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## Microstructural and Mineralogical Transformation of Hydraulically Disposed Fly Ash—Implications to the Environment

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### ABSTRACT

Increasing amounts of coal are combusted annually to meet the ever-increasing energy demands. The inevitable by-products include fly ash and saline effluents, which require acceptable disposal. The aim of this article is to compare the effect of hydraulic disposal with dry ash dumping. The results indicate that the former carries more environmental benefits based on the physical, chemical, and mineralogical aspects that were investigated.

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### 1. Introduction

Coal is the leading and most reliable source of energy worldwide. During pulverised coal combustion to generate electricity, vast quantities of ash are produced, of which ~75% is fly ash. The properties of fly ash are well understood following decades of study by different researchers. This has resulted in myriad applications of fly ash, which include cement and concrete extension, agriculture, and waste treatment (Kruger, 1997; Rethman et al., 1999; Truter et al., 2001; Reynolds et al., 2002; Alam et al., 2006; Gitari et al., 2008; Nochaiya et al., 2009; Ben-Haha et al., 2010; Meaward et al., 2010). Nevertheless, only a small portion of total fly ash production is utilised, leaving the majority (over 420 Mt/yr) for either storage, on-site disposal, or landfill (Gitari et al., 2009; Ahmaruzzaman, 2010; Green et al., 2012). All three options block off some land use while on-site disposal and landfill are becoming prohibitively expensive (Ciccu et al., 2003; Ahmaruzzaman, 2010).

There are generally two ways in which fly ash is disposed: dry and hydraulic ash disposal. Concurrently, the shortage of water necessitates liquid-effluent reuse wherever possible, especially by industry. However, some of the effluents are no longer suitable for further water recovery and thus require disposal. Some companies, therefore, use these redundant effluents for the hydraulic disposal of fly ash. The present authors have previously reported the potential benefits of using saline effluents in thickened slurries or paste for backfilling purposes (Mahlaba et al., 2011a,c).

Several researchers have investigated the effect of chemical weathering on dumped ashes, mainly from a geochemical point of view, and most concluded that coal ash leaches heavy metals (Sareesh et al., 1998; Zevenbergen et al., 1999; Baba and Usman, 2006; Gitari et al., 2008). Limited literature was found on the characterisation of dumped ash for either understanding its transformation or potential utilisation (Spears and Lee, 2004; Donahoe et al., 2007; Lee et al., 2007; Sarkar et al., 2007; Dey and Gandhi, 2008). Donahoe et al. (2007) and Mahlaba et al. (2011b) also reported promising results of chemical fixation in fly ash when reacted with a suitable liquid solution.

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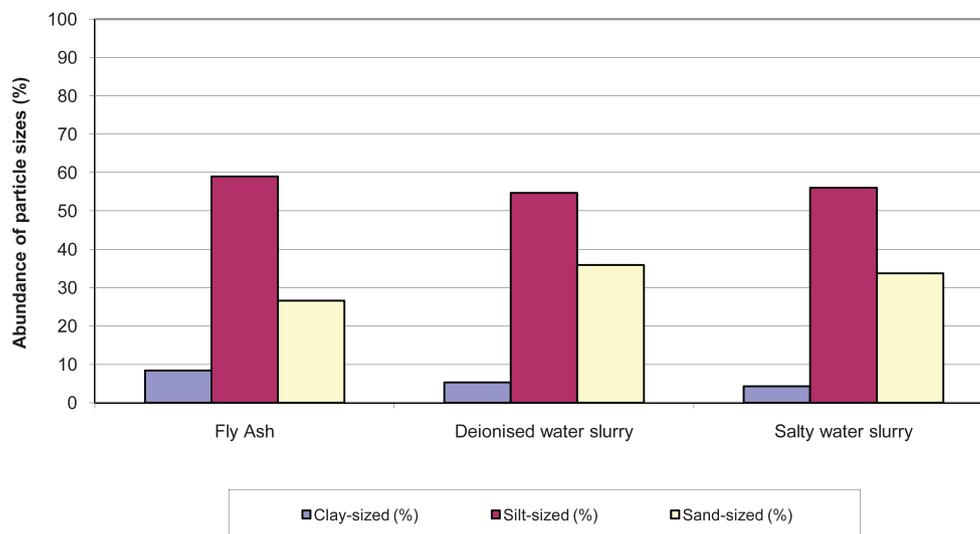


Fig. 1. Illustration of PSD profiles for cured slurries and fly ash.

