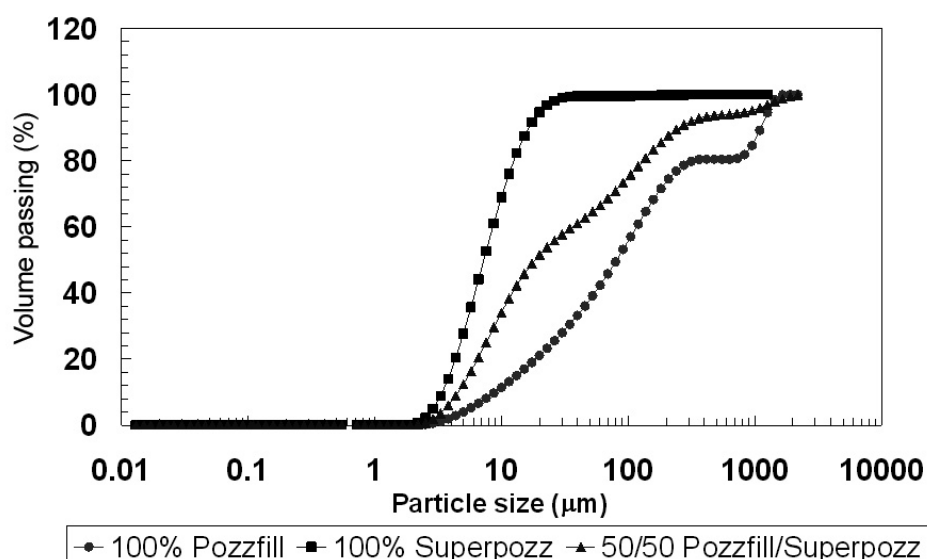
3.2   Pipe test results

To ensure that the results obtained in the rheometer with the coarser slurries was not due to artefacts produced by the rheometer, another series of tests was conducted in a pipe rig. The pipe rig consisted of a positive displacement pump, a mass flow meter, a set of 16, 13 and 9 mm pipes across which the pressure was measured using pressure transducers.

3.3   Ash characteristics

This time, ash from a different power station was used that was fractionised as given in Figure 5. The Pozzfill is the standard ash obtained from the power station with a d_{50} of 64.7 µm. Superpozz consisted mainly of the fines fraction of the Pozzfill. Approximately 98% was smaller than 20 µm and a d_{50} of 6.3 µm. A quantity of Pozzfill and superpozz was mixed to obtain a mixture with a d_{50} of 16 µm. Figure 5 shows the particle size distribution of the ash.

Table 4   Summary of particle size distribution of Letabo ash slurries

Material	d10	d50	d90	< 10 um	< 20 um	<100 um	>20<100 um	>100um
Pozzfill	7.9	64.7	279	15.02	26.1	64.3	38.2	35.7
50/50	3.97	16.0	221.2	45.5	59.3	74.3	15	25.7
Superpozz	2.98	6.33	14.3	81.8	97.9	99.57	1.67	0.43

Figure 5   Particle size distribution of Letabo ash slurries
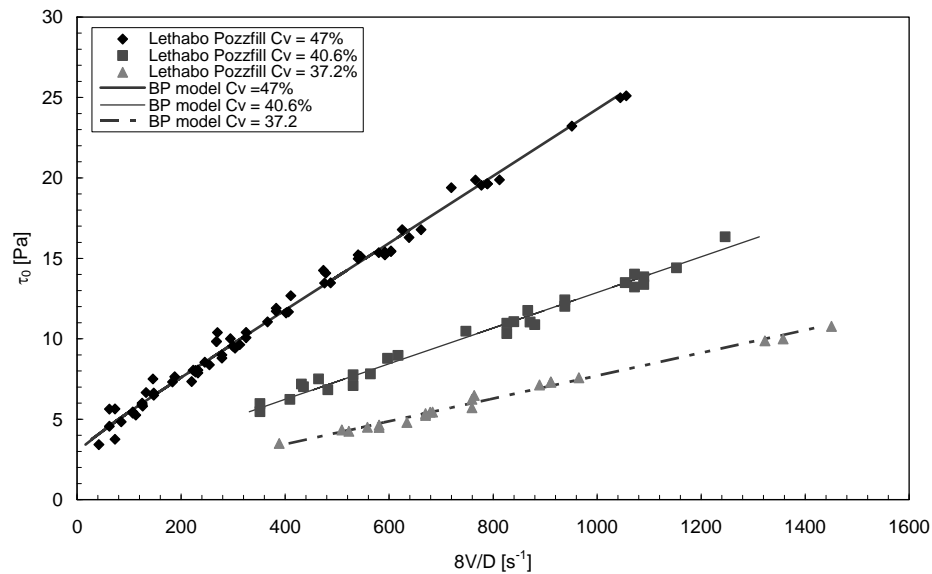
3.4   Lethabo ash

