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Evaluation of workability and strength development of fly ash pastes prepared with industrial brines rich in $SO_4^{=}$ and Cl^- to expand brine utilisation

Jabulani S. Mahlaba [a,b,*], Elsabé P. Kearsley [a], Richard A. Kruger [c], P.C. Pretorius [b]

[a] University of Pretoria, Civil Engineering, Pretoria 0002, South Africa
[b] SASOL Technology Pty (Ltd.), R&D, Environmental Sciences and Engineering, P/Bag x1034, Secunda, South Africa
[c] Richonne Consulting, P.O. Box 742, Somerset Mall, Cape Town 7137, South Africa

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ABSTRACT

Anthropogenic pollution is an unavoidable consequence of both producing energy from coal and desalination of water. Coal ash and brines are partially utilised due to vast volumes and stringent legal environmental requirements. Therefore innovative management for these wastes is essential. This manuscript presents the initial results of research showing that brine chemistry dominates the behaviour of fly ash pastes. The outcome could expand the utilisation of brines in mortars and mass concrete to conserve potable water. The tests involved varying paste consistency and brine characteristics. The results demonstrated that chemical composition of brine plays a more important role than salinity in determining both paste rheology and strength development. An optimum brine salinity range for pastes was obtained with a specific fly ash. The results suggest that an opportunity exists for utilising industrial brines rich in Cl^- and $SO_4^{=}$ as mixing waters in the co-disposal or mine backfilling with fly ash pastes. This would reduce operational costs and liability of energy generation from coal.

1. Introduction

The scarcity of potable water and escalating energy demands are arguably the major contributors to anthropogenic pollution in terms of saline brines and coal fly ashes, respectively. The management of industrial brines resulting from water recovery poses an environmental concern especially inland (Nassar et al., 2008; Souilah et al., 2004; Vedavyasan, 2001); where the option of oceanic disposal is often uneconomical or may have detrimental effects on marine life over the long-term (Souilah et al., 2004; Ahmed et al., 2003; Korngold et al., 2009).

Conventional disposal of brines along with fly ash as a slurry uses copious volumes of water which makes the transportation simple. The excess water required presents a risk of leaching heavy metals and contaminate fresh water resources and soil. Paste disposal increases the ratio of fly ash to water which will conserve water and reduce leaching. The co-disposal of brines with fly ash has been proposed by several researchers as a means to mitigate the environmental footprint (Palarski et al., 2011; Mahlaba et al., 2008; Muntingh et al., 2009; Ilgner, 2002; Mahlaba, 2007). Transportation of fly ash paste to a disposal site is a major challenge to operators and technology suppliers (Steward and Slatter, 2009; Naik et al., 2009; Jewell and Fourie, 2006). This is often due to the sensitivity of rheology to fly ash properties such as particle size distribution, particle morphology, and mineralogy (Boger et al., 2008). The matter is further exacerbated in cases where brines exhibit variable characteristics.

The variability of brines as well as failure to meet legal environmental requirements restrict their potential utilisation in applications such as a carrier medium of solid wastes, crystallisation of marketable salts, and mixing water in concrete. Literature focuses on the deleterious impact of chlorides in reinforced concrete (Balonis et al., 2010; Neithalath and Jain, 2010; Arya et al., 1990; Barberon et al., 2005) and sulphates to explain concrete deterioration (Medveščček et al., 2006; Collepardi, 2003; Klemm, 1998). These anions pose a durability issue if they come from the external environment such as the interaction of concrete with seawater.

Nevertheless, a few researchers have investigated the utilisation of seawater as mixing water in concrete and discovered that resultant concrete was stronger than a control which was prepared with potable water (Borsoi et al., 2009; Akinkurolere et al., 2007). The major components in seawater are chloride, sodium, calcium and sulphate (Taylor and Kuwairi, 1978). The examination of most saline brines also demonstrates that calcium, sodium, sulphates and chlorides are the major constituents (Ahmed et al., 2003; Ravizky and Nadav, 2007; Mooketsi et al., 2007; Koch, 2002). Therefore close similarity exists between saline brines and seawater. Furthermore, the use of Cl-bearing compounds to accelerate strength development and improve mechanical properties is common

* Corresponding author at: SASOL Technology Pty (Ltd.), R&D, Environmental Sciences and Engineering, P/Bag x1034, Secunda, South Africa. Tel.: +27 (0)17 619 2500.
E-mail address: sam.mahlaba@sasol.com (J.S. Mahlaba).