This article presents the results of the investigation where the influence of different liquid media used for hydraulic ash disposal was studied and compared with dry ash disposal. The findings being reported contribute toward environmentally acceptable management of coal combustion by-products.

## 2. Materials

A class F fly ash was collected from a power station at the Sasol Synfuels plant, Secunda, South Africa, which produces approximately 2.5 Mt/yr of fly ash. Salty water and deionised water represent two scenarios for the liquid carrier medium of fly ash. The salty water is an effluent (reject) produced as waste stream in this facility with the following typical composition:  $\text{Na}^+$  (21,000 mg/L),  $\text{Ca}^{2+}$  (2100 mg/L),  $\text{Mg}^{2+}$  (1550 mg/L),  $\text{Cl}^-$  (34,300 mg/L),  $\text{SO}_4^{2-}$  (15,200 mg/L), and pH 8.8.

High-density slurry was prepared by mixing 68% (m/m) fly ash with 32% (m/m) deionised water and salty water, which improves consolidation and reduces environmental impact (Odler, 2004; Mahlaba et al., 2011a,c). The resultant mixtures were allowed to cure under atmospheric conditions for 1.5 years in a laboratory controlled at a temperature of  $21 \pm 2^\circ\text{C}$ .

To determine the degree and nature of transformation, various analyses were conducted on cured slurries with reference to fresh fly ash as detailed below.

## 3. Methods

Chemical composition and mineralogy were determined using X-ray fluorescence (XRF), X-ray diffraction (XRD), differential scanning calorimetry (DSC), and field emission gun scanning electron microscopy (FEG-SEM). The samples were pressed as briquettes and introduced to the ARL 9400XP+ XRF, and analysis was based on UniQuant software. XRF results were normalised since no loss-on-ignition (LOI) was determined. XRD data were collected using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence and receiving slits with Fe-filtered  $\text{Co-K}\alpha$  radiator. The phases were identified using X'Pert Highscore plus software, and 20% Si (Aldrich 99% pure) was added to samples, which were then milled in a McCrone

micronising mill for the determination of amorphous content. The relative phase amounts were estimated using the Rietveld method (Autoquan Program). Thermal analysis was performed on a Mettler Toledo DSC 822<sup>e</sup> Star<sup>e</sup> System with an FRS5 sensor. The heating rate was  $10^\circ\text{C}/\text{min}$  from  $25^\circ\text{C}$  to  $150^\circ\text{C}$  followed by cooling from  $150^\circ\text{C}$  to  $25^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ . The second heating from  $25^\circ\text{C}$  to  $500^\circ\text{C}$  was again at  $10^\circ\text{C}/\text{min}$  and final cooling was at  $20^\circ\text{C}/\text{min}$ . A Zeiss ULTRA plus 55 FEG-SEM with InLens detector was operated at 1 keV to analyse surface properties on the carbon-coated samples.

Leachability was determined and interpreted according to the South African Standard Leaching Procedure (SASLP), which is adopted from the Australian Standard Leaching Procedure, namely, AS 4439.3-1997 (Crous, 2010). This test is similar to the Toxicity Characterisation Leaching Procedure (TCLP), except for the leachant options and the fact that the particle size of the sample must pass through a 2.4-mm sieve.