To investigate the effect of particle size distribution on the rheology of the ash, slurries were prepared using the Pozzfill slurry with additional fines fractions from the Superpozz fraction and ultimately testing a 100% Superpozz slurry with almost 98% of particles less than 20 μm. All the ash slurries were tested for three concentrations.

3.5   Pozzfill (100%)

The Pozzfill is the 'standard ash' obtained from the mine. The physical and chemical properties of the Pozzfill ash slurry of three different concentrations are given in Table 5. A maximum solids concentration of 67% by weight was obtained after allowing settling overnight. It displayed Bingham plastic behaviour (Figure 6). The yield stress for the maximum concentration was 2.6 Pa.

Table 5   Lethabo Pozzfill (100%) ash properties

Property	Lethabo Pozzfill 1	Lethabo Pozzfill 2	Lethabo Pozzfill 3
Moisture [%]	33.30	39.02	43.63
Density [kg/m^3]	1.563	1.487	1.446
Cw [%]	66.70	60.98	56.37
Cv [%]	46.92	40.58	37.17
pH	9.120	9.190	8.810
EC [mS/cm]	1.050	1.720	1.990
τ_y [Pa]	2.60	1.36	0.460
K [Pa.s^n]	0.021	0.011	0.0070
n	1.000	1.000	1.000

Figure 6   Pseudo-shear diagram for Lethabo Pozzfill (100%) ash slurries

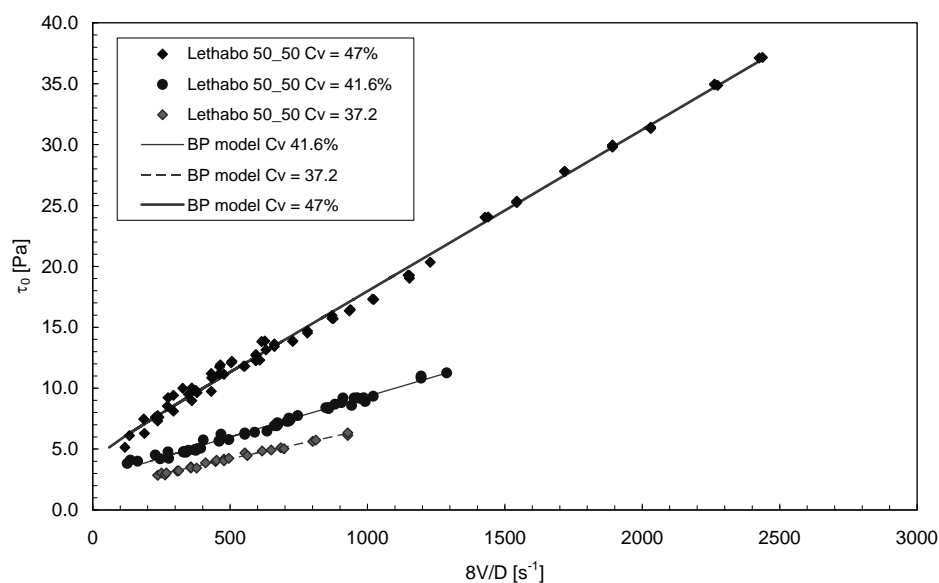## 3.6   Pozzfill/Superpozz 50/50

In this case, the particle size distribution was altered by the addition of Superpozz to double the fraction less than 20 μm. The ash slurry properties are given in Table 6. The actual results obtained were that it was altered from 26 to 59%. The d_{50} was changed to 16 μm. This slurry also displayed Bingham plastic behaviour (Figure 7). The yield stress for the maximum concentration was 3.5 Pa.

