THE INFLUENCE OF BRINE CHEMISTRY ON THE WORKABILITY, STRENGTH DEVELOPMENT AND MINERALOGY OF FLY ASH PASTES

by

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A thesis submitted in fulfilment of the requirements for the degree of

PHILOSOPHIAE DOCTOR (CIVIL)

in the

FACULTY OF ENGINEERING, BUILT ENVIRONMENT AND
INFORMATION TECHNOLOGY

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

PRETORIA

January 2011

THE INFLUENCE OF BRINE CHEMISTRY ON THE WORKABILITY, STRENGTH DEVELOPMENT AND MINERALOGY OF FLY ASH PASTES

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ABSTRACT

The ever-increasing demand for energy due to industrialisation and population growth necessitates the combustion of more coal, which results in enormous fly ash production. The scarcity of potable water as well as high water consumption during mineral and coal processing leads to inevitable saline brine production. Both saline brines and fly ashes pose an environmental threat, where utilisation of fly ashes is negligible. The management of industrial brines is a concern for inland industries because oceanic disposal is uneconomical.

It is therefore imperative to develop an innovative waste disposal practice. Consequently, a research study was initiated to investigate the suitability of brines for mine backfilling as fly ash pastes. The objective was to examine and understand the influence of brine chemistry on the paste behaviour with a specific fly ash. The tests involved varying paste consistency, brine and fly ash characteristics.

A redundant Fine Ash Dam (FAD) was studied to establish what transpires over the long-term when brines interact with fly ash. Results showed that a FAD possesses distinctive chemical, mineralogical and physical properties which reach equilibrium within 4 years. The presence of approximately 60% amorphous content and the intrinsic nature of some properties of weathered ash suggest its viability for utilisation as a pozzolan. Identified secondary phases include ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O$), pyrrhotite ($Fe_7S_8$), analcime ($NaAlSi_2O_6 \cdot H_2O$), C-S-H gel, magnetite (Fe_3O_4), Strätlingite ($Ca_2Al_2SiO_2(OH)_{10}.8H_2O$), Friedel's salt ($Ca_3.Al_2O_6.CaCl_2.10H_2O$), sillimanite ($Al_2SiO_5$), periclase ($MgO$), calcite ($CaCO_3$), gypsum ($CaSO_4.2H_2O$) and halite ($NaCl$).

Experimental results demonstrated that both salinity and chemical composition of brines determine the paste behaviour. Optimum brine salinity exists between 40 - 60 g/l for both synthetic and industrial brines, where synergistic advantage of individual constituents is realised in a typical brine. Conversely, acid solutions showed undesired paste behaviour hence should be excluded in paste preparation.

Chlorides seemed to accelerate the strength development while the use of sulphate solutions to make paste will necessitate stringent monitoring. In contrast, it was discovered that both physical and chemical properties of fly ash, not just alkalinity determine its effectiveness in immobilising prevalent inorganic species from brines in the paste.

This doctoral thesis has demonstrated that co-disposal of brines with fly ash as paste if properly engineered will mitigate environmental pollution.

Keywords: brines, salinity, coal fly ash, fine ash dam, paste, workability, rheology, strength development, chemical weathering, analcime, C-S-H gel, Strätlingite, mineralogy, leaching, immobilisation

ACKNOWLEDGEMENTS

My sincere gratitude goes to my supervisors Prof Elsabé Kearsley and Dr Richard Kruger (editing) for their excellent guidance, dedication, encouragement as well as immense knowledge transfer and coaching/mentoring. The following UP personnel are thanked: Mr Derek Mostert, Mrs Rita Peens, Ms Vanessa Doman (PSD analysis), Mr Andre Botha (FEG SEM analysis) and Mr Jaco Snyman. I can’t forget Ms Wiebke Grote (UP) and Dr Spha Hadebe (SASOL) for assisting with XRD and DSC analyses, respectively. Dr Sabine Verryn (XRD Analytical and Consulting) is thanked for her inputs on the mineralogy (XRD). I am indebted to Dr Henry Matjie for positive builds to my thesis including mineralogy and proof-reading. Mr PC Pretorius is acknowledged for constructive comments on the thesis. Ms Kelly Reynolds (ESKOM) is thanked for kindly supplying the Matimba fly ash.

I also thank SASOL Technology R&D for providing financial support which made this research possible. The management of Environmental Sciences & Engineering is thanked for believing in me, especially Mrs MP Augustyn and Dr TD Phillips. Gratitude is also due to Tracey Laban (language editing), Andisa Mahlamvu (G_s analysis), GE Madlala, CH van de Meeberg, NP Molipane, and David Mogale (NMISA). Dr Sarushen Pillay and Mr Pierre Greeff are thanked for guiding the IP approval process.

Finally, I thank my family for allowing me the time to invest in my PhD studies. Ngibonga kakhulu umndeni wonke wakithi kaMahlaba eSwayimana (KZN), ikakhulukazi umama wami uMaDladla ngegalelo lakhe. *Ngibonga kubaba wami ongasekho uSibango Mahlaba ngokungifisela imfundo ephakeme*. Thanks to my beloved wife Pamella and our children Tumelo, Mandiswa and Sonwabile (Sam junior) for love, support & understanding when I neglected them during tough hours of research and thesis preparation.

Ngiyibekile induku ebandla nani qhubekani lapho ngigcine khona Mabunjwa!!!

“What is impossible to man is possible with God.”

“Success is often achieved by those who don't know that failure is inevitable.” Coco Chanel

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NOMENCLATURE

$[Cl^-]$	Chloride Concentration
$[SO_4^{2-}]$	Sulphate Concentration
ASTM	American Society for Testing and Materials
CAE	Clear Ash Effluent
C-S-H	Calcium Silicate Hydrate
D_{50}	Diameter passed by 50% particles
DSC	Differential Scanning Calorimetry
Dwater	Deionised Water
EC	Electrical Conductivity
FA	Fine Ash
FAD	Fine Ash Dam
FEG SEM	Field Emission Gun Scanning Electron Microscopy
LC	Leachate Concentration
LOI	Loss on Ignition
pH	The degree of acidity or basicity
PSD	Particle Size Distribution
RO	Reverse Osmosis
S/S	Solidification/Stabilisation
S:L	Solid to Liquid ratio
SANS	South African National Standard
SASLP	South African Standard Leaching Procedure
SASTC	South African Standard Total Concentration
SEM	Scanning Electron Microscopy
TDS	Total Dissolved Solids
TGA	Thermal Gravimetric Analysis
UCS	Unconfined Compressive Strength
US EPA	United States Environmental Protection Agency
WFA	Weathered Fine Ash
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

TERMINOLOGY

There are several possible definitions in literature for some of the terms used in this thesis. The author therefore defined those imperative for the understanding of this multidisciplinary research thesis.

Amorphous: It refers to the non-crystalline phase of solid material without a definitive chemical composition according to XRD.

Bleed: It is a supernatant effluent that forms when ash settles, requiring further management

Brine: Is a salinated waste stream which is produced as a by-product during the desalination or demineralisation of water.

Brine chemistry: It refers to the combination of salinity and chemical composition of brine

Clear Ash Effluent: It is the supernatant (water) that segregates from the slurry when fine ash settles in the fine ash dam.

Desalination: Is a process which uses membranes to recover water under pressure.

Fine Ash: A combination of 17% gasification fines (particles < 250 µm) and 83% fly ash.

Fine Ash Dam: A name given to a disposal site of hydraulically deposited fly ash and gasification fines with brines at SASOL Synfuels.

Flowability: See workability.

Fly ash: Is a fine solid by-product collected from the precipitators, resulting from the coal-fired boilers during electricity generation.

Glass: See amorphous.

Hydration: Refers to a process where cement or ash reacts with water in the presence of lime to form mainly calcium silicate and aluminate hydrates. Other researchers refer to hydration as *pozzolanic* or *cementitious reactions*.

Hydration products: See secondary phases.

Immobilisation: It refers to the ability to retain pollutants during leaching conditions.

Leaching: Can be defined as the indication of components which dissolve when a material contacts a liquid medium.

Mineralogy: Refers to the identification of chemical compounds present in a solid material using techniques such as XRD.

Paste: Is a viscous suspension containing more than 62% fly ash that does not segregate nor settle when left idle with the ability to harden as concrete over time.

Pozzolanicity: refers to the tendency of a material to form calcium silicate hydrate and aluminate hydrate when its glassy phase (mainly silica, alumina and free lime) reacts with water.

Regeneration: Is a process of recovering the activity of ion-exchange resins using chemicals for water purification to meet boiler quality.

Regen brine: Is the brine which results during the regeneration of resins.

Retention: See immobilisation.

Rheology: Is the study of the flow and deformation of matter.

Salty water: Salty water is the most diverse brine at Synfuels complex with 10 - 11% dissolved salts.

Settling: Refers to segregation of solids and supernatant in a slurry until no visual changes occur.

Secondary phases: Are the phases which form when chemical weathering occurs between coal combustion by-products including fly ash and water-based solutions.

Slurry: Is a dilute suspension containing < 30% solid content such as fly ash which segregates and solids settle when left idle.

Sustainability: Refers to economic viability and environmental friendliness of a technology.

Tailings: Waste which results from the recovery of precious metals e.g. gold and platinum in the mining industry.

Weathering: Weathering is a process of alteration by mechanical, chemical or biological action which significantly affects the behaviour of a material.

Workability: Is the study of flow characteristics which is synonymous with transportability, pumpability and flowability.

Yield stress: Is the critical shear stress which must be exceeded before irreversible motion is initiated.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The economic development of South Africa will depend upon the country's ability to utilise its natural resources in an efficient and sustainable manner. One of the cornerstones of such progress is the adequate supply of energy in the form of gas, liquid fuels and electricity. The supply of liquid fuels is predominantly provided by imports of crude oil; while power generation is essentially based on domestic coal and minor contribution from nuclear power. The escalation of crude oil prices in the period between 2007 and 2008 had a detrimental effect on South Africa's economic growth. However, the country has significant coal resources which can alleviate the problem if correctly utilised to produce both liquid fuels and electrical energy.

The processing of coal to generate liquid fuels (gasification) and electricity (combustion) must be sustainable i.e. economically viable and environmentally benign. The main challenge with coal processing is the management of the wastes that inevitably arise. Coal is and has been for more than two centuries, the leading inexpensive and most reliable source of energy worldwide but it is also the most polluting of the fossil fuels (Vejahati et al., 2010; Arvelakis and Frandsen, 2010; van Dyk et al., 2006, 2008; Jorgenson et al., 2006; Litto et al., 2007; Auner and Holl, 2006; Younger, 2004). Most power utilities and other coal consuming industries are therefore regarded as major polluters (Zhu et al., 2007; Collot, 2006). The major by-products of both coal gasification and combustion are coal ash, salt-laden wastewaters (brines), as well as gaseous emissions to the atmosphere (Baba et al., 2010; Fu et al., 2010; Bealey et al., 2007; Auner and Holl, 2006; Stergaršek et al., 2008; Younger, 2004).

The Republic of South Africa views availability and access to a clean and healthy environment as a fundamental human right enshrined in the country's constitution. Compliance with this mandate is the legislated responsibility of several governmental departments, namely, Department of Water Affairs (DWA), Department of Environmental Affairs (DEA), and the Department of Mineral Resources (DMR). In an attempt to comply with the country's mandate, a study was initiated to investigate the problem.

This thesis presents the findings of a novel application of known paste technology that could provide a solution for the disposal of saline brines and coal fly/fine ash. The study contributes towards reducing the impact on South Africa's water resources and sustainability of using coal as a primary energy resource.

"If knowledge can create problems, it is not through ignorance that we can solve them." Isaac Asimov (American professor: 1920 - 1992)

1.2 OPERATIONAL CHALLENGES

This investigation is based on the operation of SASOL Synthetic Fuels (Synfuels) plant in Secunda, 120 km south-east of Johannesburg, South Africa. SASOL is an internationally recognised petrochemical company using the Fischer-Tropsch coal gasification process. It was established in South Africa during the 1950's to produce liquid fuels and chemicals from low-grade coal. The Secunda plant is a second plant of SASOL Limited (the first being the Sasolburg plant), which has been operational since 1979, producing over 150 000 barrels of liquid fuels and chemicals per day (Skhonde et al., 2009). SASOL also has power plants to generate its own electricity through coal combustion. The gasification and combustion of approximately 45 million tons of low-grade bituminous coal consequently yields approximately 12 million tons of coal ash per annum.

Figure 1.1 outlines the current waste handling practices at the SASOL Synfuels' facility. A hydraulic ash removal system is used both at the gasification and steam plants. The two streams of coal ash are separated at the ash handling plant, where the bottom ash from the steam plant and coarse gasification ash are mixed, dewatered and conveyed to the ash disposal site. The remaining ash, a combination of 17% gasification fines (particles < 250 µm) and 83% fly ash hereafter referred to as *fine ash* is slurried to the Fine Ash Dams (FADs). In excess of 4 million ton/annum of fine ash is disposed along with over 17 000 m^3/annum of saline brines. The consistency of the slurry is ensured by maintaining a specific gravity of 1.3. Almost 200 of the 320 ton/day of salts on dry basis entering Synfuels plant report to the FADs as brines (Maree, 2008). Approximately 60% of the salts ending up in the FADs originate from regeneration and desalination processes (Pretorius and Nieuwenhuis, 2002; Maree, 2008).

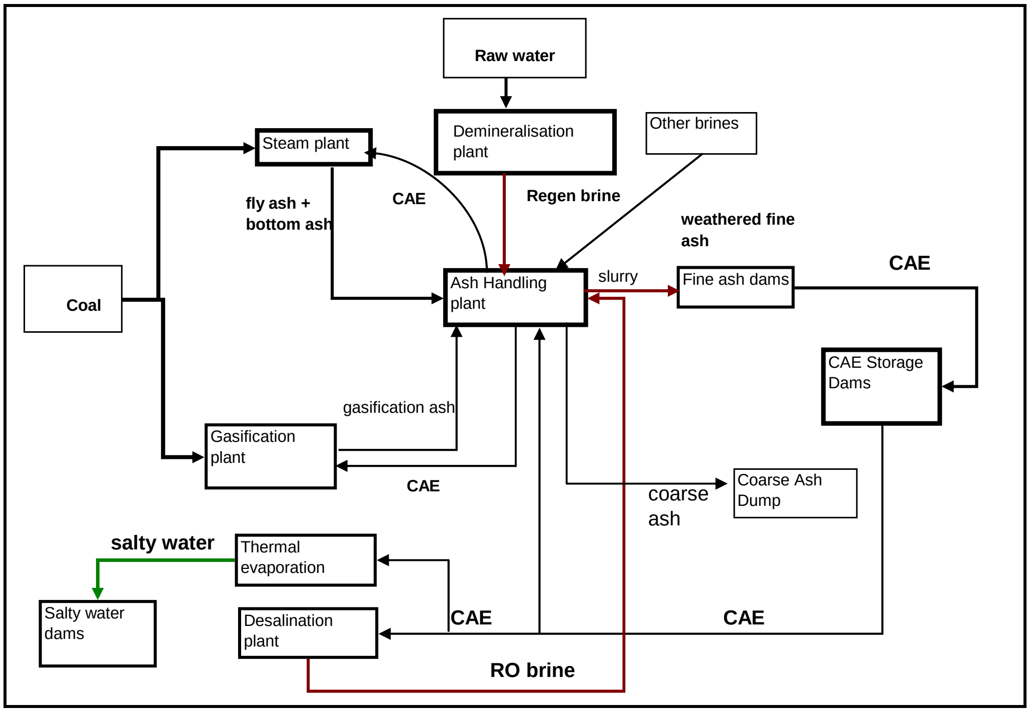

Figure 1.1 Overview of current waste management at Synfuels

Note: CAE = Clear Ash Effluent, RO = Reverse Osmosis

The regeneration of resins at the demineralisation plant uses sulphuric acid (H_2SO_4), sodium hydroxide (NaOH) and sodium chloride (NaCl), and yields regeneration brine hereafter referred to as *regen brine*. The regen brine contributes approximately half of the salts transported to the FADs.

Clear Ash Effluent (CAE) refers to the supernatant that is recovered from the FADs. This is stored in the CAE reticulation water dam before further utilisation either as make-up water for fresh ash collection, thermal evaporation or desalination by Reverse Osmosis (RO). This results in a RO brine effluent. Thermal evaporation of CAE to recover good quality water yields the highly saline brine which is stored at dedicated salty water dams hence its name; *salty water* effluent.

There are other minor streams in terms of salinity such as spent Fe-based catalyst, blow-down of process cooling water, and sludge from flocculation units all of which also end up in the ash disposal system.

During coal gasification and production of liquid fuels the formation of brines is inevitable (Arnal et al., 2005; Bloetscher et al., 2005; Gordon, 2001; Al-Faifi et al., 2010). Further processing and treatment to recover salts from these complex brines through evaporation and crystallisation technologies are limited, due to the inefficiency of the processes available and shortage of markets for the products.

The current practice is considered unsustainable due to both a build up of dissolved salts in the reticulating water (CAE) and the accumulation of large tonnages of fine ash. This has an adverse impact on the quantity and quality of the recovered water from desalination and also poses an adverse environmental legacy. The development of a sustainable waste management process is a pre-requisite for an acceptable coal processing facility.

The fundamental background to this research was obtained using dry fly ash from the power plant at SASOL Synfuels. For operational reasons at SASOL Synfuels, dry fine ash is not available. The latter is a combination of gasification fines and fly ash which results from the thickening of hydraulically removed ashes. The gasification and power generation processes at SASOL Synfuels use the same coal feedstock, which suggests similar chemical compositions in gasification ash and fly ash (Matjie et al., 2008). The mineralogy of gasification ash (Matjie and van Alphen, 2008) is comparable to that of fly ash despite the different burning conditions. *It was therefore justified to use dry fly ash to ascertain the characteristics of pastes where brines are mixed with the coal fly ash*. This would facilitate their co-disposal by either using the paste to backfill voids within the coal mines adjacent to SASOL or placed above ground at suitably designed disposal sites. Furthermore, water saving will be obtained.

Co-disposal in this manner (i.e. mixing brine with fly ash to form paste) would result in a highly alkaline blend which should, theoretically, immobilise any contaminants present in the brines. An alkaline environment lends itself to waste immobilisation as reported by several researchers (Bouzalakos et al., 2008; Kim, 2005; Ciccu et al., 2001; Pandian, 2004; Cohen et al., 2003; Theschamps et al., 2008; Meawad et al., 2010).

Paste disposal is a proven technology developed in the early 1970’s with dominant application in the metallurgical industry for backfilling and surface disposal of sulphide-rich tailings. A good quality paste is known to decrease the mobility of toxic components through a combination of physical and chemical phenomena (Jewell and Fourie, 2006; Stropnik and Južnič, 1988; Joshi et al., 1994; Kaneko et al., 2001; Chindaprasirt et al., 2005). An example of a good paste is depicted in Figure 1.2.

Figure 1.2 Typical consistency of a good paste (Source: unknown)

The region in which a paste rather than a slurry exists varies according to the characteristics of the materials being used. Therefore, paste is ore-related and site specific, and hence there are no universally accepted parameters defining a paste. Figure 1.3 provides, an indicative way of describing a region in which paste exists in terms of solids concentration (Kwak et al., 2005; Kesimal et al., 2005; Jewell and Fourie, 2006). The transition from slurry to paste occurs as water content decreases.

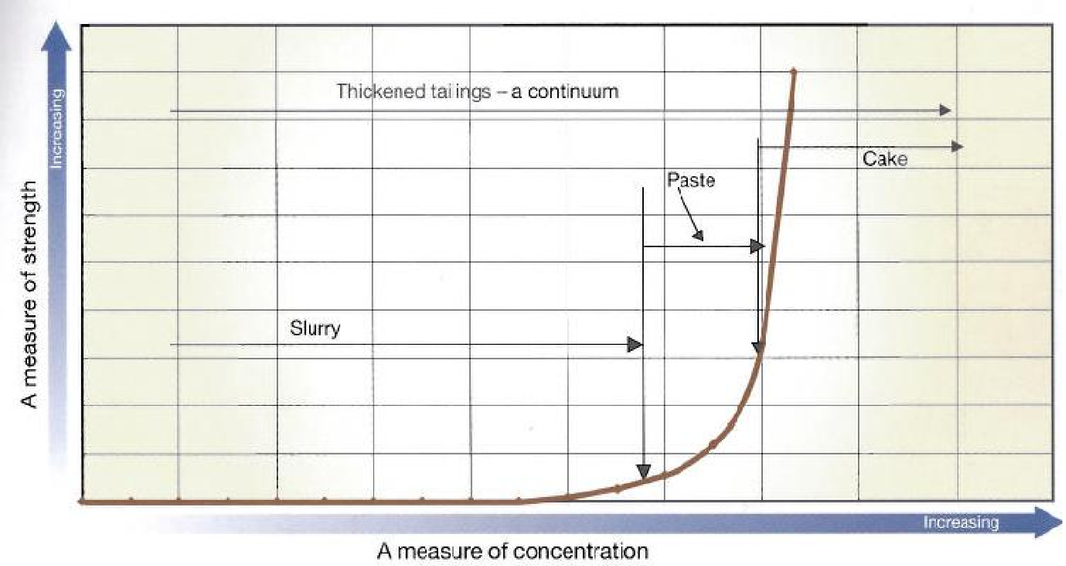

Figure 1.3 Graphical representation of solids concentration for a paste (Jewell and Fourie, 2006)

No legislative guidelines in terms of physical parameters could be found from the South African governmental agencies on the minimum requirements for FADs and paste facilities.

The United States Environmental Protection Agency (US EPA) (1989) recommends that stabilised/solidified waste should have a hydraulic conductivity that is at least two orders of magnitude lower than the surrounding land (Paria and Yuet, 2006; Asavapisit and Ruengrit, 2005). The difference in hydraulic conductivity will minimise the infiltration of water into the stabilised waste and hence reduce the risks of leaching.

From the aspect of stability, there is no consensus on the minimum compressive strength for paste backfill. An Unconfined Compressive Strength (UCS) of 500 kPa is used in this work as the lower limit of strength applicable to paste, which is higher than the minimum UCS values recommended by other researchers (Potvin et al., 2005; Laugesen and Erickson, 2006; Bouzalakos et al., 2008). The yield stress of a typical paste is approximately 200 Pa (Boger et al., 2006; Hallbom, 2010). The design and stability of an impoundment has direct cost implications in terms of pump sizes and energy requirements. Some of the above-mentioned parameters were used in the current study to define a desired paste quality in addition to leachability.

“Engineering is the art of modelling materials we do not wholly understand, into shapes we cannot precisely analyse so as to withstand forces we cannot properly assess, in such a way that the public has no reason to suspect the extent of our ignorance.” A R Dykes

1.3 OBJECTIVES

The principal objective of the study is to investigate and understand the chemical characteristics of brines which control the observed behaviour of fly ash pastes. The relevance of undertaking such a study is to provide a solution to SASOL’s problem of disposing saline brines and fly ash in a sustainable manner using paste technology. The implementation of paste disposal will mitigate the environmental impact associated with the production of synthetic fuels, chemicals as well as electricity from coal. The clear conclusions and recommendations made also provide a measurable contribution to the advancement of engineering science.

1.4 HYPOTHESIS

The author believes that paste technology can be developed to immobilise contaminants present in saline brines from SASOL Synfuels when these are mixed with the alkaline fly ash. The hypothesis is based on the knowledge that the hydration reactions of coal fly ashes are similar to those undergone by cement (Bouzalakos et al., 2008; Bin-Shafique et al., 2002; Joshi et al., 1994; Tishmack et al., 2001; McMurphy et al., 1996; Baltakys et al., 2007; Krolo et al., 2003; Pacewska et al., 2006). These are known to immobilise several toxic species including any heavy metals present. It is postulated that the use of brines does not exacerbate the leaching characteristics of the stabilised waste.

1.5 SCOPE OF RESEARCH

To restrict variability within certain boundaries, the research was limited to materials from the SASOL Synfuels plant at Secunda. The brines, fly ash, and samples drilled from the FAD were investigated. In addition fly ash from Matimba power station (ESKOM) was used to compare the influence of fly ash on paste. This would ensure that the effect of variable consistencies in the brines and differences in fly ash are taken into consideration.

Measurement of workability, strength development, and other properties (Particle Size Distribution, pore water quality, moisture content, and specific gravity) in conjunction with Scanning Electron Microscopy, X-ray Fluorescence, X-ray Diffraction, and Differential Scanning Calorimetry analyses were used to characterise the materials (fly ashes, pastes, drilled samples). Leach tests were carried out to assess the chemical behaviour of these materials. The research was principally based on laboratory tests.

The following tasks were conducted to investigate the technical feasibility of co-disposing brines with fly ash:

- Critical review of literature and standard procedures to provide the basic information.
- Samples drilled at various locations within a redundant FAD were used to establish long-term weathering patterns when brines interact with fine ash.
- Two industrial brines (regen brine and salty water) were sampled at the Secunda site. These were used to determine the chemical composition of brines that can typically arise in the process of production of liquid fuels from coal.
- Representative samples of fly ashes from two power stations (Synfuels and Matimba) using different coal sources in South Africa were collected.

- Both synthetic and industrial brines were used to investigate the influence of brine chemistry on paste characteristics.

The study does not include the following:

- The effect of gasification fine ash on the paste behaviour.
- Effect of predominant brine constituents on paste mineralogy.
- Leaching behaviour of toxic and trace elements.
- Deterioration of paste due to chemical attack.

1.6 METHODOLOGY

The application of paste technology to immobilise major components present in the brines is considered novel. Hence a multidisciplinary approach was adopted to investigate the characteristics of the paste and the ability of fly ash to provide a suitable chemical environment for realising the objective. The tested hypothesis states that ***any alkaline fly ash can immobilise saline brines where resultant paste properties are determined by the predominant brine components; and the mineralogy of the paste resembles that of a Weathered Fine Ash***. The following approach was used to validate the hypotheses:

- Identify the various methods used in paste research, select and test those pertinent to this investigation.
- Establish the effect of any of the predominant brine components (Ca^{2+}, Na^{+}, Cl^{-} and SO_4^{2-}) on paste behaviour and develop a simplified brine model to predict the influence.
- Investigate the influence of both brine and fly ash composition on the paste properties including workability and strength development.
- Establish which secondary phases were present in the samples drilled from the existing ash slurry disposal facility, and compare these with those found in pastes.
- Get an insight to the relevant hydration kinetics.

1.6 STRUCTURE OF THE THESIS

Chapter 1

The problem statement for this investigation is introduced.

Chapter 2

Literature review on brines and coal fly ashes with their management challenges is presented. Case studies of the proposed disposal solution are summarised.

Chapter 3

The experimental procedures including sampling strategy and preliminary workability testing are presented.

Chapter 4

Presents the drilling and detailed characterisation of Weathered Fine Ash from a disused Fine Ash Dam; and the effect of curing time is discussed.

Chapter 5

Provides the analysis and discussion of results from the laboratory simulations of paste behaviour using both industrial and synthetic materials.

Chapter 6

Compares the slurry disposal with paste placement and indicates whether the latter will provide a more environmentally acceptable solution.

Chapter 7

Summarises the principal findings of the work which answer the research questions and recommends future work that should emanate from this PhD thesis.

CHAPTER 2

LITERATURE REVIEW AND HYPOTHESIS

2.1 INTRODUCTION

The purpose of this Chapter is to review the generation of salt-laden wastewaters (brines) and coal fly ash from both the process and environmental impact viewpoints. The traditional management practices and disposal methods for these wastes are discussed.

"Discovery consists of seeing what everybody has seen and thinking what nobody has thought."
Albert Szent-Gorgyi (Hungarian biochemist: 1893 – 1986)

A potential solution to the problems presented is proposed. The hydration of cement and weathering of disposed fly ash are used to explain the alteration in the physical, chemical and mineralogical characteristics of fly ash after interaction with the brines.

2.2 BRINE

Fresh water sources are increasingly becoming depleted owing to the current industrial development, population and economic growth, agriculture and climatic conditions (Yidana et al., 2008; Barwani and Purnama, 2008; Haldenwang, 2005; Hartter and Boston, 2007; Bhandari and Grant, 2007). This is exacerbated by the intensive water requirements of the mineral processing and coal consuming industry in South Africa. The legislative requirements have consequently become more stringent towards raw water intake; hence a concerted effort is required to reuse effluents (Madwar and Tarazi, 2002; Schutte et al., 1987).

It is imperative for the industries to save water and reduce preventable losses (Aqil et al., 2007; Gemitzi et al., 2007) as well as maximise the reuse of effluents (Gordon, 2001; McPhail et al., 2004; Glater and Cohen, 2003; Lynch et al., 2005; Svensson, 2005; Ahmed et al., 2003). Effluent reuse is conventionally achieved through the utilisation of desalination and ion-exchange demineralisation technologies (Al-Kudsi and Waring, 2000; Gordon, 2001; Glater and Cohen, 2003; Walton et al., 1999; Lynch et al., 2005; Downward and Taylor, 2007; Souilah et al., 2004; Collares-Pareira et al., 2003; Mooketsi et al., 2007; Madwar and Tarazi, 2002; Schutte et al., 1987).

Examination of most saline brines demonstrates that calcium, sodium, sulphates and chlorides (Ahmed et al., 2003; Ravizky and Nadav, 2007; Mooketsi et al., 2007; Koch, 2002) are the major constituents. The composition of many of the brines resembles that of seawater. As a matter of fact, seawater desalination to recover potable water is ubiquitously practised at coastal facilities (Voutchkov, 2010; Del Bene et al., 1994; Ravizky and Nadav, 2007).

The necessity to dispose desalination brines resulting from water purification poses environmental concern especially inland, where the option of oceanic disposal is uneconomical due to the distance and maintenance costs (Zodi et al., 2010; Nassar et al., 2008; Swift and Becerra, 2002; Arnal et al., 2005; Khoury et al., 2004). Moreover, oceanic disposal may have detrimental effects on marine life over the long-term (Haley et al., 2008; Ahmed et al., 2003; Nassar et al., 2008; Korngold et al., 2009; Fernández-Torquemada et al., 2005).

There are several options for brine disposal and/or management as thoroughly discussed (Glater and Cohen, 2003; Smith, 1990; Korngold et al., 2009; Swanepoel, 2001). These include solar ponds, crystallisation of salts, irrigation of crops and deep well injection. The disadvantage of solar ponds includes large land requirement, regular removal of precipitated salts and dependence on climate. Crystallisation of salts is usually limited in the market and variability of the brine quality upsets the crystallisation process. Crop irrigation and deep well injection are opportunistic rather than generic solutions.

None of these brine management options can address the problems of the SASOL Synfuels complex being investigated in this thesis. Deep well injection is undesirable because SASOL Synfuels plant is located on the water divide of the Vaal and Olifant rivers. The high salinity of the brine prevents any possibility of crop irrigation.

2.3 FLY ASH

Coal is the primary and reliable source of energy which is readily available at a low cost, more so because environmental impacts are not properly cost. Most coal consumers in South Africa use low-grade coal either as a source of electrical energy or for the production of liquid fuels and chemicals.

The chemical composition and mineralogy of South African bituminous coals were studied by a few researchers (van Dyk et al., 2006; Moitsheki et al., 2010; Matjie et al., 2008). Matjie et al. (2006) and Van Alphen (2005) report that bituminous coal has kaolinite ($Al_2Si_2O_5(OH)_4$) and quartz (SiO_2) as the major minerals while minor minerals are calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and pyrite (FeS_2). According to Glasser (2004) quartz, feldspars ($(K,Na)AlSi_3O_8$) and clay minerals are also typical constituents of coal.

Kaolinite is the most abundant clay mineral (Glasser, 2004; Van Alphen, 2005) which during combustion converts to metakaolin (dehydroxylated phase) and eventually transforms to mullite ($Al_6Si_2O_{13}$). Mullite can be regarded as a characteristic mineral of South African fly ash according to Kruger (2010). During combustion calcite and dolomite alter into lime (CaO) and a mixture of lime and periclase (MgO), respectively with the liberation of carbon dioxide. Concurrently, pyrite or its polymorph marcasite is oxidised to form hematite (Fe_2O_3) and/or magnetite (Fe_3O_4) in fly ash (Tishmack and Burns, 2004; Fan et al., 2005). Van Alphen (2005) in his PhD thesis provides a detailed description of the mineralogical transformation occurring during the combustion of pulverised South African coals in a power utility boiler.

2.3.1 Formation of Fly Ash

There are two major technologies that can be used to combust coal, namely, fluidised bed combustion (FBC) and pulverised coal combustion (PCC). The principal difference between FBC and PCC technologies lies in the temperature and residence time of coal in the combustion chamber. The former operates at temperatures between 800 and 900 ºC in the presence of an absorbent such as limestone to capture over 90% of sulphur (Haynes, 2009). This temperature range is below the fusion temperature for most silicate minerals hence FBC fly ash contains a high concentration of crystalline phases, iron oxide and anhydrite (Haynes, 2009; Tishmack and Burns, 2004; Glasser, 2004). In the circulating configuration, the coal particles can spend up to several minutes in combustion chamber while the residence time is about 4 – 7 seconds in the case of PCC (Kruger, 2010). The principal benefit of FBC technology is its mitigation of sulphur dioxide and nitrogen oxides emissions (Baba et al., 2010; Glinicki and Zieliński, 2008) as well as the ability to combust low-quality coal.

On the other hand PCC operates between 1 300 and 1 700 ºC which is above the fusion temperature of most minerals thereby resulting in the formation of high content of amorphous or non-crystalline (glassy) phase; during rapid cooling (Kutchko and Kim, 2006; Glasser, 2004; Haynes, 2009; Font et al., 2010). From their origin it is evident that these fly ashes differ in many aspects (Sulovský, 2002). At present no power station uses FBC technology to combust coal in South Africa hence subsequent discussions are limited to PCC fly ash.

2.3.2 Production Rates of Fly Ash

Combustion of low-grade coal inherently generates large quantities of ash of which approximately 75% is fly ash. Ahmaruzzaman (2010) and Chen et al. (2010) estimate the world's annual production of fly ash to be 500 million tons. Due to the rapid industrial expansion in China and India there has been a significant escalation in fly ash production. It was assumed to be approximately 370 million ton/annum in 1992 (Ozdemir et al., 2001; Dutta et al., 2009).

The world's average utilisation of fly ash is 16% (Ahmaruzzaman, 2010). This is inadequate and raises concern about the excess of 420 million tons of fly ash being stored and disposed of annually. It is important to take a closer look at the properties of fly ash which should bring to light the limitations and opportunities of this underutilised potential resource.

2.3.3 Physical Properties of Fly Ash

Fly ash can generally be defined as a very fine by-product from a coal-fired power station (Nochaiya et al., 2009; Joshi et al., 1999; Raghavendra et al., 2002; Fernández-Jiménez et al., 2006; Fan et al., 2005). The physical properties of fly ash have contributed to its popular application in cement extension (Kesimal et al., 2005; Sear, 2001; Jozić and Zelić, 2006). Fly ash particles range from 0.01 µm to 100 µm, with 50 µm being a characteristic mean particle size (Pando and Hwang, 2006; Mishra and Patel, 2004; Cohen et al., 2003). It is reported in literature that the finest particles are richer in glass and thus more reactive. Unburned carbon tends to be prevalent in coarse particles (Campbell, 1999; Payá et al., 1995).

The use of high quality spherical fly ash allows for a reduction in the water demand of concrete which promotes a durable product with less porosity (Kruger, 2010). Furthermore, the sphericity of fly ash promotes workability in cement pastes and concrete by reducing friction between the particles making it easier to pump and place (Ferraris et al., 2001; Chindaprasirt et al., 2005; Yijin et al., 2004; Mahlaba and Pretorius, 2006).

Reduced water requirements result in a more cohesive paste with minimal bleed formation and low hydraulic conductivity; the cornerstones of good paste (Pagé and Spiratos, 2000; Bergeson et al., 1988; Chindaprasirt et al., 2005; Shi, 1996). Typical morphology of fly ash is shown in Figure 2.1.

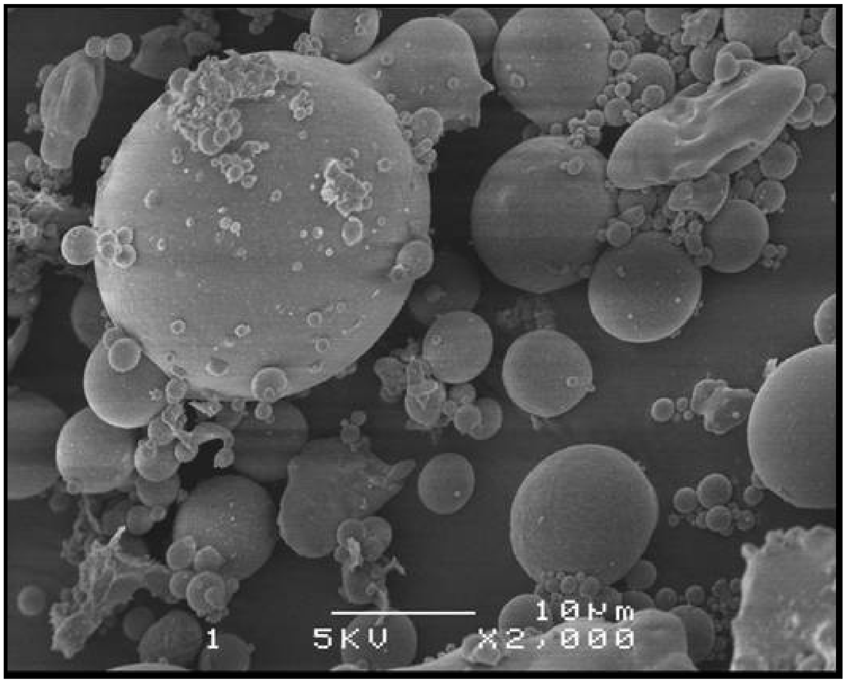

Figure 2.1 Typical morphology of Synfuels fly ash

Other physical properties of fly ash which are pertinent to its utilisation are specific gravity or relative density, surface area, and Particle Size Distribution (PSD). A range of typical physical properties of fly ash is presented in Table 2.1 (Tischmack and Burns, 2004; Koch, 2002).

Table 2.1 Typical physical properties of coal fly ash (Tischmack and Burns, 2004; Koch, 2002; Haering and Daniels, 1991)

Physical Property	**Fly Ash**
Specific gravity	1.59 – 3.10
Surface area (m^2/g)	0.20 – 3.06
Mean particle diameter (µm)	20 – 80
Hydraulic conductivity (cm/s)	$5x10^{-8}$ – $1x10^{-6}$
Dry bulk density (g/cm^3)	1.0 – 1.6

2.3.4 Chemical Composition of Fly Ash

Research over the years has shown that fly ash is a useful resource by virtue of its chemical and mineralogical composition as well as its morphology (Diaz et al., 2010; Nochaiya et al., 2009; Chancey et al., 2010; Raghavendra et al., 2002; Mobasher et al., 1996; Thomas et al., 2001; Dutta et al., 2009; Williams and van Riessen, 2010). Both the coal type and method of combustion influence the crystallinity and mineralogy of coal ash. The actual chemical composition of Synfuels fly ash, to be used in the study is presented in Table 2.2 (Mahlaba et al., 2011). These results are similar to those found by other researchers in the previous investigations, indicating that fly ash composition remains rather constant over time (Swanepoel, 2001; Matjie et al., 2004; Mahlaba, 2007; Williams and van Riessen, 2010).

Table 2.2 Typical elemental composition of Synfuels fly ash (Mahlaba et al., 2011)

Chemical Species	**Synfuels Fly Ash (%)**
SiO_2	49.7
Al_2O_3	26.2
Fe_2O_3	2.7
CaO	10.5
MgO	2.1
K_2O	0.9
Na_2O	0.7
TiO_2	1.5
SO_3	0.5
$^{\#}$LOI	4.1
Other	0.4

$^{\#}$LOI = Loss on ignition

The mineralogy of Synfuels fly ash is presented in Table 2.3 showing an appreciable content of 66% amorphous phase, which falls within the 60 – 90% range suggested by Chancey et al. (2010). There is no major change in the mineralogy of Synfuels fly ash to that presented previously by other researchers (Matjie et al., 2004; Mahlaba, 2007). The significance of amorphous phase lies in its chemical reactivity during utilisation. This is similar to volcanic rocks which also contain an amorphous phase (Ward and French, 2006; Font et al., 2010; Nochaiya et al., 2009).

Besides the susceptibility of the glassy phase to dissolution, the fineness of ash (i.e. available surface area) also influences its leaching behaviour, and ultimately its environmental impact during disposal or utilisation where it comes into direct contact with soil or water.

Table 2.3 Mineralogy (XRD) of Synfuels fly ash (Mahlaba et al., 2011)

Minerals	**Chemical Formulae**	**Synfuels Fly Ash (%)**
Mullite	$Al_6Si_2O_{13}$	20.5
Quartz	SiO_2	10.2
Hematite	Fe_2O_3	0.7
Lime	CaO	2.2
Glass	Amorphous phases	66.3
Total	N/A	**99.9**

(a) Classification of Fly Ash

Class C fly ash normally results from the combustion of lignite or subbituminous coal and exhibits self-cementing properties due to its high calcium content and reactivity. Therefore some researchers refer to it as *cementitious* or calcareous fly ash.

On the other hand, class F fly ash originates from the combustion of anthracite or bituminous coal and contains less calcium (Nochaiya et al., 2009; Bin-Shafique, 2002; Jozić and Zelić, 2006). Class F is referred to as *pozzolanic* or siliceous.

Fly ash is categorised as either class C or class F in accordance with ASTM C 618, see Table 2.4. Diamond (1983) elaborates on the differences between the two fly ash classes with regards to reactivity and chemical composition of their glassy phase.

Table 2.4 ASTM standard classification of fly ash (ASTM C 618- 03)

Components	**Class C**	**Class F**	**Synfuels fly ash**
$SiO_2 + Al_2O_3 + Fe_2O_3$, min (%)	50.0	70.0	78.6
SO_3, max (%)	5.0	5.0	0.5
Moisture content, max (%)	3.0	3.0	N/A
LOI, max (%)	6.0	6.0	4.1

The summation of SiO_2 + Al_2O_3 + Fe_2O_3 components in Synfuels fly ash gave 78.6% which is greater than the minimum of 70% for class F (Table 2.4). Thus Synfuels fly ash is a class F according to ASTM C 618 – 03, which agrees with the report by Bezuidenhout (1995) that South African fly ashes are generally class F.

(b) Pozzolanicity

South African fly ashes including that from Synfuels power station exhibit pozzolanic properties. A pozzolan is defined as a "siliceous or siliceous and aluminous material that will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties"(ASTM E 2201 – 02a). Concurrently, pozzolanic activity is defined as "the phenomenon of strength development that occurs when lime and certain aluminosilicates react at ambient temperatures in the presence of water" (ASTM E 2201 – 02a). Pozzolanic materials have been studied by several researchers who report their usefulness in various applications like cement, concrete, mortars, grout, and road stabilisation (Donatello et al., 2010; Pando and Hwang, 2006; Ozyildirim, 1998; Steenari et al., 1998; Cohen et al., 2003; Nochaiya et al., 2009; Giergiczny, 2004).

2.3.5 Status Quo

South Africa and many other countries such as Poland, United States of America, India and China rely on coal as a primary source of energy (Vejahati et al., 2010; Meawad et al., 2010). The coal combustion process yields vast quantities of fly ash which require disposal or storage in a responsible manner (Baba et al., 2010; Pandian, 2004; Wiszniowski et al., 2007; Kumar, 2004; Donahoe et al., 2007; Kostakis, 2009). Some countries are considering the classification of coal ash as a hazardous material (Diaz et al., 2010; Fongsatitkul et al., 2009). Environmentalists and the public have a concern about coal ash despite its utilisation applications which include addition in cement and concrete manufacturing, agriculture, and waste stabilisation (Ahmaruzzaman, 2010; Cheng, 2005; Mahlaba and Pretorius, 2006; Fernández-Pereira et al., 2002; Shang and Wang, 2005; Ilgner, 2002; Kruger and Krueger, 2005; Pandian, 2004; Gitari et al., 2008; Kearsley and Wainwright, 2003; Kruger and Surridge, 2009; Haynes, 2009; Pengthamkeerati et al., 2010; Truter et al., 2001).

SASOL (petrochemical) and ESKOM (power utility) are the largest coal processing companies in the Southern Africa. All their facilities are situated inland (van Dyk et al., 2006; Feeley, 2003; Sheng et al., 2003). South Africa produces in excess of 30 million tons of fly ash per annum of which only 5% is utilised (Bada and Potgieter-Vermaak, 2008; Gitari et al., 2009).

Generally ash utilisation only consumes a small fraction of total fly ash production (Antiohos and Tsimas, 2004; Ahmaruzzaman, 2010) leaving the majority for onsite disposal or landfilling. The latter is becoming increasingly more costly especially since rehabilitation of onsite disposal sites is required before closure (Haynes, 2009; Ahmaruzzaman, 2010). Authorities are also reluctant to issue new permits for waste disposal sites (Ciccu et al., 2003).

2.4 ASH DISPOSAL SYSTEMS

During the production of liquid fuels and electricity from coal a variety of saline brines and coal ash are inevitably produced, the disposal of which requires environmentally sound management policy and strategy. There are generally two methods in which fly ash can be disposed. These are either hydraulic or dry ash disposal. The former is more common and has been practised over seven decades (Tu et al., 2007; Jakka et al., 2010).

2.4.1 Hydraulic Ash Disposal

SASOL Synfuels is an example of a facility using hydraulic ash disposal where fine ash is co-disposed with saline brines as slurry onto the Fine Ash Dam (FAD) as shown in Figure 2.2. The same slurry disposal method is commonly practised in gold and copper metallurgical industries for tailings disposal (Nengovhela et al., 2006). Tailings essentially pose higher environmental risks than coal ash such as liquefaction (stability) and ubiquitous acid generation (Sracek et al., 2010; Vermeulen, 2001; Heikkinen, 2009; McPhail et al., 2004; Fourie, 2006; Chang, 2009; Nengovhela et al., 2006; Nehdi and Tariq, 2007; Mendez and Maier, 2008; Dey and Gandhi, 2008).

Significant volumes of water are lost in hydraulic disposal of coal ash and tailings (Stephenon and Odirile, 2008; Jewell and Fourie, 2006) and its recovery is adversely affected by the accumulation of dissolved salts in the reticulating effluents (Schutte et al., 1987; Simpson and Buckley, 1987). The situation is further exacerbated by the accumulation of solid residues of coal ash which ultimately necessitates rehabilitation of the FADs.