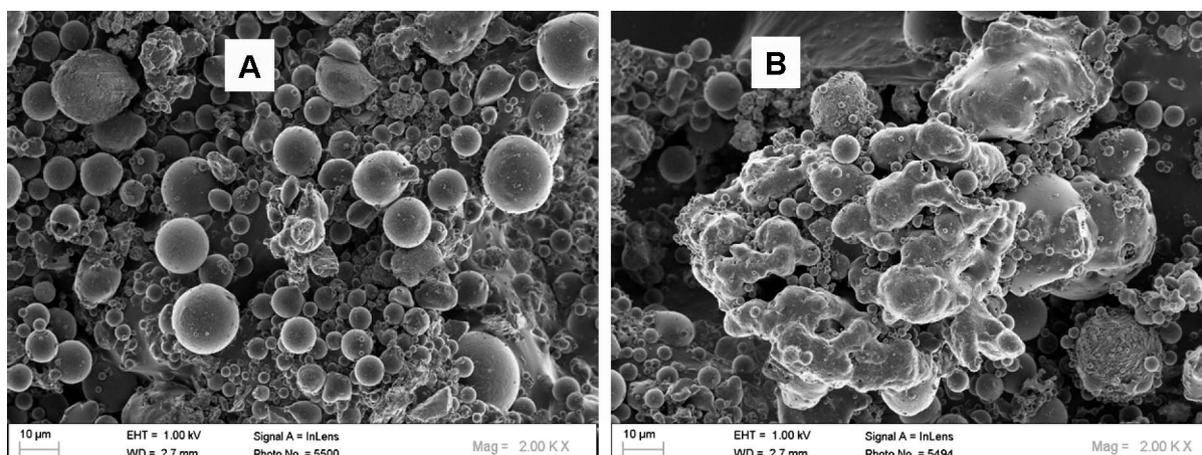
The cementitious wastes, such as fly ash, are leached with water at a solids-to-liquid (S:L) ratio of 1:20 and gently shaken for 18 hours (Halim et al., 2004). The aliquot for metal determination was preserved with nitric acid to pH 3 or lower while the other fraction was used for the remaining analysis including electrical conductivity (EC).

## 4. Results and Discussion

The results of the analyses on chemical, physical, and mineralogical properties as well as leachability are presented next.

### 4.1. Particle size distribution

Particle size distribution (PSD) data were classified into clay-sized, silt-sized, and sand-sized particles according to ASTM D422-63 (ASTM International, 2002). There is no obvious difference between the slurries (hydrated ashes), implying that hydration reactions did not alter the range of particle sizes (Figure 1). These samples in turn have PSD profiles similar to that of fly ash in terms of silt-sized particles, which is the predominant particle range. The content of clay-sized particles in fly ash is about twice that of the cured slurries. Finer particles are richer in glass and are consequently more reactive (Payá et al., 1995; Campbell, 1999).



**Fig. 2.** Morphology of characteristic fly ash particles: spherical (A) and fused (B).

#### 4.2. Particle morphology

Some morphological transformation is to be expected due to the hydration of fly ash and chemical weathering (Zevenbergen et al., 1999; Donahoe, 2004). From Figure 2, it is evident that the majority of fly ash particles are spherical (image A), although some particles are fused (image B).

In contrast, cured slurry prepared with deionised water showed a mixture of unreacted spherical particles reminiscent of fly ash designated in Figure 3C, and the presence of secondary phases depicted in Figure 3D.

The slurry prepared with salty water displayed significant morphological transformation in Figures 4E and 4F, indicative of prominent degree of chemical weathering (Donahoe, 2004).

#### 4.3. Chemical composition

The chemical analysis obtained using XRF is presented in Table 1. Results are similar except for Na, Cl, and S species, which are appreciably higher in the salty water-bearing slurry, and that can be ascribed to the composition of the salty water.

#### 4.4. Mineralogy

##### 4.4.1. X-ray diffraction

The X-ray diffraction (XRD) results (Table 2) demonstrated that salty water-bearing slurry formed new minerals that were not

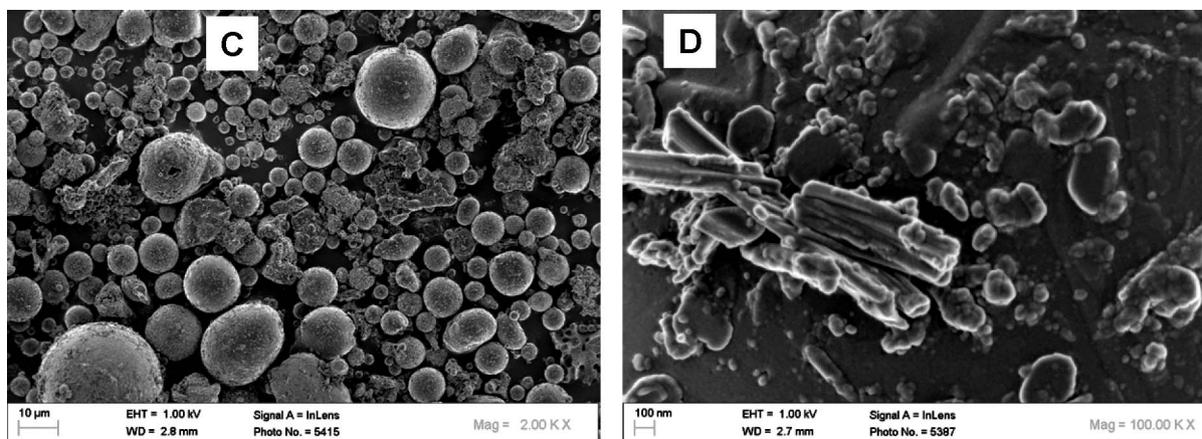
originally present in the fly ash. Deionised water-based slurry, on the other hand, remained very similar to unreacted (fresh) fly ash except for the formation of periclase (MgO) and calcite (CaCO<sub>3</sub>). This observation highlights the importance of chemical constituents in the carrier medium (effluent) in the hydration process. Salty water-bearing slurry formed analcime (NaAlSi<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O), calcite, gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), and halite (NaCl) as hydration products. Analcime is a hydrated sodium aluminosilicate that is very scarce in weathered coal ashes, but it has been identified in some South African coal seams in the Mpumalanga province (Kim and Burley, 1980; Van Alphen, 2005). Its identification provides scientific evidence supporting the immobilisation of sodium in the ash matrix observed previously (Mahlaba, 2011).