Table 6   Lethabo Pozzfill/Superpozz (50/50) ash properties

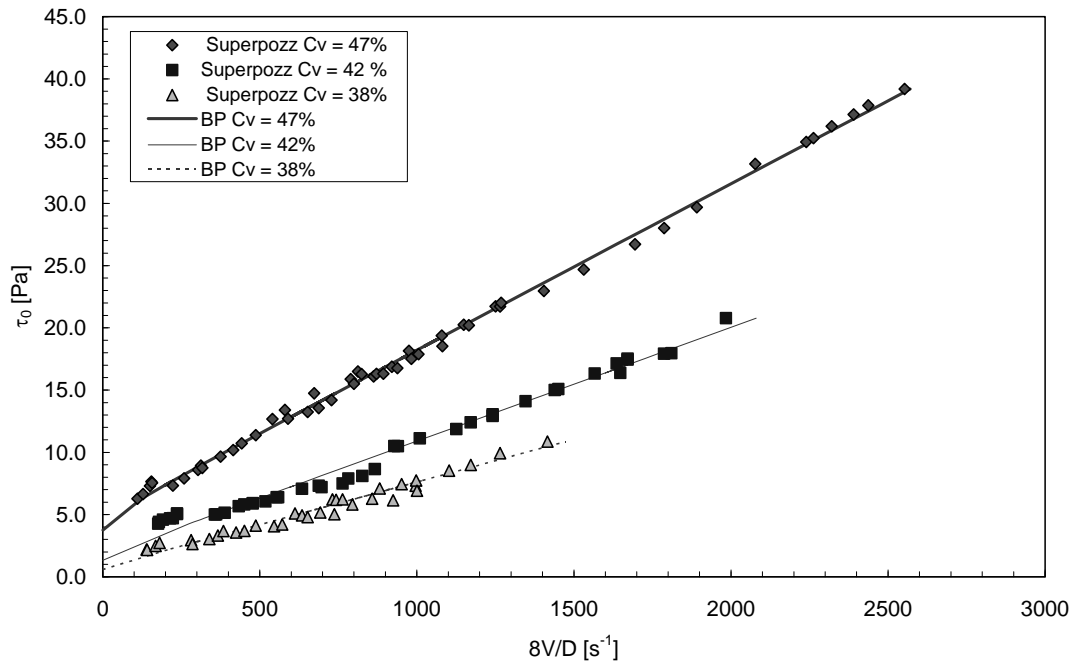| Property	Lethabo 50-50 1	Lethabo 50-50 2	Lethabo 50-50 3
Moisture [%]	35.68	40.15	44.08
Density [kg/m^3]	1.564	1.499	1.453
Cw [%]	64.32	59.86	55.92
Cv [%]	47.00	41.58	37.75
pH	8.340	8.240	8.050
EC [mS/cm]	2.000	3.140	3.290
τ_y [Pa]	3.55	2.03	1.33
K [Pa.s^n]	0.013	0.0070	0.0050
n	1.000	1.000	1.000

Figure 7   Pseudo-shear diagram for Lethabo Pozzfill/Superpozz (50/50) ash slurries

3.7   Superpozz 100%

A 100% Superpozz slurry was tested next. The slurry properties are given in Table 7. In this case, 98% was less than 20 μm. The fines fraction was increased from 59 to 98% compared to the Pozzfill/Superpozz 50/50 mixture. The d_{50} was changed from 65 to 16 μm. In order to change only one parameter at a time, it was attempted to prepare the same concentrations as for the Pozzfill 100% slurry. It displayed Bingham plastic behaviour (Figure 8). The yield stress for the maximum concentration was only 3.5 Pa.