Figure 2.2 Deposition of fine ash-brine slurry onto a Fine Ash Dam

Ash is hydraulically collected with saline effluents from both gasification and steam plants. The sluiced 17% gasification fines (particles < 250 μm) and 83% fly ash are thickened to yield fine ash slurry, pumped and deposited at the FADs. After deposition the slurry flows towards the penstock. The coarse particles are expected to settle near the discharge points whereas the fine ash particles are transported closer to the penstock (Jakka et al., 2010; Vermeulen, 2001). This phenomenon is termed hydraulic sorting and is responsible for inhomogeneity of PSD and consequently hydraulic conductivity and density in the dam (Chang, 2009).

The dam is divided into regions which are alternatively used. The deposition of slurry occurs in cycles around the dam to allow deposited material to desiccate thereby resulting in a layered vertical profile (Chang, 2009). Vermeulen (2001) reported that layers in a tailings dam vary between 1 and 20 cm thickness by alternating fine and coarse deposits. Further details on the hydraulic ash disposal method are discussed in Chapter 4.

2.4.2 Dry Ash Disposal

Some ESKOM power stations (Tutuka, Lethabo, Matimba and Kendal) employ a dry ash removal system where fly ash is conditioned with 10 - 15% brines and placed on a conveyor belt for transportation to the disposal site (see Figure 2.3). This practice significantly reduces water losses encountered with hydraulic disposal.

Figure 2.3 Disposal of dry fly ash at ESKOM's Tutuka plant

Dry ash disposal may, however, pose dust and leaching threats to the environment. The deficiency of water content in the dry ash disposal may limit or prevent hydration and consequently the formation of secondary phases (Donahoe, 2004). The findings of a study conducted by Gitari et al. (2009) at the Tutuka disposal site are summarised later in the Chapter (section 2.7.2).

2.4.3 Sea Disposal of Ash

Some countries (Japan, India and Israel) have the option to dispose of coal ash into the sea either as slurry or dry. One of the drivers for this practice is the shortage of space for landfilling or storage (Jakka et al., 2010; Horiuchi et al., 2000; Shoham-Frider et al., 2003). There are obviously environmental threats posed to the marine life and eventually the food chain

(Shoham-Frider et al., 2003). No sea disposal of ash takes place in South Africa hence no further review is presented in this thesis.

The popularity of hydraulic ash disposal and a poor understanding of the associated hydration and weathering processes necessitate a dedicated endeavour of research to bridge the knowledge gap. Such an understanding could lead to the development of environmentally benign disposal technologies or abatement of pollution potential in the existing disposal facilities.

2.5 WEATHERING

2.5.1 Background

Weathering can generally be defined as the process of alteration and breakdown by mechanical, chemical or biological action which significantly affects the behaviour of a material (Barth et al., 1990; Moon and Jayawardane, 2004). It can be broadly categorised into physical and chemical weathering where the former refers to breakdown due to mechanical interference and involves little or no alteration to chemical composition.

Chemical weathering on the other hand involves a change in composition of a material due to processes such as hydrolysis, carbonation, oxidation and hydration. Fly ash undergoes this type of weathering which alters its properties such as surface area, cationic exchange capacity and pH (Zevenbergen et al., 1999).

2.5.2 Weathering of Coal Ash

Coal fly ash principally contains high-temperature solids hence will convert into thermodynamically stable minerals under atmospheric conditions (Donahoe, 2004; Zevenbergen et al., 1996, 1999). Research suggests that weathering of coal fly ash is analogous to that of volcanic ash because both ashes have high content of aluminosilicate glass which is thought to form clay minerals during weathering (Zevenbergen et al., 1996, 1999).

Zevenbergen et al. (1999) discovered that the initial high pH of alkaline coal fly ash accelerates the dissolution of glass, which later decreases and leads to Al and Si precipitation to form amorphous aluminosilicate. This as a result increases the surface area and cation exchange capacity of weathered ash. It is also found that weathering of coal fly ash for 10 years produces an amorphous clay content exceeding that of a 250 year-old volcanic ash (Zevenbergen et al., 1999).

The high degree of amorphous content and metal immobilisation during weathering of coal fly ash imply that the long-term environmental impact of its disposal is less deleterious than generally expected. Thus extended weathering exposure of fly ash may result in the formation of fertile soil that could support agriculture (Zevenbergen et al., 1999).

Donahoe (2004) defines secondary phases as the phases which form when chemical weathering occurs between coal combustion by-products including fly ash and water-based solutions. Table 2.5 presents a detailed list of both observed and predicted secondary phases in weathered fly ash and the number of references that either identified or predicted the existence of a specific phase. It is further reported that some secondary phases cannot be identified because they either occur in minute quantities or they are too fine for identification with current XRD techniques. It is therefore important to carefully select analytical techniques for studying mineralogy.

Table 2.5 Observed and predicted phases in old coal ashes (Donahoe, 2004)

Phase	**Composition**	**Observed in references***	**Predicted in references***
Böhmite	$AlO(OH)$	-	1
Gibbsite	$Al(OH)_3$	-	7
Al-hydroxide (amorphous)	$Al(OH)_3$	1	7
Hydrous Al-sulphate	$Al(OH)SO_4$	-	3
Imogolite/allophone	Hydrous aluminate silicate	2	-
Halloysite	$Al_2Si_2O_5(OH)_4$	-	1
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	-	1
Smectite	$(Ca,Na)_{0.3}Al_2Si_4O_{10}(OH)_2.nH_2O$	-	2
Arsenolite	As_2O_3	1	-
Barite	$BaSO_4$	1	5
Witherite	$BaCO_3$	1	1
Ba-arsenate	$Ba_3(AsO_4)_2$	-	2
Ba-chromate/sulphate	$Ba(Cr,S)O_4$	-	2
Ba/Sr-sulphate	$(Ba,Sr)SO_4$	-	3
Gypsum	$CaSO_4.2H_2O$	13	2
Calcite (aragonite)	$CaCO_3$	10	2
Dolomite	$CaMg(CO_3)_2$	1	2
Ca-aluminate	$Ca_3Al_2O_6$	2	-
Ca-silicate	$CaSiO_3$	1	1
Portlandite	$Ca(OH)_2$	7	1
Ettringite	$Ca_6Si_2(SO_4)_3\ (OH)_{12}.26H_2O$	10	1
Thaumasite	$Ca_6Si_2(SO_4)_2(CO_3)_2(OH)_{12}.24H_2O$	4	-
Anhydrite	$CaSO_4$	1	3
Hannebachite	$CaSO_3.0.5H_2O$	5	1
Tobermorite	$Ca_9Si_{12}O_{30}(OH)_6.4H_2O$	2	-
Whitlockite	$Ca_9(Mg,Fe)H(PO_4)_7$	-	1
Apatite	$Ca_5(PO_4)_3OH$	-	1
Powellite	$CaMoO_4$	-	2
Fe-(oxy)hydroxide	$Fe(OH)_3$, $FeOOH$	3	4
Maghemite	Fe_2O_3	1	-
Hematite	Fe_2O_3	1	1
Fe-sulphate	$FeSO_4$	1	-
Ferric arsenate	$FeAsO_4$	-	1
Fe/Cr-hydroxide	$(Fe,Cr)(OH)_3$	-	4
Fe-vanadate	$FeVO_4$	-	1
Magnesio-ferrite	$MgFe_2O_4$	-	1
Magnesite	$MgCO_3$	-	1
Talc	$Mg_3Si_4O_{10}(OH)_2$	1	-
Brucite	$Mg(OH)_2$	2	2
Mg-sulphates	$MgSO_4$ etc	1	-
Zeolite Na-P1	$Na_6Al_6Si_{10}O_{32}.12H_2O$	2	-
Phillipsite	$NaKAl_2SiO_{16}.6H_2O$	-	1
Laumontite	$CaAl_2Si_4O_{12}.4H_2O$	-	2
Wairakite	$CaAl_2Si_4O_{12}.2H_2O$	-	3
Nosean-haüyne	$(Na,Ca)_8Al_6Si_4O_{24}(SO_4)_{1-2}.H_2O$	2	-
Thernadite	Na_2SO_4	1	-
Na/K,Ca-sulphates	e.g. $Na_2Ca_5(SO_4)_6.3H_2O$	3	-
Amorphous silica	SiO_2	-	2
Al-Si amorphous phase	Undetermined	1	-
Mg-Ca-Na-K-Al-Si phase (amorphous)	Undetermined	1	-
Strontianite	$SrCO_3$	-	3
Celestine	SrO_4	-	4
Willemite	Zn_2SiO_4	-	2

* The numbers represent references which either predicted and/or identified a phase

2.6 CEMENT CHEMISTRY

The preceding and the present section attempt to provide a basis for explaining the reactions occurring between brines and fly ash by using a combination of chemical weathering (natural process) and cement hydration (industrial process). The literature survey was limited to Ca, Na, Mg, Fe, Al, Si, Cl^-, and SO_4^{2-} which are the dominant constituents in brines and fly ashes.

It is generally accepted that fly ash undergoes hydration reactions similar to cement. This is substantiated by similarity of both physical and chemical characteristics of these materials and hence utilisation of fly ash in the extension of blended cements. Different opinions nonetheless, exist on the knowledge and understanding of cement hydration (Pagé and Spiratos, 2000; Tommaseo and Kersten, 2002; Mehta and Monteiro, 2006).

The major minerals in Portland cement are tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite (García-González et al., 2007; Medveščček et al., 2006; Double, 1983). The tricalcium silicate and dicalcium silicate content makes up to 75 – 80% of cement while tricalcium aluminate and tetracalcium aluminoferrite range from 4 – 11% and 8 – 13%, respectively (Ramachandran et al., 2002). Table 2.6 provides the elemental composition of Portland cement.

Table 2.6 Typical elemental composition of ordinary Portland cement (Mehta and Monteiro, 2006; Lam et al., 2000)

Component	**Weight (%)**
CaO	63.0
SiO_2	20.7
Al_2O_3	4.0
Fe_2O_3	3.0
Na_2O	0.5
MgO	4.0
LOI	1.5
Other	3.3
Sum	100.0

The need to reduce carbon footprint of cementitious binders has necessitated cement extension with fly ash, slag or limestone. The result is that pure Portland cement is no longer readily available commercially (Ramachandran et al., 2002; Gabrovšek et al., 2006), but its classic chemistry is still used for comparative purposes in this research.

2.6.1 Hydration of Cement

Cement hydration can generally be defined as a chain of reactions that occur between aluminosilicate, lime and water to form a hardened product. Literature states that the rate of hydration reactions cannot be predicted based on the reactant proportions but it is controlled by the availability of reactive components (Ward and French, 2006). For instance, materials may contain equivalent amounts of lime but the material with free lime will be more reactive than that containing bound lime due to different degrees of availability.

Cement contains approximately 50% tricalcium silicate (Ca_3SiO_5), which has high reactivity. Tricalcium silicate undergoes early hydration to form calcium silicate hydrate (C-S-H) as shown in equation 2.1:

$Ca_3SiO_5 + nH_2O \rightarrow$ C-S-H + $Ca(OH)_2$………………………………………………(2.1)

Calcium silicate hydrate is the main binding component in concrete which provides strength and durability (Ylmén et al., 2009; Coleman and Mcwhinnie, 2000; Le Bellégo et al., 2000; Chen et al., 2004; Memon et al., 2002; Richardson, 2008). It is a gel with the variable composition $xCaO.ySiO_2.zH_2O$; where x, y and z, are the coefficients (Chatveera and Lertwattanaruk, 2009; Chen et al., 2004; Klemm, 1998; Ramachandran et al., 2002; Odler, 2004). The C-S-H gel is an extremely fine and amorphous or poorly crystalline material contributing over 60% (m/m) of hydrated cement paste (Baur et al., 2004; Bensted, 1983; Chen et al., 2004; Thomas et al., 2001).

Dicalcium silicate (Ca_2SiO_4) on the other hand, contributes to long-term strength (Ylmén et al., 2009; Thomas et al., 2001) by forming calcium silicate hydrate as shown in equation 2.2:

$Ca_2SiO_4 + nH_2O \rightarrow$ C-S-H + $Ca(OH)_2$ ....(2.2)

The C-S-H phase can act as a centre of adsorption for hazardous ions including heavy metals (Johnson, 2004; Plank and Hirsch, 2007; Klemm, 1998; Delagrave et al., 1997). Gougar et al. (1996) compiled a list shown in Table 2.7 from literature of contaminants that can be immobilised in C-S-H.

Table 2.7 A list of contaminants immobilised by C-S-H (Gougar et al., 1996; Odler, 2004)

Description	**Typical elements**
Monovalent cations	Li, Na, K, Rb, Cs
Divalent cations	Mg, Ni, Co, Hg, Zn, Cd, Pb
Trivalent cations	Al, Fe, Cr
Actinide	U
Anions	Cl^-, I^-, OH^-, CO_3^{2-}, SO_4^{2-}

The C-S-H gel is not readily identifiable with XRD because of its low degree of crystallinity; hence several researchers used thermal analysis and other techniques for identification of C-S-H gel (Murat, 1983; Coleman and Mcwhinnie, 2000; Balonis et al., 2010; Nochaiya et al., 2009). According to Chen et al. (2004) more than 30 phases of C-S-H have been identified.

Tricalcium aluminate ($Ca_3Al_2O_6$) has a significant influence on the early reactions despite its existence in relatively small quantities. It undergoes hydration quicker than both dicalcium silicate and tricalcium silicate to form tricalcium aluminate hydrate (C-A-H), according to equation 2.3:

$Ca_3Al_2O_6 + nH_2O \rightarrow C\text{-}A\text{-}H + Ca(OH)_2$……………………………………….(2.3)

The formation of C-A-H phase liberates more heat but has less contribution to strength development. The formation of C-A-H is favoured under sulphate deficient conditions due to *retardation* caused by the presence of sulphates (Radwan and Heikal, 2005; Hartman et al., 2006). Gypsum addition can be used to control the setting of cementitious materials (Double, 1983; Medvešček et al., 2006).

Tetracalcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$) reacts with lime and water to form hydrogarnet ($Ca_6Al_2Fe_2O_{12}.12H_2O$) according to equation 2.4:

$Ca_4Al_2Fe_2O_{10} + 2Ca(OH)_2 + 10H_2O \rightarrow Ca_6Al_2Fe_2O_{12}.12H_2O$ ……………(2.4)
This reaction is of less importance to cement properties compared to the first three.

2.6.2 Effect of Pozzolans

It is observed that portlandite ($Ca(OH)_2$) forms as a by-product during cement hydration. Depending upon the availability of additional silicates from a pozzolan e.g. silica fume, this portlandite can react further to form C-S-H (Ylmén et al., 2009; Livingston and Bumrongjaroen, 2005; El-Alfi et al., 2004; Hekal, 2000), according to equation 2.5:
$SiO_2 + Ca(OH)_2 \rightarrow$ C-S-H ....(2.5)
Formation of the additional C-S-H gel reduces porosity and hydraulic conductivity of the hardened material (Memon et al., 2002; Donatello et al., 2010).

Mehta and Monteiro (2006) distinguish between the hydration of cement and the pozzolanic reaction. The former is explained in the above discussion using equations 2.1 to 2.3, where portlandite forms as a by-product. The pozzolanic reaction on the other hand is a slow reaction where portlandite is consumed in the presence of water as illustrated in equation 2.6:
Pozzolan + $Ca(OH)_2 + nH_2O \rightarrow$ C-S-H ....(2.6)
The consumption of lime shown in equation 2.6 is vital for the durability of hydrated paste under acidic conditions.

The replacement of Portland cement with fly ash (pozzolan) in high volumes reduced the early strength development in concrete (Shi, 1996; Shehata, 2001). This attracted a research focus on evaluating the accelerators such as $CaCl_2$, Na_2SO_4 and silica fume to accelerate pozzolanic reactions (Nochaiya et al., 2009; Shi, 1996; Shi and Day, 2000; Shehata, 2001). These admixtures reduce the setting time and accelerate early strength development of concrete essential in commercial application (Ramachandran et al., 2002).

2.6.3 Effect of Gypsum

Under sulphate-rich conditions tricalcium aluminate reacts with gypsum ($CaSO_4.2H_2O$) to form a sparingly soluble mineral, ettringite according to equation 2.7 (Yuan et al., 2009; Black et al., 2006).

$Ca_3Al_2O_6 + CaSO_4.2H_2O + nH_2O \rightarrow$ Ettringite ……………………………… (2.7)

Ettringite is a complex mineral of hydrated calcium aluminosulphate with the chemical formula $Ca_6[Al(OH)_6]_2(SO_4)_3.xH_2O$ where x = 26 or 32 (Baur et al., 2004; Prasad et al., 1999). Its occurrence is very rare in nature but prevalent in cementitious systems under specific conditions (Hartman et al., 2006).

The formation of ettringite is generally unwanted in hardened concrete because it causes expansion which leads to structural damage (Prasad et al., 1999). However, research has revealed that only the delayed ettringite formation is deleterious and not early ettringite formation which occurs immediately in fresh concrete with sufficient sulphates (Collepardi, 2003).

If there is insufficient sulphate for the formation of ettringite with tricalcium aluminate, calcium monosulphoaluminate hydrate forms. Sulphate attack occurs when hardened cement paste (or concrete) is exposed to a sulphate-rich environment. Over time this facilitates the conversion of calcium monosulphoaluminate hydrate to ettringite i.e. delayed ettringite formation (Collepardi, 2003; Klemm, 1998), see equation 2.8.

$Ca_4.Al_2O_3.SO_4.12H_2O$ + gypsum + $16H_2O \rightarrow$ Ettringite……………………………(2.8)

There are benefits associated with the formation of secondary minerals from an environmental perspective. Ettringite is a very insoluble mineral (details in section 2.6.5) which serves as a “sink” for sulphates, calcium ions and water molecules by virtue of its chemical structure shown in Figure 2.4 (Baur et al., 2004; Klemm, 1998; Tishmack et al., 2001).

Additionally, ettringite has the ability to exchange sulphates for oxyanions from heavy metals in its structure (Baur et al., 2004; Klemm, 1998; Klemm and Bhatty, 2002; Tishmack et al., 2001). Oxyanions that can replace sulphates include AsO_4^{3-}, $B(OH)_4^-$, SeO_4^{2-} and VO_4^{3-} (Baur et al., 2004;

Johnson, 2004) of which $B(OH)_4^-$ has the highest affinity (Chrysochoou and Dermatas, 2006). Gougar et al. (1996) compiled a comprehensive list of pollutants that can be immobilised in the ettringite structure, illustrated in Table 2.8. Moreover, ettringite adds strength and reduces hydraulic conductivity (Heebink and Hassett, 2001).

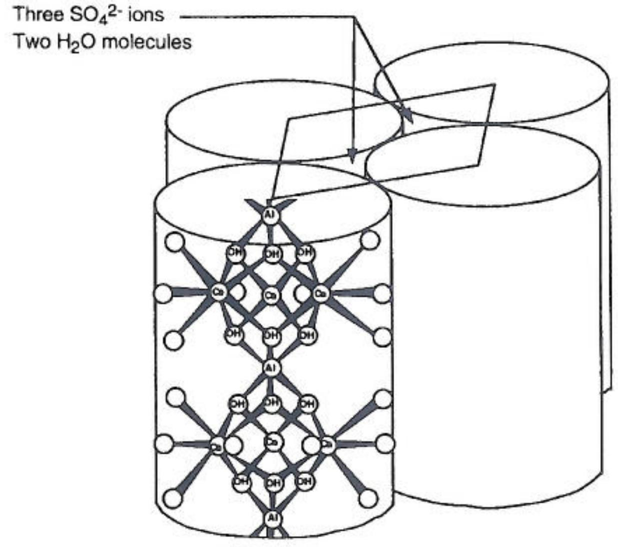

Figure 2.4 Crystal structure of ettringite, showing a projection of the partial structure of one column (Klemm, 1998)

According to Chrysochoou and Dermatas (2006) the formation of ettringite is favoured over calcium monosulphoaluminate hydrate at temperatures below 50 °C while the pH stability of ettringite generally lies between 10.5 and 13. These minerals with many molecules of water of crystallisation can dry wet sites by binding large volumes of water in their structures (Heebink and Hassett, 2001).

Table 2.8 A summary of pollutant substitutions in the ettringite structure (Gougar et al., 1996)

Ca^{2+} site	**Al^{3+} site**	**SO_4^{2-} site**	**OH^- site**
Sr^{2+}	Cr^{3+}	$B(OH)_4^-$	O^{2-}
Ba^{2+}	Si^{4+}	CO_3^{2-}	
Pb^{2+}	Fe^{3+}	Cl^-	
Cd^{2+}	Mn^{3+}	OH^-	
Co^{2+}	Ni^{3+}	CrO_4^{2-}	
Ni^{2+}	Co^{3+}	AsO_4^{3-}	
Zn^{2+}	Ti^{3+}	SeO_4^{2-}	
		VO_4^{2-}	
		BrO_3^-	
		NO_3^-	
		MoO_4^{2-}	
		ClO_3^-	
		SO_3^{2-}	
		IO_3^-	

2.6.4 Immobilisation of Chlorides

Calcium chloride ($CaCl_2$) is commonly used in relatively small quantities to *accelerate hydration* reactions in cement pastes (Allen and Thomas, 2007; Valls and Vàzquez, 2000; Anthony et al., 2003). However, the presence of dissolved chloride in large quantities elevates the risks of steel corrosion in reinforced concrete (Beaudoin et al., 1990; Abdel-Wahab and Batchelor, 2002; Sumranwanich and Tangtermsirikul, 2004; Arya et al., 1990). This is particularly so where the thickness of the concrete is insufficient to protect steel.

It is well documented in literature that chlorides can be chemically immobilised by the formation of Friedel's salt ($Ca_3.Al_2O_6.CaCl_2.10H_2O$) or be physically adsorbed onto C-S-H gel (Balonis et al., 2010; Pagé and Spiratos, 2004; Justnes, 2004; Walcarius et al., 2001; Sugiyama et al., 2003; Zibara et al., 2008). The formation of Friedel's salt (chloroaluminate) is subject to the availability of calcium aluminate ($Ca_3Al_2O_6$) or aluminoferrite ($Ca_4Al_2Fe_2O_{10}$), soluble chloride and sufficient curing time (Sumranwanich and Tangtermsirikul, 2004; Dhir and Jones, 1999; Pruckner and Gjørv, 2004; Zuquan et al., 2007). The chemical reaction of its formation is given in equation 2.9.

$CaCl_2 + Ca_3Al_2O_6 \rightarrow Ca_3.Al_2O_6.CaCl_2.10H_2O$ ……………..............………… (2.9)

Friedel's salt provides a sink for chlorides and calcium and has the ability to attract anions by ion exchange (Walcarius et al., 2001; Balonis et al., 2010). Friedel's salt is however only stable under high pH conditions (pH > 12) below which it is destroyed (Csizmadia et al., 2000).

Besides the formation of Friedel's salt other mechanisms by which chlorides can be immobilised in paste, include formation of a complex calcium oxychloride, and through bonding with C-S-H gel (Csizmadia et al., 2000; Dhir and Jones, 1999; Delagrave et al., 1997; Beaudoin et al., 1990). It is also reported that the cation associated with the sulphate influences the efficiency of chloride immobilisation. Better chloride retention was obtained from pastes containing $CaSO_4$ than those with Na_2SO_4, for equivalent sulphate concentrations (Csizmadia et al., 2000).

There is consensus in literature that chloride binding improves in the presence of calcium compared to sodium although the mechanism is still poorly understood (Nielsen et al., 2005; Pruckner and Gjørv, 2004; Arya et al., 1990; Tritthart, 1989; Hussain et al., 1994). Yuan et al. (2009) reported that binding of chloride in cementitious materials is affected by a myriad factors including concentration of chloride, sulphate and hydroxyl ions, cation associated with chloride salt, and temperature.

Nakamura et al. (1999) discovered that only 15% of chloride adsorbed onto the C-S-H gel leaches whereas as much as 65% leached from Friedel's salt. This indicates that the former provides a more sustainable sink of chlorides than the latter which is only stable at pH > 12. To maintain a highly alkaline environment is difficult because carbonation reduces pH (Chi et al., 2002; Klemm, 1998; Donahoe, 2004).

2.6.5 Limiting Factors of Hydration

The most obvious factors which limit hydration and the formation of secondary phases are free lime and time (Ćojbašić et al., 2005; Lam et al., 2000; Ben-Haha et al., 2010). Additionally, the availability of aluminates control the formation of ettringite and Friedel's salt. Sulphates have a stronger affinity for aluminates than chlorides hence either ettringite or calcium monosulphoaluminate hydrate will be formed before Friedel's salt (Csizmadia et al., 2000). The latter will only form upon depletion of sulphates and the availability of aluminates.

2.6.6 Solubility of Secondary Phases

Consideration of solubility products for major hydration products provides one indicative way of stability of immobilisation. Ebbing (1996) defines solubility product (Ksp) as "the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound." The lower the Ksp value the more insoluble the compound (Table 2.9). A secondary phase with a high solubility product is therefore undesirable because it will easily dissolve in water and leach any bound and/or adsorbed pollutants.

The Ksp values of selected compounds are illustrated in Table 2.9. Being fairly soluble, calcium precipitates (calcite, gypsum and portlandite) have high Ksp values. In contrast hydration products have extremely low solubilities especially ettringite, which is essential for the stability of immobilised contaminants (Klemm, 1998).

Table 2.9 Ksp values of common secondary phases (Klemm, 1998; Ebbing, 1996)

Compound	**Chemical Formula**	**Ksp value at 25 °C**
Calcite	$CaCO_3$	3.8×10^{-5}
Gypsum	$CaSO_4.2H_2O$	3.7×10^{-5}
Portlandite	$Ca(OH)_2$	8.9×10^{-6}
Gibbsite	$Al(OH)_3$	4.6×10^{-33}
Ettringite	$Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O$	2.8×10^{-45}
Friedel's salt	$Ca_3.Al_2O_6.CaCl_2.10H_2O$	1.0×10^{-30}
Calcium monosulphoaluminate hydrate	$Ca_4. Al_2O_3. SO_4.12H_2O$	3.7×10^{-30}

2.6.7 Deterioration Mechanisms

The preceding discussion has demonstrated that pollutants can be retained in cementitious materials via the formation of hydration products (secondary phases), some of which are pH sensitive. It is imperative to understand that some hydration products are, over time, susceptible to destructive mechanisms such as carbonation, sulphate and magnesium attack. This section sheds light on the causes of deterioration of characteristic secondary phases in cementitious pastes.

2.6.7.1 Carbonation

Carbonation is one of the major causes of reinforced concrete deterioration. It involves the reaction of carbon dioxide (carbonates) with the hydration products, which reduces the pH of pore water (Song and Kwon, 2007; Chi et al., 2002; Ramachandran et al., 2002; Klemm, 1998; Borges et al., 2010). The stability of mineral phases depends on pH and can be destroyed by carbonation also known as decalcification (Klemm, 1998; Yuan et al., 2009; Borges et al., 2010). The C-S-H is decalcified in the presence of carbonic acid (H_2CO_3) to form calcite ($CaCO_3$), silica gel and water (Yuan et al., 2009; Borges et al., 2010), see equation 2.10.

$$\text{C-S-H} + H_2CO_3 \rightarrow CaCO_3 + SiO_{2(gel)} + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.10)$$

Carbonation has adverse consequences on the stability of adsorbed contaminants. Huijgen et al. (2005) postulate the carbonation of ettringite according to equation 2.11 to form calcite, gypsum and aluminate gel ($Al_2O_3.xH_2O$) as disintegration products.

Ettringite + $CO_2 \rightarrow CaCO_3 + CaSO_4.2H_2O + Al_2O_3.xH_2O + (26\text{-}x)H_2O$ ....(2.11)

Gibbsite ($Al(OH)_3$) has reportedly formed instead of aluminate gel in some cases (Campbell, 1999; Lange et al., 1997).

Other researchers have succeeded to ameliorate paste properties through accelerated carbonation (Kashef-Haghighi and Ghoshal, 2010; García-González et al. 2007). Lange et al. (1996; 1997) reported that carbonation of C-S-H can be advantageous in light of acid-stable silica gel formation with the same morphology as C-S-H; thereby improving bonding of certain metals. It is important to note this discovery for future but it is not a priority in meeting the objectives of this research.

2.6.7.2 Magnesium attack

Prasad et al. (2006) found that Mg-bearing compounds can react with C-S-H to form magnesium silicate hydrate (M-S-H) and gypsum, illustrated in equation 2.12.

$MgSO_4$ + C-S-H → M-S-H + gypsum..(2.12)

M-S-H is softer than C-S-H hence its formation reduces structural integrity and has lower binding capacity (Chatveera and Lertwattanaruk, 2009). The transition reaction between $MgSO_4$ and portlandite produces brucite ($Mg(OH)_2$) which is stable at a pH of 10.5 thereby destabilising ettringite and C-S-H (Eglinton, 2004).

2.6.7.3 Formation of thaumasite

Formation of thaumasite ($Ca_6[Si(OH)_6]_2(SO_4)_2(CO_3)_2.24.H_2O$) is one of the deterioration mechanisms associated with sulphate attack and carbonation in concrete (Mulenga et al., 2003; Arandigoyen et al., 2006; Klemm, 1998). Thaumasite is a soft non-cohesive mass which causes a significant (over

90%) reduction in compressive strength and an increase in the hydraulic conductivity of pastes (Köhler et al., 2006).

It is reported in literature that thaumasite can either be derived from ettringite or C-S-H (Irassar et al., 2005). The Al^{3+} ions and $[(SO_4^{2-})_3 (H_2O)_2]$ in ettringite are replaced by Si^{4+} ions and $[(SO_4^{2-})_2 (CO_3^{2-})_2]$ in thaumasite with long exposure to very cold conditions (Köhler et al., 2006; Irassar et al., 2005; Klemm, 1998; Lachowski et al., 2003). Pajares et al. (2003) suggest a temperature range of 1 – 5 °C whereas Köhler et al. (2006) believe a temperature below 15 °C is required.

The use of fly ash in concrete increases the resistance to thaumasite formation (Mulenga et al., 2003; McCarthy et al., 2009). The formation of thaumasite is therefore not expected in brine-fly ash pastes because of copious volume of fly ash used in paste and relatively high temperatures in Secunda.

2.6.7.4 Alkali Silica Reaction

The high concentrations of sodium and potassium in industrial brines from SASOL Synfuels could cause the occurrence of alkali silica reaction (also known as *alkali aggregate reaction*). Alkali silica reaction (ASR) is a slow reaction which occurs in concrete between dissolved alkalis (sodium and potassium) and reactive silica or silicate present in the aggregate (Owsiak, 2003; Hicks, 2007). The alkalis originate from either the cement content or the surrounding environment such as brines and seawater (Kurtis and Monteiro, 2003). The ASR forms a gel which absorbs water, expands and eventually cracks the hardened structure (Hicks, 2007; Kurtis and Monteiro, 2003). Hicks (2007) and Justice (2005) point out that ASR leads to destructive phenomena such as loss of strength and increase in hydraulic conductivity.

It is important to note that the occurrence of ASR involves large particles of aggregate in hardened concrete. A pozzolanic fly ash and absence of aggregates make the occurrence of ASR highly unlikely in brine-fly ash pastes. Moreover, fly ash is one of the important admixtures used to mitigate deterioration of concrete due to ASR gel (Chengzhi and Aiqin, 2007; Kurtis and Monteiro, 2003; McCarthy et al., 2009; Shehata, 2001). The ASR gel is also unstable in the presence of calcium which can result in its conversion to C-S-H.

2.6.8 Concluding Remarks on Cement Chemistry

It is appreciated that the terms “cementitious” and “pozzolanic” have different meanings but for the purposes of this thesis the term cementitious will be used to indicate either or both of these terms. Other than that, there is considerable information on how pollutants can be immobilised in cementitious materials. The combination of chemical weathering and cement hydration serves as an important source of information, to explain and develop an understanding how brines and fly ash can be utilised to develop a sustainable solution for their environmentally friendly disposal.

2.7 CASE STUDIES ON ASH DISPOSAL METHODS

This section presents selected case studies on the different types of ash disposal practices with specific focus on the consequences of each method and identification of any shortcomings.

2.7.1 Hydraulic Ash Dam

A closely related study was conducted at two FADs of SASOL Synfuels where three boreholes were drilled using a rotary core drill (Koch, 2002). The dam was constructed by disposing of saline brines and fine ash as slurry in a 5:1 ratio. Two boreholes were drilled in an operational FAD, one near the centre (24 m deep) and another closer to the edge (27 m deep). The 33 m deep borehole was drilled near the centre of a redundant FAD. The findings of this study are summarised as follows:

- Ash mineralogy in the central borehole of a disused FAD remained unchanged from top to bottom. Using XRD; ettringite, calcite, magnetite and hematite were identified. Ettringite and calcite occurred at all depths of the borehole whereas magnetite and hematite only existed in certain depths.

- A variation in the mineralogical profile with depth was found on the outer borehole of the operational FAD while that of the central borehole was rather consistent. Secondary minerals on the central borehole were calcite and sillimanite (Al_2SiO_5). Conversely the borehole near the edge contained magnetite, calcite and sillimanite.
- The central boreholes exhibited consistent mineralogy throughout the depths. The redundant FAD contained ettringite while the operational FAD had sillimanite but no Fe-bearing minerals.
- The redundant FAD possessed mineral phases not detected in the operational FAD e.g. ettringite. This mineralogical difference was attributed to the different age (curing periods) of the two dams and hence the degree of chemical weathering that occurred.
- Koch (2002) further performed laboratory column simulations where she identified sillimanite and low concentrations of Fe-bearing minerals as secondary phases. No ettringite was detected probably due to the short duration of experiment.

The three boreholes investigated by Koch (2002) were important in highlighting the basic difference between operational and disused FADs. However, the study was very preliminary and superficial as certain aspects were not investigated.

The drilling described in Chapter 4 of this work advances from Koch (2002) by providing special focus on the physical, chemical and mineralogical characteristics across a specific disused FAD. This led to a better understanding of the variability and mineralogical transformation that occurred over time (Mahlaba et al., 2011).

2.7.2 Dry Ash Disposal

An investigation was performed by the University of Western Cape on the dry ash disposal of Tutuka power station near Secunda. Fly ash is conditioned with brine before conveyance to the ash disposal. Gitari et al.

(2009) conducted a study to ascertain whether the conditioning of fly ash with brines could be used to provide a salt sink.

The study was conducted to also improve the understanding of the weathering process in this ash disposal because little knowledge exists on what transpires when fly ash interacts with brines. A few boreholes were drilled in the disposal on which geochemistry and mineralogy were determined.

The findings are summarised as follows:

- The predominant soluble constituents were found to be Ca, K, Na and SO_4^{2-} according to standard leach tests.
- Hydraulic conductivity tests showed that more salts are leached during the first flush with water since infiltration was higher initially although it decreased over time.
- The highest degree of weathering was found in the oldest part (15 years) of the disposal site.
- The pH of various cores collected at the top of the dam stabilised at a pH of 8 - 9. This was attributed to the dissolution of aluminosilicate as a controlling mechanism of pore water pH.
- No major mineralogical differences were observed among the cores. Gypsum was detected on samples collected near the surface while mullite, quartz and calcite were observed in all samples.
- On the contrary, SEM images indicated different particle morphologies suggesting that chemical weathering took place in the disposal site.
- Comparison of dry and hydraulically dumped ashes suggested that the latter possessed evident mineralogical changes. This difference was inferred to the availability of sufficient water required for hydration in the latter case.
- It was concluded that the dry ash disposal does not provide a sustainable salt sink.

When assessing weathering, less attention was given to the fact that coal fly ash contains high percentages of amorphous content compared to crystalline phases. The limitations of XRD were overlooked. No comment was made on whether the disposal site is heterogeneous or not by for instance comparing properties of the cores taken at different lateral locations.

It is therefore believed that additional investigation is required to reach a conclusive answer on the sustainability of a dry disposal site. For instance the contradiction between XRD and SEM results can be resolved by using more advanced analytical techniques to study solid state chemistry of the cores.

2.7.3 Landfill of Fly Ash

A study was conducted by Yeheyis et al. (2009) to characterise landfilled class C fly ash in Canada and evaluate its potential for future applications. Mineralogy and chemical composition were determined using a variety of techniques while geochemical methods were employed to determine the environmental impact and ash characteristics.

The important observations made are highlighted hereunder:

- SEM micrographs demonstrated changes in the surface morphology from spherical particles to particles coated with secondary minerals.
- Agreement on mineralogical composition was reached between spectroscopic and thermal techniques. Changes in mineralogy include the formation of ettringite, calcite, and gypsum. The reduction in the amorphous content was attributed to the chemical weathering.
- A greater degree of carbonation was observed on the sample collected near the surface compared to those procured deeper within the landfill.
- No appreciable alteration was observed in the concentration of major elements among the samples, which is indicative of immobilisation.
- The pH of landfilled ash was lower than that of fresh fly ash due to the depletion of alkaline oxides such as CaO and Na_2O during chemical weathering.

Yeheyis et al. (2009) attributed the increase in loss on ignition (LOI) of the weathered fly ash to dehydration as well as decomposition of secondary minerals compared to fresh fly ash which was significantly lower. His explanation was substantiated by thermal analysis.

This investigation was thorough in terms of chemistry and mineralogy. However, no attention was given to physical characteristics and variability across the landfill.

2.7.4 Consolidation of Case Studies

The case studies discussed above provide a useful insight on the chemical weathering of coal ashes although there are different viewpoints on the immobilisation of pollutants. The findings (Koch, 2002; Yeheyis et al., 2009; Mahlaba et al., 2011a) demonstrate that disposal of fly ash results in the immobilisation of pollutants due to chemical weathering. However, Lee and Spears (1994) concluded from core drilling in an almost 20 years old fly ash dump that disposed fly ash contaminates groundwater, which agrees with Suresh et al. (1998). It was also concluded from the work of Gitari et al. (2009) that dry ash dumping is not sustainable due to high hydraulic conductivity and leaching.

There are also different opinions on whether fly ash is hazardous or not. The availability of land for disposal is of unanimous concern worldwide. With their heavy load of chemicals, brines pose a different type of environmental threat. The author therefore finds it scientifically justifiable to evaluate the potential of immobilising some of the components of saline brines in fly ash pastes with a view of developing a sustainable disposal solution in terms of chemical, mineralogical and physical properties.

2.8 PASTE AS A PROPOSED SOLUTION

2.8.1 Background

Paste is a homogeneous, viscous mixture of solids and liquid which does not bleed nor segregate, with the ability to harden. Bouzalakos et al. (2008) suggest a maximum of 2% bleed[1] formation.

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[1] Bleed refers to the supernatant effluent that forms after ash settling, requiring further management

There are a few parameters that can be used to define a paste such as solids concentration and yield stress. As a rule of thumb, a paste must contain at least 15% by weight of particles smaller than 20 μm (Jewell and Fourie, 2006; Kwak et al., 2005). Nonetheless paste properties principally depend on the characteristics of both solid and liquid materials (Jewell et al., 2002; Verburg, 2001; Kwak et al., 2005).

Paste technology can essentially be defined as one of the solidification/stabilisation (S/S) processes used to immobilise hazardous wastes in an environmentally acceptable manner. Immobilisation of contaminants is attained via the combination of physical and chemical phenomena. Solidification is defined as the act of physically encapsulating hazardous species in a matrix without necessarily converting its characteristics while stabilisation refers to the conversion of a hazardous material into a chemically more stable form (Chen et al., 2009; Li et al., 2001; Paria and Yuet, 2006; Laugesen and Eriksson, 2006).

It is a known fact that both dry disposal and hydraulic placement of fly ash have flaws which adversely affect the environment. To address some of the shortcomings, several researchers have proposed the co-disposal of fly ash with brines as a paste (Mahlaba and Pretorius, 2006; Muntingh et al., 2009; Ilgner, 2002, 2006; Mahlaba et al., 2008).

Paste provides an opportunity to exploit the advantages of both hydraulic and dry disposal methods. The potential of developing paste technology to immobilise saline brines with fly ash due to the pozzolanicity of South African fly ash is novel. This application has a significant potential for environmentally friendly waste disposal.

2.8.2 History of Paste

The first attempt to thicken and dispose of tailings as paste on the surface was made in Canada in 1973. A different approach was independently evaluated in Germany around the same time, where underground disposal of thickened tailings (paste) was the objective (Jewell et al., 2002). Backfill application of paste requires mechanical properties which are much higher than those associated with surface disposal (Jewell and Fourie, 2006).

2.8.3 Advantages and Disadvantages of Paste

The main hydration products of cementitious pastes are portlandite, C-S-H and ettringite where the immobilisation of pollutants such as Ca, Na, Cl^- and SO_4^{2-} is achieved by physical and/or chemical phenomena i.e. S/S (Klemm and Bhatty, 2002; Verburg, 2001; Querol et al., 1997).

Some of the advantages of paste over slurry (or tailings) include:

- High content of solids to liquid reduces the bleed formation and water loss.
- Minimisation of bleed eliminates the need for further effluent treatment.
- Relatively low hydraulic conductivity is achieved which reduces infiltration and leaching.
- High strength enables mine backfill and improved ore extraction.
- Backfilling also avails disposal land for more beneficial utilisation.
- Paste placement can prolong the life-span of a surface disposal site.
- Less or no rehabilitation effort is required.

A good quality cementitious paste is known to have a low hydraulic conductivity and the ability to harden as concrete (Stropnik and Južnič, 1988; Joshi et al., 1994; Kaneko et al., 2001; Chindaprasirt et al., 2005). Solidification and reduced hydraulic conductivity enable the physical encapsulation of the contaminants including those that do not easily form secondary minerals such as certain monovalent species (Li et al., 2001; Paria and Yuet, 2006).

Some of the few disadvantages of paste are:

- Paste is a highly specialised field requiring skilled personnel.
- Paste properties are site-specific and ore related.
- Pumping of paste requires installation of expensive equipment e.g. positive displacement pumps that may not be afforded by small companies.

2.8.4 Applicability of Paste

Application of paste technology is very attractive in both the metallurgical industry yielding acid generating tailings and in countries with water shortages such as South Africa, Botswana and many parts of Europe.

Most research has been performed on the application of paste technology for waste immobilisation using cementitious materials for mine backfill (Baur et al., 2004; Paria and Yuet, 2006; Rojas, 2006; Potvin et al., 2005; Ouellet et al., 2008). This application implies a thickening step of the tailings which is often followed by the addition of a pozzolan such as fly ash or a binder like cement. Therefore the success of paste relied on the development of efficient thickeners and powerful pumps (Fourie, 2009).

The primary objectives of paste disposal in the mining industry are usually to recover water for reutilisation and to maximise ore extraction by using the tailings to fill voids in the mined out areas (Sivakugan et al., 2006; Huynh et al., 2006; Benzaazoua et al., 2004b, 2008; Jewell and Fourie, 2006). As a result paste backfill has been successfully practised by the metallurgical industry for over a decade.

2.8.5 Case Studies on Paste

The application of paste disposal technology has been applied in various scenarios throughout the world to mitigate the environmental impact of various operations (Benzaazoua et al., 2002, 2004a; Gitari et al., 2008; Sheoran and Sheoran, 2006).

(a) Iowa power plant

A coal-fired power plant in Iowa (USA) needed to dispose of large tonnages of fly ash without compromising the environment. A comprehensive characterisation of the Iowa fly ash was conducted to evaluate the possibility of extending its applications (Bergeson et al., 1988). Potential usage still left an appreciable volume requiring disposal.

Paste was identified as one option for surface disposal of the excess fly ash since a small portion could be utilised as an additive in the cement industry (Ahmaruzzaman, 2010; Bergeson et al., 1988; Baba et al., 2010; Pandian, 2004; Wiszniowski et al., 2007). The study evaluated the influence of fly ash properties such as LOI and chemical composition on the paste characteristics, such as compressive strength, hydraulic conductivity and mineralogy.

The results indicated that the mode of curing (either air curing or humid curing) is important for the stability of the paste. The mineralogy and chemistry of the paste were dependent on the PSD of fly ash. The sodium, sulphur, lime and tricalcium aluminate content of the fly ash affected the formation of hydration products. Among the identified secondary phases in cured paste were ettringite, monosulphoaluminate and Sträetlingite ($Ca_2Al_2SiO_2(OH)_{10}.8H_2O$) for which preliminary correlation with compressive strengths was attempted. It should be noted that the relationship between mineralogy and strength was not thoroughly investigated.

Bergeson et al. (1988) covered most aspects of the paste characterisation except the evaluation of environmental impact and workability. The intended research will try to bridge this gap and additionally investigate the effect of brine properties, which is more complex than the water used. The Iowa fly ash is a class C with high reactivity and cementitious characteristics hence not all the hydration products identified in these pastes can be expected in the present study.

(b) Osborne Mine: thickened tailings

Osborne Mine is a copper-gold operation that mines ironstone deposits containing pyrite, chalcopyrite ($CuFeS_2$) and magnetite in Australia. It generates approximately 112 000 ton/month of tailings. Considerable quantities of water are lost through evaporation in the tailings dams (McPhail et al., 2004).

Water is a scarce resource in northern Queensland (Australia) hence there was a drive from the authorities to minimise water utilisation. This necessitated the identification of a more efficient technology which led to the implementation of a thickened tailings (paste) discharge. The presence of sulphides was of concern since it has a potential to generate acid mine drainage and destabilise secondary minerals (Sracek et al., 2010; McPhail et al., 2004; Benzaazoua et al., 2002, 2004a; Widerlund et al., 2005; Klemm, 1998). Addition of lime to neutralise the effect of sulphides did not solve the problem because acid generation is slow thereby posing a long-term environmental liability (McPhail et al., 2004; Deschamps et al., 2008).

The implementation of paste disposal at Osborne Mine provided both economic and environmental benefits. Reduction in operational costs and better rehabilitation potential were realised in addition to water conservation (McPhail et al., 2004; Benzaazoua et al., 2004b).

(c) Bulyanhulu Gold Mine: thickened tailings

The rehabilitation of sites contaminated by gold mine tailings poses a huge environmental concern (Mckinnon, 2002; Mendez and Maier, 2008). Bulyanhulu gold mine experiences high evaporation rates owing to the semi-arid climate in northern Tanzania. It was therefore imperative to minimise water losses.

Bulyanhulu Gold Mine with Golder Associates took an audacious step to design, manufacture and commission a paste plant for surface disposal of tailings in 2001. The decision to go for 75% surface disposal and 25% mine backfill was unique while 100% mine backfill is more traditional (Jewell et al., 2002). The paste plant is running successfully according to the design and environmental issues are minimal.

2.8.6 Concluding Remarks

The literature review has shown that there are challenges with regards to the management of brines and fly ash. Additionally, the knowledge gaps were identified from both similar studies and paste technology which necessitate this investigation.

As expected countless methods and techniques exist for evaluating the effectiveness of different disposal options. It yet remains a challenge to identify a set of suitable methods; hence the following Chapter examines this matter.