Presence of calcite was expected because it forms when CO<sub>2</sub> reacts with lime or hydration products (Borges et al., 2010). Depletion of lime was observed in slurries as chemical weathering occurred (Donahoe, 2004).

##### 4.4.2. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to thermally analyse the samples. The results suggested the presence of calcium silicate hydrate (C-S-H) gel and Friedel's salt from the salty water slurry, while no additional phase was detected in both fly ash and deionised water slurry (Figure 5).

Friedel's salt provides a salt sink for chlorides (Sugiyama et al., 2003; Balonis et al., 2010; Mahlaba et al., 2011b). A C-S-H gel can



**Fig. 3.** Mixed particle morphologies of deionised water-based slurry: spherical (C) and needle-like (D).

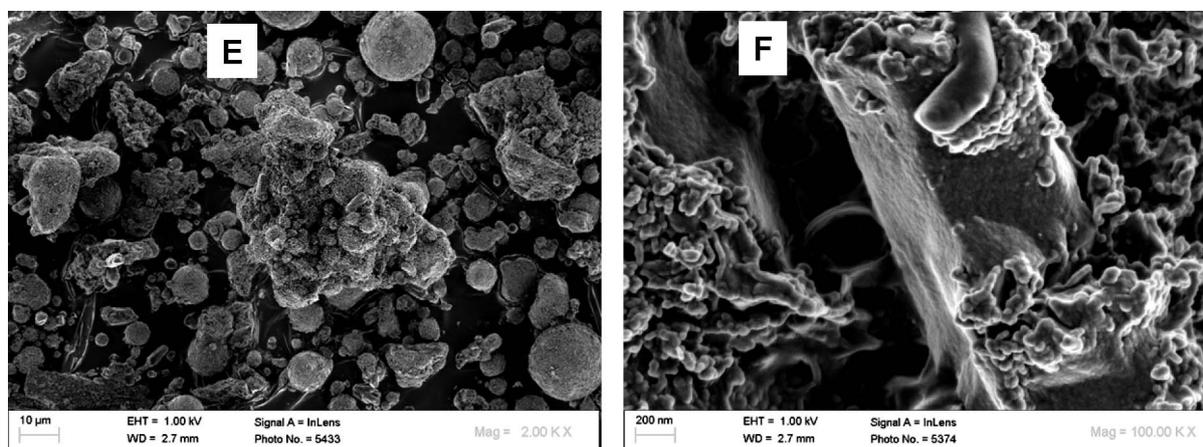


Fig. 4. Significant degree of morphological change showed by salty water-bearing slurry.

adsorb various pollutants, including sulphates, chlorides, and heavy metals (Gougar et al., 1996; Mahlaba, 2011). This reduces leachability and the harm of pollutants to the environment.