Table 7   Lethabo Superpozz ash properties

Property	Superpozz 1	Superpozz 2	Superpozz 3
Moisture [%]	37.75	42.01	46.03
Density [kg/m^3]	1.566	1.507	1.458
Cw [%]	62.25	57.99	53.97
Cv [%]	47.17	42.25	38.17
pH	8.250	8.050	8.020
EC [mS/cm]	1.930	2.120	2.350
τ_y [Pa]	3.65	1.32	0.572
K [Pa.s^n]	0.013	0.0090	0.0070
n	1.000	1.000	1.000

Figure 8   Pseudo-shear diagram for Lethabo Superpozz (100%) ash slurries

4   Comparison of results and conclusions
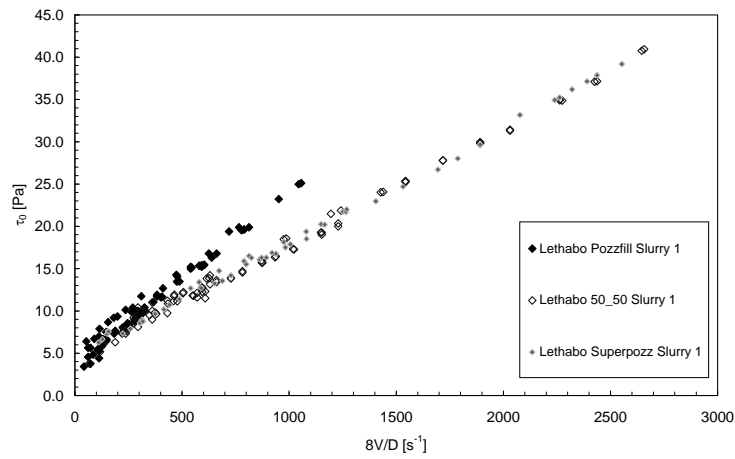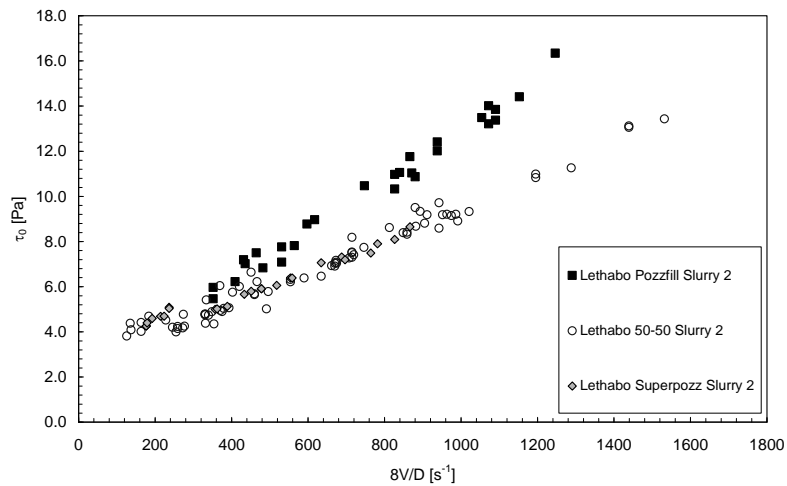
It is expected that the viscosity of slurries will decrease with increasing d_{50} (Heywood et al., 1993). It is also claimed that the finest fraction of the particle size distribution dominates the non-Newtonian behaviour of slurries (Iyer and Stanmore, 2000). Hanks and Hanks (1982) suggested that slurry can be considered to consist of discrete coarse solids suspended in a continuous vehicle of water and fine solids. For FA, the fine fraction is considered to be the fraction less than 10 μm and greater than 10 μm as coarse (Iyer and Stanmore, 1999). They also found that the addition of