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 INTRODUCTION

"The experimenter who does not know what he is looking for will not understand what he finds."
Claude Bernard (French scientist: 1813 – 1878)

There are many analytical techniques that can be employed to investigate the physical, chemical and mineralogical properties of pastes derived from brines and fly ash. These brines and fly ash are essentially variable because they are formed as by-products hence do not conform to any production specifications. Thus the paste resulting from combining these wastes is complex both in terms of its composition and behaviour. To this end the sampling strategy and the selected materials need to simulate the expected variance to enable a better understanding of the factors influencing the behavioural properties of an industrial paste.

This Chapter discusses the experimental procedures and materials used in this investigation as well as the preliminary results of workability tests on the paste. Standard methods were used to ensure the credibility of data and to keep focus on the project rather than on method development. This also makes it easier for other researchers to repeat the work in future.

3.2 MATERIALS

The sampling strategy adopted was to collect fresh fly ash and two industrial brines from the petrochemical plant in Secunda. These brines represent the expected chemical variation in the desalination facility. An additional (different) Matimba fly ash was sourced to evaluate the effect of variation of the fly ash on the paste characteristics and behaviour. Finally, it was also decided to drill several boreholes in a disused Fine Ash Dam (FAD) to establish a historic record of weathering for comparison with laboratory findings.

3.2.1 Fly Ashes

The bulk sample of fly ash was collected from the precipitators in the power station supplying the SASOL Synfuels plant with both steam and electricity. This power station combusts low-rank bituminous coal (Matjie el al., 2006; Bunt and Waanders, 2009; Moitsheki et al., 2010; Matjie, 2008) and yields fly ash. Additionally, a small sample (approximately 50 kg) of fly ash was obtained from ESKOM's Matimba power station located in the northern part of South Africa combusting coal from a different feedstock. Both of these power stations use pulverised coal combustion technology hence physical properties (such as Particle Size Distribution and particle morphology) are expected to be similar while chemical properties could vary slightly due to feedstock differences.

3.2.2 Weathered Fine Ash

The drilling was performed at various locations of the FAD of SASOL Synfuels by a contractor (Dump and Dune Drillers (Pty) Ltd) using a portable Auger drill. Details on the characterisation and implications thereof are provided in Chapter 4.

3.2.3 Brines

Bulk samples of fresh saline brines (namely, regen brine and salty water) were collected. Salty water and regen brine represent the extreme cases which can be encountered in the desalination process at Secunda. These brines originate from the thermal evaporation of Clear Ash Effluent (CAE) and ion-exchange demineralisation of raw water dominated by dosed regeneration chemicals (H_2SO_4, NaOH and NaCl), respectively.

3.2.4 Pure Chemicals

The investigation required the preparation of synthetic brines from pure chemicals. A list of those analytical grade chemicals used to prepare these brines is appended in Table A3.1.

3.3 RESEARCH METHODOLOGIES

This section presents in detail the experimental work which was conducted in this study. Justification for the inclusion of each experiment is given.

3.3.1 Industrial Brines

SASOL Synfuels plant contains a variety of brines with significant variation in chemical composition and salinity. With the industrial implementation of paste disposal technology in mind, it is imperative to test the robustness of paste properties to variations in brine and fly ash characteristics.

Fly ash was mixed with various quantities of deionised water, regen brine, and salty water to prepare a variety of pastes with fly ash content between 62% and approximately 70%. These solutions differ in terms of salinity and chemical composition which in this work will be referred to as *brine chemistry*. Typical composition of brines and seawater (Alahmad, 2010) is illustrated in Table 3.1.

Table 3.1 Chemical composition of regen brine, salty water and seawater (Alahmad, 2010)

Component	**Unit**	**Regen brine**	**Salty water**	**Seawater**
pH	-	7.4	8.8	8.2 – 10.0
EC	mS/cm	70.4	124.0	-
Ca^{2+}	g/l	0.34	2.10	0.50
Mg^{2+}	g/l	0.24	1.55	1.55
Na^{+}	g/l	19.23	21.00	12.00
Cl^{-}	g/l	14.67	34.30	22.00
SO_4^{2-}	g/l	5.93	15.20	3.00
TDS	g/l	44.40	108.00	39.81 – 45.00

(a) Effect of salinity

The effect of salinity on paste properties was also investigated. Salty water was selected for this aspect owing to its diverse chemical composition and adequately high salinity (108 g/l TDS). Deionised water was used as a control with theoretically zero salinity. The dilution of salty water with deionised water was performed as follows; 20:80 (20%), 40:60 (40%), etc with 100% being the salty water in its original form. Figure 3.1 shows the increasing colour intensity with salinity of the resultant solutions.

Figure 3.1 Photo showing increasing salinity of salty water

Mixes containing 68% fly ash and brines of different salinities were separately prepared to investigate the influence of salinity on paste characteristics. A fly ash content of 68% provides a paste consistency that is suitable to study induced behavioural differences (Mahlaba, 2007; Mahlaba et al., 2008).

3.3.2 Synthetic Brines

It is understood that the composition of industrial brines is complex hence synthetic brines were used to pinpoint the influence of individual components on rheological, chemical and mechanical properties of the paste. This would also avoid the impact of organics in industrial brines.

Synthetic brines were prepared in an attempt to develop a model towards understanding the influence of the predominant components (Na^+, Ca^{2+}, Cl^- and SO_4^{2-}) in the brines (Koch, 2002; Mooketsi et al., 2007; Ahmed et al., 2003; Ravizky and Nadav, 2007), on the paste. A wide variety of chemicals can be used to prepare solutions containing these anions but the significance of their association with a particular cation needs to be considered. For instance HCl and NaCl at equivalent [Cl^-] can influence paste behaviour differently because of pH and the presence of Na^+/H^+.

(a) Effect of chlorides

The effect of Cl^- in solutions with a maximum [Cl^-] of 24 g/l was investigated by altering the cations between H^+, Na^+ and Ca^{2+} (hydrochloric acid, sodium chloride and calcium chloride). Dilution of the 24 g/l Cl^- was carried out to prepare solutions containing 6, 12 and 18 g/l Cl^- to also evaluate the effect of [Cl^-] in pastes containing 68% fly ash.

(b) Effect of sulphates

Sulphuric acid (H_2SO_4), sodium sulphate (Na_2SO_4), and calcium sulphate dihydrate ($CaSO_4.2H_2O$) were used to prepare and adjust the [SO_4^{2-}] of the synthetic brines, to a maximum [SO_4^{2-}] of 12 g/l. The [SO_4^{2-}] of the industrial brines is usually about half that of [Cl^-].

(c) Influence of acidic mixing waters

A need was identified to separate the effect of pH from that of salinity in the mixing water for paste. H_2SO_4 and HCl were used to adjust the pH of deionised water to range between 1 and 8. Suitable paste consistency and workability tests were used to assess the influence of pH on the paste behaviour.

3.3.3 Establishment of a Predictive Brine Protocol (Model)

It is to be expected that there will be significant behavioural differences in pastes containing Cl^- and SO_4^{2-} especially in terms of workability and compressive strength. During this investigation various formulations were blended in different ratios such that the four major brine constituents (Ca^{2+}, Na^+, Cl^- and SO_4^{2-}) are in solution at a pre-determined salinity range. This aspect would demonstrate whether the characteristics of the resultant brine matrix depend on individual compounds used to prepare it.

The calibration of a protocol (model) was achieved by simulating the composition of the industrial brine through synthesis with commercial compounds and comparing yield stress and compressive strength of resultant pastes.

3.3.4 Influence of Fly Ash Properties

Fly ash is the predominant component of the paste. Its chemical composition is therefore expected to influence the paste behaviour. Matimba (ESKOM) and Synfuels fly ashes which originate from the combustion of different coals were used to establish whether the composition of the fly ash affects the characteristics of the resultant pastes.

(a) Pore water quality

Pore water can be defined as the free water available in the pores of a porous material which can provide information about its chemical environment. It was considered fundamentally important to extract pore water from the two fly ashes and compare the results, which would provide initial basis of comparison.

(b) Response to brine chemistry

Another test was to subject both fly ashes to specific brines (regen brine, salty water and deionised water) which differ in terms of chemical composition and salinity. Comparing the properties of the paste would indicate the effect of fly ash chemistry on paste. Based on the scientific literature (Chapter 2) there should be significant differences.

3.4 PHYSICAL CHARACTERISTICS

This section presents the details of analytical techniques and methods used to measure various physical properties of the paste. The emphasis was put on workability and compressive strength since they are essential for the engineering design of the disposal methodology. Other methods were used to supply additional data required to shed light on the observed paste behaviour.

Due to similarities of properties this work followed the approach of viewing fly ash as a soil (Hürlimann et al., 2001; Carraro and Salgado, 2004). It was for this reason that certain physical parameters (moisture content, pore water quality, Particle Size Distribution and specific gravity) were determined on both the samples drilled from the FAD as well as pastes prepared for evaluation.

3.4.1 Moisture Content (MC)

The determination of moisture content (MC) was only conducted on samples from the drilling exercise in a disused FAD. In accordance with ASTM D 2216-98 moisture content was determined based on mass loss during drying at 110 ± 5 ºC to a constant mass. The result is the amount of free water which is used to design stabilisation processes and indicates the available water for hydration (Barth et al., 1990; Donahoe, 2004).

3.4.2 Pore Water Extraction

The samples were dried overnight in an oven set at 35 ºC to minimise the sample alterations. A temperature of 35 ºC is a typical high which drilled samples in Secunda are thought to have experienced while in the FAD. The desiccator-cooled samples were then mixed with deionised water in a 1:2 (m/m) ratio, stirred for 10 minutes at 130 rpm, and allowed to stand for 60 minutes before recording the pH and electrical conductivity (EC) of the supernatant. The described method was adapted from ASTM D 4972-01 to suit the materials being evaluated.

3.4.3 Particle Size Distribution (PSD)

Particle Size Distribution (PSD) of the ash was determined using a Mastersizer from Malvern Instruments (Demers et al., 2008; Ntshabele et al., 2008; Deschamps et al., 2008). The PSD affects reactivity, porosity and surface area of the solid material. The results of PSD were used to measure the abundance of clay-sized, silt-sized and sand-sized particles in the samples according to ASTM D 422-63. This test provides material characteristics required to choose appropriate engineering applications (Barth et al., 1990). These data were also used to check whether the fly ashes meet the minimum threshold value of 15% for particles < 20 µm for good paste formation (Jewell and Fourie, 2006) and to indicate the influence of weathering on PSD (Zevenbergen et al., 1999).

3.4.4 Specific Gravity (G_s)

The specific gravity (G_s) of dried samples as defined in ASTM D 854 – 02 was determined using a Le Chatelier flask as illustrated in Figure 3.2. Other researchers refer to G_s as relative density. Paraffin was used as a liquid medium for the displacement of ash particles since ash is insoluble in organic solvents.

Specific gravity provides information on the settling velocity of a particle due to gravitational force. This has a direct influence to the settling rate and flowability of a viscous suspension such as paste (Deschamps et al., 2008; Kesimal et al., 2004; Demers et al., 2008).

Figure 3.2 Apparatus for the determination of specific gravity

3.4.5 Workability of Paste

Workability is a term used in civil engineering to define the ease with which a material e.g. fresh concrete can be pumped and placed. According to the definition of paste provided earlier it is necessary to understand the relationship between paste consistency and workability, which basically drives the economic feasibility and engineering design of a paste plant (Jewell and Fourie, 2006; Pullum et al., 2006; Slatter, 2004). Workability of paste can be influenced by many factors (Potvin et al., 2005; Gawu and Fourie, 2004; Huynh et al., 2006; Boger et al., 2008).

There are over 100 different methods to determine workability; not all of which are applicable at every level of consistency (Yücel, 2006). It is therefore critical to select an appropriate, reliable, sensitive and reproducible method for the intended application (Potvin et al., 2005). The workability of fly ash pastes and tailings has been investigated by different researchers using techniques such as slump, flow table, flow cones and measurement of rheology (Sofra, 2006; Gawu and Fourie, 2004; Clayton et al., 2003; Nguyen et al., 1998, 2006; Vietti and Dunn, 2006).

Despite the popularity of slump it suffers from low repeatability, is operator dependent and does not cater for shearing (Sofra, 2006; Gawu and Fourie, 2004; Clayton et al., 2003; Nguyen et al., 2006; Mahlaba and Pretorius, 2006), hence it was excluded. As an example Boger et al. (2006) evaluated three pastes derived from coal, gold and lead-zinc tailings which all produced a slump of 203 mm but their yield stresses were 160 Pa, 275 Pa and 330 Pa, respectively. This discrepancy can lead to incorrect pump sizing and other engineering problems if one were to only rely on the slump test as a measure of workability.

Only methods that are perceived pertinent to this investigation are reviewed and evaluated for suitability. A thorough elucidation of workability techniques can be obtained from Koehler and Fowler (2003) and Pretorius (2002).

(a) Flow table

The flow table test is a method often used instead of the standard slump test to determine the workability of mortars by providing more appropriate information (Koehler and Fowler, 2003). The flow table test also uses a cone to mould the specimen on top of a metal surface where after the sample is raised and dropped 25 times in 15 minutes from a height of 12.7 mm (ASTM C 230/C 230-03). The horizontal spread of the sample is measured and divided by the diameter of the lower part of the cone (100 mm). The apparatus is depicted in Figure 3.3a.

Figure 3.3a Picture of a flow table apparatus

The jolting simulates the shearing which will be applied during the pumping of the paste. This method could provide a simple and reliable method to determine the workability of brine-fly ash paste. The result depicted in Figure 3.3b illustrates a typical paste overflowing the table top. This observation was made with several paste batches and a decision was consequently taken that flow table is unsuitable in this investigation. Obviously one could reduce the height to below 12.7 mm or enlarge the diameter of the table but this would prevent any data being compared to values quoted in literature.

Figure 3.3b Illustration of paste overflowing the table top

(b) Flow cones

Flow cones are one of the funnel-based methods that can be used to measure the workability of grouts and pastes (Koehler and Fowler, 2003). In accordance with ASTM C 939, the test involves filling the flow cone to the standard level with paste and measuring the time taken to drain the cone until it is empty. This time is called efflux time and gives an indication of workability of the material being tested. Figure 3.4 is a graphical representation of the apparatus for a flow cone test. The results of this test are only acceptable for mixtures with an efflux time not exceeding 35 seconds, above which a different method must be employed.

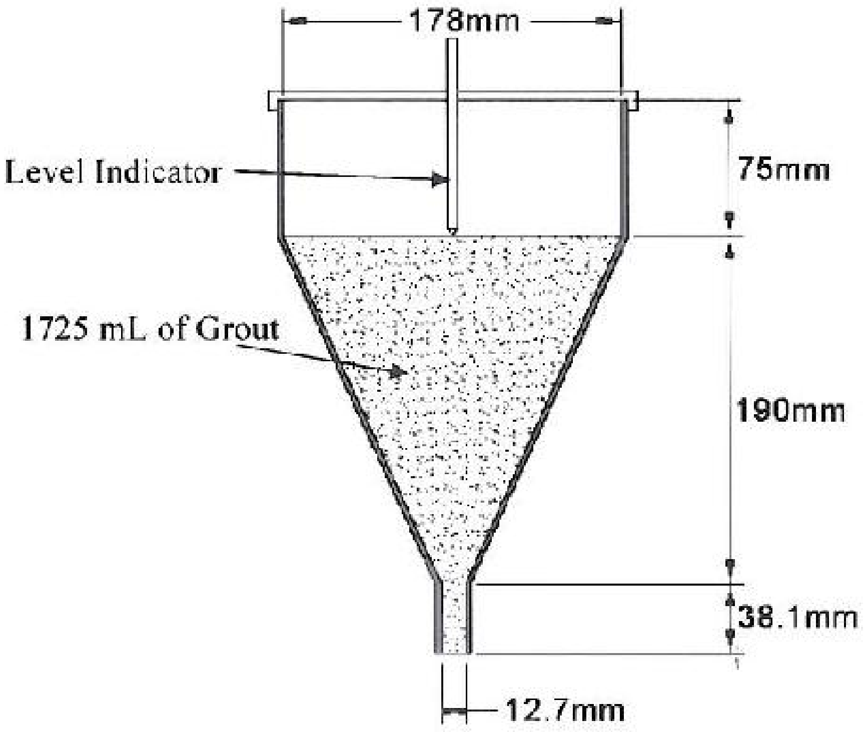

Figure 3.4 Standard flow cone test apparatus (ASTM C 939)

A standard flow cone requires approximately 1 750 ml of material which is arduous when doing replicates and requires large volumes of material. A smaller flow cone was therefore developed and evaluated in parallel with the standard flow cone. The immediate advantage of a modified flow cone is that it requires a 10th of the volume of the standard flow cone hence its development would simplify the evaluation process.

Figures 3.5a and 3.5b depict the standard flow cone and modified flow cone during successful runs where efflux times were recorded. The results of a correlation test between the two flow cones for pastes at low to medium consistencies are presented in Chapter 5.

Figure 3.5a Standard flow cone

Figure 3.5b Modified flow cone

It was observed that the application of flow cones is limited to low-viscosity pastes beyond which blockages were encountered as depicted in Figures 3.6a and 3.6b. It was unfortunate that blockages occurred in the region of high interest, which obviously restricts the applicability of the technique in this study.

Figure 3.6a Blockage in a standard flow cone

Figure 3.6b Blockage in a modified flow cone

(c) Rheological measurements

Rheology can be defined as the science of deformation and flow of matter (Malkin and Isayev, 2006). It measures the response of a system when a force is applied to a suspension. The major advantage of a rheometer is its capacity to characterise the flow behaviour of fluids (Boger et al., 2006; Malkin and Isayev, 2006). It can also be used to determine the impact of temperature on workability. Figure 3.7 depicts a rheometer (Rheolab QC model) from Anton Paar, which was used in this investigation.

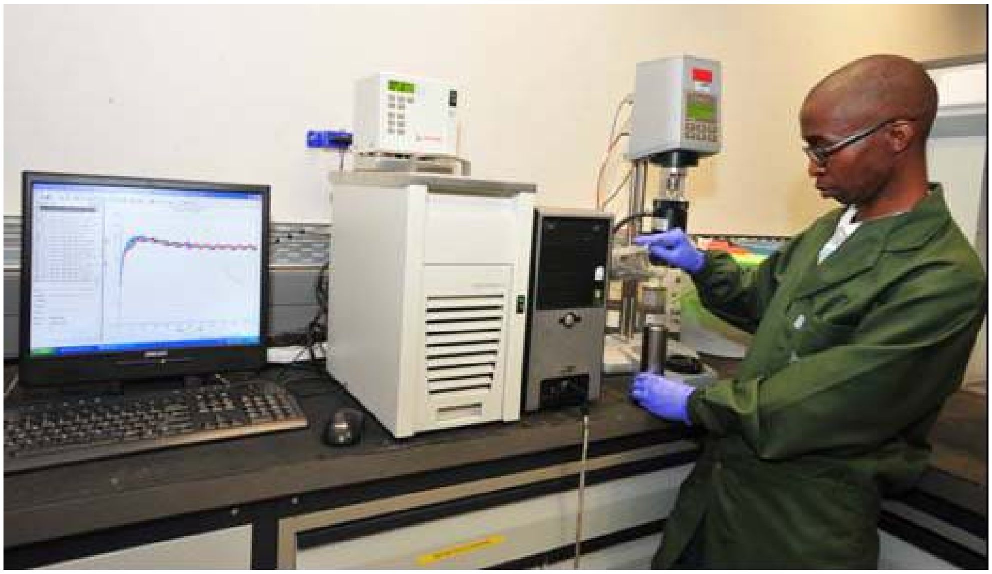

Figure 3.7 Photo of a modern vane rheometer in use

Rheometers are commonly used for the determination of *yield stress* and flow of viscous materials. Yield stress can be defined as a minimum shear stress that must be applied to a viscous material to initiate a significant flow (Alejo and Barrientos, 2009). Rheometers find application in construction, waste management and the food industry (Kwak et al., 2005; Huynh et al., 2006; Nguyen et al., 2006; Nguyen and Boger, 1998; Jewell and Fourie, 2006; Alejo and Barrientos, 2009).

The first attempt at using a rheometer to study the workability of the fly ash paste was based on measuring shear stress as a function of shear rate. Poor reproducibility was obtained and uncertainty exists as to where yield stress should be read because the rheometer has a lowest shear rate of 10 s^{-1} (see Figure 3.8). For instance, sample containing 71% fly ash had a higher shear stress than that with 70% fly ash content below 140 s^{-1} shear rate but the trend became reversed thereafter. Extrapolation of the shear stress curves to intercept the y-axis and obtain yield stress is inaccurate.

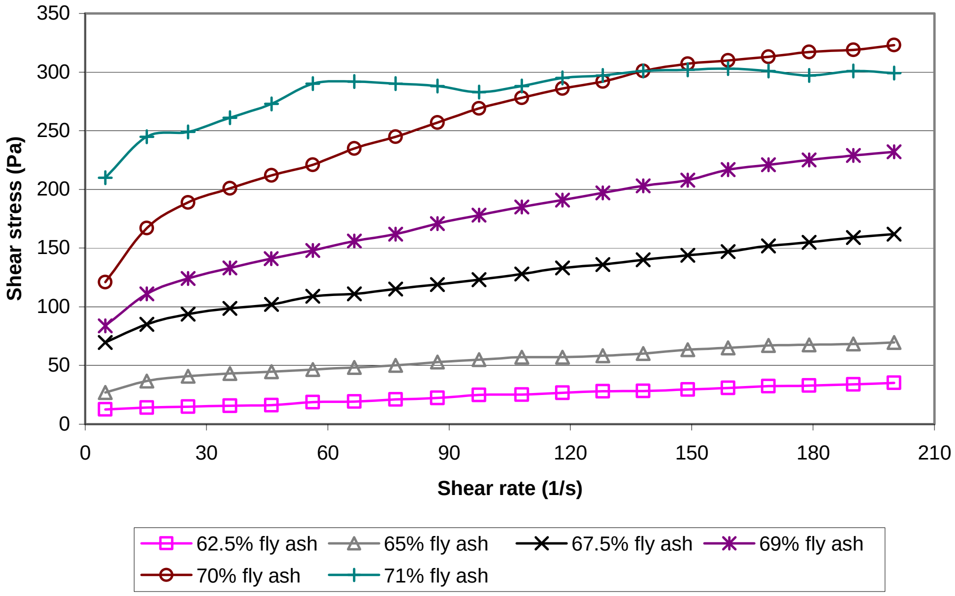

Figure 3.8 Illustration of a rheogram of shear stress against shear rate

The uncertainty and the fluctuation of these curves make it difficult to draw conclusions on the paste behaviour. It was therefore decided to evaluate the effect of time on a specific sample and see if improvement of data reproducibility occurs. Figure 3.9 shows that at least 15 minutes must be allowed as wetting time for paste to equilibrate before collecting rheological data. This observation was substantiated by Naik et al. (2009) who also allowed fly ash slurries to stand for 60 minutes before conducting rheological analysis. The reason for difference in wetting times is because the materials are different.

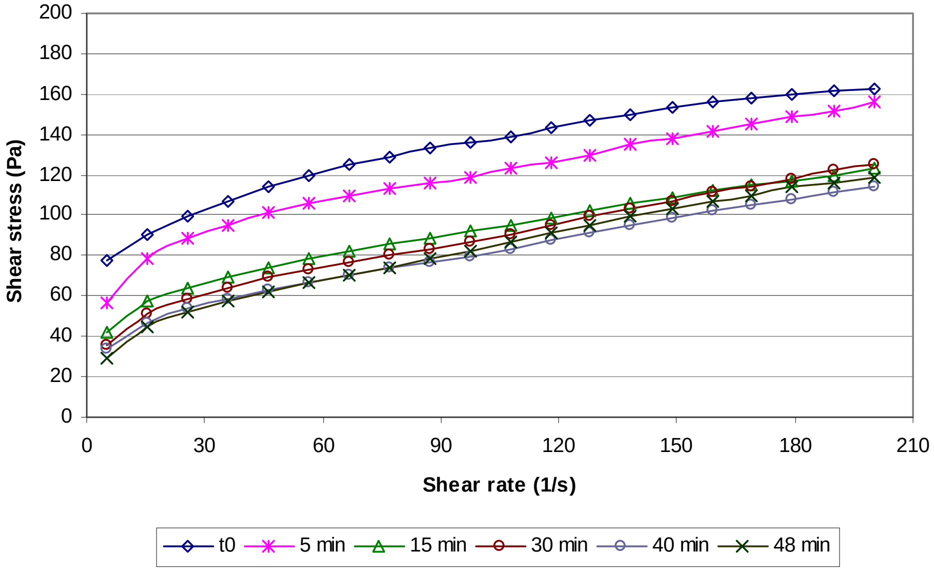

Figure 3.9 Illustration of time effect on the rheology

It was further discovered that by virtue of its solid configuration a bob which is a recommended measuring system could not penetrate the pastes with high fly ash content. On the other hand, a vane system penetrated the paste over the entire range due to its bladed configuration. The systems are depicted in Figure 3.10 where vane and bob are on the left and right hand side in the picture, respectively.

Figure 3.10 Photo of vane and bob systems

Further investigation on the use of a rheometer to study workability of pastes led to the generation of a reproducible data as shown in Figure 3.11. The method determines yield stress directly by using a vane at low speeds between 0.1 and 0.9 rpm (Boger et al., 2006, 2008; Nguyen et al., 2006) after allowing at least 15 minutes of wetting time for the sample to reach equilibrium. The exerted torque is measured as a function of time at a controlled shear rate (Nguyen et al., 2006).

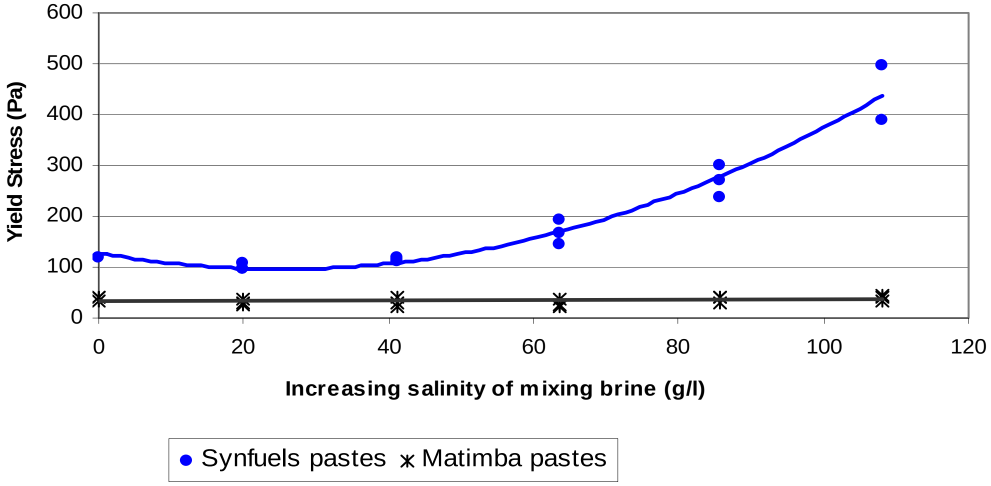

Figure 3.11 Illustration of reproducible vane yield stress determination

(d) Settling test

The slurries were prepared instead of pastes to study the settling behaviour because trends are expected to be clearer due to low solid-to-liquid (S:L) ratio. A settling test can be used to obtain information about the suspension. It has a direct application and relevance on measuring the workability of pastes and may give early indications on how different slurries behave.

The author of this thesis has developed a simple settling test where the slurry containing approximately 27% fly ash and a respective brine was prepared and transferred into a graduated measuring cylinder. The time taken by ash to settle was recorded at regular intervals until a steady state was attained. A photograph was taken at that point to provide visual evidence of the pattern.

(e) Concluding Remarks on Workability

It is concluded that for this investigation the rheometer is the most appropriate technique for the determination of yield stress as a measure of workability of fly ash pastes. However, the use of flow cones is restricted to low viscosity pastes due to blockages. The flow cone can be used to study flow properties which are influenced by shearing of the material.

3.4.6 Unconfined Compressive Strength (UCS)

Unconfined Compressive Strength (UCS) sometimes is referred to as Uniaxial Compressive Strength (both terms share the same acronym UCS) serves as a measure of performance for cementitious materials under mechanical stress (Pari and Yuet, 2006; Bouzalakos et al., 2008; Saw and Villaescusa, 2011; Palarski et al., 2011). It is important to choosing a suitable placement option for the utilisation or disposal of paste.

The development of UCS is a result of several reactions that occur during hydration of cementitious materials. It will therefore indicate the occurrence of those phenomena (Khoury et al., 2004) and suitability of paste for the intended application. Many environmental researchers have also used UCS as a measure for mine backfill, solidification/stabilisation materials and cohesive soils (Nehdi and Tariq, 2007; Pari and Yuet, 2006; Khoury et al., 2004).

Paste samples were poured into 100 mm cubes and left to stand for 24 hours to set. The samples were then removed from the moulds and wrapped in plastic as shown in Figure 3.12, to retain moisture required to sustain further hydration. The temperature was controlled at 21 ± 2 °C during curing.

Figure 3.12 Curing of paste samples under controlled conditions

The samples were cured for 28 days unless otherwise stated before being subjected to a uniaxial load to failure according to ASTM C 109. A pre-load of 10 N was applied to a specimen before data collection. The samples were subjected to force at a compression rate of 2.5 mm/min until failure. A Z050 Zwick Roell compression machine equipped with testXpert II software having a capacity of 50 kN (depicted in Figure 3.13) was used to measure UCS.

Figure 3.13 Picture of UCS determination in a Z050 Zwick Roell compression machine

3.4.7 Definition of Desired Paste

The main distinction between a paste and slurry lies in the solids content which directly influences both workability and compressive strength. A conservative approach was taken with both parameters. Yield stress was identified as the rheological parameter capable of providing a reliable, reproducible and a sensitive measure of workability for the evaluation of paste. There is no universally accepted range of yield stress for a paste due to its complexity and dependence on numerous factors. A yield stress of 200 Pa was selected as the maximum threshold value in this work. This figure was deduced from preliminary tests and it falls within the typical range for paste backfill materials of 100 – 500 Pa yield stress recommended by Hallbom (2010). Besides, Boger et al. (2006, 2008) mention that centrifugal pumps can handle pastes up to 200 Pa yield stress. The advantage of centrifugal pumps is that they are well known, relatively inexpensive and consume less energy than positive displacement pumps for instance.

The exact criterion for mine backfill materials in terms of the minimum UCS is unclear. According to Laugesen and Eriksson (2006) the minimum UCS for stabilised/solidified materials should exceed 100 kPa. Some researchers (Potvin et al., 2005) recommend a minimum UCS of 200 kPa to avoid subsidence whereas others (Bouzalakos et al., 2008) suggest 440 kPa to support construction and vehicle loads.

A more conservative approach was taken by the author of this thesis to propose a minimum UCS value of 500 kPa, which is higher than those recommended by other researchers. This value applies to either surface disposal or underground backfilling with brine-fly ash pastes.

3.5 SOLID STATE CHEMISTRY

It is important to understand the solid state chemistry of materials in order to determine the immobilisation mechanisms. This will also help in assessing the long-term liability based on the knowledge of hydration products (such as solubility and thermodynamic stability). The results can further be used to complement the leaching results (aquatic chemistry) and to explain the physical behaviours. The chemical composition and mineralogy were determined using X-ray Fluorescence, X-ray Diffraction, Differential Scanning Calorimetry, and Field Emission Gun Scanning Electron Microscopy.

3.5.1 X-ray Fluorescence (XRF)

X-ray Fluorescence (XRF) spectroscopy is one of the widely used spectroscopic techniques to acquire bulk chemical information on solid materials. The X-rays are used to excite the inner electrons hence valency of the element is usually immaterial for XRF analysis (Loubser and Verryn, 2008). The XRF is unexpectedly not immune to errors such as interference. Therefore its correct use depends on proper calibration and background information on the sample.

The samples were pressed as briquettes and introduced to the ARL 9400XP+ XRF and analysis was based on UniQuant software. The results were reported in normalised state since no loss-on-ignition (LOI) was determined in this procedure as with fused beads (Loubser and Verryn, 2008).

3.5.2 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) is arguably the most commonly used technique to identify and quantify crystalline phases of solid materials. The application of XRD is found in mining, pharmaceuticals, organic synthesis, and cement industry. Detection is based on the understanding that crystals are comprised of atoms or molecules that are arranged in a regular pattern (Ward and French, 2006). This pattern is unique for each compound and can be determined when a specimen is bombarded by X-rays. Due to the irregular scattering of X-rays the amorphous phase appears as a broad band (Loubser and Verryn, 2008; Ward and French, 2006). However, it is critical to provide the spectroscopic analyst with as much information about the sample as possible e.g. sample origin.

The majority of mineralogy was principally determined using XRD on dried samples using a PANalytical X'Pert Pro powder diffractometer with X' Celerator detector and variable divergence- and receiving-slits with Fe-filtered Co-Kα radiator. The phases were identified using X' Pert Highscone plus software. A 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). Lab B added calcium fluoride (CaF_2) instead of 20% Si for the determination of amorphous content.

3.5.3 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a thermo-analytical technique that records loss of mass as a function of temperature where results are generated by heating the sample. Long history exists on the successful use of this technique to identify hydration products in cementitious materials (Ray, 2002; Gabrovšek et al., 2006; Stefanović et al., 2007). Some of their advantages include small sample requirements, ability to detect both amorphous and crystalline phases, and quick generation of results (Ray, 2002; Voigt and Shah, 2003). Besides, thermal analytical techniques provide a greater degree of sensitivity for the identification of phases than XRD (Ramachandran et al., 2002; Gabrovšek et al., 2006).

A DSC basically measures the difference in the amount of heat required to increase the temperature of a sample and compared to a reference which was an empty sample holder in this case. The phase transitions such as dehydration can be observed and can be used to tell whether a transition is endothermic or exothermic. Moukwa et al. (1992) used DSC to determine calcium hydroxide in hydrated cement pastes. Other researchers have used Differential Thermal Analysis (DTA) which operates on the same principle as DSC to identify mineral phases (Nochaiya et al., 2009; Rojas, 2006; Pane and Hansen, 2005; Radwan and Heikal, 2005; Coleman and Mcwhinnie, 2000; Murat, 1983).

Data in this study were collected using a Mettler Toledo DSC 822^e Star^e System with an FRS5 sensor. The heating rate was 10 ºC/min from 25 ºC to 150 ºC, cooling from 150 to 25 ºC at 20 ºC/min. The second heating from 25 to 500 ºC was again at 10 ºC/min and the final cooling rate was 20 ºC/min.

3.5.4 Field Emission Gun Scanning Electron Microscopy (FEG SEM)

Particle morphology influences water requirements and workability of slurries and pastes. Scanning Electron Microscopy (SEM) is a very useful tool that is widely employed to determine the morphology of particles and detection of new phases (Plank and Hirsch, 2007; Fernández-Jiménez et al., 2005; Chan and Dudeney, 2008).

A Zeiss ULTRA plus 55 FEG SEM with InLens detector operated at 1 keV was used to analyse surface properties. To ensure electrical conductivity the samples are carbon-coated prior to analysis. FEG SEM stands for Field Emission Gun Scanning Electron Microscopy and provides high resolution micrographs compared to ordinary SEM.

3.5.5 Leaching (Aquatic Chemistry)

The utilisation of waste materials in applications where they can come into contact with surface and groundwater, carries a risk of polluting the environment (Klemm and Bhatty, 2002; Bin-Shafique et al., 2002; Gupta, 2005; Krolo et al., 2003). Contaminants may leach whenever water interacts with a permeable material such as soil or stabilised wastes (Asavapisit et al., 2003; Bin-Shafique et al., 2002; Hartwil and Calovini, 1999; Kharna et al., 1998). Most trace elements are remobilised under acidic conditions while those present as oxyanions are more soluble under alkaline conditions (Kim, 2005; Font et al., 2005).

Many researchers have evaluated various leaching methods and there are still debates on the suitability and differences in results obtained. This thesis is not focused on leaching, which is only required to obtain comparative data on different paste formulations. A South African standard leach test which will be used for regulatory purposes in the near future was employed in this study.

South African Standard Leaching Procedure (SANS 10234 – GSH)

The Republic of South Africa is working on a draft of regulations and standards for waste classification and management (SANS 10234 – GSH) which is based on the Australian Standard Leaching Procedure, namely, AS 4439.3-1997 (Crous, 2010). This test is similar to toxicity characterisation leaching procedure (TCLP) except for the leachant options and 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 S:L ratio of 1:20 and gentle shaking for 18 hours (Halim et al., 2004, 2005). 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.

Four categories are specified in the South African Standard Leaching Procedure (SASLP) to classify the risk profile of the material being studied, see Table 3.2 (Crous, 2010). The threshold values for inorganic contaminants are provided in Table A3.2 (appendix) for each of the four categories.

Table 3.2 Classification criteria of waste based on SASLP (Crous, 2010)

Contaminant Concentration Criteria	Waste Risk Profile	Description
LC > SASLP2	**A: Extreme Risk**	Considered very high risk waste with a very high potential for contaminant release. Requires very high level of control and ongoing management to protect health and the environment.
SASLP1 < LC ≤ SASLP2	**B: High Risk**	Considered high risk waste with high potential for contaminant release. Requires high level of control and ongoing management to protect health and the environment.
SASLP0 < LC ≤ SASLP1	**C: Moderate Risk**	Considered low risk waste with some potential for contaminant release. Requires proper control and ongoing management to protect health and the environment.
LC ≤ SASLP0 and TC ≤ SASTC0	**D: Very Low Risk**	Very low risk waste with low potential for contaminant release. Requires some level of control and ongoing management to protect health and the environment.

Note: LC: Leachate Concentration; SASTC: South African Standard Total Concentration

The discussion of leaching data was restricted to Ca, Na, SO_4^{2-} and Cl^- in this thesis since the focus of immobilisation was put on the predominant constituents of brines (contaminants). The first batch of pertinent data using SASLP from the upcoming legislation (expected to be passed by the end of 2011 during preparation of the thesis) were generated.

3.6 CONCLUDING REMARKS

The author believes that the above-mentioned techniques and methods will enable the attainment of project goals. It is, nevertheless, known that there are other advanced techniques such as microprobe and QEMSCAN which can also be used to identify both crystalline and amorphous phases (Moitsheki et al., 2010; Buhre et al., 2006; Goodall, 2008; Matjie et al., 2008; Liu et al., 2005).

CHAPTER 4

DRILLING AND CHARACTERISATION OF A FAD

4.1 INTRODUCTION

SASOL Synfuels disposes of over 4 million tons of Fine Ash (FA) with more than 17 000 m^3 of brines in the fine ash dams annually. There is a ubiquitous drive towards environmental sustainability from the public, authorities and industry (Auner and Holl, 2006; Bealey et al., 2007). Investigating a Fine Ash Dam (FAD) provides one step towards understanding the extent of environmental impact, rehabilitation and re-utilisation opportunities of Weathered Fine Ash (WFA).

A disused FAD under investigation was commissioned in March 1993 and decommissioned in the first half of 2005, implying that the bottom and the top ash samples were at least 16 and 4 years old, respectively, during sampling in June 2009.

FADs form an integral part of managing energy generation by-products from coal combustion operations. A fundamental understanding of weathering of disposed FA is mandatory for the improvement of fly ash-brine operations. Of particular relevance to this thesis is an insight into the long-term chemical processes taking place during weathering; and the associated mineralogical as well as microstructural transformation.

4.2 FINE ASH DAM CONSTRUCTION

A FAD was built from the disposal of slurry having a specific gravity of 1.3. An excess of 4 million tons of FA and 17 000 m^3 of brines having a typical salinity of 10 g/l TDS are disposed annually in this manner. The slurry is pumped onto the FADs by means of centrifugal pumps in 300 mm (diameter) pipelines as illustrated in Figure 4.1. With time the solids in the slurry settle on top of a FAD whereas the supernatant called Clear Ash

Effluent (CAE) drains through a penstock (Figure 4.2) to the temporary storage area known as CAE dams depicted in Figure 4.3.

There seems to be precipitation of dissolved inorganic species taking place in the CAE channel due to high pH (see Figure 4.3), which was found to be gypsum and calcite in unpublished work. Another portion of CAE percolates the FAD and collects at the toe drain which also flows to CAE dams. Toe drains have lower contaminants compared to CAE owing to the longer contact time with FA, suggesting slow reaction kinetics (Koch, 2002).

Figure 4.1 Deposition of slurry onto a FAD

Figure 4.2 Penstock in a disused FAD

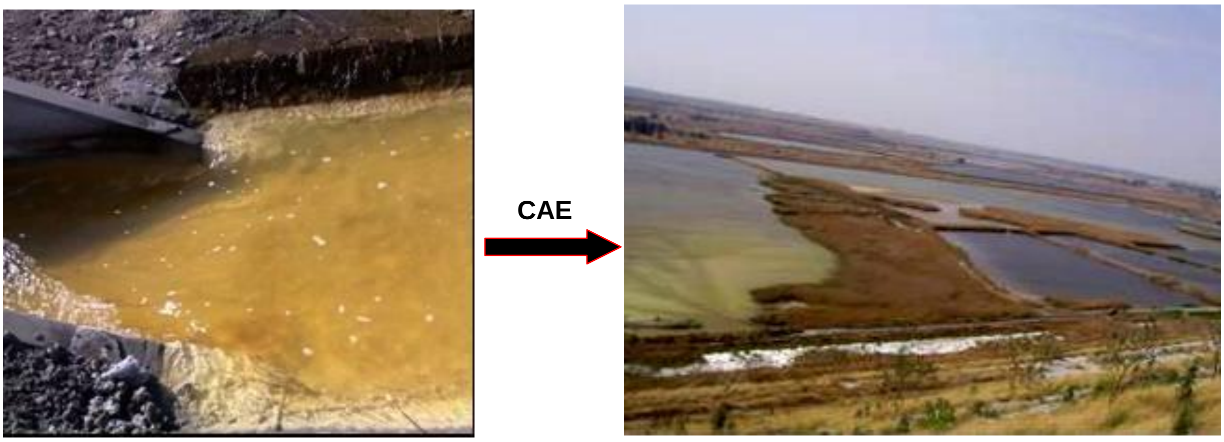

Figure 4.3 The view of CAE flowing into CAE dams

A small portion of the CAE is returned to the Synfuels factory and used as make-up water for fresh ash collection. The major portion is desalinated using Reverse Osmosis (RO), thereby producing RO brine. Demineralisation of raw water to meet boiler feed quality involves regeneration of resins with chemicals. This results in producing a regen brine, which is the largest contributor of salts at SASOL Synfuels complex.

Figure 4.4 shows a typical FAD that can be found within SASOL. Several 300 mm (diameter) discharge lines which are approximately 250 m apart, are used to ensure an equitable distribution of fine ash on the FAD.

Figure 4.4 Side view of the disused FAD

Slurry disposal is common practice in the mining industry. Most literature (e.g. Benzaazoua et al., 2002; Gitari et al., 2008; Sheoran and Sheoran, 2006) discusses the issues of relevance to acid generating tailings dams. Very little literature exists on the weathering of coal ash disposal sites despite increasing coal utilisation by developing countries including China, India and South Africa (Lee and Spears, 1994; Lee et al., 2007; Sarkar et al., 2007; Tu et al., 2007).

The study presented here was aimed at understanding the weathering process occurring in a FAD and the associated environmental impact of ash disposal if any.

4.3 DRILLING

The general layout of the FAD can be seen in Figure 4.5 with arrows indicating several deposition points across the dam which were interchangeably used to achieve even rate of vertical growth. The penstock is normally located near the centre of the dam, however, that of the FAD under investigation lies towards the north eastern end of the dam, as designated by a black spot (Figure 4.5). The position of the penstock is due to geological slope of the area, and could influence the layering of the dam.

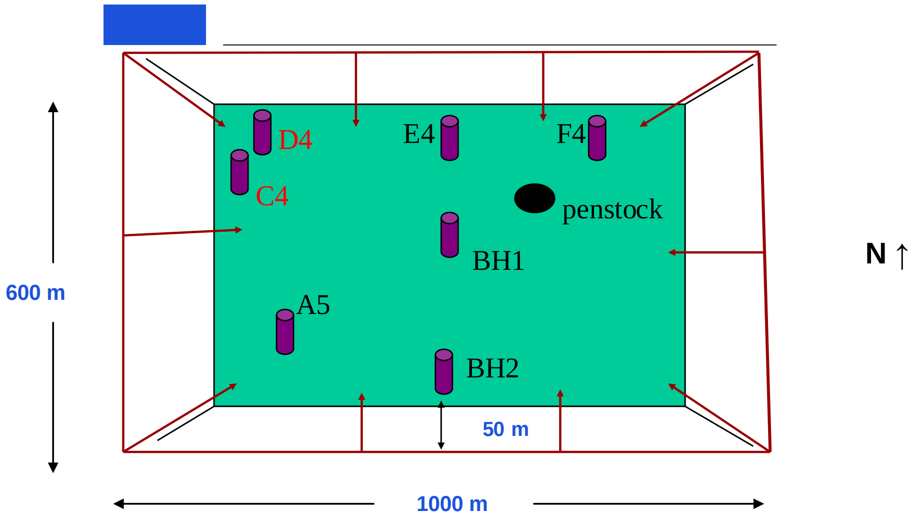

Figure 4.5 Schematic representation of the location of the boreholes on the FAD

Seven boreholes were drilled to the base of the FAD as schematically shown in Figure 4.5. Only BH1, BH2, A5, E4 and F4 were utilised in this investigation because boreholes C4 and D4 were saturated due to irrigation with CAE which takes place at set intervals post decommissioning (details are appended in Figures B4.1 – B4.2). No sampling could be performed on the eastern side of the dam due to excavations.

Dump and Dune Drillers (Pty) Ltd used a portable Auger drill as illustrated in Figure 4.6. The material collected vertically over a 1.5 m length was blended to make up the samples for the 50 m depth in the above-mentioned boreholes. Samples were sealed immediately in plastic bags under natural conditions to minimise atmospheric contact and retain original moisture.

Figure 4.6 Illustration of sampling in a FAD using Auger drill

4.4 RESULTS AND DISCUSSION: WEATHERED FINE ASH

This section presents the results of moisture content, PSD, pore water quality, chemical and mineralogical properties of WFA taken from the FAD.

4.4.1 Moisture Content Profiles

The moisture content (MC) presented in Figure 4.7 demonstrates that the degree of wetness increases with depth. The MC lies predominantly between 27% and 37% which indicates a significant water holding capacity likely to provide sufficient moisture for long-term hydration reactions.