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practice in concrete (Akinkurolere et al., 2007; Taylor and Kuwairi, 1978; Shi, 1996). Preliminary work by Mahlaba (2007) and Mahlaba and Pretorius (2006) indicated that, compared to water, brines have an advantageous effect on the workability of fly ash pastes.

The shortage of potable water and similarity between industrial brines and seawater motivated this research which can hopefully contribute towards sustainability. The primary objective was to investigate the role of brine chemistry on the behaviour of fly ash pastes in order to develop a sound co-disposal method for these wastes. Achieved results could also moot the extension of brine utilisation as mixing water in cementitious materials e.g. concrete and mortars.

State-of-the-art techniques were employed to investigate the effect of brine characteristics on the paste behaviour. This manuscript sets the scene and presents the preliminary results on how brine chemistry influences the workability and strength development of fly ash pastes.

2. Materials

2.1. Brines

Brine A and brine B originate from ion-exchange demineralisation (including regeneration chemicals) and thermal evaporation of water at a South African petrochemical plant, respectively. These industrial brines represent the worst case scenarios of brines from most desalination facilities in terms of chemical composition and salinity and to a certain degree simulate seawater. The chemical composition of these brines and typical seawater are shown in Table 1. These industrial brines were used to study the influence of brines on the rheological and hardening properties of paste. Deionised water was used as a control and also to present the best case scenario of the mixing water for paste preparation without chemical influence. Salinity is expressed in terms of total dissolved solids (TDS) in this manuscript.

2.2. Fly ash

Fly ash was obtained from a South African petrochemical plant which combusts low-grade bituminous coal for the production of steam and electricity to meet its process requirements. The elemental composition of this fly ash is provided in Table 2.

The mineralogical data of the fly ash is presented in Table 3. The presence of lime and high content of glassy phase indicate that this fly ash should be reactive upon contact with water to form materials with cementitious properties (Ward and French, 2006; Kolay and Singh, 2001; Donahoe, 2004). This is referred to as a pozzolanic reaction.

Table 1
Chemical composition of brine A, brine B and seawater (Mahlaba et al., 2011a).

Component	Unit	Brine A	Brine B	Seawater
pH	–	7.4	8.8	8.2
EC	μS/cm	70,400	124,000	–
Ca	mg/L	341	2100	500
Mg	mg/L	238	1550	1550
Na	mg/L	19,227	21,000	12,000
Cl^-	mg/L	14,668	34,300	22,000
$SO_4^=$	mg/L	5931	15,200	3000
TDS	mg/L	44,400	108,000	39,806

Table 2
Elemental composition of fly ash (%).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	SO_3	LOI[a]	Other	Sum
49.7	26.2	2.7	10.5	2.1	0.9	0.7	1.5	0.5	4.1	0.9	99.8

[a] LOI = loss on ignition.

Table 3
The mineralogy of fly ash used in the study (%).

Phase	Chemical formula	Abundance (%)
Mullite	$Al_6Si_2O_{13}$	20.53
Quartz	α-SiO_2	10.24
Hematite	Fe_2O_3	0.68
Lime	CaO	2.22
Glassy phase	N/A	66.33
Total	N/A	100.00

Table 4
The specimen mixes used in the study (% m/m).

Fly ash content (%)	Brine type (%)
62	38
64	36
66	34
68	32
70	30

3. Experimental

Workability and compressive strength are the critical parameters which determine the suitability of cementitious materials for engineering applications. Rheology measurements are commonly used in a variety of applications including construction, waste management and food industry to study the flow behaviour of viscous materials such as pastes (Jewell and Fourie, 2006; Kwak et al., 2005; Huynh et al., 2006; Nguyen and Boger, 1998; Nguyen et al., 2006). Yield stress was used as a measure of the workability of pastes. Yield stress defines the minimum shear stress required to initiate significant flow. A value of 200 Pa was selected as the maximum threshold value of yield stress for paste. This figure coincides with the limit for centrifugal pumps (Boger et al., 2006) falling within a yield stress range of 100–500 Pa suggested by Hallbom (2010) for paste backfill materials.

An unconfined compressive strength of 500 kPa is used in this work as the lower limit of strength applicable to paste. This is higher than the minimum values recommended by other researchers (Potvin et al., 2005; Bouzalakos et al., 2008).

3.1. Yield stress

An Anton Paar rheometer was used to determine yield stress. To improve the reproducibility measurements were taken after 15 min of paste wetting at a low vane speed of 0.5 rpm (Boger et al., 2008).

3.2. Unconfined compressive strength

The paste specimens were wrapped in plastic and allowed to cure for 28 days before determining the unconfined compressive strength (UCS). A pre-load of 10 N was first applied before data