fines increased the yield stress. This effect was evaluated for the Lethabo ash. The results are given in Figure 9 to 11. For the higher concentrations above $C_v = 40\%$, it is clear that the Pozzfill slurry with the highest d_{50} (65 μm) has higher viscosities that those – the 50/50 mix and Superpozz - with lower d_{50} values (16 and 6 μm respectively). At $C_v < 40\%$, this behaviour is not evident. The Pozzfill slurry with a slightly higher concentration has the same viscosity as the other two with a concentration of 38%. This behaviour is inconsistent with the literature, which suggests that, by increasing the particle size and size distribution, the viscosity will be decreased. This work shows that for the FA tested, this is not so. For ash from two different power stations, with different base rheological behaviours, one Bingham and the other yield pseudoplastic, an increase in the viscosity occurred with the addition of a significant percentage of coarse particles using both rotational and tube viscometry.
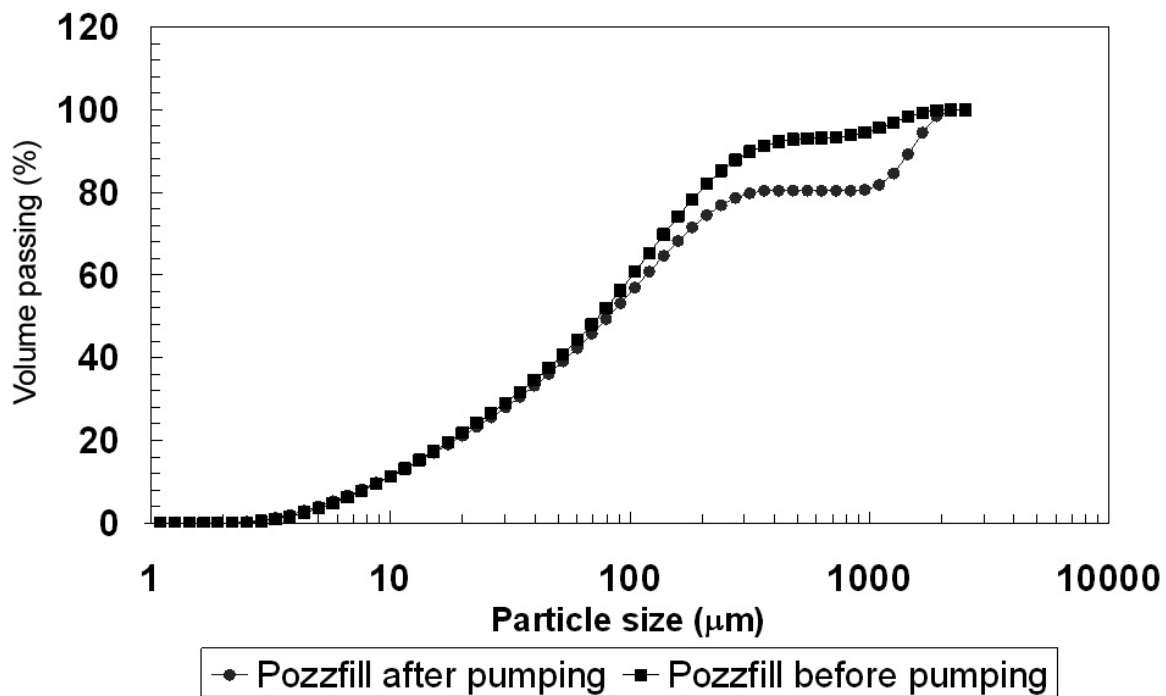
Figure 9   Comparison of Lethabo ash at C_v = 38%