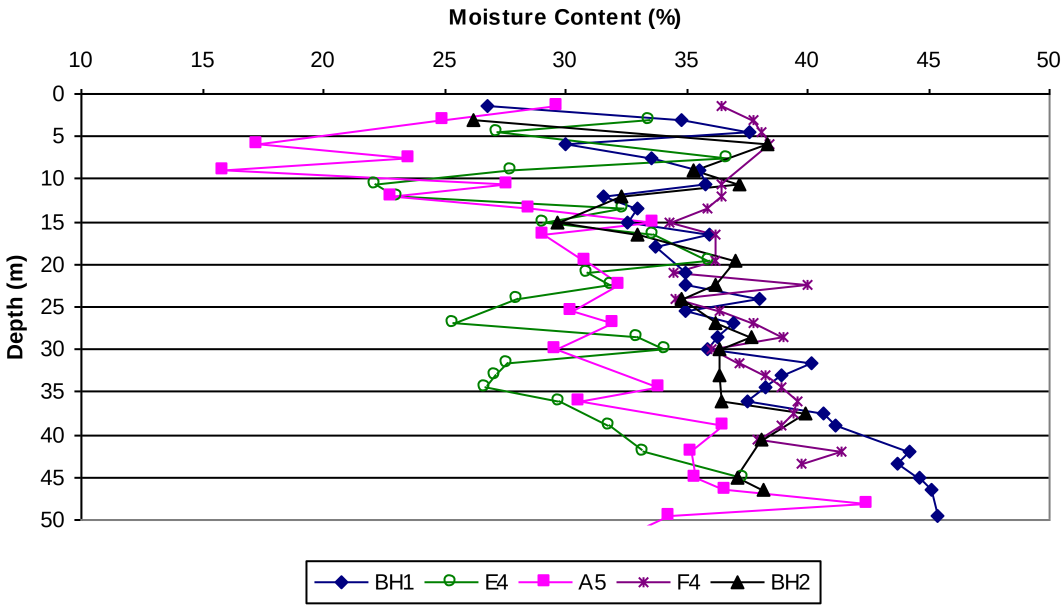

Figure 4.7 Moisture content profile of FAD

4.4.2 Pore Water Quality

The pH seemed to stabilise at around 9.5 (Figure 4.8), which is three units lower than the pH 12.5 of fresh slurry and fly ash. Donahoe (2004) attributes such drop in pH to carbonation, hydrolysis and precipitation (*i.e. chemical weathering*) upon depletion of portlandite. This observed pH reduction in an alkaline FAD correlates with the data reported by Zevenbergen et al. (1999) during their study of a fresh and 8-year old alkaline fly ash disposal in India. Mehta and Monteiro (2006) also suggest that the hydration of a pozzolan consumes lime; hence the pH is consequently decreased.

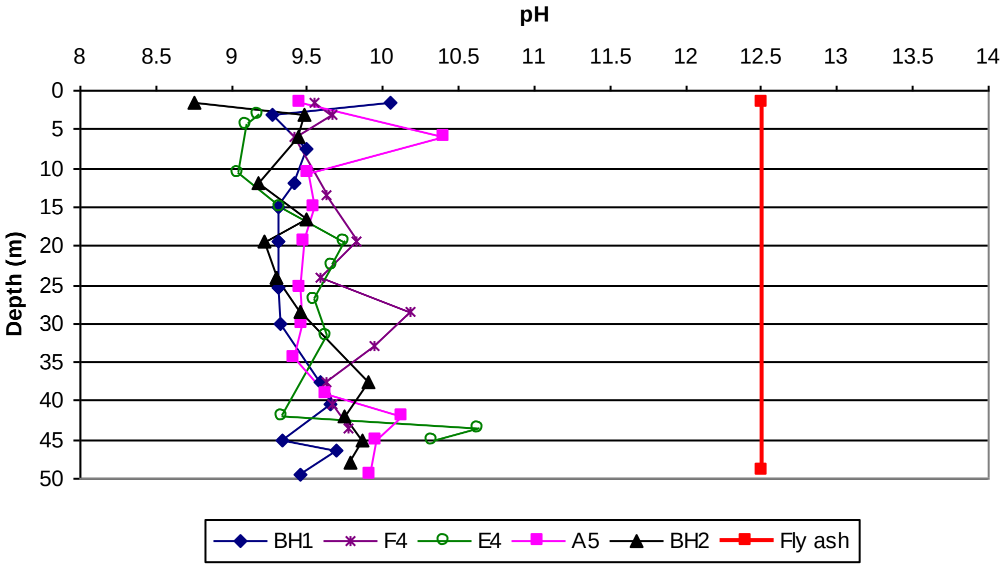

Figure 4.8 The pore water pH profile of boreholes

The samples taken at the top of the dam generally have lower pH values than those found deeper in the FAD, which can be explained in terms of a reaction with carbon dioxide. There is variation in some pH curves (boreholes) which could be attributed to analytical limitations, heterogeneity in the dam as well as the sampling procedure of making 1.5 m composite samples.

The EC data of extracted pore water are erratic at the top and bottom layers of the FAD. Such variation is not uncommon as was also found by Koch (2002) and Fourie (2006). The results shown in Figure 4.9 have the average EC of 2.2 mS/cm for WFA whereas fresh fly ash gave a value of 8 mS/cm, which is almost four times higher. The difference in leaching potential is ascribed to the formation of hydration products in the case of WFA (Donahoe, 2004; Gitari et al., 2009; Yeheyis et al., 2009; Koch, 2002).

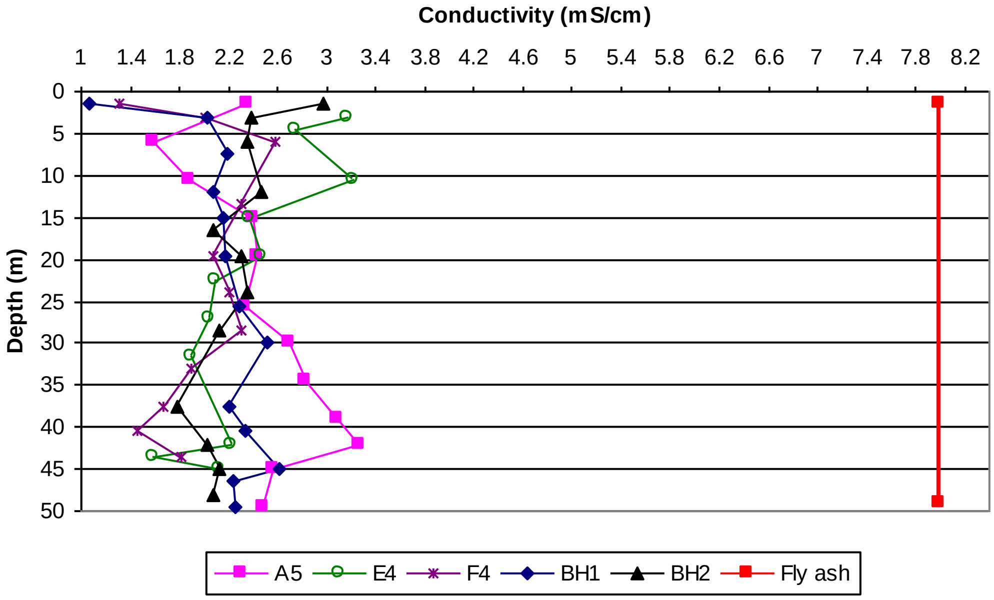

Figure 4.9 The pore water EC profile of boreholes

In isolation, this observation suggests that hydraulic ash disposal with brines provides a potentially better management than disposing dry ash. However, examination of all data will lead to an encompassing conclusion on the matter.

4.4.3 Particle Size Distribution

The PSD of WFA was classified into clay-, silt- and sand-particle sizes according to ASTM D 422-63 where:

Clay-sized = particles greater than 1 µm and smaller than 5 µm
Silt-sized = particles greater than 5 µm but smaller than 75 µm
Sand-sized = particles greater than 75 µm but smaller than 425 µm

The summary of PSD data presented in Table 4.1 demonstrates that the characteristic PSD of the FAD closely resembles that of fly ash. However, there is substantial variation in the overall data when examining the individual PSD profiles including the D_{50} values appended as Figures B4.3 to B4.6. This was attributed to plant disruptions such as boiler efficiency although no proper records exist for verification (Mahlaba and Pretorius, 2006; Glasser, 2004).

Table 4.1 Summary of PSD data for the FAD and fly ash

Particle size	**WFA**	**Median**	**Fly ash**
Clay-sized (%)	5 – 77	16	14
Silt-sized (%)	23 – 83	60	59
Sand-sized (%)	0 – 64	30	27
[2]D_{50} (µm)	3 – 120	23	27.5

It is nevertheless concluded that WFA is silty and has a characteristic PSD profile resembling that of fresh fly ash, despite the existence of relatively finer and coarser fractions such as found in boreholes E4 and A5, respectively.

4.4.4 Variation in Elemental Composition

The range of elemental composition as oxides in the FAD is summarised in Table 4.2 along with figures obtained for fresh FA and fly ash. The comparability of tabulated results validates the use of fly ash as a reference material for WFA apart from the brine influence. Elemental forms were used for the classification of elements into major, minor and trace elements.

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[2] D_{50} is defined as the diameter of sieve through which 50% of particles pass

Table 4.2 Elemental composition of WFA, fresh FA and fly ash

Component	Range in WFA (%)	Median of WFA (%)	[3]Fresh FA	Fresh fly ash
SiO_2	43.10 - 43.11	43.10	43.31	52.29
Al_2O_3	26.01 - 30.89	28.68	31.09	27.51
Fe_2O_3	1.91 - 16.62	3.87	2.14	2.77
CaO	8.46 - 11.05	9.06	8.22	10.64
MgO	1.50 - 2.33	1.97	1.15	2.24
SO_3	1.45 - 7.44	2.90	4.43	0.40
Na_2O	0.98 - 3.51	1.98	4.48	0.71
K_2O	0.71 - 1.10	0.97	0.79	0.99
TiO_2	1.05 - 1.55	1.46	1.38	1.59
SrO	0.32 - 0.55	0.45	0.39	-
BaO	0.19 - 0.35	0.28	0.25	-
P_2O_5	0.66 - 1.02	0.89	0.85	0.70
Cl	0.19 - 1.45	0.49	1.20	-
MnO	0.05 - 0.13	0.07	0.05	0.06

[3] Fresh FA refers to fine ash which was sampled from an operational FAD and dried; fine ash is a combination of fly ash and gasification fines

Thus a range of XRF results is provided as oxides in Table 4.2 while subsequent discussion of elements and their classification into major, minor and trace will be based on using the elemental symbol. This does not imply that the actual speciation is elemental.

(a) Major Elements

Major elements are defined as those elements exceeding 10% by weight in a sample. Only silicon and aluminium can be referred to as major elements in the investigated FAD.

Silicon (Si)

Figure 4.10 shows that silicon (Si) ranges between 15% and 20% in all the boreholes throughout the ash dam while fly ash contains approximately 23% Si. There is no appreciable variation of Si with depth and borehole but the higher Si content of fly ash suggests that it leaches in the FAD.

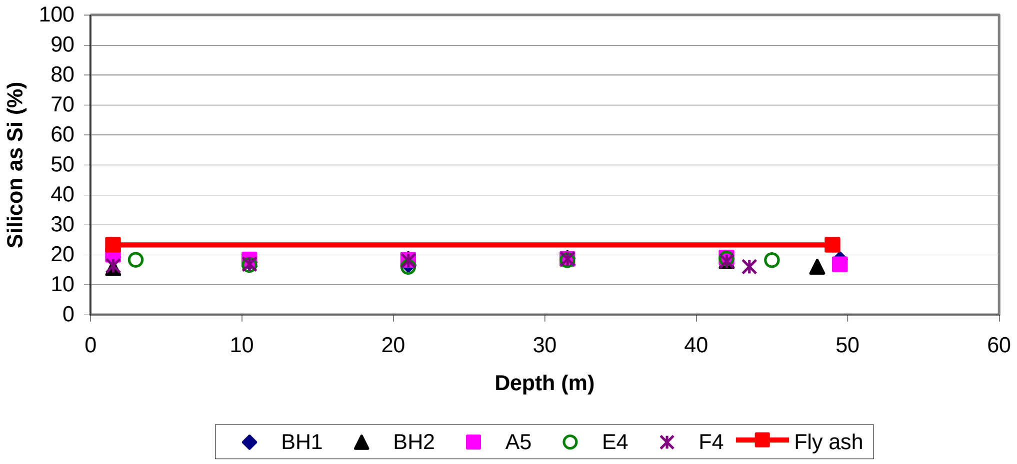


Figure 4.10 Profile of Si content in boreholes

Aluminium (Al)

The aluminium (Al) content seems to remain relatively constant between 14% and 16% throughout the FAD as illustrated in Figure 4.11. The content of Al in fly ash and WFA closely resemble each other, indicating efficient immobilisation of Al.

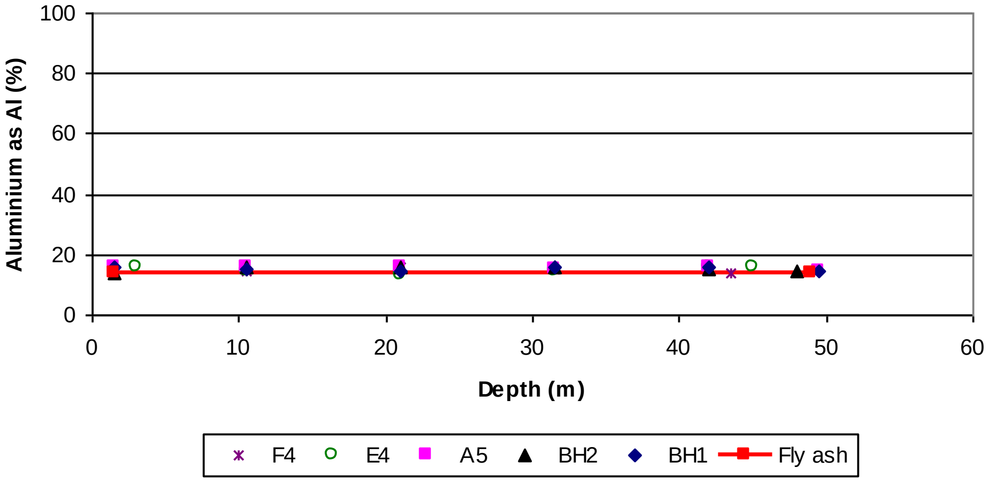


Figure 4.11 Profile of Al content in boreholes

(b) Minor Elements

Minor elements are defined as those elements with concentration ranging between 1% and 10%. They are calcium, iron, magnesium, and sodium; all of which are discussed in the following sections due to their relevance to hydration.

Calcium (Ca)

Figure 4.12 shows that calcium (Ca) profile is consistent in the FAD with some variation in borehole E4. Fly ash showed a slightly higher concentration (8%) of Ca than WFA (6%), which suggests that Ca is leaching from the FAD.

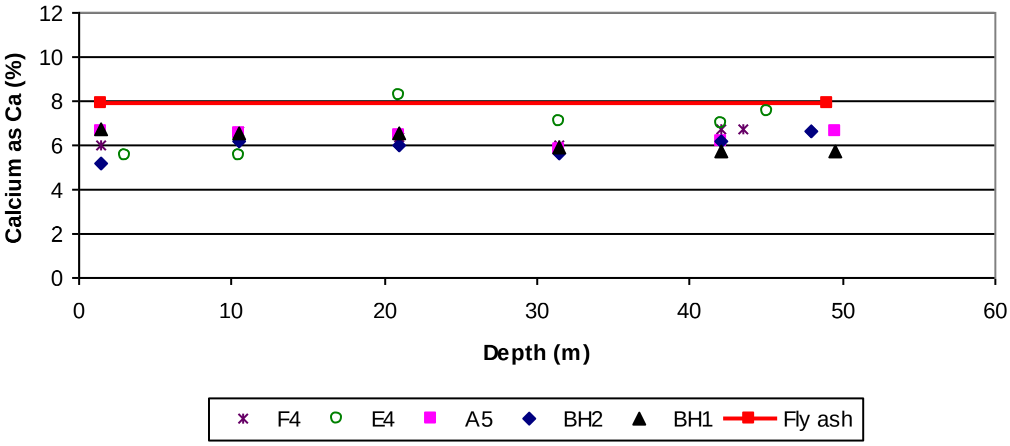


Figure 4.12 Profile of Ca content in boreholes

Iron (Fe)

The concentration profile of iron (Fe) is highly variable in some boreholes (e.g. BH1 and E4) as depicted in Figure 4.13. The variation in Fe content can be explained by the irregular dumping of spent Fe-based catalyst in the FAD. Nevertheless, there seems to be a good correlation between fly ash and WFA around 2%.

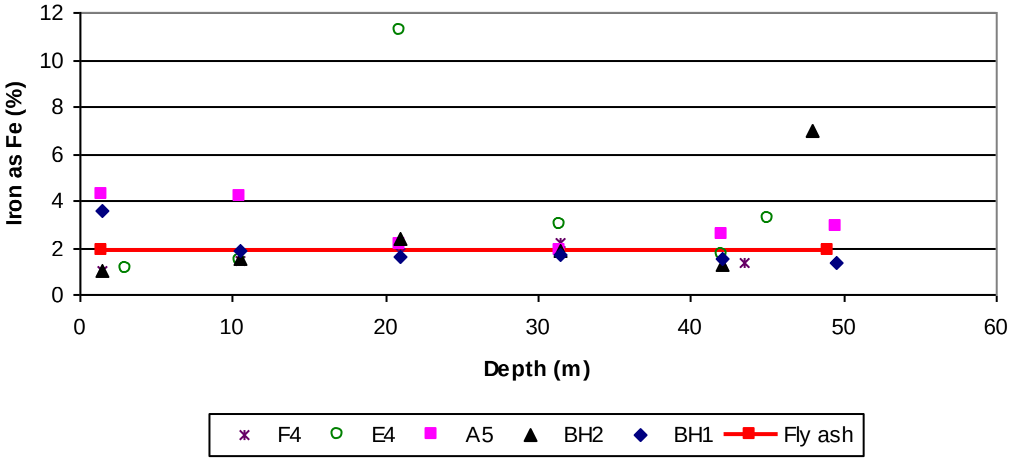


Figure 4.13 Profile of Fe content in boreholes

Sodium (Na)

The general profile of sodium (Na) is consistent with depth in most boreholes at approximately 1% as illustrated in Figure 4.14. It is important to note that WFA has a consistently higher Na content than fly ash. This difference can be associated with the regen brine the details of which were presented in Chapter 3.

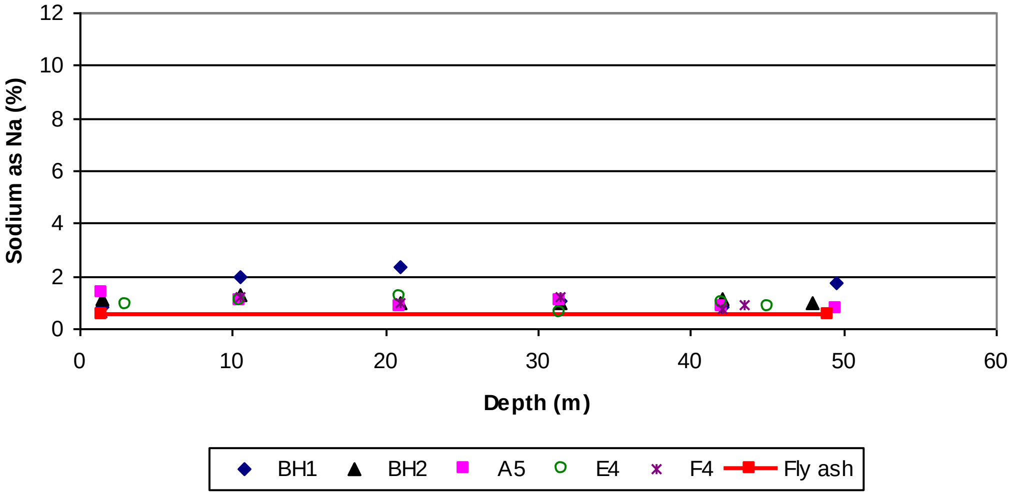


Figure 4.14 Profile of Na content in boreholes

Magnesium (Mg)

All boreholes display a consistent amount of magnesium (Mg) throughout depths which resemble that of fly ash as shown in Figure 4.15. The characteristic amount of Mg is 1%.

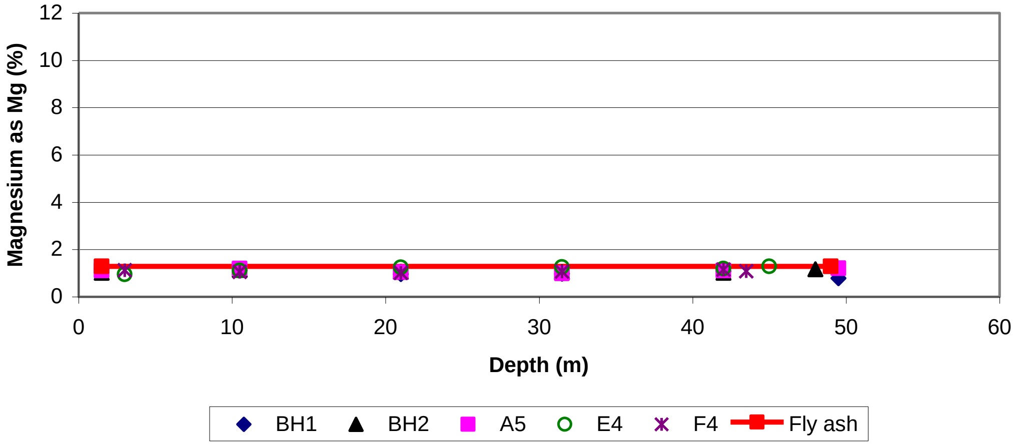


Figure 4.15 Profile of Mg content in boreholes

Minor elements seem to generally remain constant throughout the FAD and resemble fly ash with some influence of brine in the case of Na.

(c) Trace Elements

Trace elements are defined as those elements which are lower than 1% in concentration. They include chloride, potassium, sulphur, titanium, barium, strontium, and phosphorus. The trends of chloride and sulphur are presented due to their pertinence to hydration and weathering reactions whereas the others are appended in Figures B4.7 – B4.11.

Chloride (Cl)

The chloride behaviour is constant in the FAD with a typical concentration of 0.4%, and some variation in the central borehole (BH1) as shown in Figure 4.16. The fly ash showed no identifiable presence of Cl^- which suggests that it originates from the regen brine. Therefore, the variation in the quantity of Cl^- is ascribed to the disruptions during regeneration process.

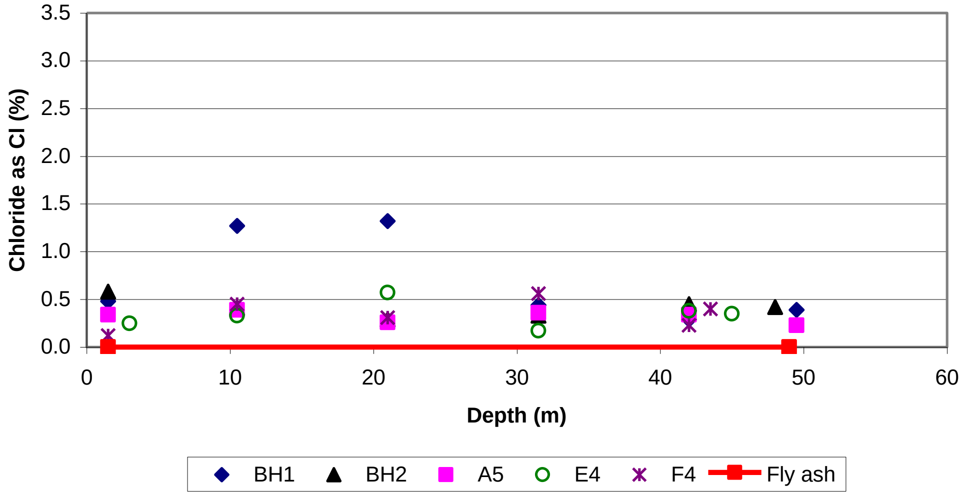


Figure 4.16 Profile of Cl^- of boreholes

Sulphur (S)

As expected, the sulphur (S) content in fly ash is low (ca 0.1%) implying that any variation in the abundance of S originates from the brines (Koch, 2002; Mooketsi et al., 2007; Mahlaba, 2007). The profile of S is slightly erratic with a gentle decline in its concentration from approximately 1.4% (top) to 0.6% (bottom) with depth in most boreholes, see Figure 4.17. This drop suggests that S either leaches at the bottom of the FAD or it results from the deterioration of ash make-up water due to desalination in terms of SO_4^{2-}.

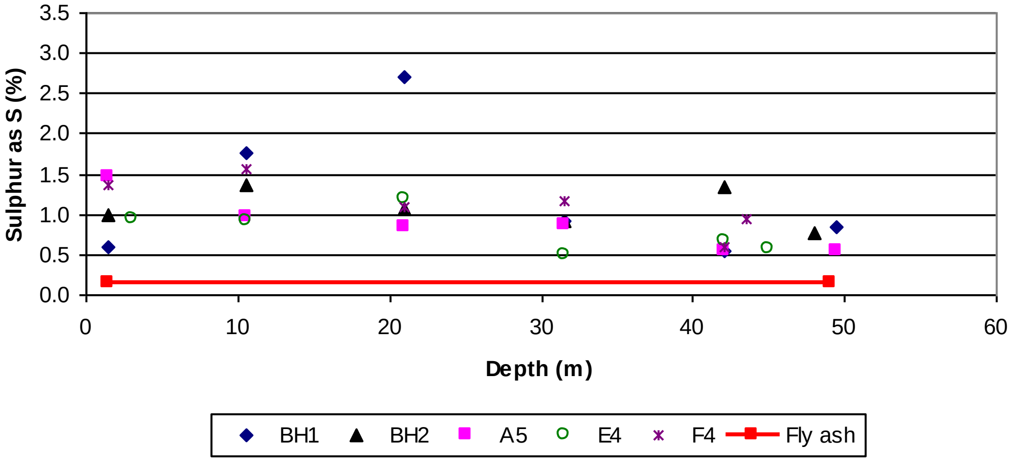


Figure 4.17 Profile of S in boreholes

(d) Concluding Remarks on Elemental Composition

The major observation from the examination of XRF data is that the quantities of S, Cl^- and Na are higher in the WFA compared to fly ash. This can be explained by the composition of the brine where these elements are predominant. Detection of lower Si and Ca quantities in WFA compared to fly ash could indicate leaching, which was unexpected since these elements partake in the hydration.

The XRF results further demonstrate that most elements remain constant throughout the depths suggesting that no measurable leaching of the elements of concern occurs in the FAD. Consequently leaching of WFA was excluded in the investigation. This conclusion agrees with the results of pore water quality in terms of EC that WFA is less leachable than fly ash.

The following section presents the mineralogy of the WFA which demonstrates that the elements are chemically immobilised in the FAD.

4.4.5 Quantitative XRD Results

There are general concerns on the reliability of XRD results due to some degree of dependence to the operator and software used for analysis. It was therefore decided to send samples to two independent laboratories for comparison. The XRD results of WFA from Lab A and Lab B are presented in Tables 4.3.

Table 4.3 The XRD results of WFA from Lab A and Lab B against fly ash

Component	**Chemical Formula**	**Lab A (%)**	**Lab B (%)**	**Fly ash**
Mullite	$Al_6Si_2O_{13}$	10.2 – 21.6	11.4 – 23.2	20.5
Quartz	SiO_2	9.3 – 13.6	6.7 – 14.7	10.2
Lime	CaO	-	-	2.2
Calcite	$CaCO_3$	2.2 – 6.3	0.9 – 6.0	-
Periclase	MgO	0.3 – 1.3	-	-
Pyrrhotite	Fe_7S_8	0.8 – 1.0	0.1 – 2.9	-
Magnetite	Fe_3O_4	0.1 – 14.1	0.1 – 9.0	-
Hematite	Fe_2O_3	0.8 – 2.0	1.0	0.7
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$	0.8 – 4.5	5.5 – 11.4	-
Sillimanite	Al_2SiO_5	0.8 – 2.0	-	-
Rutile	TiO_2	-	0.1 – 0.7	-
Anorthite	$CaAl_2Si_2O_8$	-	0.5 – 4.2	-
Analcime	$NaAlSi_2O_6 \cdot H_2O$	0.5 – 1.6	-	-
Amorphous content	N/A	56.5 – 62.5	43.6 – 76.3	66.3

It is observed and concluded from Table 4.3 that both laboratories agree that the common mineralogical constituents in the FAD are the amorphous phase, mullite, quartz, ettringite, calcite, magnetite, pyrrhotite and hematite. Lab A identified traces of sillimanite, periclase and analcime whereas Lab B identified traces of rutile and anorthite.

The agreement of results in terms of predominant phases and their abundance gives confidence in concluding that chemical weathering indeed occurred in the FAD. The difference in the trace mineral phases is inferred by the limitations of XRD and non-homogeneity in a FAD. It was decided to use the results of Lab A for the detailed discussion of mineralogy since the work was carried out by a highly skilled operator and results were provided within a reasonable period of time.

Amorphous Content

The results of amorphous content in terms of quantity and behaviour with depth per borehole are presented in Figure 4.18. The amorphous content does not change with the age of WFA between 4 and 16 years old, making it unsuitable to indicate the extent and kinetics of weathering in this investigation. The amorphous content in the FAD varies at about 60%, which is approximately 6% lower than fresh fly ash (Figure 4.18). The same pattern was also reported by Lab B in Figure B4.12 (appendix).

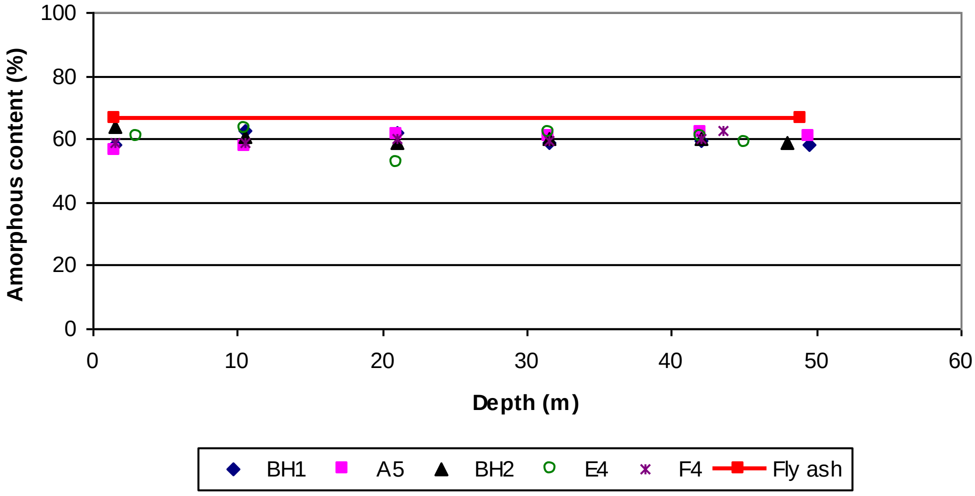


Figure 4.18 Concentration of amorphous phase (Lab A)

The high content of amorphous phase suggests that WFA can become reactive if activated with lime or cement addition (Tishmack and Burns, 2004; Glasser, 2004; Ward and French, 2006; Spears and Lee, 2004). It will be imperative to analyse the amorphous phase because it is possible that the content remains the same, but chemical composition varies since some hydration products may be amorphous e.g. C-S-H gel (Girão et al., 2010; Sakai et al., 2005); which will therefore influence reactivity and the utilisation potential of WFA. Elucidation of this aspect is beyond the scope of this thesis and will require a dedicated investigation since it is only superficially addressed here.

Crystalline phases

The mineral phases are classified into major, minor and trace minerals in terms of their relative abundance according to XRD results (Van Alphen, 2005). The same abundance ranges as for the classification of elements are applicable in the mineralogy.

(a) Major Crystalline Phases

Only mullite and quartz exceeded 10% by weight of XRD crystalline phases in WFA, which are defined as major minerals. Mullite ($Al_6Si_2O_{13}$) is the most abundant Al-Si-bearing mineral in fly ash which forms during the combustion of coal while quartz (SiO_2) is a hard Si-mineral which persists during combustion (Tishmack and Burns, 2004; Hlatshwayo et al., 2009).

These high-temperature minerals are more stable than amorphous phase under atmospheric conditions and thus high amorphous content in WFA is expected to be more reactive (Ward and French, 2006; Solem-Tishmack et al., 1995; Tishmack and Burns, 2004; Haynes, 2009). As anticipated the quantities of mullite and quartz remained constant in the FAD (Figures B4.13 – B4.14 in the appendix).

(b) Minor Crystalline Phases

The secondary phases which qualify in the definition of minor minerals (between 1 and 10%) are magnetite, ettringite, calcite and sillimanite. They all contain one or more of the following elements: Fe, Al, Si, S or Ca, which are elements of interest and hence are discussed in detail.

Magnetite

Magnetite (Fe_3O_4) is one of the Fe-oxides which can form during the combustion of coal (Glasser, 2004) but none was identified in fresh fly ash from the Synfuels complex. The abundance of magnetite in WFA is highly erratic as illustrated in Figure 4.19 which could either be genuine or due to analytical error.

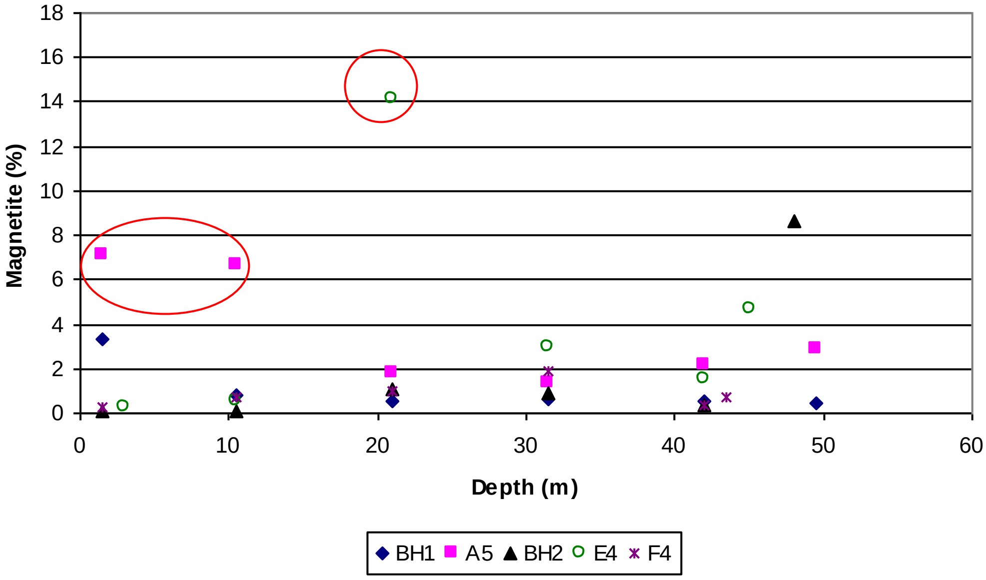


Figure 4.19 Behaviour of magnetite in each borehole

The results obtained from Lab B for the same samples were then used to verify the large variation in data of magnetite from Lab A. Figure B4.15 (appendix) demonstrates that the presence of magnetite is indeed erratic especially in boreholes A5 and E4. This variation agrees with XRF analysis and the findings made by Koch (2002). The high variation in magnetite is therefore attributed to the disposal of Fe-based spent catalyst used in the Synfuels factory.

Ettringite

The environmental importance of ettringite lies in its salt sinking capacity for calcium, sulphate and 26 – 32 molecules of water by virtue of its very low solubility (Klemm, 1998; Tishmack et al., 2001). A detailed discussion on ettringite was made in Chapter 2 with a specific reference to its solubility and stability. Appreciable quantities of ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O$) were identified in most boreholes with the majority of values ranging from 1 - 3% as illustrated in Figure 4.20.

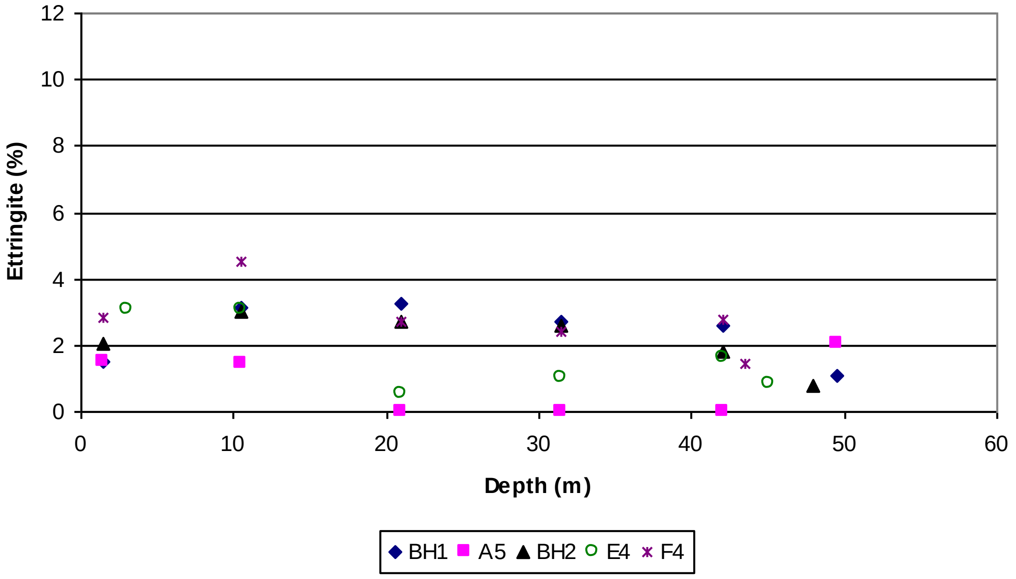


Figure 4.20 Behaviour of ettringite in boreholes

The top layer has a relatively low concentration of ettringite followed by a highest point, which in most boreholes is succeeded by a decline in the abundance of ettringite with depth (Figure 4.20). The low concentration of ettringite in the top layer is attributed to carbonation (Huijgen et al., 2005; Chi et al., 2002). Borehole A5 shows the lowest concentration and absence of ettringite at some depths.

The data from Lab B for the same samples were used for comparative purposes. It is apparent from Figure B4.16 (appendix) that indeed there is an initial increase and then a reduction in ettringite concentration with depth. The data also confirm that the top layer of the FAD has a lower abundance of ettringite than subsequent depths in all boreholes. However, the results from Lab B on borehole A5 do not confirm the absence of ettringite in certain depths. It is therefore difficult to conclude on this peculiarity because the stability of ettringite is influenced by several factors such as pH and carbonation (Klemm, 1998; Campbell; 1999; Chi et al., 2002).

Calcite

The profile of calcite ($CaCO_3$) is shown in Figure 4.21 with the characteristic abundance of approximately 3%, apart from a few exceptions. Calcite often forms when an alkaline material is exposed to the atmosphere; where carbon dioxide dissolves to form carbonic acid which dissociates and eventually reacts with lime (Muriithi et al., 2010; Johannesson and Utgenannt, 2001).

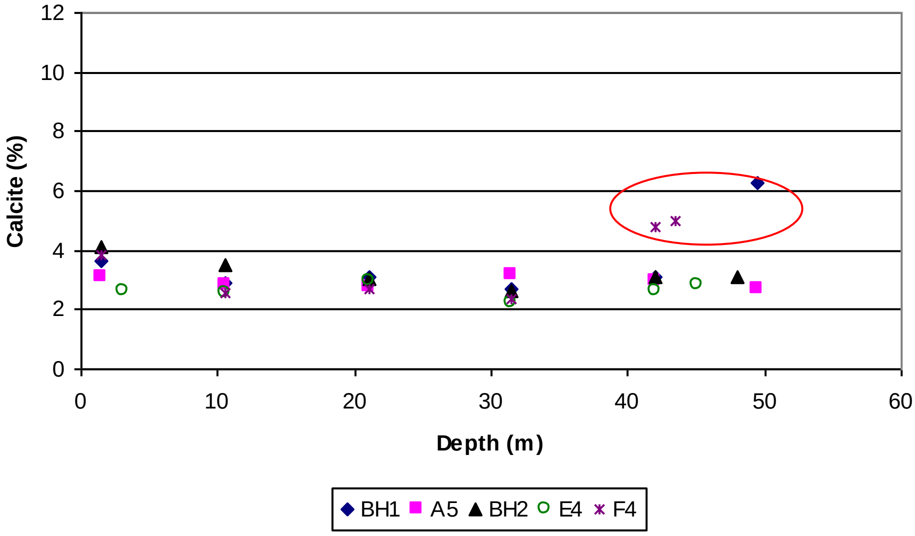


Figure 4.21 Behaviour of calcite in boreholes

The top layer seems to have the highest concentration of calcite which decreases with depth, suggesting that the dissolution of carbon dioxide does not go deep into the dam. The continuous detection of calcite is attributed to exposure of the surface during dam construction. The calcite trend from Lab B is constant as shown in Figure B4.17 (appendix), leaving the points circled in Figure 4.21 as outliers.

Sillimanite

Sillimanite (Al_2SiO_5) is the Al-Si-bearing mineral which is similar to mullite under XRD and very scarce on fly ash but was also identified by Koch (2002) in the FAD. The abundance of sillimanite predominantly varies between 1 and 1.5% of the identified phases as shown in Figure 4.22. It should be noted that the peak of sillimanite overlaps with that of mullite which can influence its identification in the ash samples. Nevertheless, the content remained relatively unchanged with depth.

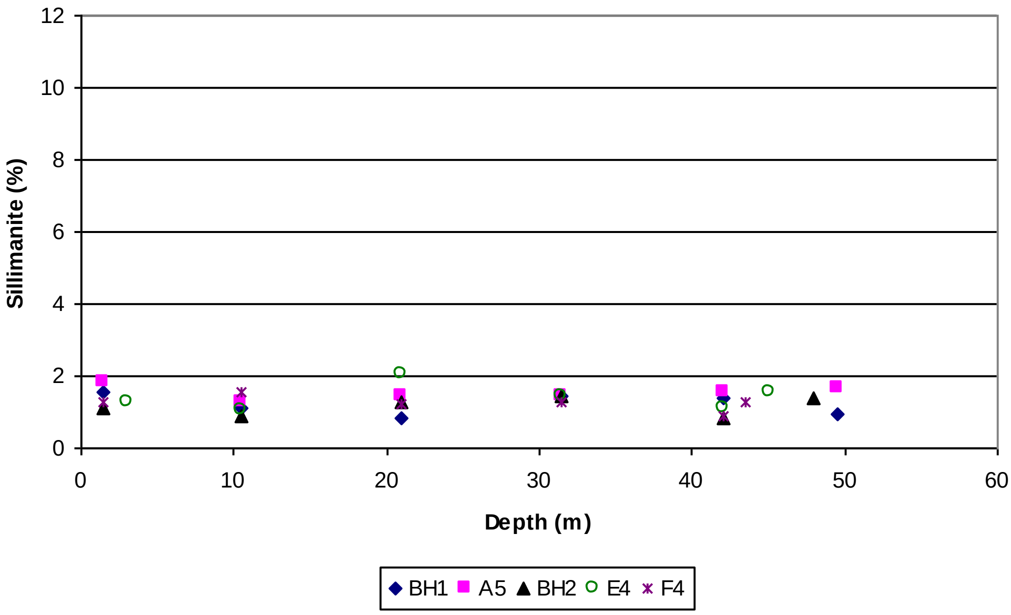


Figure 4.22 Behaviour of sillimanite in boreholes

(c) Trace Crystalline Phases

The quantities of periclase, analcime, pyrrhotite and hematite are below 1% hence these minerals are referred to as trace crystalline phases in terms of abundance in WFA.

Periclase

Periclase (MgO) is the dominant phase containing Mg in fly ash (Tishmack and Burns, 2004) which was not identified in the coal feedstock and fly ash (Matjie et al., 2008) despite Mg being present in Table 4.2 (XRF analysis). Figure 4.23 presents the behaviour of Mg bearing mineral called periclase, varying between 0.5 and 1%. It is the first time that periclase is identified at Synfuels FAD despite the knowledge of appreciable quantities of Mg which are present in several brines (Mahlaba, 2007; Mooketsi et al., 2007; Koch, 2002).

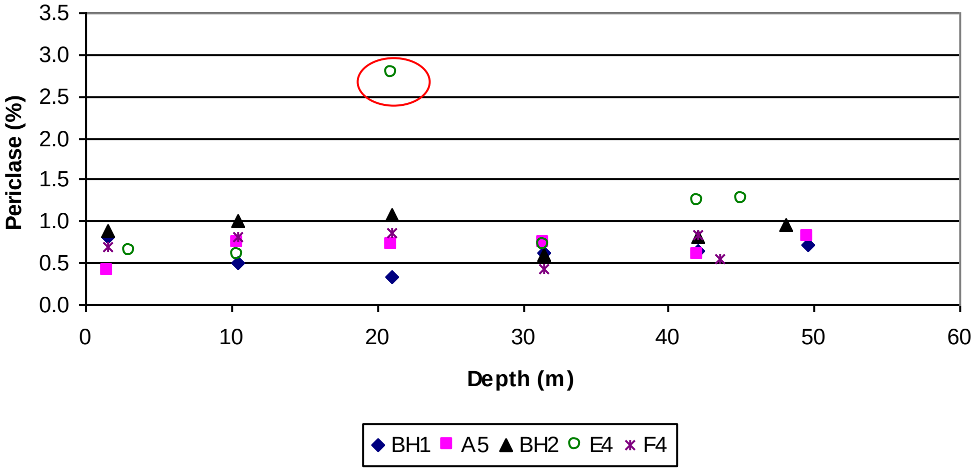


Figure 4.23 Behaviour of periclase in boreholes

One would have expected periclase to convert to brucite ($Mg(OH)_2$) under the conditions of hydraulic ash disposal. However, other researchers have made the same observation in fly ash-water pastes as old as one year (Tishmack and Burns, 2004). Campbell (1999) predicted the formation of hydromagnesite ($Mg_4(OH)_2(CO_3)_3.H_2O$) or magnesite ($MgCO_3$) in weathered ash, which was not confirmed in this study.

Analcime

Analcime ($NaAlSi_2O_6.H_2O$) is a hydrated sodium aluminosilicate which is very scarce in weathered coal ashes. However, Ward (2002) reported that analcime is found in coals from other countries while Matjie (2010) found it under certain gasification conditions of South African coal. According to Van Alphen (2005) traces of analcime are also present in some South African coal seams, namely, eMalahleni and Highveld in Mpumalanga province.

Kim and Burley (1980) reported that analcime contains 16 Na atoms which are distributed over 24 sites and that its occurrence is common in alkaline igneous rocks. Its identification provides evidence that Na is immobilised in the ash systems as has been demonstrated by geochemistry (Mahlaba, 2007; Campbell, 1999). Figure 4.24 illustrates that the abundance of analcime increases with depth in all the boreholes except beyond a depth of 40 m where a decline was observed.