#### 4.4.3. Consolidation of mineralogy

There is a significant mineralogical difference between dry and hydraulically disposed fly ash, which, in turn, depends on the water quality. Based on quantitative XRD results, approximately 4% hydration products were formed by deionised water-based slurry, and a 3% reduction in the glassy phase was observed. Concurrently, 10.8% of hydration products were obtained with salty water-bearing slurry, and a 6.6% reduction in the glassy phase content of fly ash was observed. These figures confirm that the glassy phase in fly ash reacts with liquid media during hydration. A good correlation was found between particle morphology and mineralogy. Some differences exist between the phases identified by Mahlaba et al. (2011b) from the characterisation of a 16-year-old fine ash dam and this study, probably due to curing time differences. A factor of environmental importance was the absence of ettringite, which is a salt sink for most salts (Mahlaba et al., 2011b); this was unexpected due to its abundance in cementitious systems (Klemm, 1998; Johnson, 2004; Mahlaba, 2011). The absence of ettringite can be ascribed to either (1) 1.5 years of curing being too short for its formation in this system, (2) its quantities being below the detection limit of the XRD

instrument used, or (3) deficiency of glassy aluminate in fly ash. Donahoe (2004) and Ben-Haha et al. (2010) discuss XRD limitations and alternative methods that can be used to obtain mineralogical information.

#### 4.5. Leaching

The pH and electrical conductivity (EC) of leachates are not regulated in the South African leaching method. Nevertheless, pH and EC are discussed since they indicate the effectiveness of salt immobilisation (Spears and Lee, 2004). The EC indicates the concentration of dissolved components in a leachate without differentiating whether the leachate is toxic. High EC in a sample suggests that more contaminants are leached.

Slurries have pH values that are slightly lower than that of fly ash (Figure 6). The reduction in pH indicates that mixing of fly ash with liquids to make slurries allows mineralogical transformation that consumes lime and alkalis (Zevenbergen et al., 1999; Donahoe, 2004; Spears and Lee, 2004).

Hydraulic disposal of fly ash as slurry reduces the leaching potential remarkably compared with dry fly ash disposal (Figure 7). Fly ash gave an EC value of 8 mS/cm, which is over 300% higher than for the slurries.

The leachate results of the prevalent constituents (Na, Ca, Fe, Al, Si,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$ ) of salty water and fly ash as well as common trace elements are provided in Table 3. Both  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  are below the statutory limits of 5000 mg/L  $\text{Cl}^-$  and 10,000 mg/L  $\text{SO}_4^{2-}$  based on the SASLP. SASLP has four possible categories,

Table 1

Chemical composition of fly ash and cured slurries

Component	Fly ash (%)	Deionised water slurry (%)	Salty water slurry (%)
SiO <sub>2</sub>	47.9	49.7	45.0
TiO <sub>2</sub>	1.6	1.6	1.6
Al <sub>2</sub> O <sub>3</sub>	32.8	33.4	30.6
Fe <sub>2</sub> O <sub>3</sub>	2.1	1.7	2.0
MnO	0.1	0	0
MgO	1.2	1.4	1.7
CaO	9.5	8.4	8.8
Na <sub>2</sub> O	0.7	0.7	3.4
K <sub>2</sub> O	0.9	1.0	1.1
P <sub>2</sub> O <sub>5</sub>	1.1	1.2	0.9
SO <sub>3</sub>	0.5	0.4	1.6
BaO	0.8	0.1	0.5
SrO	0.6	0.2	0.5
Cl (ppm)	7	<5	466

Table 2

XRD results of fly ash and cured slurries

Component	Chemical formula	Fly ash (%)	Deionised water slurry (%)	Salty water slurry (%)
Quartz	SiO <sub>2</sub>	10.24	12.00	10.34
Mullite	Al <sub>6</sub> Si <sub>2</sub> O <sub>13</sub>	20.53	19.66	18.53
Hematite	Fe <sub>2</sub> O <sub>3</sub>	0.68	0.58	0.60
Analcime	NaAlSi <sub>2</sub> O <sub>6</sub> ·H <sub>2</sub> O	–	–	2.37
Lime	CaO	2.22	–	–
Periclase	MgO	–	0.69	0.64
Calcite	CaCO <sub>3</sub>	–	3.54	4.92
Halite	NaCl	–	–	1.24
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	–	–	1.66
Glassy phase	N/A	66.33	63.53	59.70
Total	N/A	100.00	100.00	100.00