Figure 10   Comparison of Lethabo ash at C_v = 47%

Figure 11   Comparison of Lethabo ash at C_v = 41%

The neutralisation process reduced the pH of the FA slurries to 8 which enabled testing of the rheology of the slurries in a stable chemical environment. This process will be extended to control the pH at any level so that systematic studies of both the effect of chemistry and particle size can be observed. Since this work was done after a neutralisation process, it was assumed that any chemical effects had stabilised, and that the effect of particle size and size distribution was the dominant mechanism. The next series of tests will be conducted preparing slurries at different pH values and this can easily be done by controlling the neutralisation time. Figure 12 shows that although the there was some breakdown of larger particles (larger than 100 μm), there was not a significant increase in the fines fraction that could be the cause for the increase in the viscosity.

Figure 12   Comparison of PSD of Pozzfill slurry before and after pumping

In conclusion, this work shows that the presence of coarser particles at significant concentrations has an adverse effect on the neutralisation process as well as the pipe frictional losses that will be experienced during back fill operations, and needs to be taken into account.

Acknowledgements

References

Bournonville, B. and Nzihou, A. (2002) Rheology of non-Newtonian suspensions of fly ash: effect of concentration, yield stress and hydrodynamic interactions. Powder Technology 128, pp. 148-158.

Carlson, C.L. and Adriano, D.C. (1993) Environmental Impacts of Coal Combustion Residues. J. Environ. Qual. 22, pp. 227-247.

Cyr, M., Legrand, C. and Mouret, M. (2000) Study of shear thickening effect of superplasticizers on the rheological behaviour of cement pastes containing or not mineral additives. Cement and Concrete Research. 30, pp. 1477-1483.

Eskom Annual Report (2001) South Africa.

Gitari, M.W., Petrik, L.F., Etchebers, O., Key, D.L., Iwuoha, E. and Okujeni, C. (2006) Treatment of acid mine drainage with fly ash: removal of major contaminants and trace elements. J Environ Sci Health A Tox Hazard Subst Environ Eng. 41(8), pp. 1729-1747.

Hakan, A., Oren, A.H. and Kaya, A. (2006) Factors effecting adsorption characterstics of Zn+2 on two natural zeolites. Journal of Hazardous Materials. 131, pp. 59-65.

Hanks, R.R. and Hanks, K.W. (1982) A new viscometer for determining the effect of particle size distributions and concentration on slurry rheology, 7th International Technical Conference on Slurry Transportation, Lake Tahoe, NV, USA.

Heywood, N.I., Mehta, K. B. and Poplar, D. (1993) Assessment of flow properties of pulverized fuel ash slurries at high concentration. Proceedings 12th International Conference on Slurry Handling and Pipeline Transport: Hydrotransport 12, 28-30 September 1993, Brugge, Belgium, edited by C.A. Shook. London: Mechanical Engineering Publications.

Iyer, R.S. and Stanmore, B. (1999) The effect of water absorption and the role of fines on the yield stress of dense fly ash slurries. Cement and Concrete Research 29, pp. 765-767.

Iyer, R.S. and Stanmore, B. (2000) The distortion of the diffuse double layer and its effects on flow properties of dense flyash slurries. Colloids and Surfaces A: Physiochemical and Engineering Aspects 166, pp. 133-144.

Komnitsas, K., Bartzas, G. and Paspaliaris, I. (2004). Clean up of acidic leachates using fly ash barriers: Laboratory column studies. Global Nest: The International Journal, 6(1), pp. 81-89.

Olhero, S.M. and Ferreira, J.M. (2004). Influence of particle size distribution on rheology and particle packing of silica-based suspensions. Powder Technology 139, pp. 69-75.

Petrik, L., Gitari, M.W., Vadapalli, V.R.K., Etchebers, O., Ellendt, A., Reynolds, K., Surender, D., Hendricks, N., Klink, M.J., Somerset, V.S., White, R.A., Burgers, C., Key, D.L. and Iwouha, E.I. (2006a). Applications of ash and its derivates: water treatment, mine backfilling, lining and walling. 13th International Conference Ashes from Power Generation, 6-8 November, Krakow, Poland.

Petrik, L., Burgers, C., Gitari, W., Surender, D., Reynolds, K., Ellendt, A., Etchebers, O., Vadapalli, V.R.K., Key, D. and Iwuoha, E. (2006d) Stability and Neutralisation capacity of Potential Mine Backfill Material Formed by Neutralisation of Fly Ash and Acid Mine Drainage. Final Report submitted to Water Research Commission, K5/1458, South Africa.

Razo, I., Carrizales, L., Castro, J., Diaz-Barriga, F. and Monroy, M. (2004) Arsenic and Heavy Metal Pollution of Soil, Water and Sediments in a Semi-Arid Climate Mining Area in Mexico. Water, Soil and Air Pollution, 152, pp. 129-152.