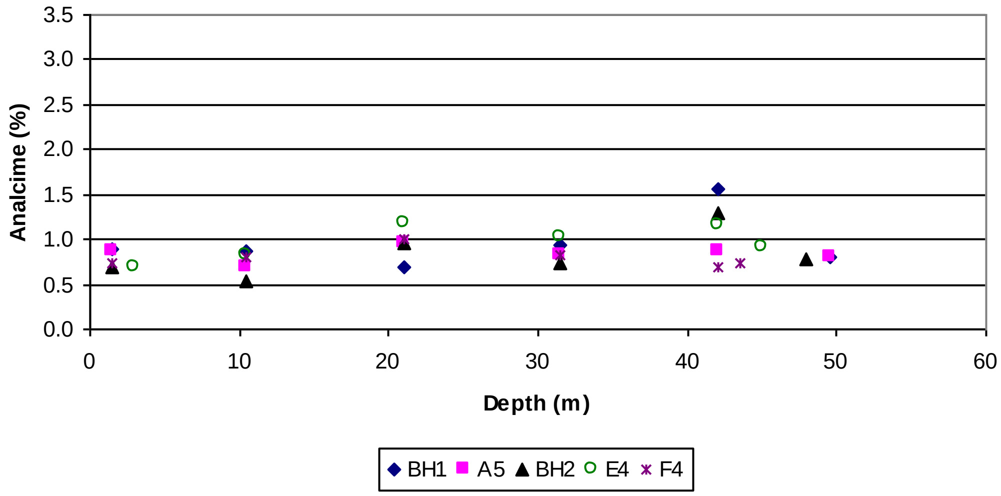


Figure 4.24 Behaviour of analcime in a FAD

The slight increase of analcime concentration with depth suggests that its formation is slow because XRF results did not demonstrate that Na dissipates in the FAD. The presence of analcime is substantiated by the identification of other Na-bearing minerals such as thernadite (Na_2SO_4),

$Na_2Ca_5(SO_4)_6.3H_2O$ and zeolite Na-P1 ($Na_6Al_6Si_{10}O_{32}.12H_2O$) in weathered coal ashes compiled by Donahoe (2004). Conversely, Medveščček et al. (2006) identified sodium calcium aluminate sulphate hydrate ($NaCa_4Al_2O_6(SO_4)_{1.5}.15H_2O$) in Portland cement hydration. Several researchers have prepared analcime by reacting fly ash with NaOH in the laboratory (Medina et al., 2010; Wałek et al., 2008; Querol et al., 1997).

Pyrrhotite

Pyrrhotite (Fe_7S_8) is the Fe-sulphide mineral which was not present in the feedstock coal (Matjie et al., 2008), indicating that some regions in the FAD are reducing since combustion process is oxidative (Glasser, 2004). Pyrrhotite was detected by both laboratories with the abundance of 0.1 – 2.9% as shown in Table 4.3 and Koch (2002) also identified this mineral in another FAD. The random existence of pyrrhotite is displayed in Table B4.1 (appendix) while further details are beyond the scope of this project.

The existence of pyrrhotite can be attributed to the once-off discharge of approximately 30 000 m^3 of biologically active sludge; from the process cooling towers to the FAD during the annual shutdown (Macholo, 2010). This practice is now discontinued at the Synfuels complex.

Hematite

Hematite (Fe_2O_3) is one of the Fe-oxides which form during the combustion of coal (Glasser, 2004). Approximately 1.2% hematite was originally present in fresh fly ash as presented in Table 4.3. Figure 4.25 shows that hematite varies between 0.3 and 0.8%, which suggests that its portion was oxidised to magnetite during weathering. It should also be noted that the abundance of phases depends on the identified minerals.

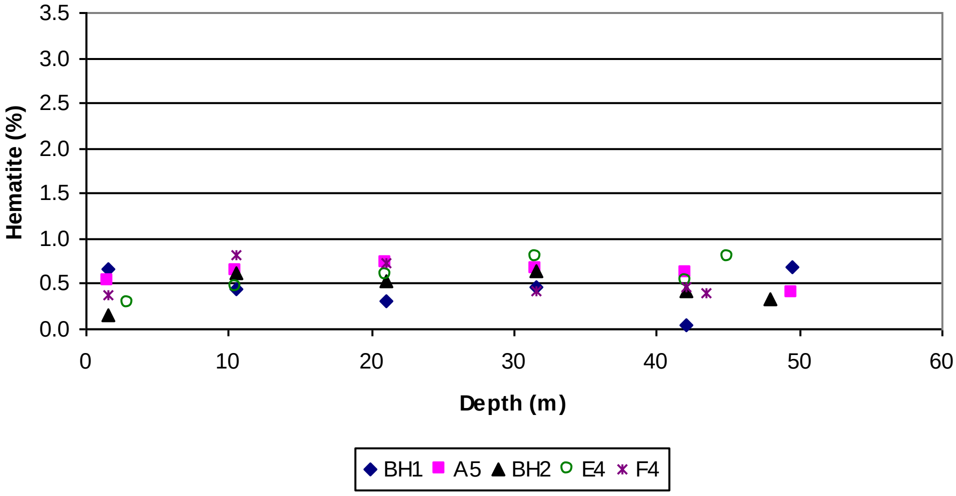


Figure 4.25 Behaviour of hematite in a FAD

4.4.6 Concluding Remarks on XRD

From the examination of XRD data, it is concluded that chemical weathering and the formation of new minerals took place in the FAD; owing to positive identification of hydration products as well as the observed reduction in pH and M-alkalinity in the leachates of WFA compared to fresh fly ash. The comparison of the quantities of crystalline phases between WFA and fly ash was avoided due to a possible confusion because mineral abundance depends on the identified minerals.

Secondary minerals identified include magnetite, ettringite, calcite, sillimanite, analcime, pyrrhotite and periclase. These minerals contain the majority of the predominant constituents found in brines and fly ash.

4.4.7 Thermal Analysis

The samples from the most representative borehole were subjected to a Differential Scanning Calorimeter (DSC) analysis to possibly acquire additional mineralogical information. The DSC results of fresh fly ash and WFA showed two peaks at 75 and 467 °C which correspond to the free water evolution and decomposition of portlandite, respectively (Pane and Hansen, 2005).

However, WFA exhibited additional peaks at approximately 110 and 180 ºC suggesting the presence of calcium hydrate silicate (C-S-H) and hydrated gehlenite ($Ca_2Al_2SiO_2(OH)_{10}.8H_2O$), respectively (Nochaiya et al., 2009; Stefanović et al., 2007; Coleman and Mcwhinnie, 2000; Murat, 1983). There was no evidence of Friedel’s salt which would exhibit a peak at around 300 ºC (Coleman and Mcwhinnie, 2000; Birnin-Yauri and Glasser, 1998). Its absence was expected because it’s stable at pH > 12 and WFA has a pH of 9.5 (Csizmadia et al., 2000). The observed immobilisation of Cl^- in the WFA is therefore ascribed to the adsorption to C-S-H gel (Saikai et al., 2006; Beaudoin et al., 1990; Sumranwanich and Tangtermsirikul, 2004; Delagrave et al., 1997).

The C-S-H is a major contributor to strength development and provides adsorption sites for numerous pollutants including chloride (see Table 2.6 in Chapter 2) in the hydrated cement pastes (Coleman and Mcwhinnie, 2000; Balonis et al., 2010). Hydrated gehlenite commonly known as Strätlingite is a calcium aluminate silicate hydrate characterised by platy crystals (Mtschei et al., 2007; Tishmack and Burns, 2004), and is reportedly strong (Ding et al., 1995). Tishmack and Burns (2004) report that Strätlingite has S as an interlayer ion while Saikai et al. (2006) state that Ca can be replaced by alkali metals.

The use of DSC has proven that XRD requires supplementary techniques in order to get a better mineralogical understanding. The DSC micrographs are attached in Figures B4.18 and B4.19 (appendix).

4.4.8 Particle Morphology

This section presents the FEG SEM data for the different ash types. The majority of fresh fly ash particles are indeed spherical as can be seen in Figure 4.26, which agrees with literature (Tishmack and Burns, 2004). It is particularly important though to note that there are some fused particles with non-spherical morphologies as illustrated in Figure 4.27.

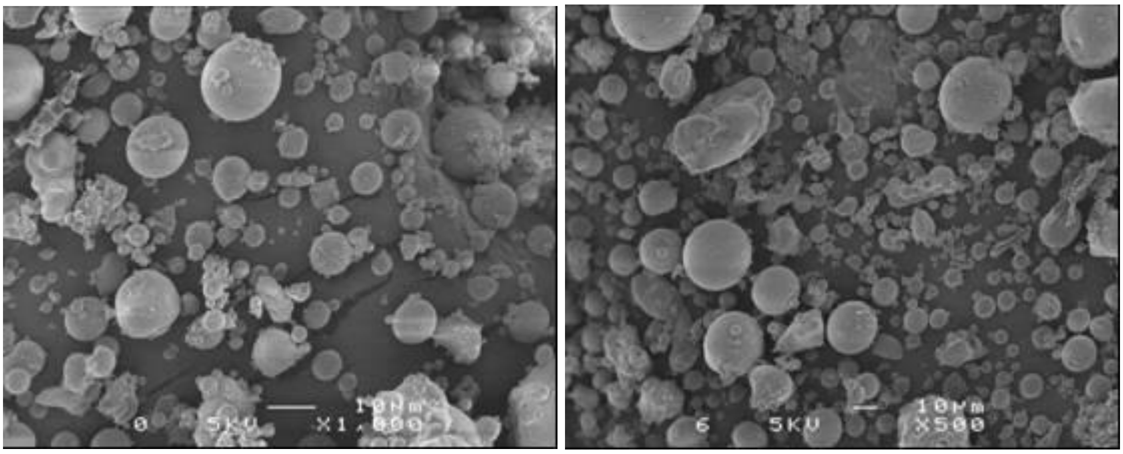


Figure 4.26 FEG SEM images for representative Synfuels fly ash particles

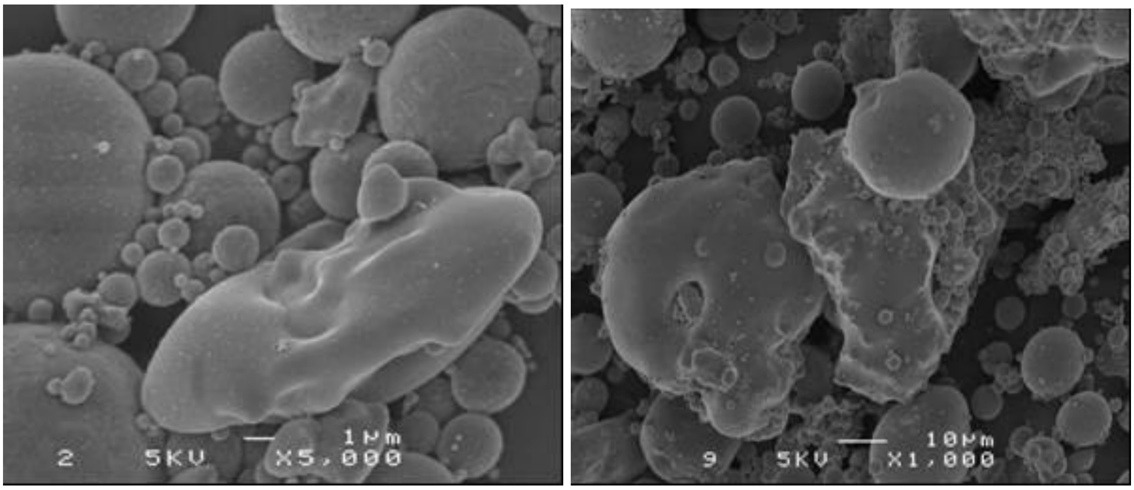


Figure 4.27 FEG SEM images for peculiar Synfuels fly ash particles

Some FEG SEM micrographs of WFA also have cenospheres as depicted in Figure 4.28. The sphericity agrees with high amorphous content of WFA from XRD analysis; see extra images appended in Figure B4.20. It further substantiates the postulate made by the present author that WFA can still be utilised as a pozzolan.

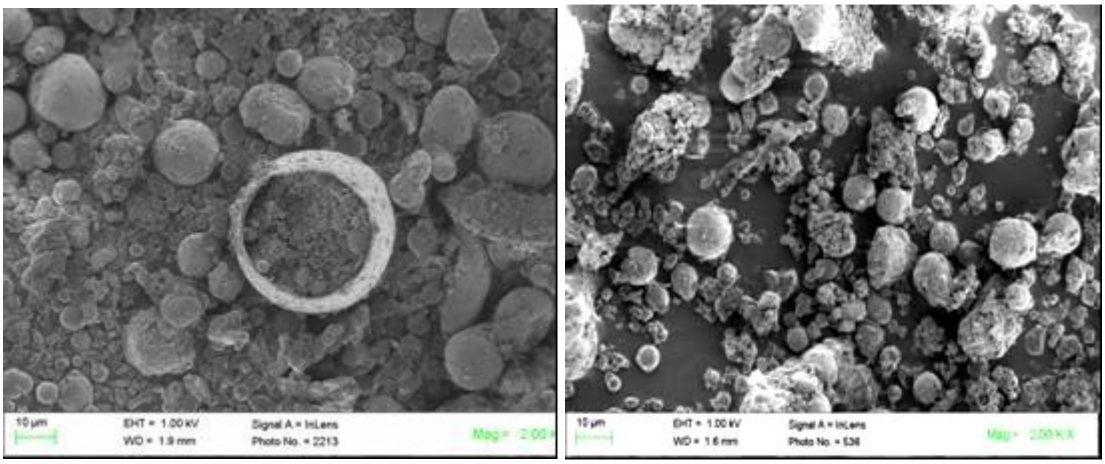


Figure 4.28 FEG SEM images showing sphericity in WFA

Figure 4.29 interestingly shows the gel-like micrographs while Figure 4.30 illustrates the presence of crystalline phases some of which are needle-like, hexagonal, and platy particles. The presence of the new particle morphologies serves as additional proof that mineralogical and microstructural transformation occurred in a FAD (Yeheyis, 2009; Zevenbergen et al., 1996; Campbell, 1999; Kolay and Singh, 2001; Lee and Spears, 1997), which agrees with both XRD and DSC results. Gitari et al. (2009) also made a similar observation when comparing the SEM micrographs of fly ash and weathered fly ash of ESKOM's Tutuka power station.

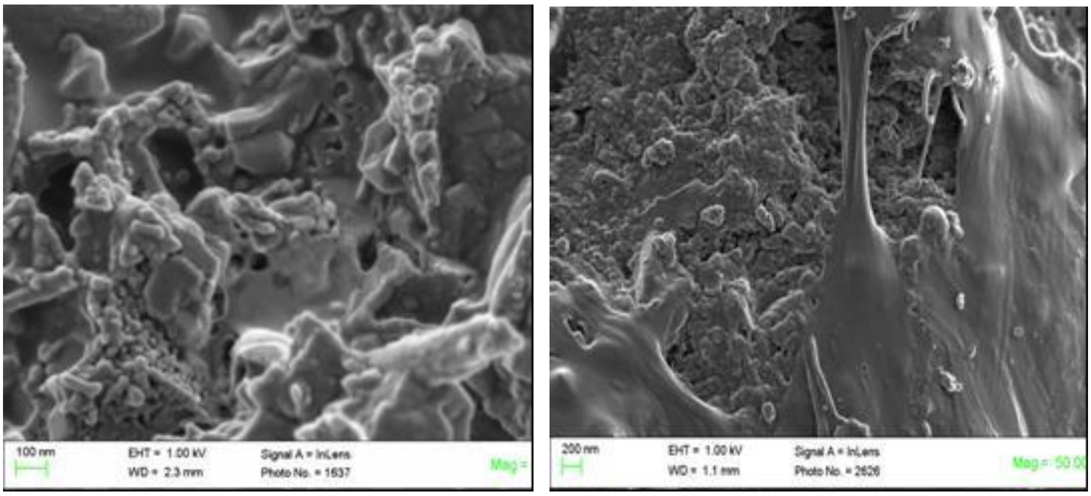


Figure 4.29 FEG SEM images depicting presence of gel in WFA

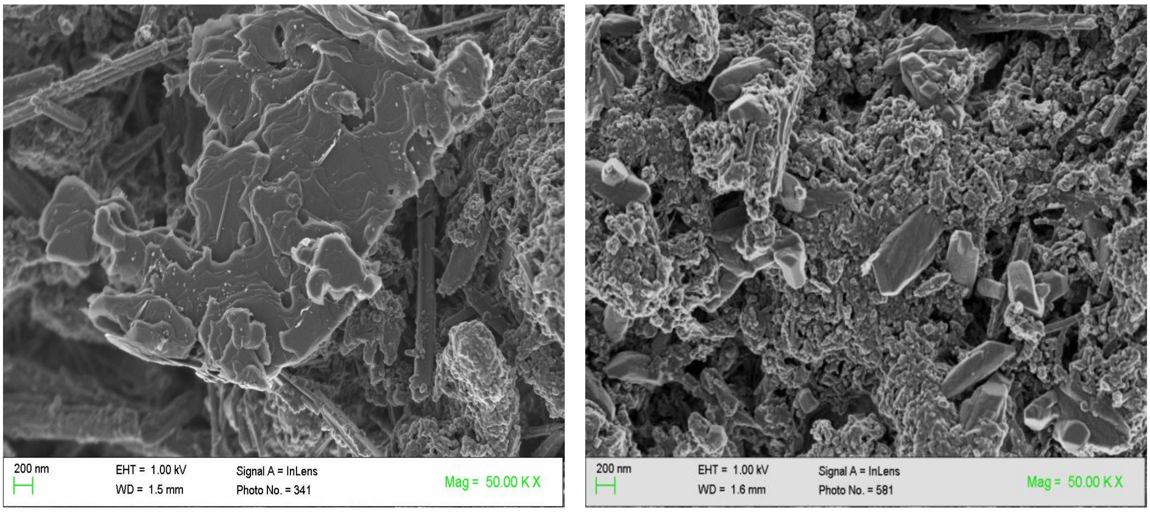


Figure 4.30 FEG SEM images showing new crystalline minerals in WFA

A study performed by Campbell (1999) on South African fly ashes also confirmed the presence of secondary phases in weathered fly ashes from ESKOM's Matla and Kriel power stations whereas SASOL's weathered fly ash in Sasolburg (Vaaltriangle) remained indifferent. The SASOL disposal site investigated by Campbell (1999) differs in many aspects from the one used for this study. The comparison of SASOL operations is outside the scope of this research.

The observed alteration in morphology may affect the workability during the reutilisation of WFA as a pozzolan, although this will depend on the nature of utilisation and quantities consumed in such an application (Kearsley and Wainwright, 2003; Vermeulen, 2001; Fester et al., 2008; Chang, 2009; Glasser, 2004; Sakai et al., 2009; Fernández-Jiménez and Palomo, 2003).

4.5 FRESH SLURRY

Fresh slurry was sampled from an operational FAD (*the same dam where Koch (2002) drilled two boreholes)* as shown in Figure 4.31a. This sample served as both a lysimeter and control in the sense that it was cured under natural conditions as illustrated in Figure 4.31b, and initial conditions were known.

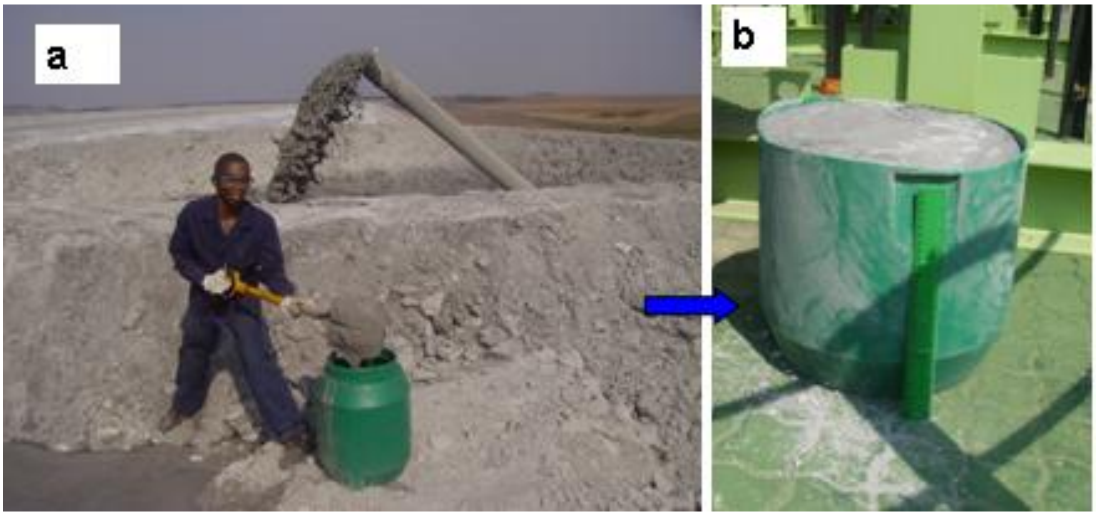


Figure 4.31 Illustration of (a) sampling of fresh slurry and (b) its curing

It would provide an insight on the kinetics of hydration (weathering process) within the duration of the investigation, and also an opportunity to compare current results with those obtained by a different researcher (Koch, 2002).

4.5.1 Results and Discussion

This section presents results of an 8-month old FA, which is younger than 4 to 16 years of the FAD presented earlier. The findings could give more insight on the short-term reaction kinetics in a slurry system.

(a) Particle Size Distribution

The PSD of the FA depicted in Figure 4.32 is distinctly finer than fly ash. This distinction can be inferred from chemical weathering (Memon et al., 2002; Zevenbergen et al., 1999).

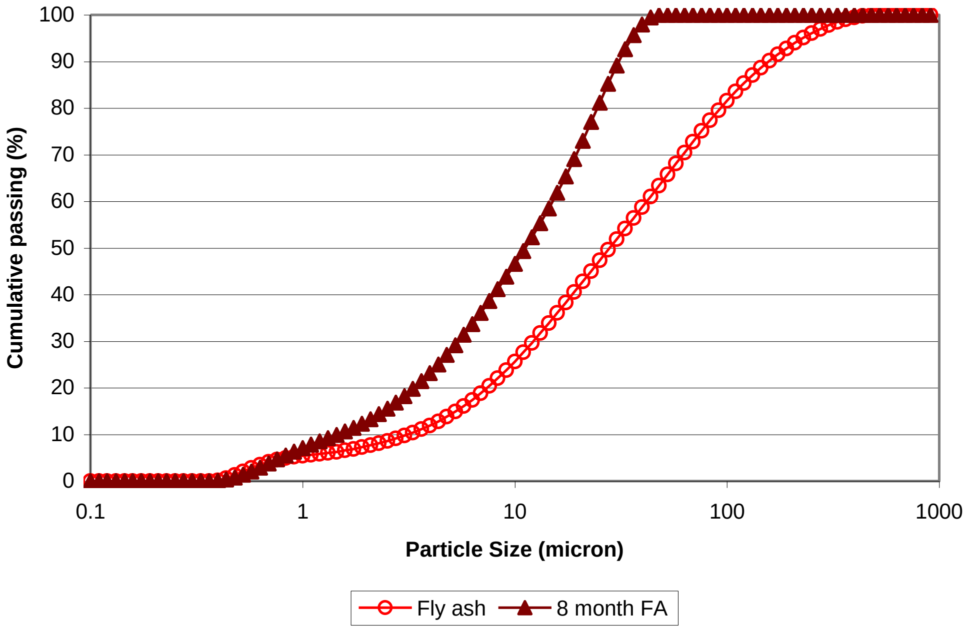


Figure 4.32 Particle size distribution of 8-month old FA against fly ash

(b) Elemental and Mineralogical Properties

The elemental composition (XRF) and mineralogy (XRD) of the 8-month old FA are compared against those of fly ash in Tables 4.4 and 4.5, respectively. It is observed in Table 4.4 that the amounts of Na and Cl^- increased whereas Ca slightly decreased in the 8-month old FA compared to fly ash. This distinction is ascribed to hydration of FA with CAE and leaching of Ca.

Table 4.4 Elemental composition of fly ash and 8-month old FA

Component	**8-month old FA (%)**	**Fly ash (%)**
SiO_2	48.50	47.92
Al_2O_3	32.80	32.78
Fe_2O_3	2.26	2.05
CaO	7.95	9.48
MgO	1.91	1.18
SO_3	0.87	0.51
Na_2O	1.06	0.67
K_2O	0.81	0.92
TiO_2	1.60	1.63
SrO	0.34	0.57
BaO	0.25	0.77
P_2O_5	1.21	1.07
Cl	0.15	<0.01
MnO	0.05	0.05
Total	**99.76**	**99.60**

Table 4.5 shows that there are mineralogical differences between the two samples indicating the formation of a Na-bearing mineral (analcime), calcite ($CaCO_3$) and traces of periclase (MgO) in the FA. Concurrently, a decrease in the amorphous content was observed and lime was below the detectable limit in the XRD instrument used.

Morphological analysis with FEG SEM supports the mineralogical data. It is clear in the images that alteration is very minimal which suggests that curing for 8 months is probably too short, see Figure B4.21 (appendix).

Table 4.5 Mineralogy of fly ash and 8-month old FA

Component	**Chemical Formula**	**8-month FA (%)**	**Fly ash (%)**
Mullite	$Al_6Si_2O_{13}$	19.44	20.53
Quartz	SiO_2	9.68	10.24
Lime	CaO	-	2.22
Calcite	$CaCO_3$	5.36	-
Periclase	MgO	0.09	-
Hematite	Fe_2O_3	0.59	0.68
Analcime	$NaAlSi_2O_6{\cdot}H_2O$	2.07	-
Amorphous content	N/A	62.78	66.33
Total	N/A	**100.01**	**100.00**

4.6 EFFECT OF CURING TIME ON FA PROPERTIES

A brief comparison is made between an 8-month old FA and drilled WFA. This attempts to establish the effect of curing time on the weathering process taking place in FA. A difference was observed in PSD and mineralogy. The absence of ettringite, for instance, indicates that 8 months of curing is not sufficient for the formation of this environmentally important mineral while 4 years was adequate in the FAD. This agrees with the findings made by Koch (2002) who identified sillimanite and calcite in the operational FAD and column experiment. Both of these investigations by Koch (2002) were short-term.

4.7 CONCLUSIONS

It is concluded that a FAD has a characteristic PSD which resembles that of fresh fly ash. This observation refutes hydraulic sorting in a hydraulic fine ash disposal despite reports that it is common in the tailings dams, which is attributed to morphological differences of particles in these systems. The WFA and fly ash can be classified as silty. It is, nevertheless, possible to find peculiar lateral locations in a FAD which are either too fine or too coarse such as boreholes E4 and A5, respectively. This deviation could be attributed to plant disruptions such as boiler efficiency and continual disposal of solid wastes for which no records exist.

The XRF data demonstrate that predominant constituents from brines such as sodium, sulphur and chloride form part of WFA. Such a discovery indicates that fly ash may immobilise pollutants present in brines if well engineered. No indication of leaching of the elements of concern was obtained in this investigation except calcium and silicon based on XRF results. Besides, higher leaching potential was exhibited by the electrical conductivity of pore water for fly ash compared to WFA. This suggests that hydraulic ash co-disposal along with saline brines may be environmentally-friendlier than dry ash disposal.

Examination of XRD data confirmed the existence of secondary phases, which are the hydration products of fly ash and brines. The newly formed phases are pyrrhotite, periclase, analcime, magnetite, sillimanite, ettringite, and calcite in an ascending order of abundance. The DSC analysis on selected WFA samples highlighted the existence of additional secondary phases, namely, C-S-H gel and hydrated gehlenite (Strätlingite). The importance of C-S-H gel and Strätlingite lies in their contribution to strength of paste and provision of adsorption sites for pollutants such as chloride, sulphur, and heavy metals.

There was no detectable increase in the abundance of these phases between 4 and 16 years, implying that chemical weathering significantly occurs within 4 years in an alkaline environment with supersaturated brines. However, the XRD analysis of 8-month old FA lacked the majority of secondary minerals, namely, ettringite, magnetite and pyrrhotite identified after 4 years. This was confirmed by morphologies of particles obtained during FEG SEM analysis.

The high content of glassy phase (amorphous) and lack of alteration in certain physical properties indicate that WFA can be utilised as a pozzolan; probably with lime addition owing to reduced pH of pore water to 9.5. It is imperative to determine the chemical composition of amorphous phase and estimate the degree of reactivity.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 BACKGROUND

The purpose of Chapter 5 is to provide detailed analysis of the results obtained during a laboratory evaluation of various pastes as described in Chapter 3. The discussion and interpretation are made against the literature survey presented in Chapter 2.

"Whenever a theory appears to you as the only possible one, take this as a sign that you have neither understood the theory nor the problem which it was intended to solve." Karl Popper (philosopher: 1902 – 1994)

5.2 EFFECT OF BRINE COMPOSITION

The effect of brine characteristics on paste behaviour is vital to this study. The workability results of fresh pastes were generated using modified and standard flow cones, as well as a rheometer. The implication of these analytical techniques to this research are mentioned and the important considerations for subsequent tests. As a measure of mechanical properties the Unconfined Compressive Strength was also determined after 28 days of curing unless stated otherwise.

The concentration of dissolved salts is principally expressed as [Y], where square brackets '[ ]' indicate the concentration of the ionic species Y in g/l. Deionised water is abbreviated as Dwater in the graphs and tables to simplify illustration of data.

5.2.1 Flow Cones

The flow cone results for pastes prepared from fly ash and brines as a function of Total Suspended Solids (TSS) i.e. excluding the influence of brine salinity are presented in Figure 5.1. Low values of efflux time indicate high workability, and vice versa. Results show that workability of fresh pastes decreases as fly ash content increases regardless of the nature of the mixing water (Torrance and Pirnat, 1984; Boger et al., 2006, 2008).

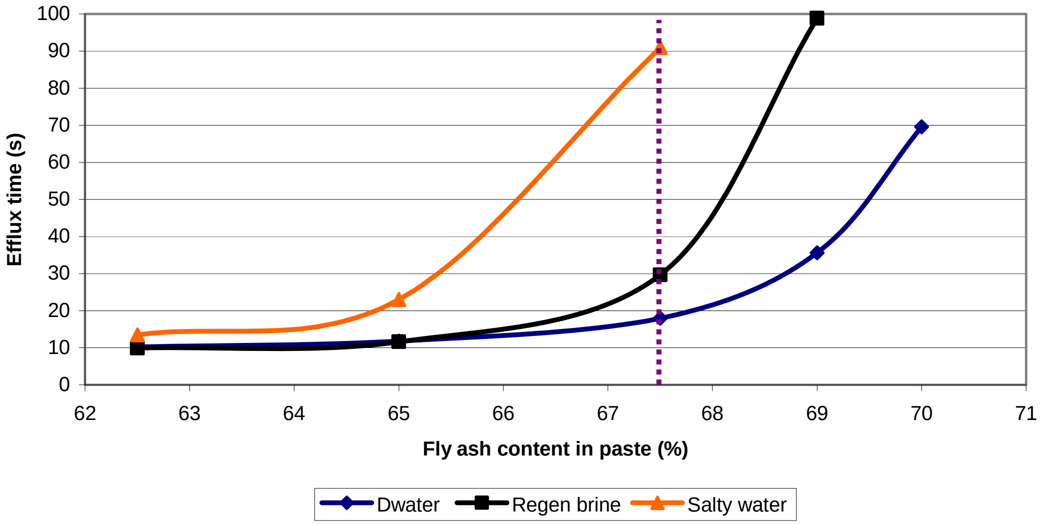


Figure 5.1 Efflux times for various pastes as a function of fly ash

Efflux time curves demonstrate that deionised water bearing pastes have (especially above 65% fly ash content) a higher workability compared to brine-based pastes, with salty water exhibiting the lowest workability and regen brine falling in between. The average efflux times of 18, 30, and 91 seconds were obtained in pastes containing 67.5% fly ash content (TSS) with deionised water, regen brine and salty water, respectively.

The flow cones gave reproducible data which are sensitive to fly ash content and brine types making it suitable for attaining goals of the study. However, ASTM C 939 recommends the use of this method for materials with efflux times not exceeding 35 seconds.

The current author disagrees with this recommendation in this research because paste is being investigated not grout. His definition of valid flow cone results includes the achievement of undisturbed flow of paste until the cone runs empty.

Salty water contains 108 g/l Total Dissolved Solids (TDS) which other researchers refer to as 10.8% salinity while regen brine contains approximately 40 g/l TDS. The chemical analyses of these brines were provided in Table 3.1 in Chapter 3.

If the Total Solids (TS) rather than just the suspended solids are taken into account, the difference in the efflux time between the three systems is reduced substantially (Figure 5.2). The curves are almost superimposed when salinity of brine forms part of the solids content in the paste formulation. It is therefore concluded that salinity must always be incorporated in the formulation of paste, in order to achieve relevant results in terms of workability. Torrance and Pirnat (1984) made a similar observation when studying marine clays.

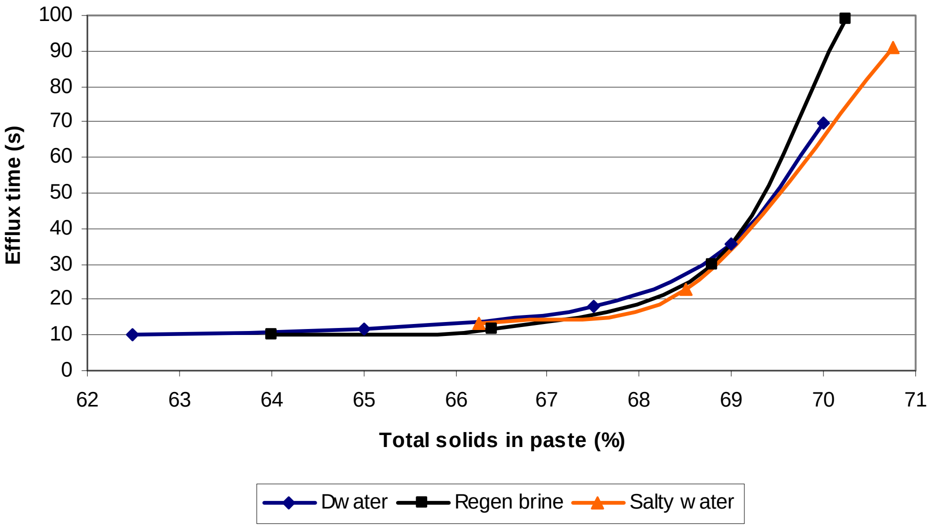


Figure 5.2 Efflux times for various pastes as a function of Total Solids

These preliminary results suggest that workability is not influenced by brine composition although diversion is observed beyond 69% TS. However, Mahlaba (2007) made a contrasting observation when he examined the time dependence of paste flowability and found that it is affected by brine composition. That experiment took approximately 96 hours during which reactions could occur significantly. The major distinction with the present flow cone investigation is the duration which was below 100 seconds.

5.2.2 Correlation of Flow Cones

The use of a standard flow cone is arduous whereas a modified flow cone is user-friendly with equivalent reproducibility of data, at a tenth of the sample volume required by the former. However, it was imperative to establish a correlation between the two flow cones.

The pastes were prepared with deionised water and increasing concentrations of fly ash for comparing the two flow cones. It is apparent from Figure 5.3 that the upper limits for standard flow cone and modified flow cone were 70% and 66% fly ash contents, respectively.

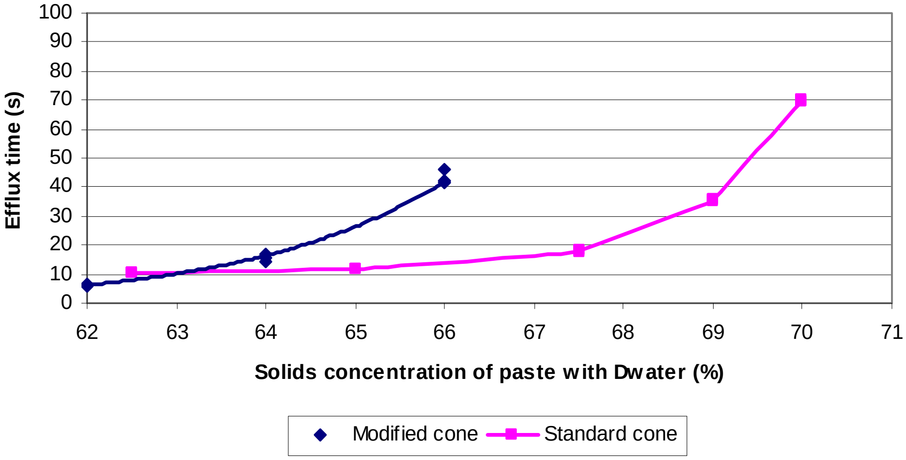


Figure 5.3 Comparison of results from two flow cones

The difference in the analytical ranges of flow cones can be explained in terms of their dimensions, as illustrated in Figure 5.4. The height and inlet diameter of the standard flow cone are almost four times those of the modified flow cone. The outlet diameter of the former is 12.7 mm while that of the latter is 8 mm.

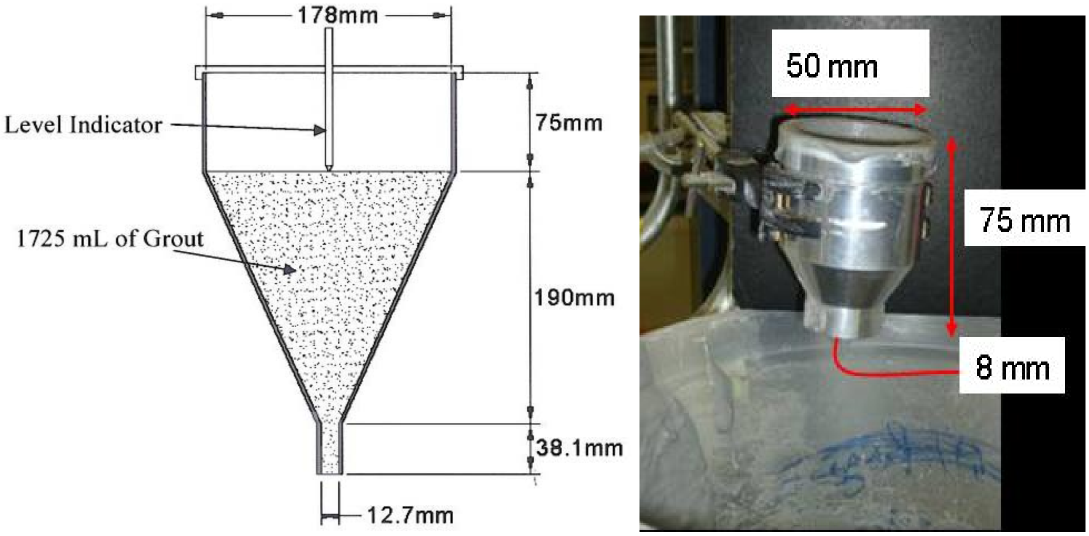


Figure 5.4 Comparison of dimensions for two flow cones

5.2.3 Rheology

The experiments presented in section 5.2.1 were repeated with the use of a rheometer to study workability instead of flow cones. Figure 5.5 demonstrates that dissolved salts in a brine solution affect yield stress. The higher the salinity of brine the less workable the paste becomes for a given fly ash content and vice versa (Torrance and Pirnat, 1984). As expected, the yield stress increases with increasing fly ash content in the paste (Boger et al., 2006, 2008).

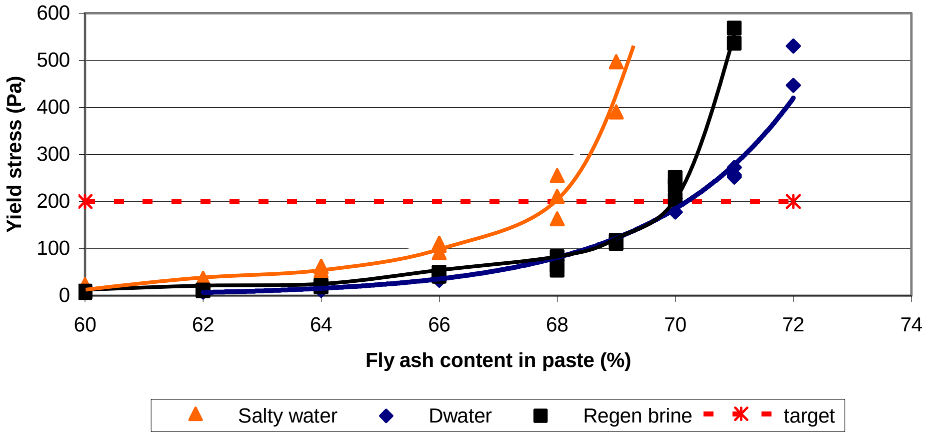


Figure 5.5 Yield stress for various pastes as a function of fly ash

The curves are almost superimposed when total solids are used to define workability of pastes as illustrated in Figure 5.6. The findings made with a rheometer substantiate the aforementioned results achieved with the flow cones. This agreement confirms the effect of salinity and it must therefore be taken into account in the subsequent tests. It is also possible to fit an equation to the data and predict yield stress as a function of TS, see appendix C (Figure C5.1).

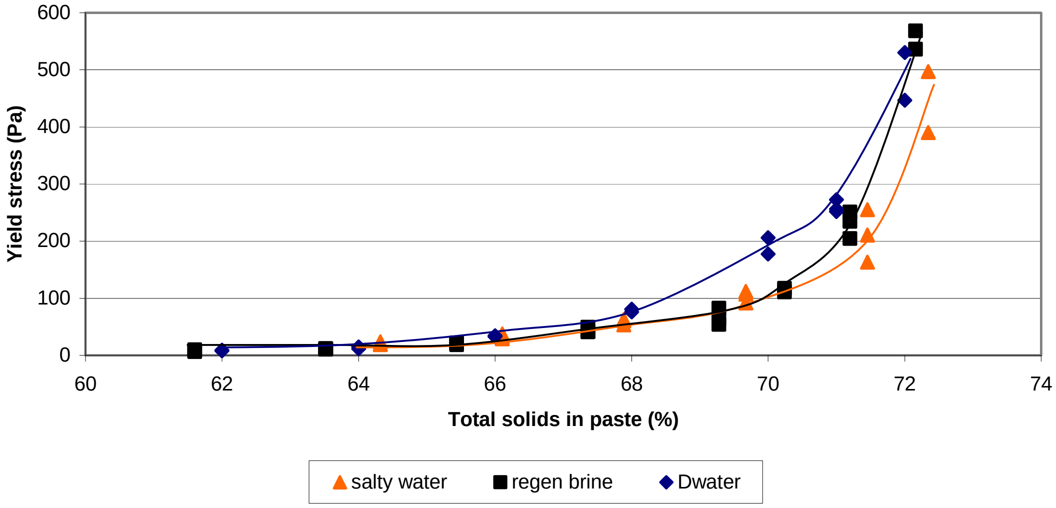


Figure 5.6 Yield stress as a function of Total Solids

5.2.4 Conclusions on Workability Tests

The use of a rheometer enabled the study of workability in terms of yield stress and reproducible data were attained. Of particular importance is that the rheometer can be used to generate rheological data in a paste consistency range of interest (i.e. including the upper limit which could not be measured with flow cones). It was therefore decided to use the rheometer as a primary technique for workability determination in this investigation.

The use of flow cones is limited to less viscous pastes due to blockages. However, the application of flow cones is useful for studying paste properties which are affected by shearing of the material, and also to provide quick readings in the field where there are no facilities.

It is also concluded from Figures 5.2 and 5.6 that the presentation of workability involving brines requires the adoption of equation 5.1 (Pretorius, 2010).

TS = TSS + TDS …………………………………………………………………… (5.1)

Where:

TS = Total Solids (g/l)

TSS = Total Suspended Solids i.e. fly ash content (g/l)

TDS = Total Dissolved Solids in brine (g/l)

5.2.5 Unconfined Compressive Strength

The results of Unconfined Compressive Strength (UCS) for pastes containing different brines and 68% fly ash are presented in Figure 5.7. The regen brine paste gave the highest UCS value of 1 840 kPa followed by salty water paste with 1 650 kPa. Deionised water bearing paste gave a markedly lower UCS value of 65 kPa. These results indicate that the composition of the brine affects the mechanical properties of paste and not necessarily according to brine salinity. This suggests the importance of chemical composition of the brine as reported by Mahlaba (2007) and Mahlaba and Pretorius (2006).

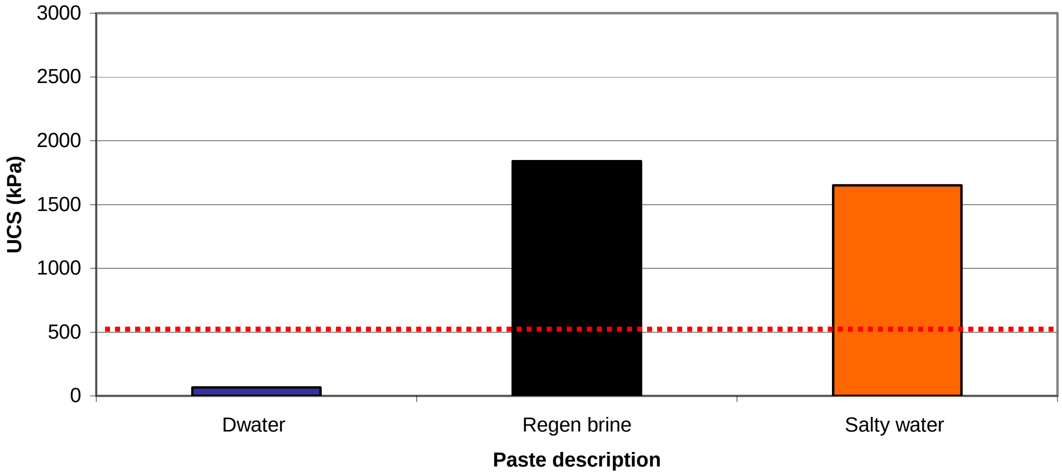


Figure 5.7 Influence of brine type on compressive strength

(a) Effect of Curing Time on UCS

The effect of curing time on the strength development of paste was assessed by comparing pastes of different ages. Figure 5.8 shows that a substantial increase in UCS occurs between 28 and 150 days. The UCS values of pastes containing salty water and regen brine increased from 1 650 and 1 840 kPa to 3 000 and 4 100 kPa, respectively. This increase in UCS within 150 days suggests a significant extent of reactions taking place between fly ash and brines.