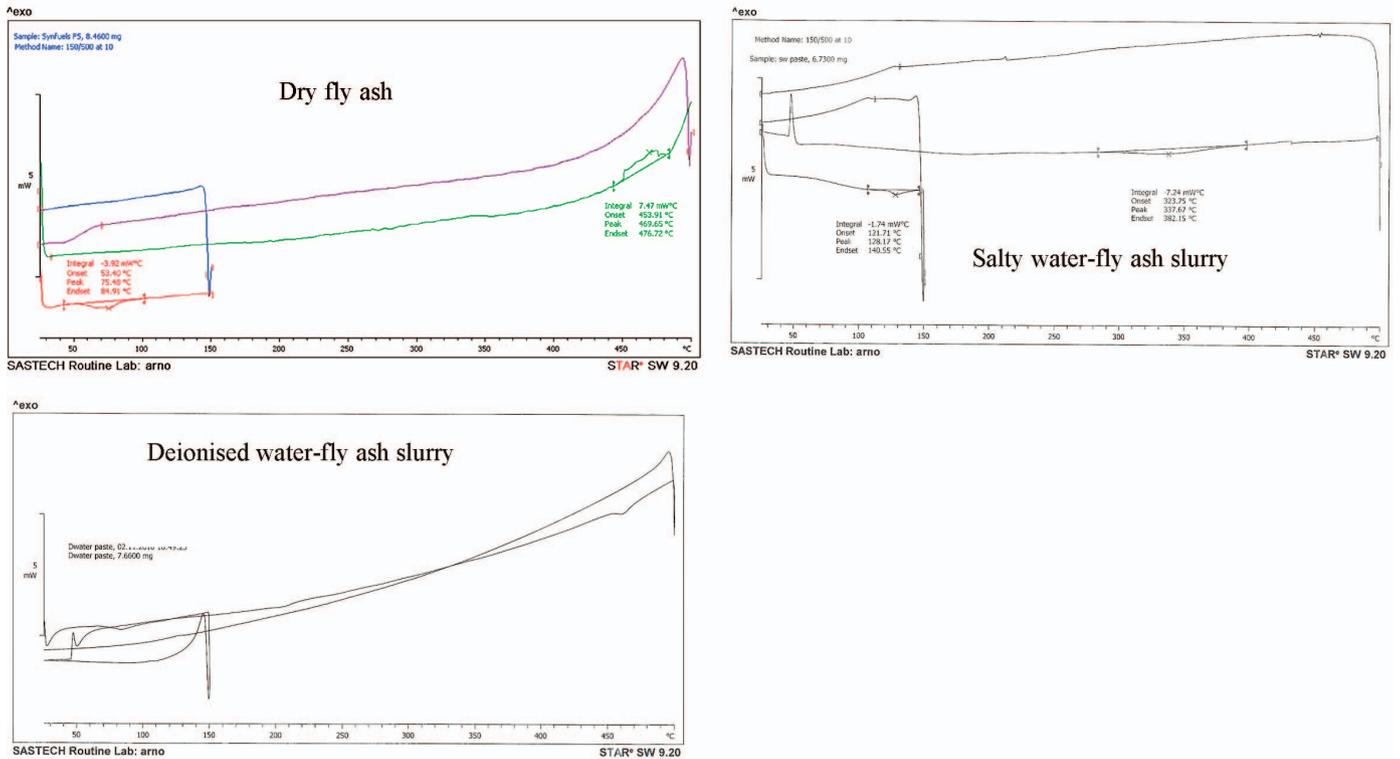


Fig. 5. Illustration of DSC micrographs for cured slurries and dry fly ash.

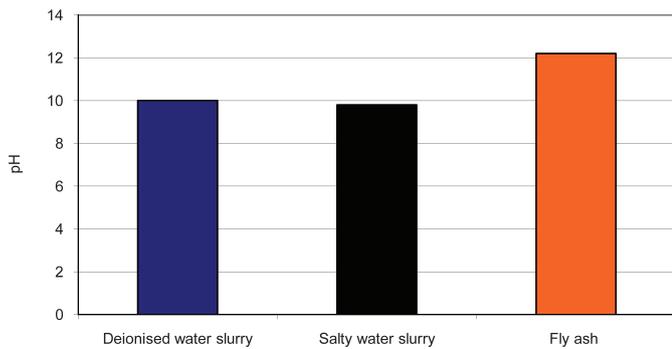


Fig. 6. pH of leachates for 1.5-year-old slurries and fly ash.