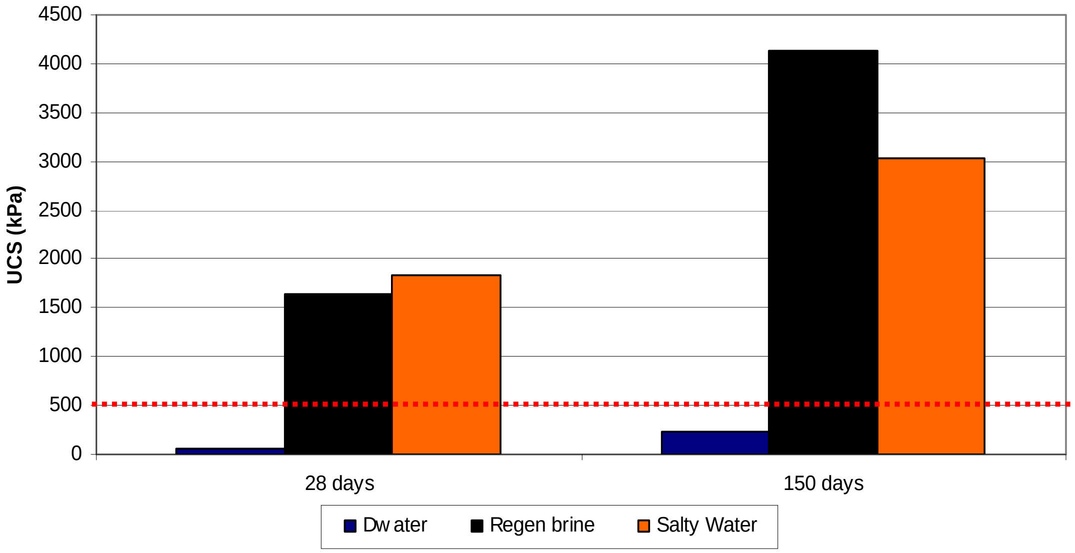


Figure 5.8 Effect of curing time on UCS development

Compared to brine pastes, no appreciable improvement in the UCS of pastes bearing deionised water was achieved since it only rose from 65 to 225 kPa, which is below the 500 kPa target. This difference in behaviour indicates that ionic components in the brine have a profound influence in the strength development of fly ash pastes (Akinkurolere et al., 2007; Taylor and Kuwairi, 1978). Other researchers have also made a similar observation and concluded that operational costs of coal mining can be reduced by using saline mine waters (Palarski et al., 2011; Saw and Villaescusa, 2011).

5.3 INFLUENCE OF BRINE SALINITY

So far it has been established that both salinity (TDS) and chemical composition of brine affect the paste behaviour. A need was identified to decouple the role of chemical composition from that of salinity of brines since it influenced the results. Salty water was diluted to different degrees of salinity using deionised water.

(a) Yield Stress

The results of yield stress as a function of brine salinity used during paste preparation are provided in Figure 5.9. It is demonstrated that salinity of brine influences the workability of paste. For instance, a paste containing 68% fly ash and brine with ≤ 40 g/l salinity has a yield stress of approximately 120 Pa whereas a paste prepared with 85 g/l saline brine gave a yield stress of 280 Pa. Such an increase in salinity resulted in over 100% increase in yield stress between these pastes.

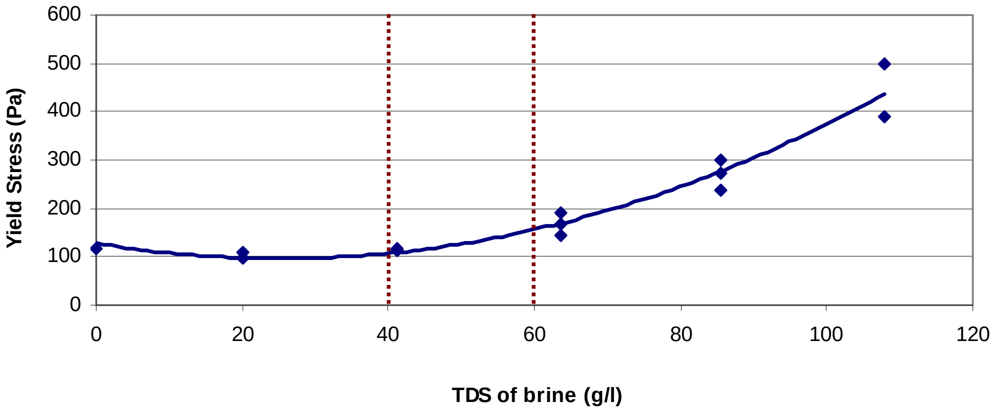


Figure 5.9 Effect of brine salinity on yield stress

It is therefore concluded that the use of a more saline brine will produce a less workable paste in a given S:L ratio (Torrance and Pirnat, 1984). The consequences of increasing salinity will encompass the elevation of energy requirements and susceptibility of pastes to pipeline blockages during transportation. The effect of brine salinity is therefore significant in the paste workability and hence will influence both the engineering design and operation of a paste disposal plant.

(b) Unconfined Compressive Strength

The results of UCS for pastes prepared with a fixed fly ash content (68%) and brine solutions of varying salinity are presented in Figure 5.10.

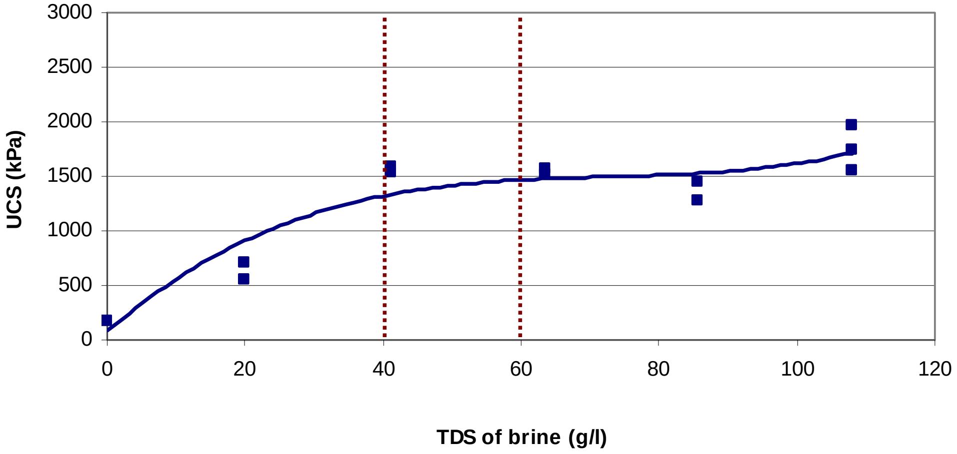


Figure 5.10 Effect of brine salinity on compressive strength

It is evident that there is an increase in UCS with salinity up to 40 g/l beyond which no further strength gain was achieved. These results suggest that a salinity of at least 40 g/l in a specific brine composition is required for optimum strength gain.

(c) Concluding Remarks on Brine Salinity

It has been discovered that brine salinity has a more profound influence on workability than on compressive strength. For instance, the use of 40 g/l and 85 g/l brine salinities as mixing liquids produced the same mechanical properties of approximately 1 500 kPa while a difference in yield stress was more than double. It is therefore recommended that the salinity of the tested brine be maintained between 40 – 60 g/l range for good paste properties, labelled in Figures 5.9 and 5.10.

Having established the influence of brine salinity on paste properties, the effect of chemical composition of brine is investigated. Attention is given to the prevalent brine components.

5.4 EVALUATION OF CHLORIDE COMPOUNDS

As discussed in Chapter 2 the majority of literature investigates the impact of chlorides on the setting and corrosion of reinforced concrete (Balonis et al., 2010; Neithalath and Jain, 2010; Arya et al., 1990; Barberon et al., 2005). The present study evaluates the influence of the increasing [Cl^-] in brines and role of the associated cations on the characteristics of paste.

(a) Settleability

The test to measure the settling rate demonstrates that chloride salts do not influence the settling of fly ash slurries (results shown in Figures 5.11 and 5.12). The initial volume of the slurries was approximately 45 ml and settling occurred within 30 minutes.

The settled ash bed was approximately 17 ml for slurries containing 12 g/l Cl^- derived from NaCl, $CaCl_2$, as well as 1:1 ratio of NaCl and $CaCl_2$ solutions, all of which resembled the settling of the slurry containing deionised water. On the other hand, the settling of the slurry with HCl stabilised at approximately 25 ml, as depicted in Figure 5.11. The time dependence of the settling rate is illustrated in Figure 5.12.

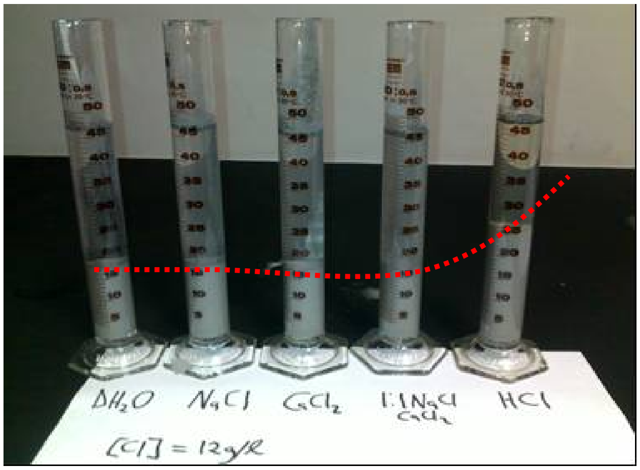


Figure 5.11 Illustration of chloride influence on slurry settling

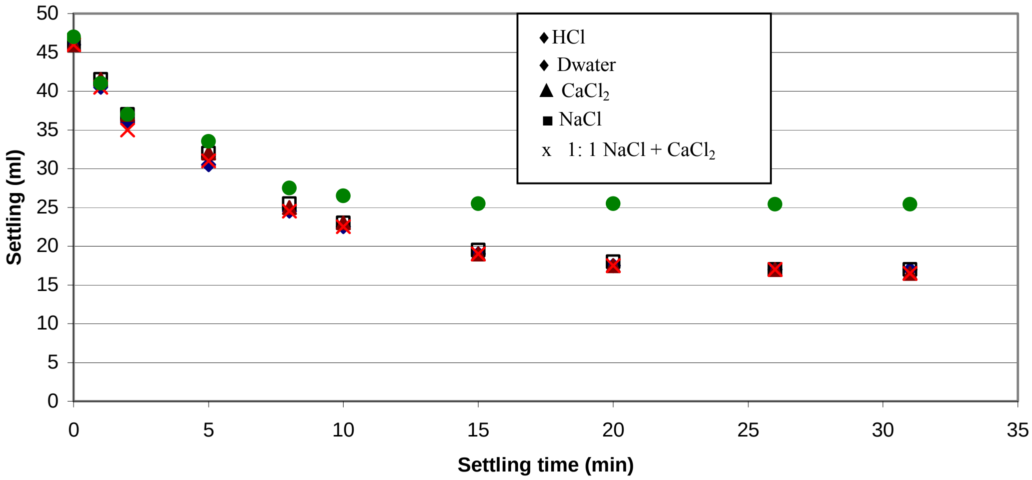


Figure 5.12 Settling rate of slurries bearing Cl^- solutions as a function of time

The pH of the supernatants was recorded at the end of the experiment i.e. after 30 minutes. The pH was approximately 12.0 for all the slurries except that containing HCl which gave a value of 7.8.

The results suggest that while chloride salts do not significantly influence the settling of fly ash slurries since their settling was identical to that of slurry bearing deionised water, the pH plays a role. The HCl solution reduced the extent to which settled fly ash consolidated and formed a thicker fly ash bed by 47%. In practical terms this implies an increase in hydraulic conductivity and leaching potential.

The expansion of the ash bed with HCl could be a result of repulsive forces due to differences in the surface charge (Donahoe, 2004; Vietti and Dunn, 2006; Stocks, 2006). Zeta potential is likely to provide a definitive answer in this matter. The determination of zeta potential is indirectly calculated by measuring the mobility of suspended particles and is known to change with pH and dilution (Vietti and Coghill, 2006). From the viewpoint of practical implementation the HCl scenario is highly unlikely. It is necessary to be aware of this fact that pH plays a role but does not require thorough investigation in this thesis.

(b) Yield Stress

With gained knowledge on brine salinity the sequence of yield stresses was expected to be: yield stress $_{(HCl\ paste)}$ << yield stress $_{(NaCl\ paste)}$ < yield stress $_{(CaCl2\ paste)}$ according to the TDS (or molar masses of the cations) at the equivalent [Cl^-]s.

The pattern of the curves is very similar for the chloride compounds compared with previously observed differences. The deviation of results shown in Figure 5.13 from the above prediction, affirms that chemical composition of brine is a vital factor determining the rheological behaviour of paste. NaCl seemed to slightly reduce paste workability whereas $CaCl_2$ gave a marginally higher workability and HCl fell in between.

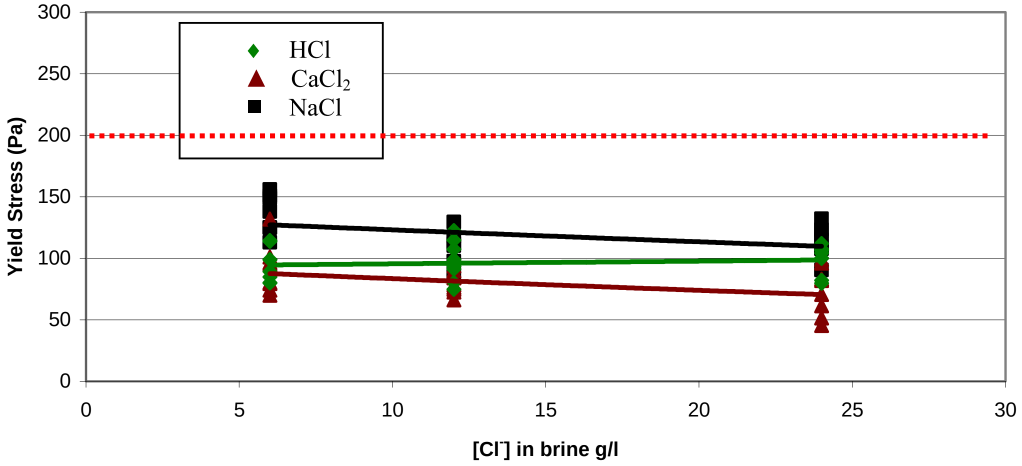


Figure 5.13 Effect of chloride compounds on yield stress

The increase in [Cl^-] from 6 to 24 g/l did not seem to appreciably affect the workability of paste except providing some kind of lubrication with NaCl and $CaCl_2$. This unclear trend was ascribed to salinities being lower than 40 g/l as established earlier.

The effect of time on the observed trend was studied using brines with a concentration of 12 g/l Cl^- derived from HCl, NaCl and $CaCl_2$ solutions. The results presented in Figure 5.14 affirm that NaCl solution produces a paste that is less workable than $CaCl_2$ solution even after 2.5 hours, which is the expected time of paste transportation to the disposal site.

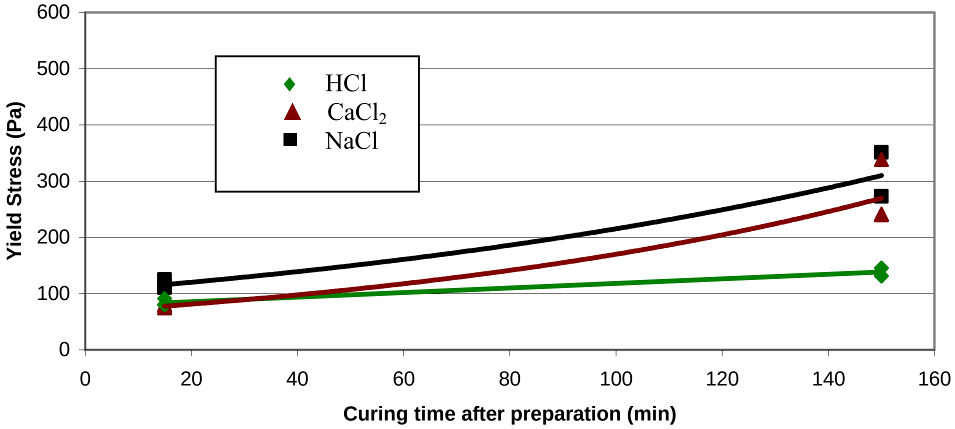


Figure 5.14 Time independence of yield stress of paste bearing chloride compounds

The yield stress values of NaCl and $CaCl_2$ bearing pastes increased from 110 and 80 Pa after 15 minutes to approximately 300 and 270 Pa after 2.5 hours, respectively (Figure 5.14). Conversely, HCl-based paste gave a gentle increase in yield stress from approximately 80 Pa to approximately 140 Pa. The rheological behaviour of pastes bearing Cl^- has been confirmed and it is substantiated by flow cone data where NaCl is less flowable than $CaCl_2$, see Figure C5.2 in appendix C.

(c) Unconfined Compressive Strength

The UCS results indicate that chloride compounds have a significant influence on the mechanical properties of paste (Akinkurolere et al., 2007; Taylor and Kuwairi, 1978). The increase in UCS occurred regardless of the associated cation in the lower range of $[Cl^-]$ i.e. 6 – 12 g/l as shown in

Figure 5.15. Nevertheless, pastes containing HCl and NaCl solutions showed maximum UCS values of 1 100 kPa beyond 12 g/l Cl^- as well as 1 700 kPa at a $[Cl^-]$ of 35 g/l, respectively. On the contrary, the UCS of pastes bearing $CaCl_2$ showed the potential to exceed 3 000 kPa at a $[Cl^-] \geq 40$ g/l. The UCS values of pastes achieved with $[Cl^-] > 6$ g/l significantly exceed the minimum UCS of 500 kPa, targeted in this study.

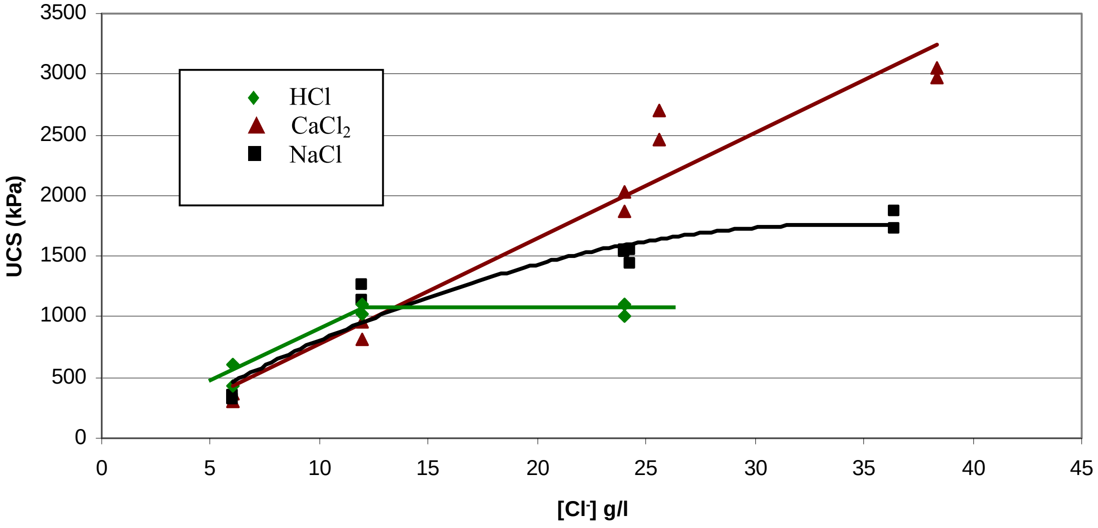


Figure 5.15 Influence of chloride solutions on UCS of paste

(d) Concluding Remarks on Chloride compounds

From the stability viewpoint (deduced from settling and UCS results), it is concluded that HCl is not an appropriate source of chlorides for pastes. The use of $CaCl_2$ solution provided the most effective form of chloride speciation in pastes, which increased their compressive strength (Shi, 1996; Akinkurolere et al., 2007; DOW, 2006; Ramachandran, 1978). Furthermore, pastes bearing $CaCl_2$ provided better workability in the short-term. NaCl on the other hand, produced pastes with satisfactory strength development albeit a slightly lower workability. Thus pastes based predominantly on Ca, Na and Cl^- have the suitable properties for disposal either on the surface or in mine backfill.

5.5 EVALUATION OF SULPHATE COMPOUNDS

Sulphate attack and subsequent deterioration in concrete are well documented in literature (Schmidt et al., 2009; Medveščček et al., 2006; Collepardi, 2003; Klemm, 1998; Collepardi et al., 2003). The present study investigates the effect of different sulphate compounds (as solutions for paste preparation) on paste properties with emphasis on workability and compressive strength. The study aims to establish the effect of sulphate and its associated cations on the paste behaviour, to reveal the suitable formulation.

(a) Settleability

The results depicted in Figure 5.16 suggest that sulphate salts do not influence the settling of fly ash slurries, which closely resemble those achieved with deionised water. However, the use of H_2SO_4 reduced the degree of consolidation in the settled bed.

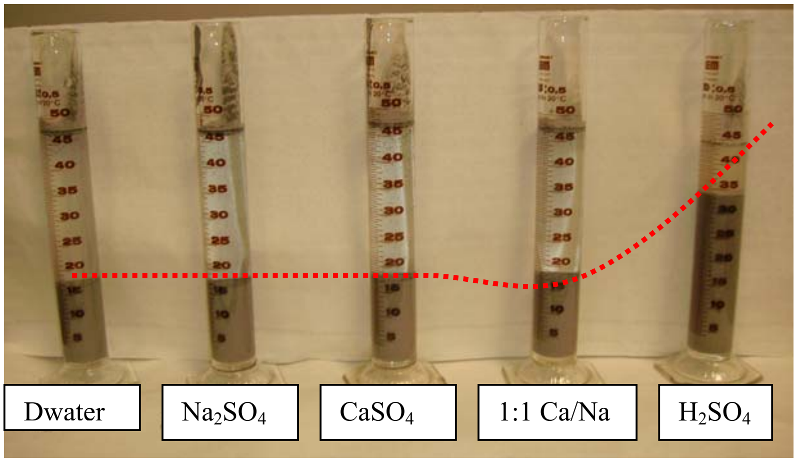


Figure 5.16 Illustration of slurry settling with sulphate solutions

There is no difference in the settling rate of slurries containing sulphate except when the source is H_2SO_4. The time dependence of settling is graphically shown in Figure 5.17. Solutions containing sulphate salts exhibit the same extent of settling of fly ash slurries as deionised water which achieved 17 ml of settled ash from 46 ml. The slurry containing H_2SO_4 stabilised at 34 ml, which is 100% thicker than other slurries. This decrease in settling is probably caused by the imbalance of surface charges (zeta potential) due to additional hydronium (H_3O^+) ions as pH decreases (Vietti and Coghill, 2006; Vietti and Dunn, 2006). The presence of H_2SO_4 in solutions may expand the volume of material to be landfilled, making it more porous and environmentally less acceptable.

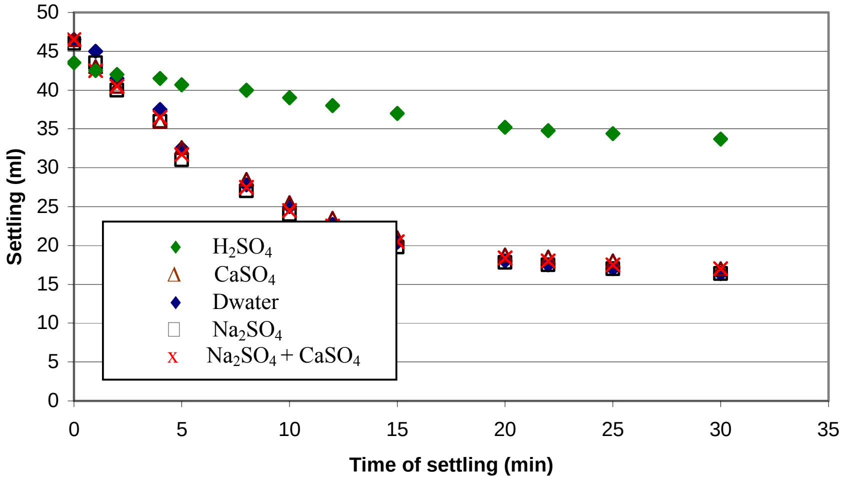
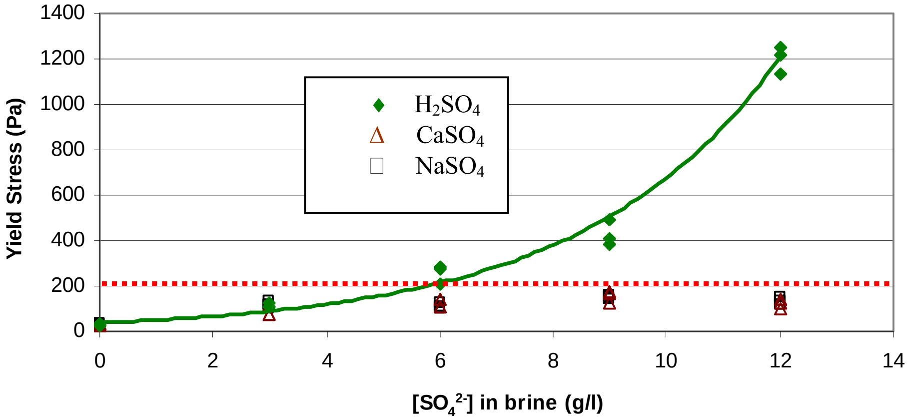


Figure 5.17 Settling behaviour of slurries with sulphate solutions

After settling reached equilibrium, the pH of the supernatants was measured and gave approximately 12.3 for most slurries except the H_2SO_4 bearing slurry which gave pH of 4.4. The acidic pH suggests that the buffering capacity of fly ash was exceeded during the 30 minutes of experimentation.

(b) Yield Stress

The rheological results of pastes demonstrate that sulphate salts achieved very similar yield stress even at high $[SO_4^{2-}]$s. An exponential increase in yield stress with $[SO_4^{2-}]$ was obtained in pastes containing H_2SO_4 solution as shown in Figure 5.18. Moreover, paste bearing H_2SO_4 underwent a substantial temperature rise from 21 to 33.5 °C while other pastes did not liberate measurable heat. This observation suggests the occurrence of a vigorous reaction between fly ash and the H_2SO_4 solution.



[4]Figure 5.18 Influence of sulphate compounds on yield stress

(c) Unconfined Compressive Strength

The achieved UCS results in Figure 5.19 indicate that sulphate compounds have distinct influence on the mechanical properties of paste. The increase of [SO$_4^{2-}$] from 6 to 30 g/l in the form of Na_2SO_4 solution raised UCS from 250 to approximately 2 000 kPa, which was followed by a decline. The H_2SO_4 bearing paste produced a relatively poor strength development with the maximum UCS value of 1 000 kPa at 6 g/l SO$_4^{2-}$. Concurrently, the use of $CaSO_4$ solution showed a gentle increase in UCS without indication of a maximum threshold in the studied range.

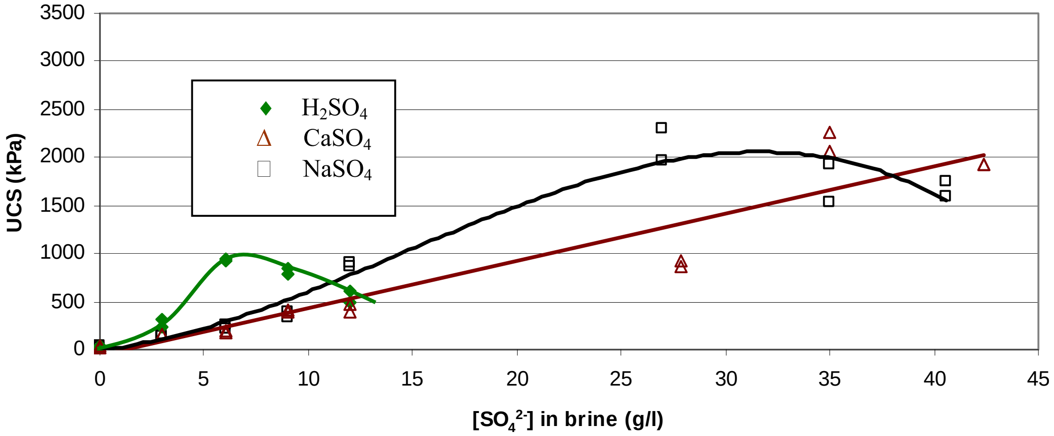


Figure 5.19 Influence of SO$_4^{2-}$ solutions on UCS of paste

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[4] The scale of yield stress was increased to 1400 to appreciate the behaviour of sulphuric acid

Pastes containing SO_4^{2-} ions derived from H_2SO_4 and Na_2SO_4 gave maximum UCS values corresponding with 6 and 30 g/l [SO_4^{2-}]s, respectively. However, a balance between UCS and yield stress must be obtained for an effective paste disposal.

The use of H_2SO_4 would introduce operational complications both from workability and compressive strength viewpoints; hence it must be avoided as a feed stream to the paste plant. Addition of at least 12 g/l SO_4^{2-} in solution as Na_2SO_4 or $CaSO_4$ will produce pastes exceeding the minimum targeted UCS of 500 kPa for mine backfilling at a yield stress of approximately 150 Pa.

5.6 DEVELOPMENT OF PREDICTIVE BRINE PROTOCOL (MODEL)

The purpose of this section was to apply brine chemistry knowledge gained in this study to predict and verify paste characteristics in terms of yield stress and compressive strength.

So far it has been established that brine must have a salinity of 40 - 60 g/l TDS; applicable to both industrial and synthetic brines. Suitable fly ash paste properties were individually achieved with $CaCl_2$ and Na_2SO_4 solutions compared to NaCl and $CaSO_4$, respectively. The pH of the paste must remain in the alkaline region.

The following discussion is aimed at providing the best combinations of the dominant constituents, namely, Ca, Na, Cl^- and SO_4^{2-} in synthetic brines to attain the desired paste properties.

5.6.1 Blending of $CaCl_2$ and Na_2SO_4 Solutions

This section examines the influence of blending $CaCl_2$ and Na_2SO_4 in various ratios as the mixing solutions in the preparation of fly ash pastes. Yield stress and compressive strength are used to indicate the effect on paste both at 40 g/l and 60 g/l salinities.

In Figure 5.20 it is shown that the yield stress of pastes containing the individual solutions is lower than those with blended solutions. The trend is more marked in the 60 g/l series. The increase in yield stress was probably caused by the precipitate which formed during the blending of these solutions as shown in Figure C5.3 (appendix). It is believed that the precipitate formed is gypsum ($CaSO_4.2H_2O$), likely to co-exist with NaCl. The findings could highlight the conversion from one set of compounds to another but results will probably enable the author to make conclusive statement on the matter.

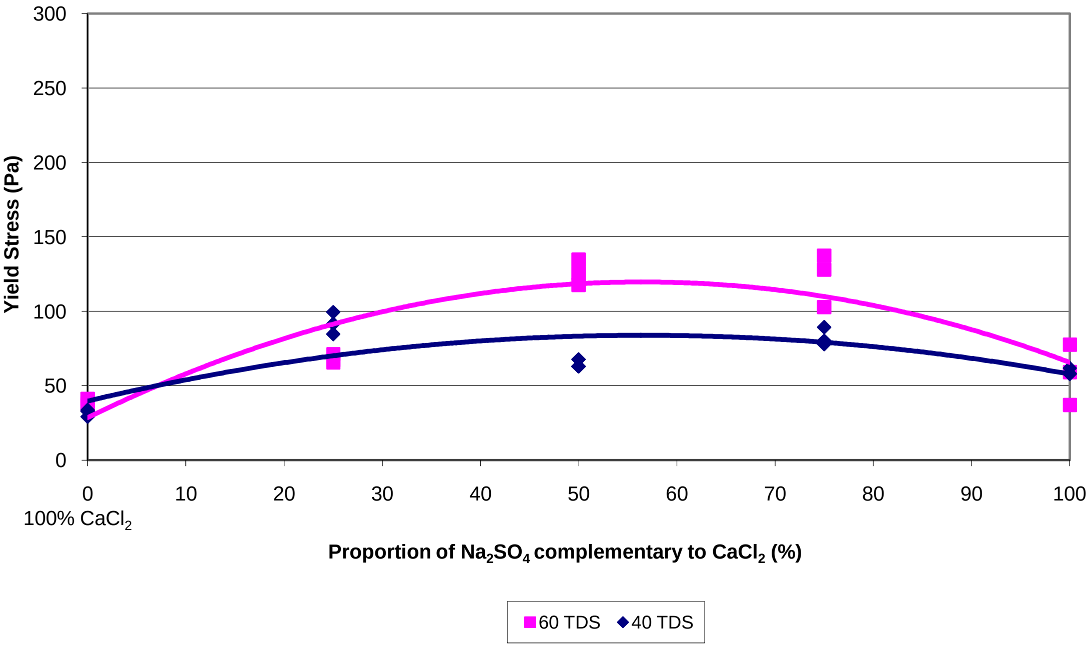

Figure 5.20 Effect of Na_2SO_4 and $CaCl_2$ blends on yield stress of paste

The results of UCS illustrated in Figure 5.21 are slightly erratic probably because of precipitation in the mixing solution since some salts could not be quantitatively transferred into the paste mixing vessel. Nonetheless, data indicate that pastes containing blended solutions provide better strength development than pastes prepared with individual solutions. For instance at 40 g/l salinity, pastes prepared with 100% solutions of Na_2SO_4 and $CaCl_2$ individually gave the UCS values lower than 2 000 kPa whereas a paste with 1:1 blended solution exceeded 2 200 kPa. $CaCl_2$ solution produced pastes which are stronger than those of Na_2SO_4.

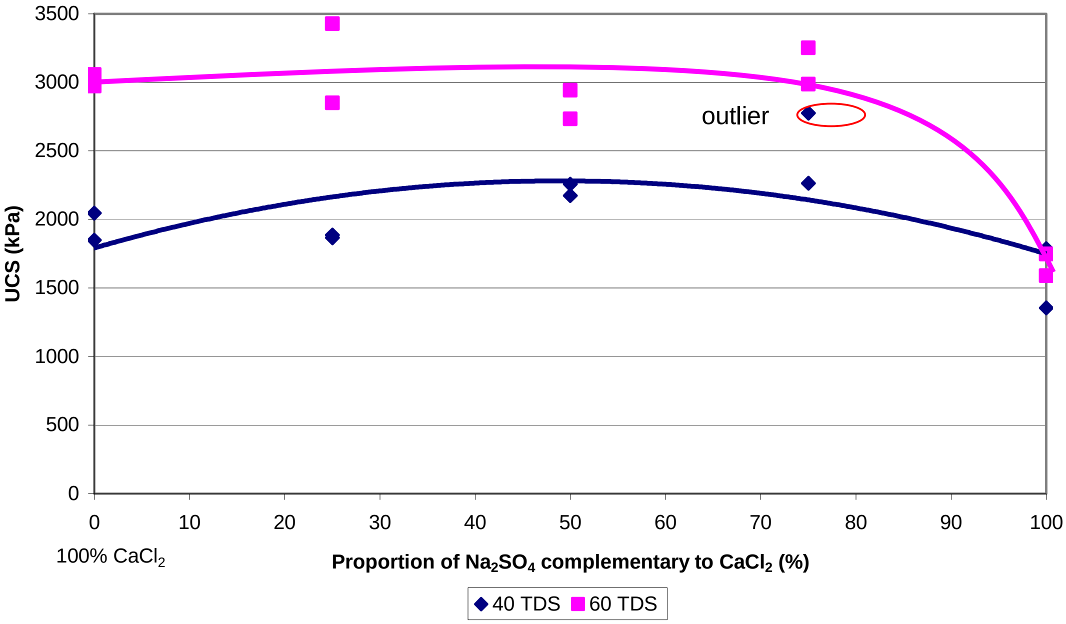

Figure 5.21 Effect of Na_2SO_4 and $CaCl_2$ blends on compressive strength of paste

5.6.2 Blending of NaCl and $CaSO_4$ Solutions

The pastes containing $CaSO_4$ solution were less workable compared to those prepared with blended NaCl and $CaSO_4$ solutions, as well as NaCl solution at both 40 g/l and 60 g/l salinities. According to Figure 5.22, it can be concluded that the yield stress remains almost constant between the two salinities. This reaffirms the validity of the prescribed brine salinity range of 40 – 60 g/l.

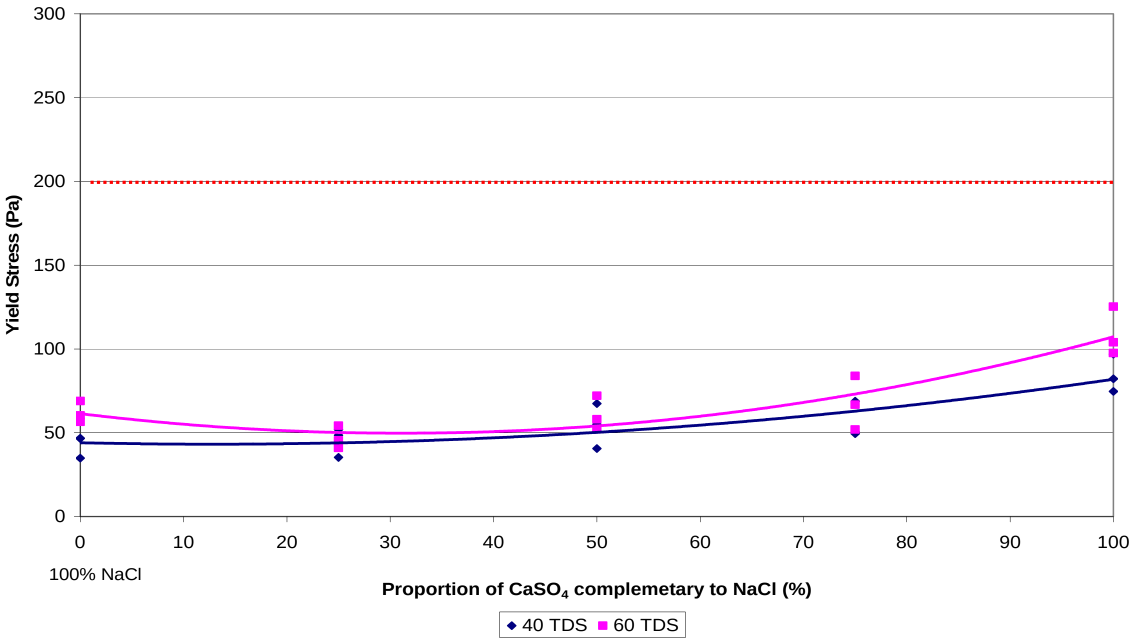

Figure 5.22 Effect of NaCl and $CaSO_4$ blends on yield stress

The blending of NaCl and $CaSO_4$ produced pastes with better precision of data as can be seen with UCS results in Figure 5.23. The UCS values for the pastes with blended solutions were approximately 2 000 and 2 500 kPa for 40 and 60 g/l salinities, respectively. The pastes with individual solutions were slightly weaker. The difference between pastes prepared from individual and blended solutions suggests a synergistic effect in the latter.

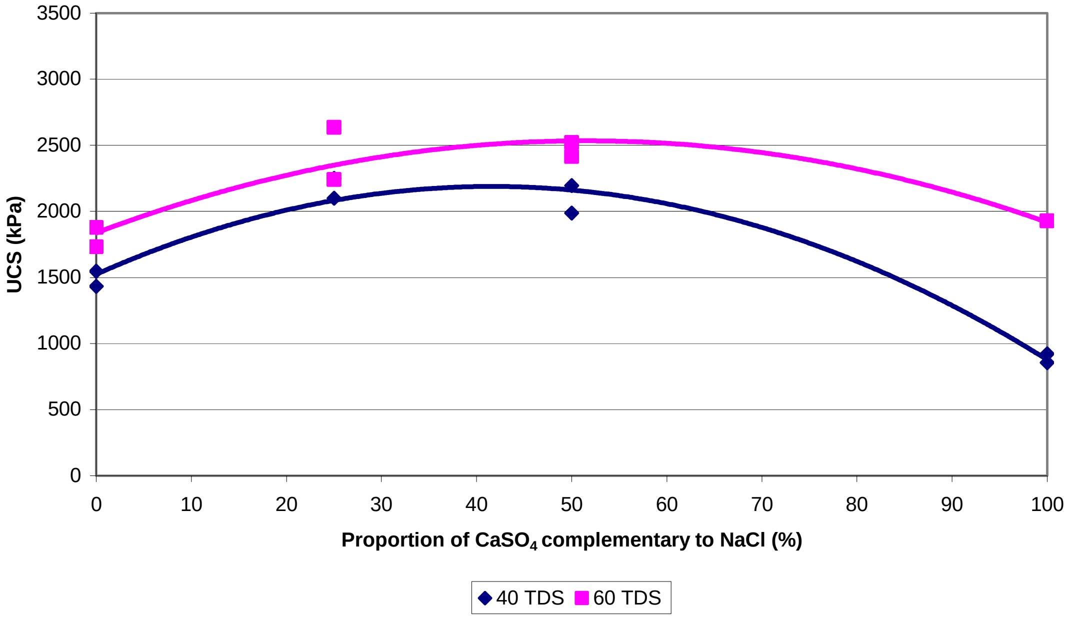

Figure 5.23 Effect of NaCl and $CaSO_4$ blends on compressive strength

5.6.3 Comparison of Brine Sets

The statistical analysis of yield stress data using t-test, assuming equal variance showed that the workability of pastes containing the blends of NaCl and $CaSO_4$ solutions was not significantly different from that of blended Na_2SO_4 and $CaCl_2$ solutions. The details are appended in Table C5.1.

However, the pastes with Na_2SO_4 and $CaCl_2$ solutions were somewhat stronger than those with NaCl and $CaSO_4$, which correlate with the use of the Na_2SO_4 and $CaCl_2$ to accelerate the early strength development in concrete (Shi and Day, 2000; Erlin and Hime, 1976, 2004). The observed trends were consistent in both salinities, which improves confidence in the conclusions made here.

The degree of reproducibility of UCS was relatively low with the blends of NaCl and $CaSO_4$ solutions probably due to precipitation which introduces non-homogeneity in the resultant pastes. It can be concluded that the salinity range of 40 – 60 g/l also holds true for synthetic brines investigated here. The optimum blending ratios could not be established although 1:1 was more promising. A concerted study for optimisation may be required in future.

5.6.4 Calibration of the Brine Protocol

This section aims to test the accuracy of the developed predictive brine protocol (model). The results of the simulated salty water with and without pH adjustment are presented. The closeness of the results will mean that major components in brine are sufficient to dominate the paste behaviour. Otherwise, the effect of minor/trace elements as well as treatment chemicals such as flocculants and antiscalants should be considered.

To calibrate the developed model, salty water was simulated with pure chemicals where one of the simulations was acidic, see Table C5.2 in the appendix. The yield stress for salty water and acidic synthetic brine (acidic synbrine) bearing pastes is approximately 200 Pa (Figure 5.24). Based on the previous observations made during settling, it was necessary to adjust the pH 0.3 of acidic synbrine to emulate that of salty water (pH 8.8). NaOH pellets were used for pH adjustment to 10.0 at an additional 38% salinity in the synbrine.

The yield stress of paste with synbrine (i.e. after pH adjustment) conspicuously decreased from 200 Pa to 70 Pa as shown in Figure 5.24. The effect of pH on the paste behaviour observed asserts the testimony made during settling tests. It is speculated that the addition of NaOH neutralised the surface charge imbalance caused by H_3O^+ ions, which Stocks (2006) refers to as coagulation. This resulted in the reduction of yield stress and the paste became more workable (Vietti and Dunn, 2006; Vietti and Coghill, 2006).

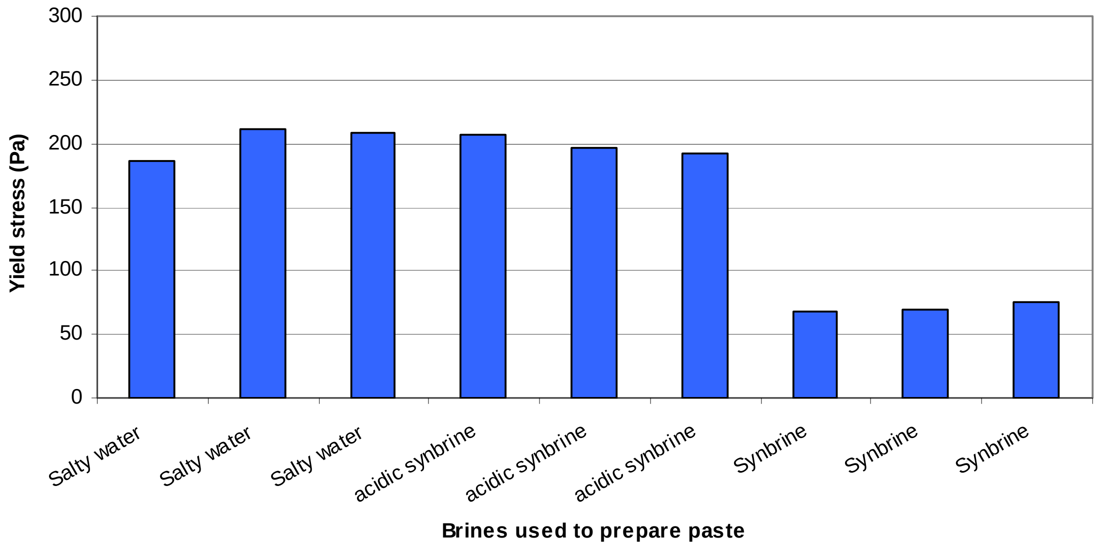

Figure 5.24 Calibration of the brine protocol in terms of yield stress

The UCS data presented in Figure 5.25 revolve around 2 000 kPa for pastes containing salty water and acidic synbrine. Synbrine paste was marginally stronger than the other two pastes, implying that almost equivalent compressive strength was obtained despite the differences in salinity and pH of these brines (as appended in Table C5.2).

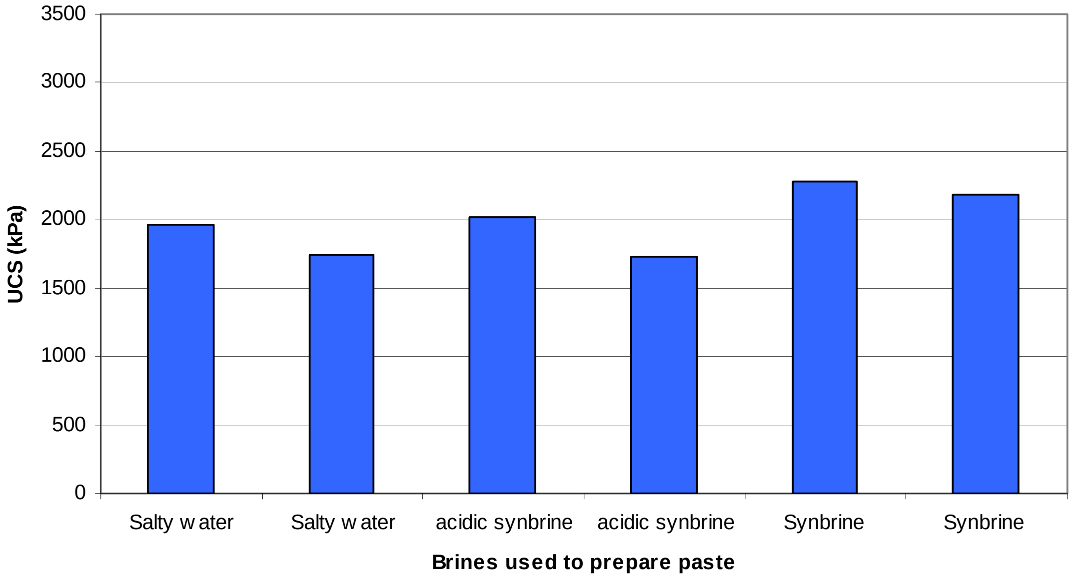

Figure 5.25 Calibration of the brine protocol using compressive strength

It is therefore concluded that brine acidity does not have a huge effect on the compressive strength compared to yield stress. The closeness of UCS results is attributed to the fact that the pH of paste rises rapidly during mixing of brine with fly ash, which nullifies the effect of initial pH of the brine as various reactions take place during 28 days of curing.

Remarks on the Protocol

The above results have proven the validity of the proposed brine protocol where predominant brine constituents were used to predict the paste behaviour as well as the acceptable salinity range of brine. Nevertheless, it was realised that a higher degree of accuracy is achieved in the UCS prediction compared with that of yield stress. This difference is attributed to the dependence of yield stress to initial pH of the brine solution while strength development is a long-term phenomenon involving a chain of reactions (Ylmén et al., 2009; Coleman and Mcwhinnie, 2000; Campbell, 1999).

5.6.5 Effect of pH on Workability

It has been established that salinity and chemical composition of brine have a profound effect on the paste properties. Acids showed a unique influence on the fresh paste properties, which is being examined using HCl and H_2SO_4 to attain solutions in a pH range of 1 to 8. These solutions were blended with 65% fly ash content prior to the determination of efflux time.

The preliminary results obtained when deionised water was acidified with HCl and H_2SO_4 to attain a range of pH are presented in Figure 5.26. The data suggest that pH has a profound effect on the workability of paste (Torrance and Pirnat, 1984; Jewell et al., 2002; Chang, 1993). It must be remembered that deionised water lacks alkalinity hence minute droplets were used to try and adjust the pH of deionised water. In spite of negligible addition of salinity during adjustment of pH, the influence on workability was conspicuous (Figure 5.26).

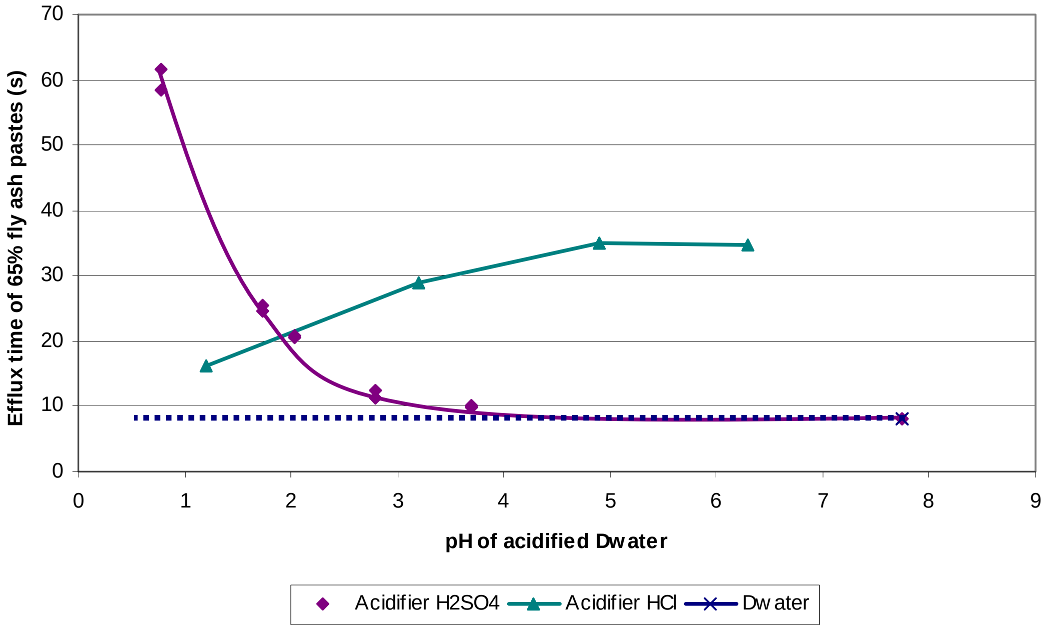

Figure 5.26 Effect acidification of deionised water on flow behaviour

A relationship seems to exist between these data and the previously made observations where H_2SO_4 reduced workability (section 5.5) although the influence of HCl was inconclusive in section 5.4. The reduction in the extent of slurry settling was demonstrated by both acids although the case of H_2SO_4 was more pronounced.

Studying the effect of pH on the paste behaviour will require a devoted research effort. In this thesis it was considered sufficient to note that acids induce undesired paste behaviour, which warrants their exclusion in paste formulations or preparation.

5.7 CHARACTERISATION OF CURED PASTES

The findings presented so far have been based on fresh and 28-day old pastes. It was considered necessary to perform some of the analyses on pastes cured for a longer period of time in order to establish whether chemical weathering takes place. This characterisation only involves pastes prepared with 68% Synfuels fly ash and salty water, regen brine as well as deionised water which were cured for 18 months under atmospheric conditions at 21 ± 2 °C.

5.7.1 Particle Size Distribution (PSD)

The PSD analysis of fly ash reveals that it contains 40.5% of particles < 20 µm, which is more than twice the generally accepted minimum threshold of 15% content required for the formation of a stable paste (Jewell and Fourie, 2006; Kwak et al., 2005). The PSD profiles of fly ash and pastes are appended in Figure C5.4.

The paste samples were dried at 35 °C and crushed by hand before PSD analysis. The PSD data of 18-month old pastes and the fly ash (control) are presented in Figure 5.27. There is no obvious difference between the pastes on their own implying that hydration reactions did not alter the range of particle sizes in 18 months. These samples in turn have PSD profiles similar to that of fly ash in terms of silt-sized particles (5 – 75 µm), which is the predominant particle size range. The content of clay-sized particles (< 5 µm) in fly ash is about twice that of the pastes whereas the sand-sized (75 – 425 µm) content is about 30% lower in fly ash.

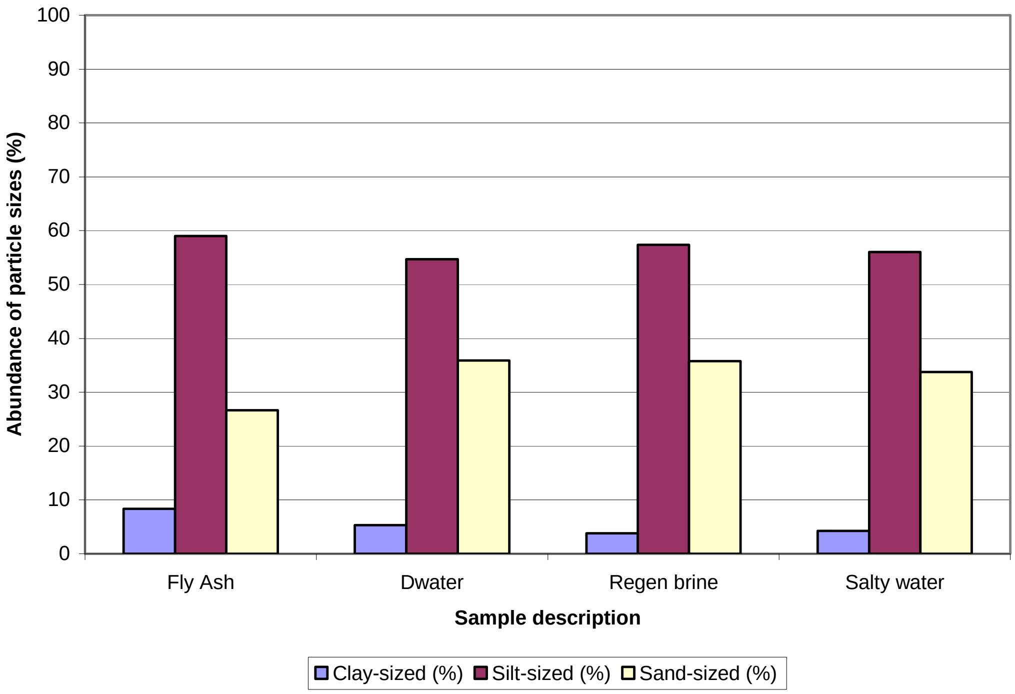

Figure 5.27 Illustration of PSD of 18-month old pastes and fly ash

5.7.2 Morphology Using FEG SEM

The FEG SEM was used to provide microstructural information of different pastes after 18 months of curing. It is demonstrated in Figure 5.28 that some morphological alteration took place in the different pastes although a great number of fly ash particles failed to react. This is not unexpected since a significant variation exists in the composition of individual spheres (Vassilev and Vassileva, 1996; Kruger, 2010; Mahlaba et al., 2011).

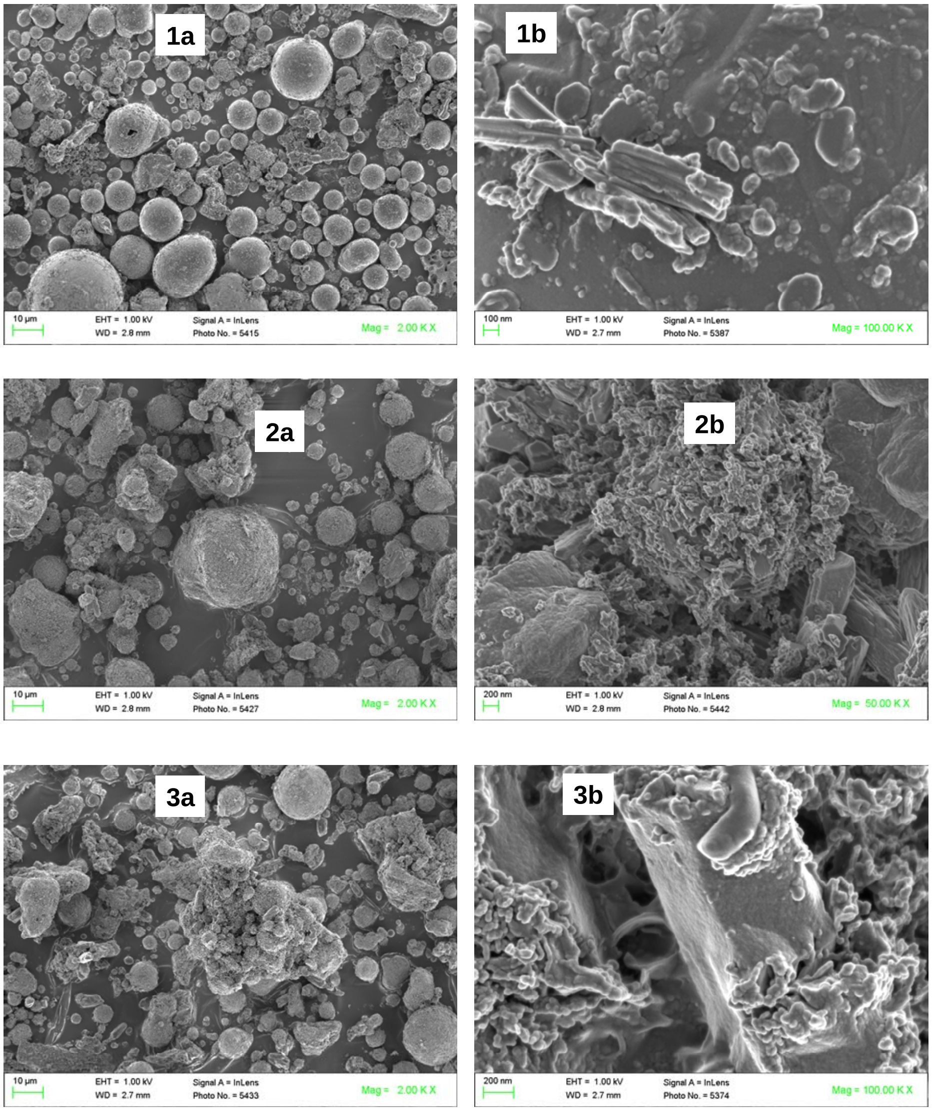

Figure 5.28 FEG SEM images of 18-month old pastes prepared with (1) deionised water (2) regen brine and (3) salty water

The FEG SEM micrograph (designated as 1a) of deionised water bearing paste shows that no reaction occurred in the fly ash particles, whereas micrographs corresponding with 2a and 3a indicate some degree of reaction (despite being spherical) in the pastes prepared with regen brine and salty water, respectively. Alternatively, images designated as 1b, 2b and 3b illustrate the distinct presence of secondary phases in pastes prepared with deionised water, regen brine and salty water, respectively. From FEG SEM analysis, it is expected to detect hydration products from the different pastes. Additional micrographs are attached in Figures C5.5 to C5.7.

5.7.3 Elemental Analysis Using XRF

The XRF technique was used to determine the elemental composition of pastes and fly ash as received, which is fully appended in Table C5.5. Selected data relevant to hydration are presented in Table 5.1. It can be deduced that the content of Si, Al, Fe and Ca remained more or less constant whereas that of Na and Cl^- increased significantly in pastes containing regen brine and salty water. This increase is inferred to the dominancy of Na and Cl^- in these brines. Concurrently, S also slightly increased in the pastes bearing regen brine and salty water for the same reason.

Table 5.1 Summary of XRF data on 18-month old pastes

Sample name	**Si (%)**	**Al (%)**	**Fe (%)**	**Ca (%)**	**Na (%)**	**S (%)**	**Cl^- (%)**
Fly ash	22.40	17.35	2.05	7.45	0.50	0.20	<0.01
Dwater paste	23.24	17.69	1.70	6.63	0.54	0.16	<0.01
Regen brine paste	22.12	16.80	1.94	6.99	1.74	0.32	0.38
Salty water paste	21.03	16.21	1.98	6.89	2.54	0.63	1.29

5.7.4 MINERALOGY

(a) XRD

The XRD results of 18-month old pastes are provided in Table 5.2. It is apparent that brine pastes formed new minerals which were not originally present in the fly ash. Deionised water bearing paste on the other hand remained similar to fresh fly ash except for calcite and periclase. This observation once again highlights the pertinence of chemical constituents in brines during hydration and chemical weathering. Regen brine paste formed analcime ($NaAlSi_2O_6.H_2O$) and calcite while salty water paste additionally formed gypsum ($CaSO_4.2H_2O$) and halite (NaCl) as hydration products.

Table 5.2 XRD results of fly ash and 18-month old pastes

Component	**Chemical Formula**	**Fly ash**	**Dwater paste**	**Regen brine paste**	**Salty water paste**
Quartz (%)	SiO_2	10.24	12.00	9.05	10.34
Mullite (%)	$Al_6Si_2O_{13}$	20.53	19.66	17.99	18.53
Hematite (%)	Fe_2O_3	0.68	0.58	0.64	0.60
Analcime (%)	$NaAlSi_2O_6 \cdot H_2O$	-	-	2.65	2.37
Lime (%)	CaO	2.22	-	-	-
Periclase (%)	MgO	-	0.69	0.09	0.64
Calcite (%)	$CaCO_3$	-	3.54	6.52	4.92
Halite (%)	NaCl	-	-	-	1.24
Gypsum (%)	$CaSO_4.2H_2O$	-	-	-	1.66
Amorphous content (%)	N/A	66.32	63.53	63.06	59.70
Total	**N/A**	**99.99**	**100.00**	**100.00**	**100.00**

Analcime was also identified in WFA and 8-month old FA in Chapter 4. Halite is a Na bearing precipitate observed in salty water paste that may easily redissolve on contact with water.

Calcite was identified in all the pastes as would be expected because it forms when carbon dioxide reacts with hydration products. Depletion of lime was observed in pastes as chemical weathering occurred and a decrease in pH is subsequently expected during leaching.

No ettringite was detected and gypsum was instead identified in the salty water paste. The absence of ettringite either implies that: 18 months of curing is too short for its formation, its quantities were below the detection limit of XRD instrument used for analysis or there is a deficiency of glassy aluminate in fly ash.

(b) DSC

The DSC results were used to supplement the mineralogical data obtained using XRD. Dehydration peak was observed below 100 °C while that of portlandite (calcium hydroxide) decomposition was detected above 400 °C in all the samples including fly ash (Pane and Hansen, 2005). Additionally, two peaks were detected in salty water paste around 130 and 340 °C corresponding with calcium silicate hydrate (C-S-H) gel and Friedel's salt ($Ca_3.Al_2O_6.CaCl_2.10H_2O$), respectively (Saikai et al., 2006; Ramachandran et al., 2002; Birnin-Yauri and Glasser, 1998). No extra peaks were observed in pastes prepared with deionised water and regen brine. The DSC micrographs are appended in Figure C5.8. The mineralogical phases obtained with DSC and XRD complement each other despite their different detection limits and degrees of sensitivity (Donahoe, 2004; Ramachandran et al., 2002).

5.7.5 Leachability

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

It can be observed in Figure 5.29 that pastes have pH values which are slightly lower than that of fly ash. The reduction in pH indicates that mixing of fly ash with liquids to make pastes allows mineralogical transformation which consumes lime and alkalis i.e. chemical weathering (Donahoe, 2004; Zevenbergen et al., 1999; Spears and Lee, 2004).

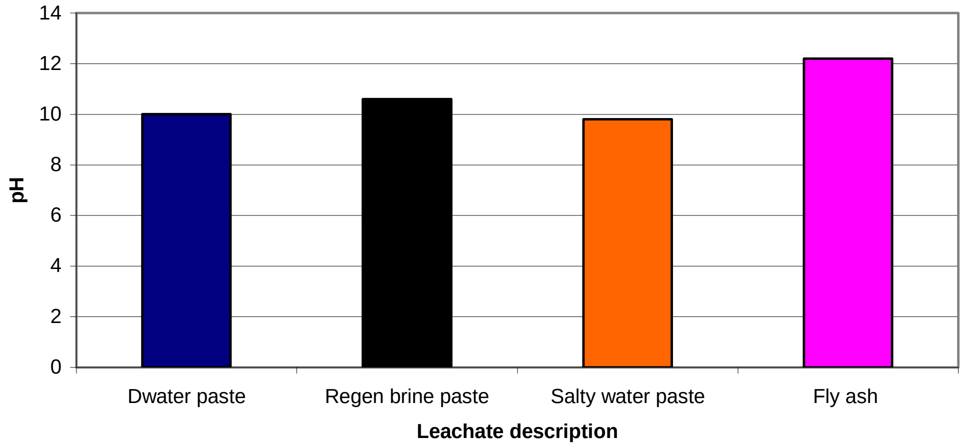

Figure 5.29 pH of paste leachates

The EC trends in Figure 5.30 illustrate that co-mixing of fly ash with brines to make paste reduced the leaching potential remarkably compared to fly ash. Fly ash gave an EC value of 8 mS/cm, which is over 300% higher than pastes.

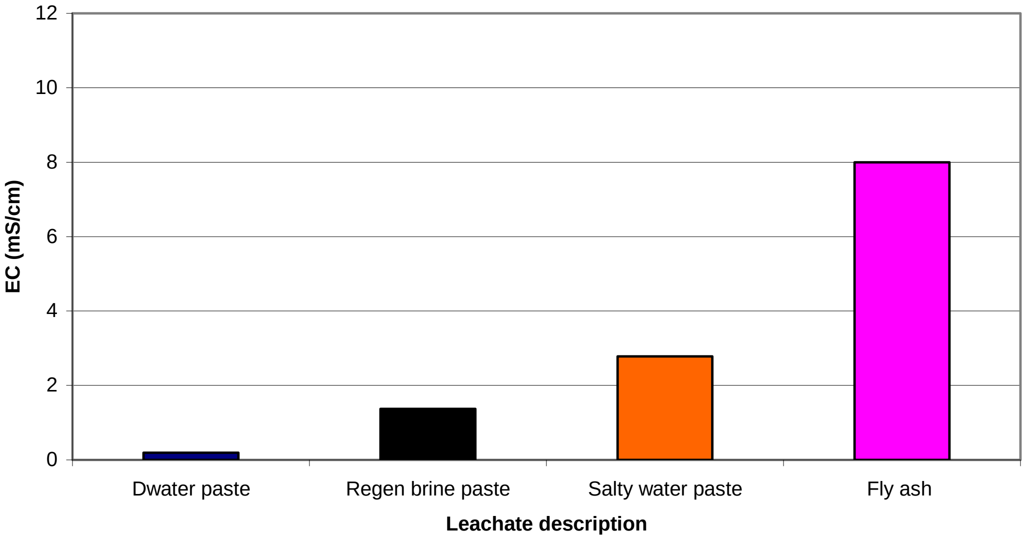

Figure 5.30 EC of paste leachates

The leachate results are summarised in Table 5.3 where it is evident that M-alkalinity (total alkalinity) of pastes decreased conspicuously from 1 800 in fly ash to approximately 100 mg/l as $CaCO_3$. Of the predominant brine and fly ash constituents (Na, Ca, Fe, Al, Si, SO_4^{2-} and Cl^-) only Cl^- and SO_4^{2-} are regulated as illustrated in Table 5.3. Both Cl^- and SO_4^{2-} are below the statutory limits of 5 000 mg/l Cl^- and 10 000 mg/l SO_4^{2-}.

Table 5.3 Summary of leachate data ([∂]mg/l)

Component	Dwater paste	Regen paste	Salty water paste	Synfuels fly ash	☼SASLP0
M-Alkalinity (mg/l as $CaCO_3$)	40	112	76	1 800	-
Cl^-	<5	218	466	7	5 000
SO_4^{2-}	35	136	466	101	10 000
Na	4	223	519	3	-
Al	5.45	9.06	6.59	<0.10	-
Si	3.4	4.9	3.8	<0.2	-
Fe	<0.025	<0.025	<0.025	<0.025	-
K	1.6	11.6	29	<1	-
Ca	27	24	21	704	-

☼ SASLP0 = provides concentration limits for classifying the material as a low risk according to SASLP

Based on the prevalent components, paste disposal method provides an environmentally acceptable solution for brines. It must, however, be noted that before any conclusions can be drawn on the environmental impact, more elements including trace elements need to be considered, which is outside the scope of this thesis.

5.8 INFLUENCE OF FLY ASH

The use of fly ash with different properties was aimed at verifying whether its composition plays a role in the behaviour of paste. The outcome of that evaluation on the rheology and UCS of pastes under varied brine conditions is discussed.

[∂] Leachate data are expressed in mg/l because g/l is too big

5.8.1 Determination of Paste Behaviours

(a) Rheological Behaviour

The rheological results presented in Figure 5.31 demonstrate that Matimba fly ash does not react to brine variance since there was no change in workability. All pastes gave a yield stress of approximately 40 Pa.

On the contrary, pastes prepared by mixing Synfuels fly ash with regen brine and deionised water gave a yield stress of approximately 80 Pa which is twice that of Matimba fly ash pastes. Salty water gave a high yield stress of 210 Pa with Synfuels fly ash. It is clear that these fly ashes respond differently to brines in terms of rheology.

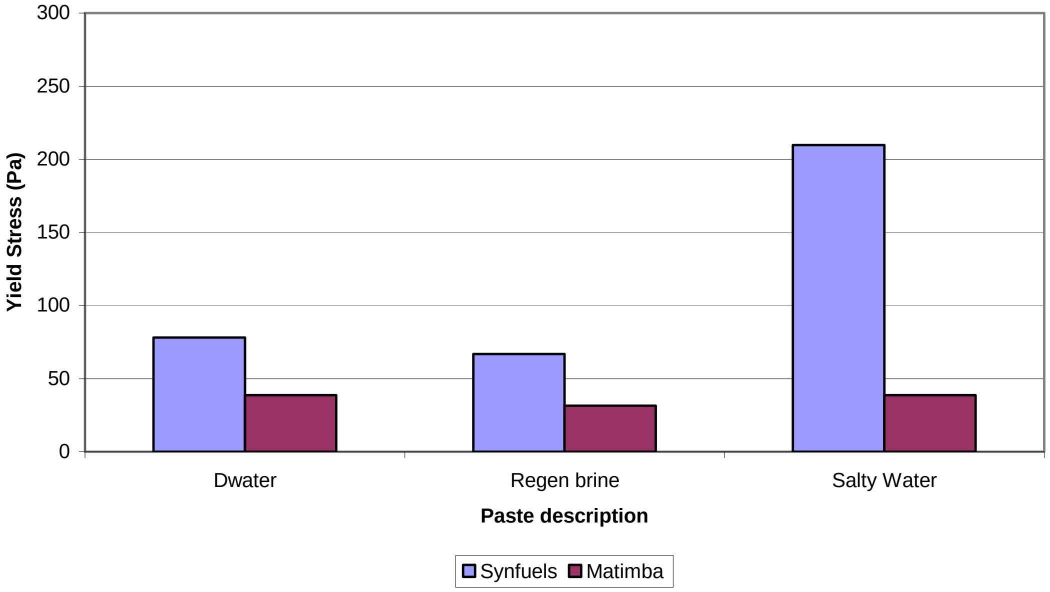

Figure 5.31 Effect of fly ash properties on workability

Figure 5.32 also shows a negligible response of Matimba fly ash bearing pastes to changes in brine salinity. In contrast, Synfuels fly ash demonstrated an exponential increase in yield stress when the TDS of the brine exceeded 40 g/l. The increase in the yield stress as a function of brine salinity for pastes derived from Synfuels fly ash indicates the occurrence of early hardening reactions (Campbell, 1999), which was not exhibited by similar pastes prepared with Matimba fly ash.

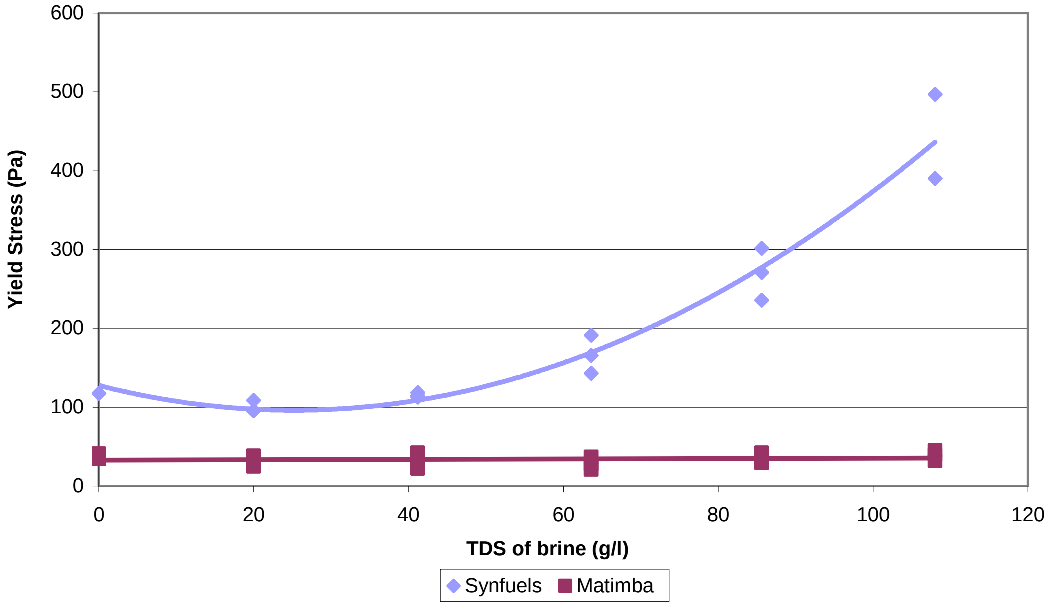

Figure 5.32 Rheological responses of pastes to salinity per fly ash type

(b) Unconfined Compressive Strength

Comparison of strength development in pastes containing different fly ashes as a function of brine composition is presented in Figure 5.33. Synfuels fly ash responds to variation in brines whereas Matimba fly ash remains essentially unaltered. The UCS of Matimba fly ash pastes is less than 200 kPa while Synfuels fly ash pastes reached 1 650 and 1 840 kPa with salty water and regen brine, respectively.

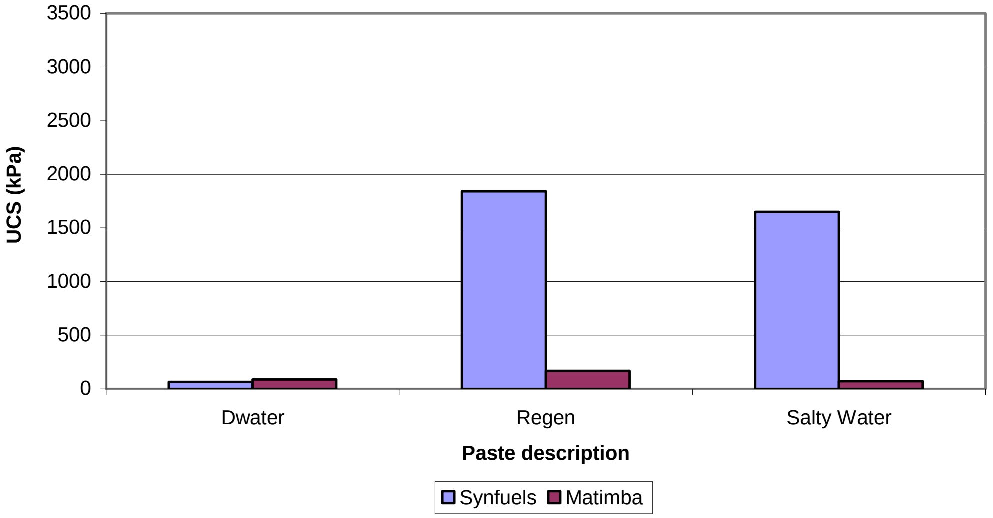

Figure 5.33 Comparison of fly ashes on UCS behaviour after 28 days

The attempt to explain the differences exhibited by pastes containing these fly ashes is made in the following section.

5.8.2 Physical Characteristics

Basic physical properties of the two fly ashes, namely, colour, PSD, and particle morphology were examined. As a matter of fact no significant differences were expected because both fly ashes originate from power stations employing pulverised coal combustion (PCC) systems, which could yield similar physical properties in fly ash.

(a) Colour

The two fly ashes are visually different (Figure 5.34), Matimba fly ash has a brownish appearance whereas Synfuels fly ash appears greyish in colour. This difference in colour serves as an indication that these fly ashes may also differ in several other aspects.

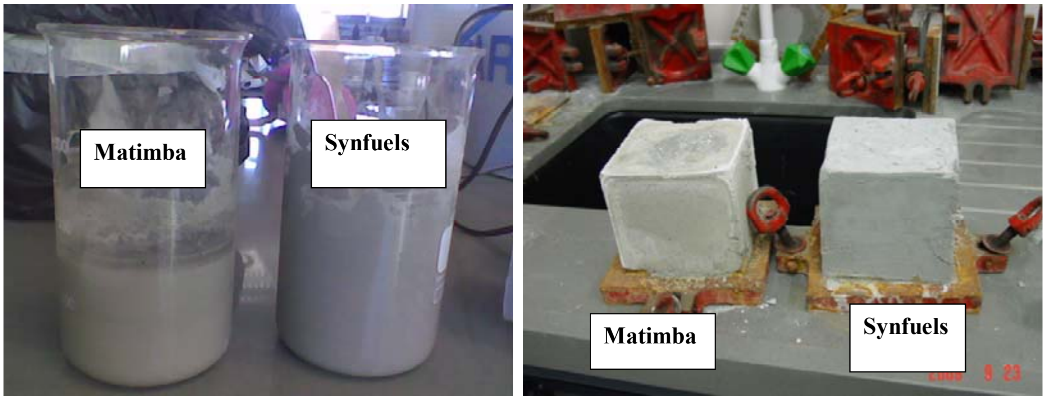

Figure 5.34 Photo of fly ashes

(b) Particle Size Distribution

The comparison of the PSD for these fly ashes shows that Matimba fly ash is coarser than Synfuels fly ash, see Figure 5.35. In terms of the required fineness (particles < 20 µm) of 15% for paste (Jewell and Fourie, 2006), Matimba fly ash has 20% while Synfuels fly ash has 40% of the minimum requirement.

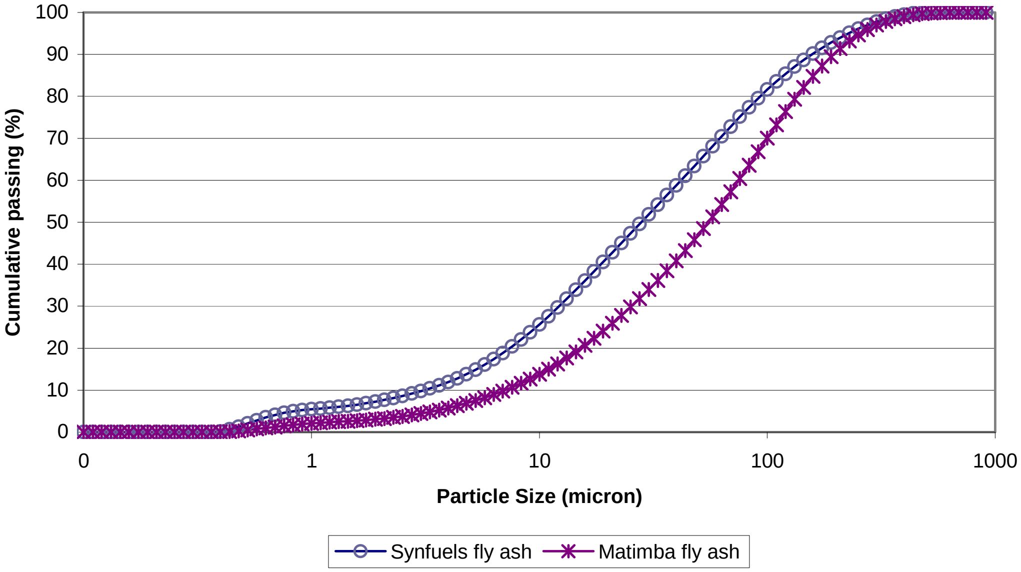

Figure 5.35 Particle size distributions of the two fly ashes

The PSD data of the two fly ashes were further classified according to ASTM D 422-63 (Figure 5.36). The abundance of clay-sized particles in Synfuels fly ash is almost twice that of Matimba fly ash while that of silt-sized particles is 17% higher (in the former).

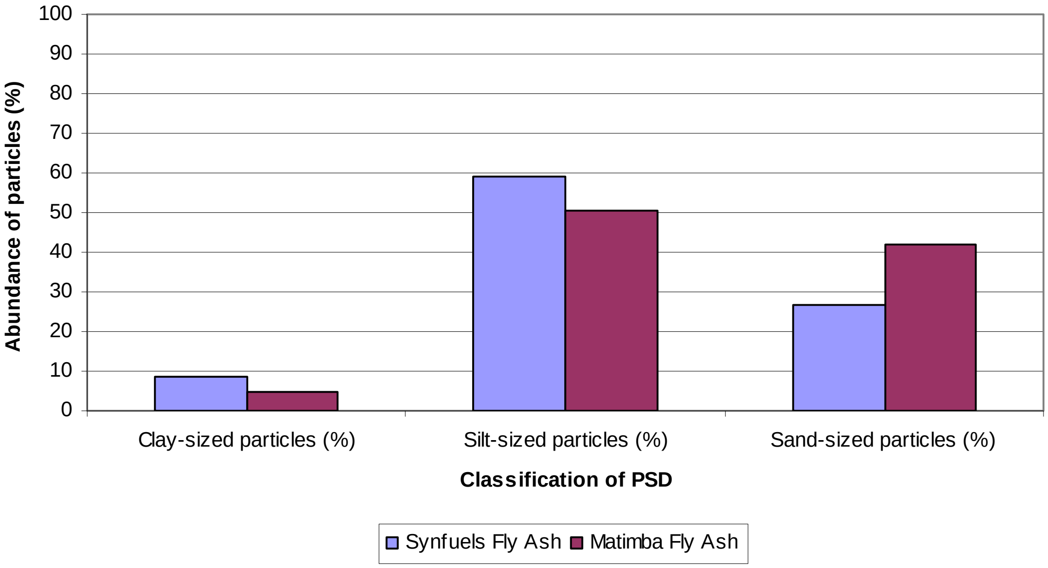

Figure 5.36 PSD profiles of the two fly ashes

As expected, the sand-sized particles are significantly higher in the Matimba fly ash. Thus Matimba fly ash is coarser than Synfuels fly ash. According to literature finer particles are more reactive than coarser particles which are usually rich in unburned carbon (Campbell, 1999; Mahlaba and Pretorius, 2006). From a PSD point of view Matimba fly ash ought to have been less reactive than Synfuels fly ash, which was indeed the case.

(c) Morphology

The FEG SEM images in Figure 5.37 show that the particles of Synfuels fly ash are predominantly spherical while those of Matimba fly ash are rather irregular as depicted in Figure 5.38. Morphology of fly ash particles affects workability and its reactivity (Kruger, 2010; Mahlaba and Pretorius, 2006).

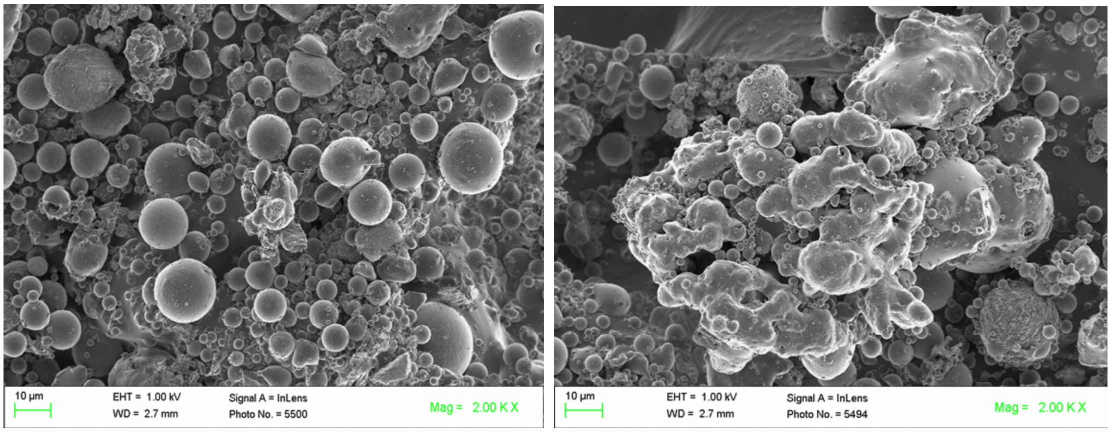

Figure 5.37 Morphology of Synfuels fly ash particles

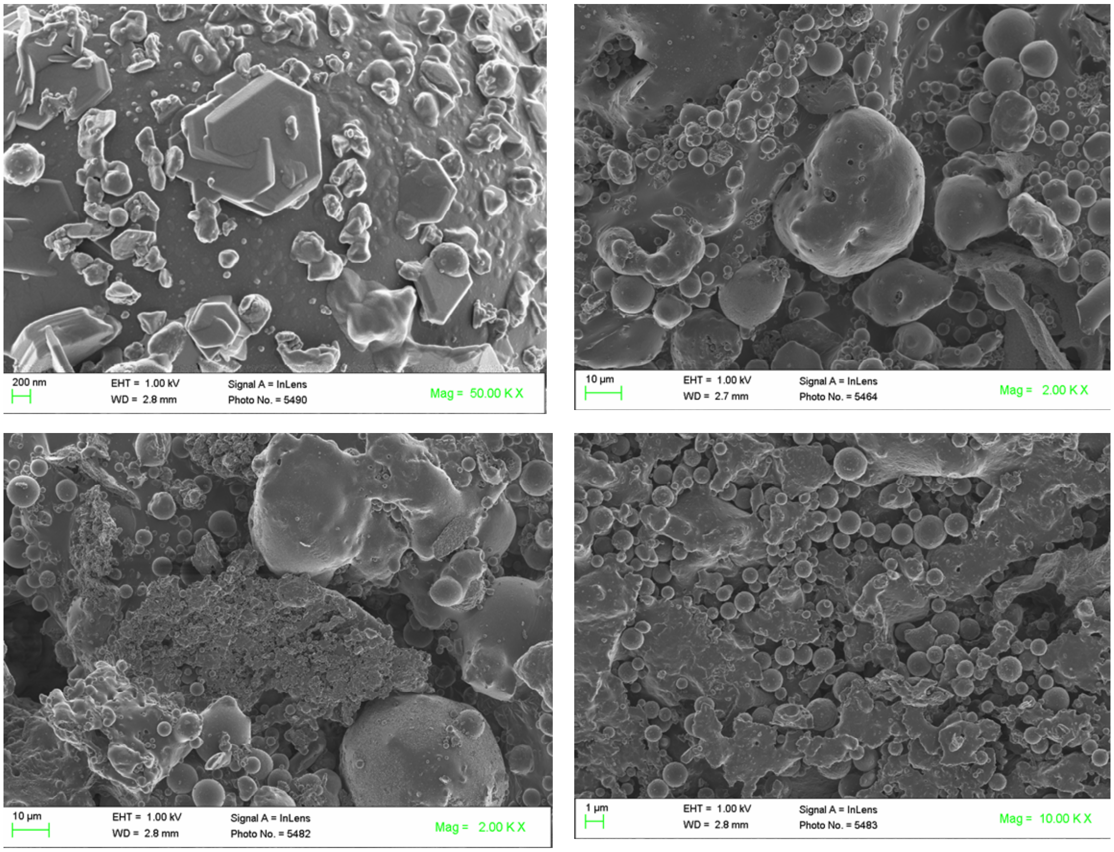

Figure 5.38 Morphology of Matimba fly ash particles

5.8.3 Chemical and Mineralogical Characteristics

(a) XRF

The elemental composition of the two fly ashes is presented in Table 5.4. It is evident that Matimba fly ash has a significantly higher content of Fe_2O_3, which could be responsible for the observed colour difference. Conversely, Synfuels fly ash has almost four times the content of CaO and slightly more Al_2O_3 and MgO compared to Matimba fly ash.

Table 5.4 Elemental composition of the two fly ashes

Component	**Matimba fly ash (%)**	**Synfuels fly ash (%)**
SiO_2	59.48	47.92
Al_2O_3	28.55	32.78
Fe_2O_3	5.91	2.05
CaO	2.33	9.48
MgO	0.38	1.18
SO_3	0.39	0.51
Na_2O	N/A	0.67
K_2O	1.00	0.92
TiO_2	1.32	1.63
SrO	0.04	0.57
BaO	0.11	0.77
P_2O_5	0.24	1.07
Cl	<0.01	<0.01
MnO	0.06	0.05
Total	**99.81**	**99.60**

(b) XRD

There are appreciable mineralogical differences (Table 5.5) between the two fly ashes which are in line with XRF data. Matimba fly ash has a higher content of hematite and mullite while Synfuels fly ash is richer in lime and amorphous phase, which are essential in hydration (Spears and Lee, 2004).

Table 5.5 Mineralogy of fly ashes

Compound	**Chemical formula**	**Matimba fly ash (%)**	**Synfuels fly ash (%)**
Mullite	$Al_6Si_2O_{13}$	28.98	20.53
Quartz	SiO_2	11.86	10.24
Hematite	Fe_2O_3	1.43	0.68
Lime	CaO	0.37	2.22
Amorphous content	N/A	57.36	66.32
Total	**N/A**	**100.00**	**99.99**

The presence of lime has a profound effect on the reactivity of fly ash to immobilise salts by providing an alkaline environment (Bouzalakos et al., 2008; Kim, 2005; Ben-Haha et al., 2010) as has already been manifested by poor response to brine variations of pastes containing Matimba fly ash.

(c) Pore Waters

This section presents the nature of extracted pore water from the two fly ashes. Figure 5.39 demonstrates that Matimba fly ash gave a pH of 11.3 while Synfuels fly ash gave 12.2, which is almost an order of magnitude difference in $[H_3O^+]$.

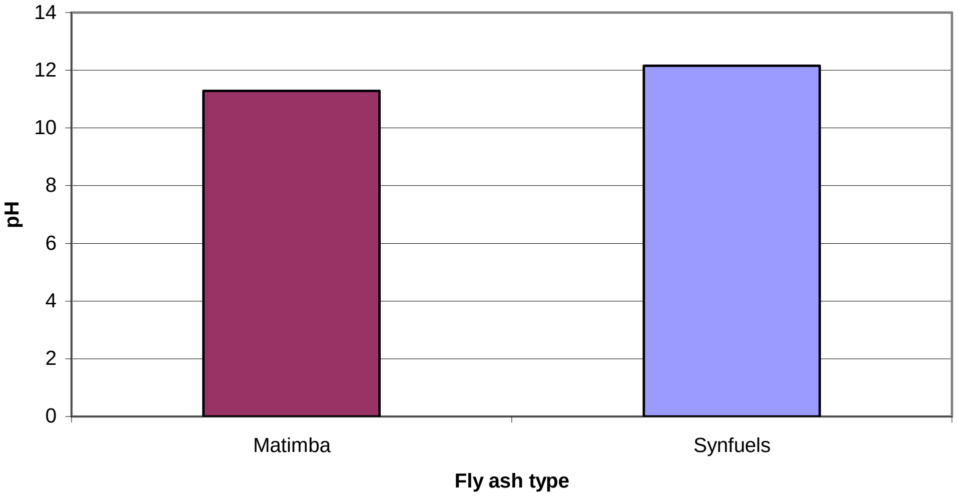

Figure 5.39 Comparison of pH for the two fly ashes

Concurrently, Matimba fly ash showed a higher leachability compared to Synfuels fly ash as shown in Figure 5.40. The former released salts corresponding with an EC of 18.02 mS/cm whereas the latter gave only about half i.e. 9.22 mS/cm. This difference could be a combination of chemical and physical factors.