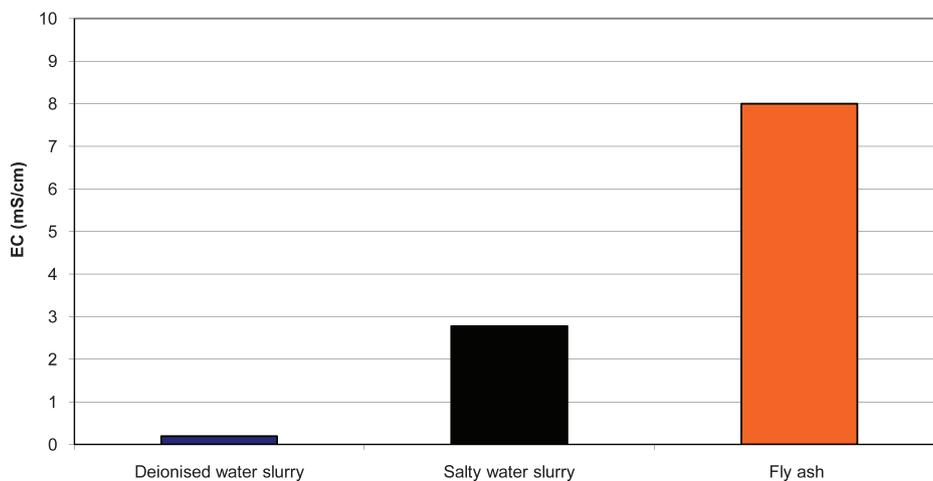


Fig. 7. EC of leachates for 1.5-year-old slurries and fly ash.

which differ in the degree of environmental risk (Crous, 2010). Of those categories, SASLPO provides the threshold values for classifying a material as a low risk. The M-alkalinity (total alkalinity) decreased conspicuously from 1800 in fly ash to approximately 100 mg/L as CaCO<sub>3</sub> in the slurries.

Based on the prevalent components and trace elements of salty water and fly ash, the hydraulic ash disposal method as thick slurry could provide a less harmful solution for fly ash and saline effluents at a single site. Despite promising results reported in this study, the leachability of more trace elements must also be considered before making conclusions on the environmental impact of the two methods.

**Table 3**

Leachate data of predominant components in fly ash and salty water effluent

Component	Deionised water slurry (mg/L)	Salty water slurry (mg/L)	Fly ash (mg/L)	SASLPO <sup>1</sup> (mg/L)
M-alkalinity (mg/L as CaCO <sub>3</sub> )	40	76	1800	–
Cl <sup>-</sup>	<5	466	7	5000
SO <sub>4</sub> <sup>2-</sup>	35	466	101	10,000
Na	4	519	3	–
Al	5.45	6.59	<0.10	–
Si	3.4	3.8	<0.2	–
Fe	<0.025	<0.025	<0.025	–
K	1.6	29	<1	–
Ca	27	21	704	–
B	2.26	4.95	1.12	25
Ba	0.14	<0.1	1.29	35
Sr	3.59	1.75	<0.1	–
Cr	0.48	0.61	0.14	5.0
Hg	<0.1	<0.1	<0.1	0.05
V	0.10	0.23	<0.1	5.0
As	<0.1	<0.1	<0.1	0.5
Se	<0.1	<0.1	<0.1	0.5
Cd	<0.1	<0.1	<0.1	0.25

<sup>1</sup> SASLPO = provides concentration limits for classifying the material as a low risk according to SASLP.

## 5. Conclusions and Recommendations

The findings made in this study can be summarised as follows:

- Hydration of fly ash seems to reduce the content of clay-sized particles while the silt-sized range remains unchanged. Conversely, coarser fractions slightly increase in the slurries.
- A morphological change was observed in some particles of cured slurry, indicative of hydration.
- The prevalent particles in hydrated ash were spherical as found in dry fly ash, suggesting that there could be appreciable reactivity remaining in cured slurries after 1.5 years. Relatively lower pH and depletion of lime would require lime addition for reuse.
- XRD analysis showed the existence of calcite and periclase (~4%) in deionised water-bearing slurry, with ~3% reduction in the amorphous phase content. On the other hand, salty water-bearing slurry formed a total of 10.8% hydration products, namely, analcime, periclase, calcite, gypsum, and halite. A reduction in the amorphous content of 6.6% was achieved.
- Friedel's salt and C-S-H gel were identified in the salty water-bearing slurry using a DSC instrument.
- Leaching showed that hydration reduces the mobility of contaminants, signifying that dry ash dumping may pose more environmental concern than properly designed hydraulic ash disposal using effluents.

This work is important in suggesting the benefits of hydration in the disposal of fly ash. Future research should examine the consequences of hydraulic disposal and ways of implementing an appropriate solution.

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