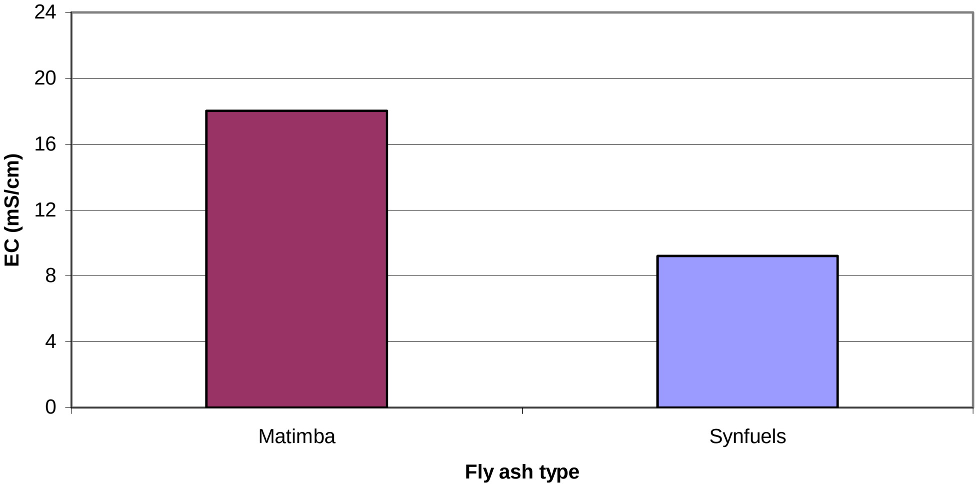

Figure 5.40 Comparison of EC for the two fly ashes

5.8.4 Concluding Remarks on Fly Ashes

Initially it was believed that physical properties of Synfuels and Matimba fly ashes would be almost identical. Examination of data demonstrated the existence of critical differences especially the PSD and morphology of particles. As expected the chemical and mineralogical characteristics of these fly ashes were different in accordance with feed coals and operation conditions. The distinctive behaviours of resultant pastes were therefore attributed to all the above-mentioned differences in the two fly ashes. The critical differences were lime deficiency, relatively lower content of the amorphous phase and the coarser nature of Matimba fly ash particles.

It is, nevertheless, believed that additives can ameliorate the reactivity of Matimba fly ash (Giergiczny, 2004; Shi, 1996). The impact of additives on the workability and strength development of paste will require good balance according to the criteria in section 3.4.7 (Chapter 3).

5.9 CONCLUSIONS

An encompassing finding made in this research is that both brine and fly ash properties have a profound effect on the paste behaviour. This was manifested in the workability, strength development, and weathering (including formation of secondary phases and leachability) of the resultant pastes.

The important aspects and observations which led to the above statement are that:

- Total solids rather than fly ash content in paste provide a better means of assessing and predicting workability. This means that salinity of brine as Total Dissolved Solids must be taken into account during paste preparation.
- An optimum range of salinity with the industrial brine was found between 40 and 60 g/l for acceptable workability and adequate strength development when mixed with Synfuels fly ash. This range was also applicable to most pastes prepared with synthetic brines, indicating its flexibility to chemical variations and hence its realism.
- The evaluation of various sulphate and chloride compounds produced pastes with comparable workability although chlorides demonstrated a pronounced contribution to strength development compared to sulphates.
- Unlike chlorides, sulphates produce pastes possessing threshold UCS values. Therefore the use of sulphate solutions would necessitate close monitoring and/or the installation of accurate control systems of the paste plant to ensure production of paste with desired characteristics.
- It was ascertained that HCl and H_2SO_4 solutions significantly reduce the extent of settling by 47% and 100%, respectively. This could increase the hydraulic conductivity and have an adverse effect on the properties of the resultant paste product, which will increase the environmental liability. Therefore highly acidic effluents must be avoided in paste.

- Using $CaCl_2$ and Na_2SO_4 as mixing solutions individually produced better results than NaCl and $CaSO_4$ at equivalent concentrations of the anions.
- Most importantly, blending of these solutions improved the properties when compared with individual solutions. This suggests synergy of components in a brine matrix.
- It is therefore concluded that solutions rich in chloride and sulphate ions can be beneficially used in cementitious products. This discovery substantiates the use of seawater in concrete as observed by other researchers.
- Calibration of the predictive brine protocol showed that the hypothesis is correct although the accuracy of UCS prediction was higher than that of the yield stress. This was inferred to the sensitivity of workability to properties of the mixing water e.g. pH and salinity while UCS is a result of various longer term phenomena.
- The mineralogy (especially CaO and amorphous content) in addition to PSD and morphology of fly ash control its suitability for use in the co-disposal of brines as paste. Thus the immobilisation of pollutants does not depend entirely on the alkalinity of fly ash; its composition is also relevant.
- It was demonstrated that brines react with Synfuels fly ash and reduced the leachability of components. This was supported by microstructural and mineralogical information.

The overall conclusion is that paste technology is a plausible option for the safe co-disposal of brines in fly ash pastes provided suitable brines and fly ash are mixed. The study has succeeded in identifying the factors of raw materials required to attain pastes with the desired characteristics and behaviour.

It cannot be overemphasised that optimisation of paste properties to suit the intended application is essential for different sets of materials and conditions due to the specificity of the paste disposal method.

CHAPTER 6

COMPARISON OF SLURRY DISPOSAL WITH PASTE PLACEMENT

6.1 INTRODUCTION

The purpose of Chapter 6 is to provide a brief comparison between hydraulic ash disposal as slurry and paste placement. The fundamental question to be answered here is whether paste disposal method will provide environmental benefits over slurry for saline brines and coal fly ash as claimed in the literature.

“It doesn't matter how beautiful your theory is, it doesn't matter how smart you are. If it doesn't agree with experiment, it's wrong.” Richard Feynman (American physicist: 1918 – 1988)

6.2 SELECTED RESULTS

The selected results are used to compare the two co-disposal scenarios of fly ash and brines. The disposal sites of slurry and paste are examined to put matters into perspective. Various locations in a disused Fine Ash Dam (FAD) are depicted in Figure 6.1. It is apparent that the FAD (dry slurry) is heterogeneous and susceptible to erosion although vegetation occurs to a limited extent. With these points in mind, the necessity to rehabilitate the FAD is inevitable, which is an independent area of research.

Figure 6.1 Illustration of various areas in a Fine Ash Dam

On the other hand, Figure 6.2 depicts a cured paste in the field. This paste facility places thickened tailings from the recovery of copper and zinc, but generic paste properties are expected to remain similar. The disposal site looks homogeneous despite cracks. It should be noted that these (cracks) become filled with the next layer of paste during subsequent deposition. The site also seems less prone to erosion and infiltration, which minimises the risk of leaching.

Figure 6.2 Illustration of homogeneity of placed paste

6.2.1 Particle Size Distribution

The PSD profile of materials provides comparative basis at the microstructural level. It is evident from Figure 6.3 that typical Weathered Fine Ash (WFA) is relatively finer than both fresh fly ash and brine-fly ash pastes.

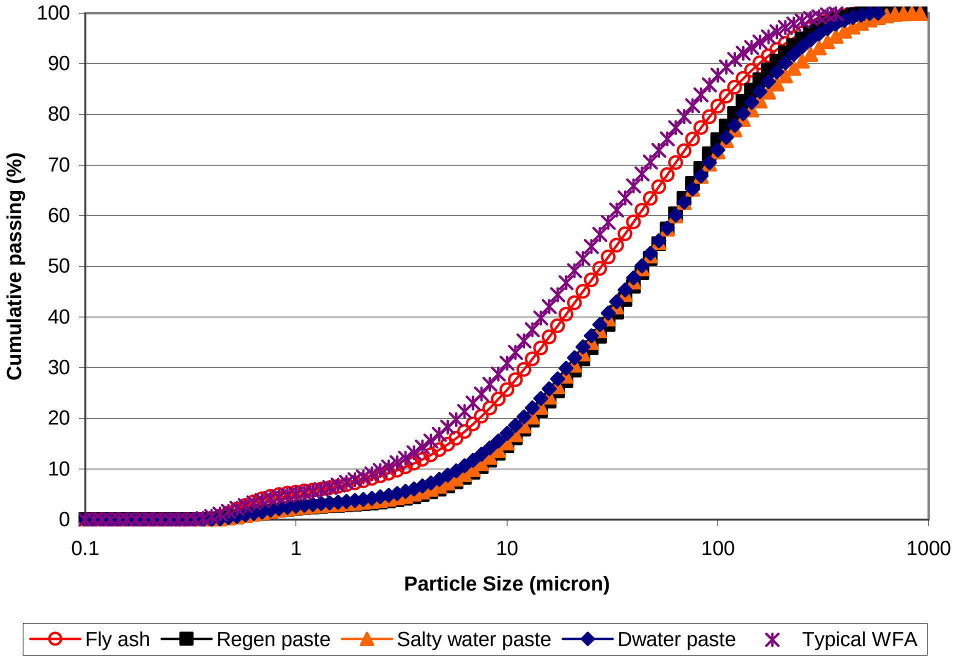

Figure 6.3 Comparison of PSD profiles of various ash materials

The distinction in PSD profiles is attributed to chemical weathering with the understanding that secondary phases are finer than particles of unreacted fly ash. This increases the surface area of the weathered ash (Zevenbergen et al., 1999).

The pastes are in contrast, coarser than fly ash which was used to prepare them. This difference can be attributed to the existence of precipitates in the short-term, which will most probably alter into finer hydration products as chemical weathering proceeds (Memon et al., 2002). Based on the results of this study, it can be concluded that 18 months of curing the pastes was insufficient for significant weathering and the establishment of equilibrium.

6.2.2 Leaching

The leaching results of both pastes and WFA provided in Table 6.1 are consistently lower than for fly ash in terms of pH, EC, alkalinity and Ca. The quantities of Na, Cl^- and SO_4^{2-} are, as expected, somewhat higher in the pastes prepared with regen brine and salty water. Nonetheless, approximately 90% concentration of these constituents present in the original brines was immobile during leaching. This bodes well for safe environmental disposal.

Table 6.1 Summary of leachate results for fly ash, pastes and typical WFA

Sample	**pH**	**EC (mS/cm)**	**M-alkalinity (mg/l) as $CaCO_3$**	**Ca (mg/l)**	**Na (mg/l)**	**Cl^- (mg/l)**	**SO_4^{2-} (mg/l)**
Fly ash	12.5	6.71	1800	704	3	7	101
Dwater paste	10.0	0.17	40	27	4	<5	35
Regen paste	10.6	1.29	112	24	223	218	136
Salty water paste	9.8	2.72	76	21	519	466	466
Typical WFA	9.7	0.57	50	53	58	36	172

These leaching data (Table 6.1) provide the scientific evidence that immobilisation of pollutants occurs when brines interact with coal ash either in the slurry or paste form. Immobilisation of contaminants contained in the brine was achieved irrespective of the brine characteristics or S:L ratio above a minimum moisture content for hydration.

6.2.3 Elemental Composition

It is apparent from the results shown in Table 6.2 that the samples are similar at an elemental composition level. The concentrations of Cl^-, Na and S are relatively higher in the regen paste, salty water paste and a typical WFA. This discrepancy was ascribed to the chemical composition of brines that were mixed with either fly ash or the Fine Ash in the case of WFA.

Table 6.2 Summary of elemental composition of fly ash, pastes and typical WFA

Sample	**Si (%)**	**Al (%)**	**Fe (%)**	**Ca (%)**	**Na (%)**	**S (%)**	**Cl^- (%)**
Fly ash	22.40	17.35	2.05	7.45	0.50	0.20	<0.01
Dwater paste	23.24	17.69	1.70	6.63	0.54	0.16	<0.01
Regen paste	22.12	16.80	1.94	6.99	1.74	0.32	0.38
Salty water paste	21.03	16.21	1.98	6.89	2.54	0.63	1.29
Typical WFA	18.62	16.14	2.45	5.98	0.98	1.07	0.39

6.2.4 Mineralogy

Mineralogy provides useful information pertinent in determining the efficacy of different disposal methods in terms of stabilisation, as well as in understanding the implications of the leaching data.

(a) XRD

The XRD results of hydrated samples and fly ash illustrated in Table 6.3 exhibit appreciable mineralogical differences. Ettringite was not identified in any of the 18-month old pastes whereas precipitates, namely, halite and gypsum were obtained in some of the pastes. Some precipitates are soluble upon contact with water implying a poor immobilisation mechanism for Ca, Na, Cl^- and SO_4^{2-}.

Table 6.3 The XRD results of fly ash, typical WFA and pastes

Component	**Chemical Formula**	**Fly ash**	**Dwater paste**	**Regen paste**	**Salty water paste**	**Typical WFA**
Quartz	SiO_2	10.24	12.00	9.05	10.34	11.03
Mullite	$Al_6Si_2O_{13}$	20.53	19.66	17.99	18.53	19.17
Hematite	Fe_2O_3	0.68	0.58	0.64	0.60	0.64
Magnetite	Fe_3O_4	-	-	-	-	0.89
Analcime	$NaAlSi_2O_6.H_2O$	-	-	2.65	2.37	0.73
Lime	CaO	2.22	-	-	-	-
Periclase	MgO	-	0.69	0.09	0.64	0.59
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$	-	-	-	-	2.58
Sillimanite	Al_2SiO_5	-	-	-	-	1.46
Calcite	$CaCO_3$	-	3.54	6.52	4.92	2.60
Halite	NaCl	-	-	-	1.24	-
Gypsum	$CaSO_4.2H_2O$	-	-	-	1.66	-
Amorphous content	N/A	66.33	63.53	63.06	59.70	60.30
Total	**N/A**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**

The XRD findings are summarised as follows:

- Lime originally present in the fly ash was not detected after hydration while calcite and periclase were identified as new phases.
- The presence of quantifiable [Na^+] in the mixing water was responsible for the formation of analcime since it was not identified in paste containing deionised water.
- Ettringite, magnetite, and sillimanite were only identified in the WFA and not in the pastes prepared and investigated during this study. This suggests that their formation requires a much longer curing time than 18 months.

(i) It is also possible that finer particles of gasification ash do catalyse the formation of ettringite and sillimanite because gasification fines are rich in aluminosilicates (Matjie and Van Alphen, 2008).

(ii) However, examination of 8-month old FA and short term experiments of Koch (2002) lacked ettringite, suggesting that time is more of an issue than distinction between the materials.

(iii) The disposal of Fe-based catalyst in the FAD could be providing the additional Fe, required to form magnetite during chemical weathering.

(b) DSC

The results of DSC analysis indicate that C-S-H gel and Friedel's salt formed within the 18-month period of curing of the salty water bearing paste. No additional phases could be identified on the pastes prepared with regen brine and deionised water probably due to salinity differences.

6.2.5 Particle Morphology

Field Emission Gun Scanning Electron Microscopy (FEG SEM) provides high resolution information about the surface properties of solid materials. The images confirm occurrence of hydration and chemical weathering in both paste and slurry environments, which are distinctly different from the particles of fresh fly ash, as illustrated in Figure 6.4.

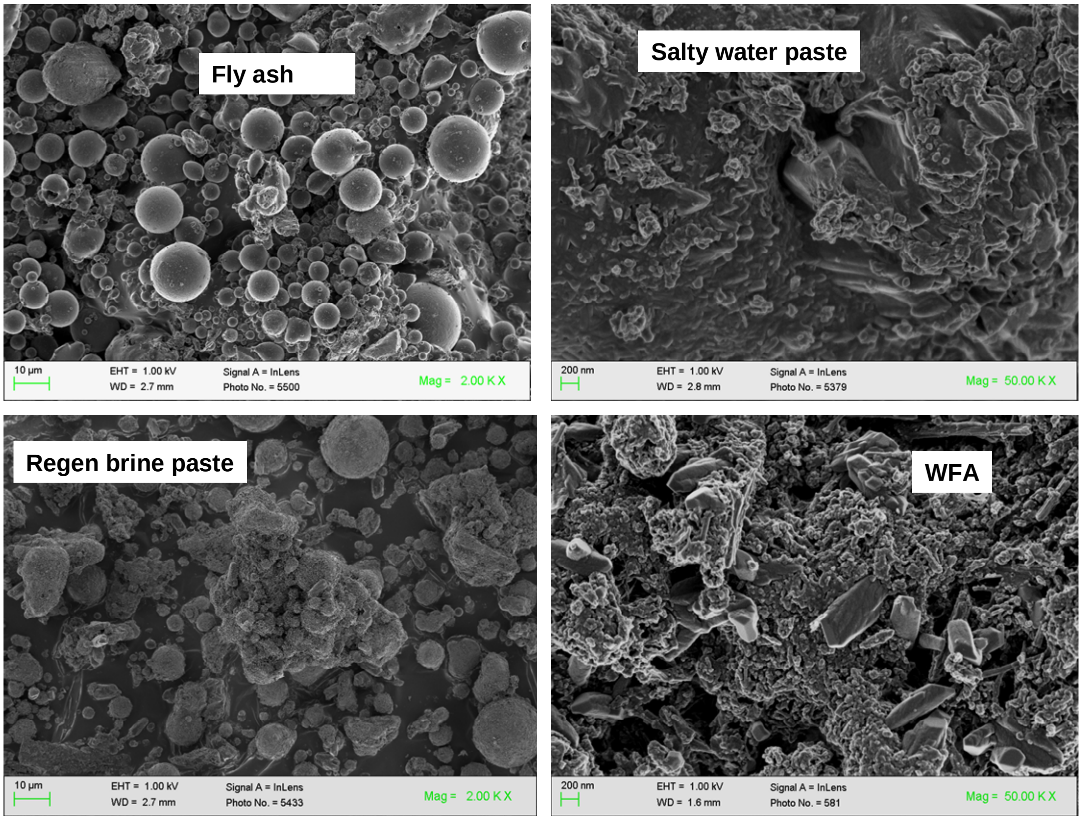

Figure 6.4 FEG SEM images of fly ash, salty water paste, regen brine paste and typical WFA

6.3 CONCLUDING REMARKS

As expected slurry and pastes differ both in terms of physical and mineralogical properties. Apart from these differences, both disposal methods reduced the extent of leaching compared to fresh fly ash.

Unlike slurry, paste does not bleed thus little or no adverse environmental legacy of return water is inherited. Another advantage of paste is the development of appreciable compressive strength making it suitable for mine backfill. Lastly, solidification is another very important characteristic of paste especially for the immobilisation of water soluble species.

It is proposed that in future comparative investigation of slurry and paste disposal, identical materials be used for preparation and be exposed to equivalent curing times under the same curing conditions.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 BACKGROUND

Production of liquid fuels, chemicals and electricity from coal produces a variety of by-products which include coal ashes and saline brines. Mitigation of anthropogenic pollution is a subject of interest to all stakeholders.

The aim of this thesis was to investigate if saline brines could be mixed with coal fly ash to make a paste that is environmentally benign using materials from the SASOL Synfuels plant in Secunda. The tested hypothesis states that “**any alkaline fly ash can immobilise saline brines where resultant paste properties are determined by the predominant brine components; and the mineralogy of the paste resembles that of a Weathered Fine Ash (WFA)**”. It was believed that the findings of this study would provide the basis for developing a sustainable solution to the disposal of brines and coal fly ash; by either using the paste to backfill voids within the coal mines adjacent to SASOL or placed above ground at suitably engineered disposal sites.

The experiments were designed such that the influence of the expected variance in the feedstock materials on the behavioural characteristics of paste is understood. The variance is due to the fact that the influents to the paste process will be industrial by-products and wastes which are obviously not controlled to any specifications. The adopted research strategy was to evaluate the effect of brine characteristics (principally, salinity and chemical composition) on the workability, strength development, microstructural properties, mineralogy and leachability of the resultant fly ash pastes. Drilling was also performed on a redundant Fine Ash Dam (FAD) to establish long-term information of brine-fly ash systems.

7.2 CONCLUSIONS FROM THE FIELD INVESTIGATION

Characterisation of a redundant FAD was performed to obtain a historical record of what transpires in the long-term, in a disposal site formed by mixing brines and fine ash in a 5:1 ratio. Fine ash is a mixture of 83% fly ash and 17% gasification fines (particles < 250 μm) which results from the thickeners after clarification of hydraulically removed ashes. It was assumed that gasification fines (17%) do not alter significantly the properties of WFA; hence fly ash was used as a reference material. Besides, both fly ash and gasification ash originate from combustion and gasification of the same coal feedstock.

The results obtained from the detailed characterisation of samples drilled from the disused FAD are summarised as follows:

- The FAD possesses a characteristic profile in terms of particle size distribution which is in contrast to hydraulic sorting commonly found in the gold tailings dams. This distinction was attributed to the morphological differences of particles present in these materials. The majority of fly ash particles is spherical which promotes flowability and better particle packing. It was also observed that chemical weathering alters the microstructure of ash.
- The XRF data demonstrate the prevalence of Na, S and Cl in WFA, which was explained as a contribution of the brine that was used as a carrier medium of fine ash to the FAD as a slurry. Most importantly, no indication of leaching was obtained except Ca and Si suggesting that the majority of pollutants were immobilised in the FAD.
- Examination of XRD, FEG SEM and Differential Scanning Calorimetry (DSC) data confirmed the existence of secondary phases, which are the hydration products of fine ash and brines. They are pyrrhotite (Fe_7S_8), periclase (MgO), analcime ($NaAlSi_2O_6.H_2O$), magnetite (Fe_3O_4), sillimanite (Al_2SiO_5), ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O$), calcium silicate hydrate (C-S-H) gel, Strätlingite or hydrated gehlenite ($Ca_2Al_2SiO_2(OH)_{10}.8H_2O$) and calcite ($CaCO_3$). Further findings are:
  (a) The positive identification of various hydration products served as scientific evidence that contaminants present in the brines could be immobilised in the ash during hydration and chemical weathering.

(b) It was further observed that chemical weathering occurred significantly within the first 4 years. No additional transformation was detected up to 16 years at the investigated FAD.

(c) Eight months of slurry curing resulted in the formation of analcime, calcite and periclase. Other secondary phases like ettringite were not present which suggests that they require longer time to form. This was also found by Koch (2002) who worked with similar materials in her MSc project.

(d) A high degree of amorphous content was retained in the WFA which suggests its potential utilisation as a pozzolan. This will require lime supplementation since it was depleted during chemical weathering as manifested by a pH reduction from 12.5 to 9.5.

7.3 CONCLUSIONS FROM LABORATORY EXPERIMENTS

The results from the laboratory experiments of paste can be summarised as follows:

- Total dissolved and suspended solids (instead of fly ash content) in paste must be taken into account during paste formulation. This parameter can also be used to assess and predict the workability of fresh pastes. The implications are that the salinity of brine as Total Dissolved Solids (TDS) must be regularly determined and form part of the paste operational procedure.
- Evaluation of workability tests for application in the paste research was performed as follows:

(a) A rheometer proved indispensable. It was chiefly used to measure yield stress since it showed high sensitivity and reproducibility of data in the desired range of paste consistency.

(b) The use of flow cones to determine flowability in terms of efflux time was limited to low viscosity pastes, due to blockages. The use of flow cones will be appropriate when measuring the flow properties of paste which are influenced by shearing. Modification of cone dimensions can be considered in future.

(c) The flow table was unsuitable to study the workability of fly ash-brine pastes in the range covered in this investigation. As with flow cones modifications could provide a suitable instrument.

- An attempt to understand and simplify the effect of brine chemistry on paste led to the following conclusions:

(a) An optimum range of salinity for both the industrial and synthetic brines was found between 40 and 60 g/l TDS for an acceptable workability (i.e. yield stress < 200 Pa) and adequate strength development (Unconfined Compressive Strength > 500 kPa) when mixed with Synfuels fly ash.

(b) The evaluation of various sulphate and chloride compounds as mixing solutions in paste demonstrated comparable degrees of workability. Chlorides had a profound effect on strength development.

(c) Unlike chlorides, sulphate solutions produced pastes possessing threshold Unconfined Compressive Strength values that may not be acceptable. This may require a stringent operating envelope or close monitoring system of a paste plant to avoid off-spec production for either utilisation or backfill/surface disposal.

(d) Both HCl and H_2SO_4 markedly reduced the consolidation of the settled mass, which was probably due to the surface charge on the ash particles. In a disposal scenario, this could increase the hydraulic conductivity and have adverse effects on the properties of the resultant paste product. Moreover such expansion can potentially increase the volume of material to be landfilled, which is costly and requires land space.

(e) When used individually as mixing solutions, $CaCl_2$ and Na_2SO_4 produced higher compressive strength than was the case for NaCl and $CaSO_4$ at equivalent concentrations of the anions. The blending of these pairs improved the results even further indicating synergy of brine constituents. However, a marginal difference was obtained between the two sets of brines, implying that a brine matrix gives more flexibility in terms of preparation.

(f) A predictive model of brine was successfully developed, which demonstrated that the dominant brine constituents are sufficient to predict paste behaviour. More accurate prediction of Unconfined Compressive Strength than workability was achieved with the model.

(g) The discrepancy in predicting the workability of fresh paste was ascribed to the dependence of various brine characteristics on the initial pH and salinity. In contrast, mechanical properties (Unconfined Compressive Strength) are the longer-term properties which involve microstructural and mineralogical alterations during paste curing.

(h) From the above points, there exists a potential to beneficially utilise non-acidic brines rich in chloride and sulphate to make cementitious products such as mortars and mass concrete. This discovery is substantiated by improvement in the strength development of concrete using seawater as mixing water as reported by other researchers. The current work has demonstrated that brines ameliorate the workability of paste.

- The effect of using a different type of fly ash on the properties of paste was investigated and findings are presented below:

(a) It was discovered that fly ash properties have a profound effect on the resultant paste characteristics such as workability, compressive strength development and leachability. This observation reiterates the site-specificity of paste disposal methodology since different plants will most probably differ in terms of combustion technology, coal sources, and brine characteristics.

(b) The author strongly believes that this technology can be tailor-made for similar operations by developing an understanding of the fundamental characteristics of raw materials.

- Mineralogical determination was conducted on 18-month old pastes that were cured under laboratory ambient conditions. The hydration products identified are calcite, analcime, periclase, C-S-H gel, Strätlingite, and Friedel's salt ($Ca_3.Al_2O_6.CaCl_2.10H_2O$), in addition to hematite (Fe_2O_3), mullite ($Al_6Si_2O_{13}$) and quartz (SiO_2), which were originally present in the fly ash. Ettringite which is a common hydration product was not identified probably due to the shorter curing time.
- An agreement was found between mineralogy and the change in particle morphology.
- Leachability of pastes was less than half that achieved with fly ash despite addition of the highly saline brines to make paste, indicating that co-disposal provides an environmental benefit.

7.4 IMPLICATIONS TO SUSTAINABILTY

Dry fly ash disposal showed higher susceptibility to leaching. In the worst case scenario, the co-disposal of brines with fly ash provides a single pollution source. The best case scenario found in this thesis, is that hydration and chemical weathering immobilise pollutants either in the slurry or paste environment. However, paste disposal has additional benefits over slurry; that includes solidification which reduces infiltration and the necessity to immediately rehabilitate the disposal site as well as water conservation. High strength development in paste also presents an option to backfill adjacent mine voids.

This thesis has demonstrated that SASOL Synfuels can employ paste disposal technology to immobilise pollutants present in saline brines via mixing with fly ash in an environmentally benign manner. The hypothesis presented in Chapter 1 was proven to be correct.

"The more original a discovery, the more obvious it seems afterwards." Arthur Koestler (Hungarian author: 1905 – 1983)

7.5 RECOMMENDATIONS FOR FUTURE WORK

The study has highlighted a number of points requiring further consideration towards the development of paste technology as a sustainable solution for petrochemical companies and power stations using coal.

The following future work is recommended:

- Evaluation of the effect of gasification fine ash or admixtures on the paste behaviour and mineralogy.
- Leaching behaviour of toxic and trace elements (heavy metals and oxyanions).
- The effect of predominant brine constituents on the mineralogy of paste.
- The influence of low pH of the mixing water on the paste properties.
- Reaction kinetics of weathering must be understood since rainfall cannot be controlled by mankind.

- Feasibility testing of the laboratory findings on a pilot scale
- A well designed study for direct comparison of slurry and paste using the same starting materials.

The research will continue towards commercialisation of paste technology in order to provide a feasible environmental solution in support of coal utilisation.

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APPENDIX A

DETAILS OF CHEMICALS USED AND COMPLIANCE TABLE

A1 CHEMICAL INFORMATION

Table A3.1 Chemicals used to prepare synthetic brines and in other experiments

Chemical Name	**Chemical Formula**	**Name of Supplier**
Sodium hydroxide pellets	NaOH	Associated Chemical Enterprises (Pty) Ltd
Sodium chloride AR	NaCl	Associated Chemical Enterprises (Pty) Ltd
95 – 97% sulphuric acid	H_2SO_4	Fluka
Calcium sulphate dihydrate	$CaSO_4.2H_2O$	Promark Chemicals
anhydrous calcium chloride 4 to 8 mesh	$CaCl_2$	Univar
anhydrous sodium sulphate	Na_2SO_4	Unilab
Nitric acid 55% CP	HNO_3	Associated Chemical Enterprises (Pty) Ltd
32% hydrochloric acid	HCl	Associated Chemical Enterprises (Pty) Ltd
paraffin	N/A	RIBAS

A2 COMPLIANCE TABLE

South African Standard Leaching Procedure (SASLP) and South African Standard Total Concentration (SASTC) threshold values for waste risk profiling and assessment of hazardous waste disposal to landfill. Only inorganic components were extracted from the comprehensive table.

Table A3.2 Compliance table used to classify leachate using SASLP (Crous, 2010)

Contaminants	SASTC0 g/kg	SASLP0[1] g/l	SASLP1 g/l	SASLP2 g/l
As, Arsenic	0.50	0.0005	0.001	0.004
B, Boron	15.00	0.025	0.05	0.20
Ba, Barium	6.25	0.035	0.07	0.28
Cd, Cadmium	0.26	0.00025	0.005	0.002
Co, Cobalt	5.00	0.025	0.05	0.20
Cr_{Total}, Chromium Total	800.00	0.005	0.01	0.04
Cr(VI), Chromium (VI)	0.50	0.0025	0.005	0.02
Cu, Copper	19.50	0.050	0.10	0.40
Hg, Mercury	0.16	0.00005	0.0001	0.0004
Mn, Manganese	12.75	0.02	0.04	0.16
Mo, Molybdenum	1.00	0.0035	0.007	0.028
Ni, Nickel	10.60	0.0035	0.007	0.028
Pb, Lead	1.90	0.0005	0.001	0.004
Sb, Antimony	0.075	0.0005	0.001	0.004
Se, Selenium	0.050	0.0005	0.001	0.004
V, Vanadium	2.68	0.005	0.01	0.04
Zn, Zinc	160.00	0.16	0.32	1.28
Cl^-, Chloride	-	5.00	10.00	40.00
SO_4^{2-}, Sulphate	-	10.00	20.00	80.00
NO_3 as N, Nitrate-N	-	0.30	0.60	2.40
F, Fluoride	10.00	0.05	0.10	0.40
CN^- (total), Cyanide Total	10.50	0.0025	0.005	0.02

Note: SASLP = South African Standard Leaching Procedure
SASTC = South African Standard Total Concentration

APPENDIX B

ADDITIONAL DRILLING RESULTS

B1 WATER TABLE

The levels of water table are presented in Figures B4.1 and B4.2 based on the readings which were taken after drilling the boreholes (A5, BH1, BH2, C4, D4, E4, and F4) located at the top surface of the dam. Boreholes C4 and D4 are located at the north-west corner of FAD which is sometimes irrigated with ash water.

This is supported by detection of water table at as high as 10 m from the top in these boreholes as shown in Figure B4.1.

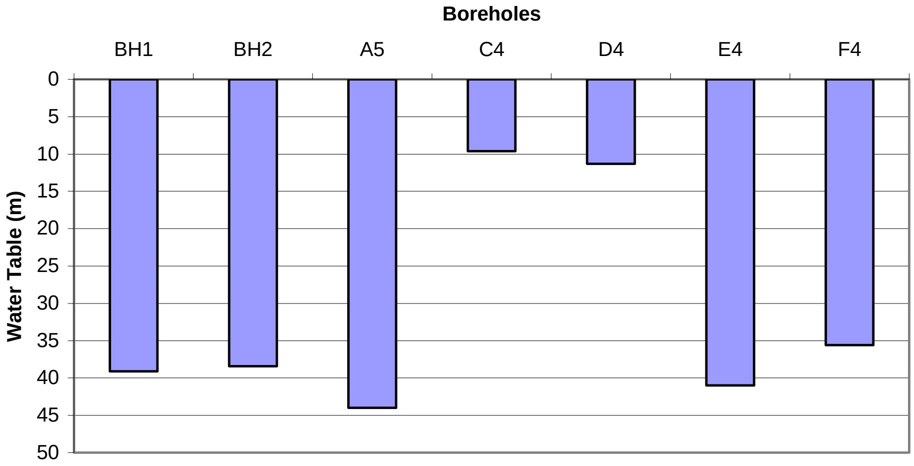

Figure B4.1 Water tables for different boreholes

Figure B4.2 also shows that boreholes C4 and D4 had the highest degree of saturation because water was obtained near the top surface.

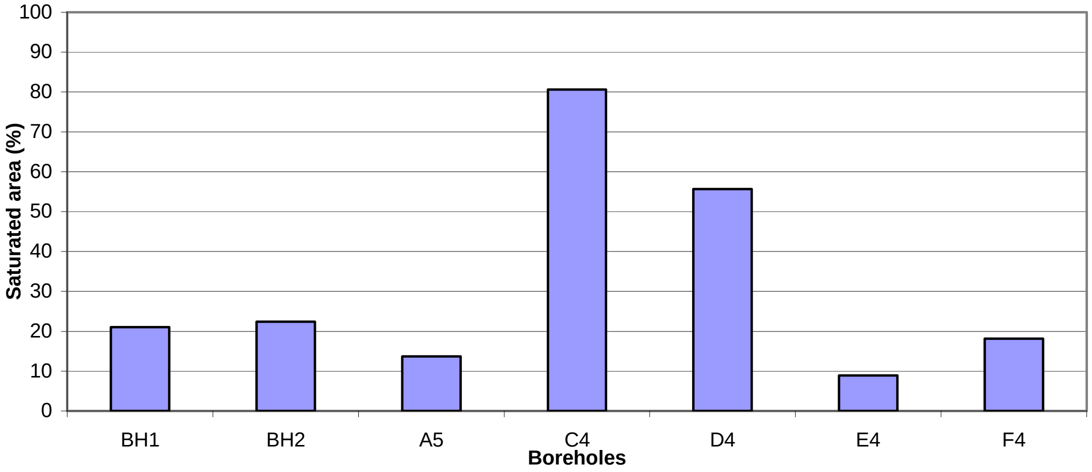

Figure B4.2 Saturation area in each borehole (%)

B2 PHYSICAL PROPERTIES OF WFA

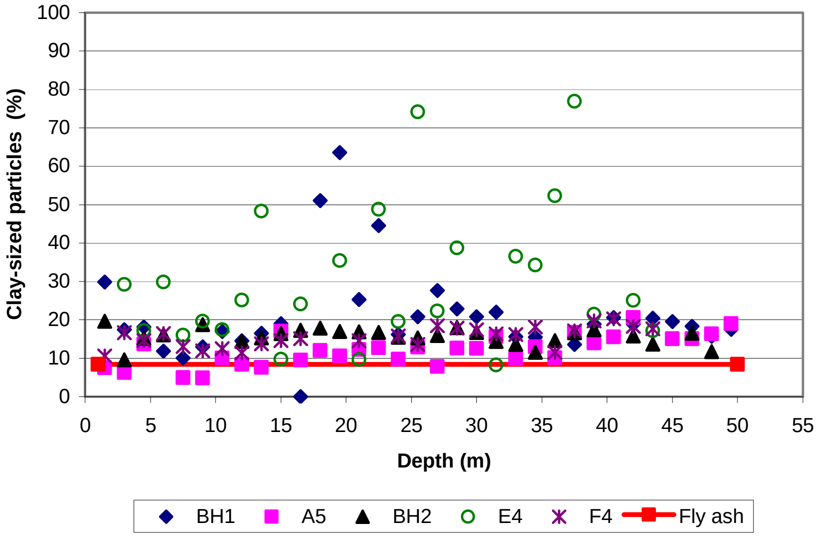

Figure B4.3 Profile of clay-sized proportions

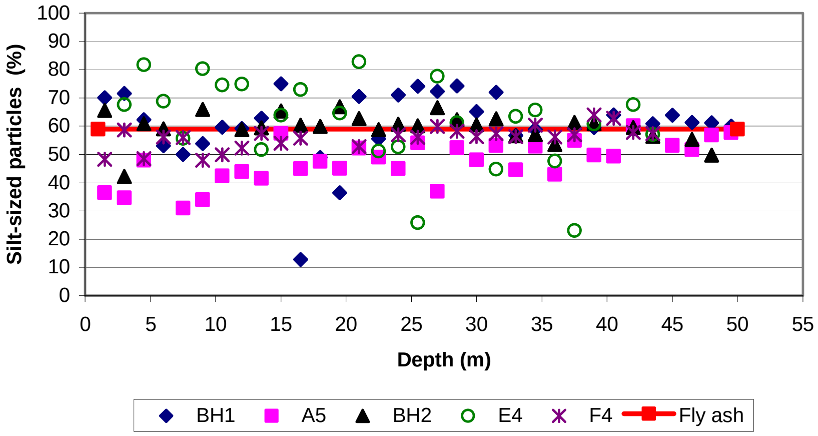

Figure B4.4 Profile of silt proportions

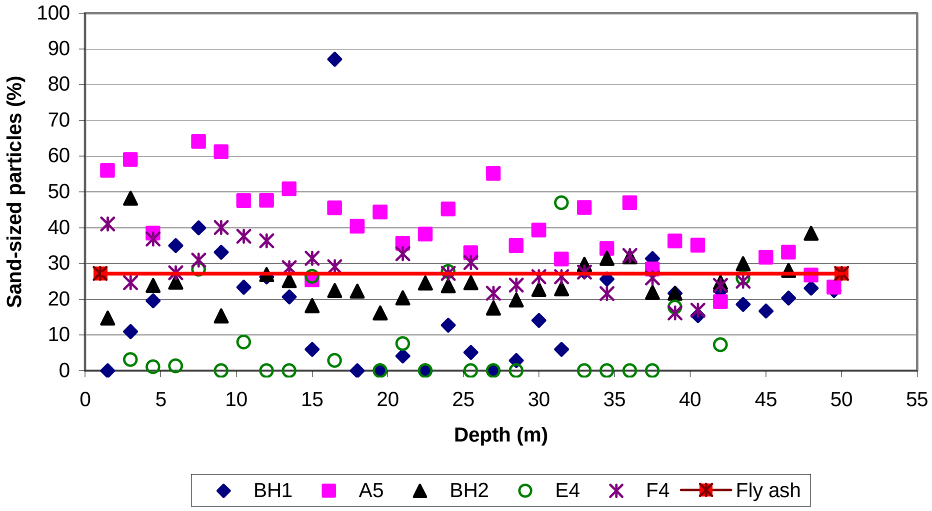

Figure B4.5 Profile of silt proportions in boreholes

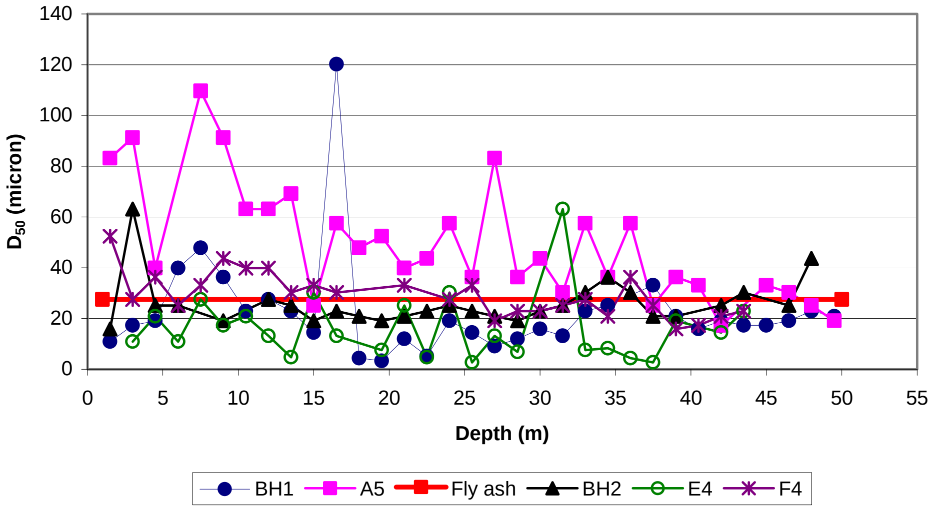

Figure B4.6 The D_{50} trend of boreholes against fly ash

B3 CHEMICAL COMPOSITION OF WFA

B3.1 Trace Elements

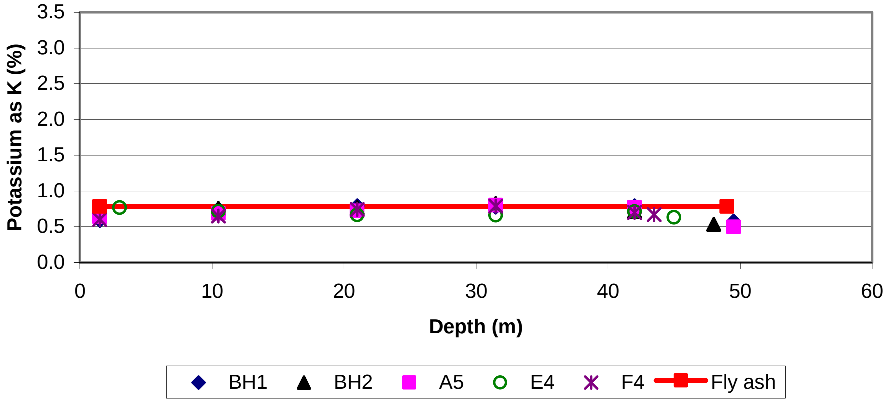

Figure B4.7 Profile of K in boreholes

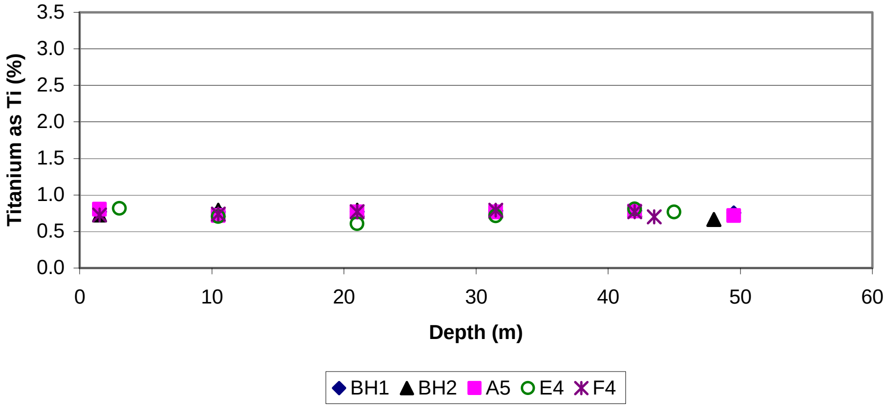

Figure B4.8 Behaviour of Ti in the WFA

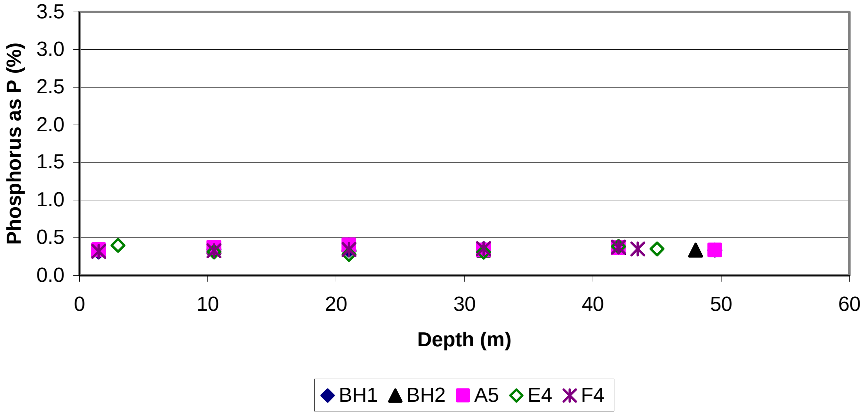

Figure B4.9 Behaviour of P in the WFA

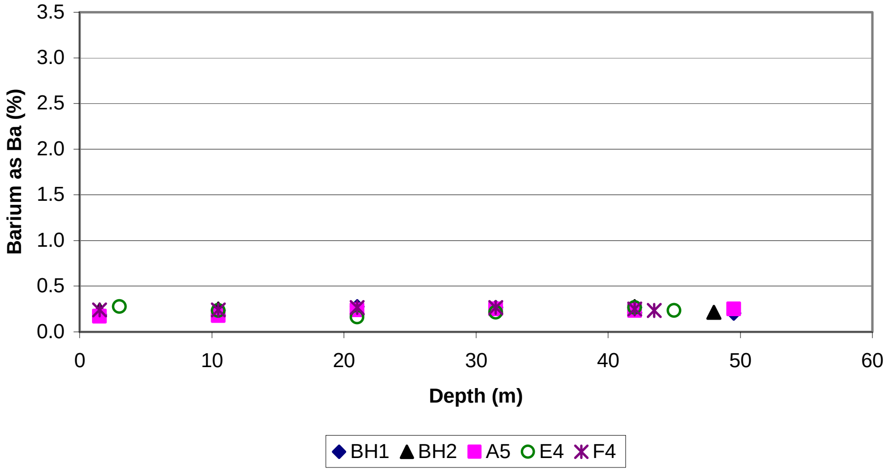

Figure B4.10 Behaviour of Ba in the WFA

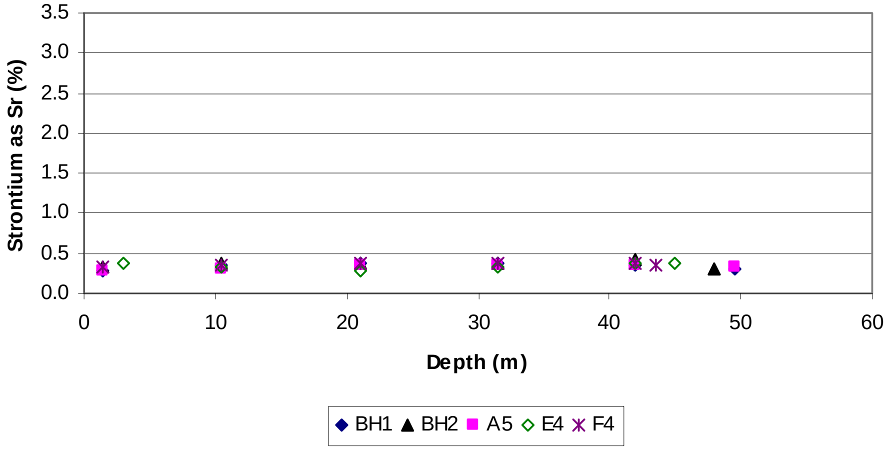

Figure B4.11 Behaviour of Sr in the WFA

B4 MINERALOGY OF WFA

We present selected mineralogical data from Lab B to supplement those of Lab A.

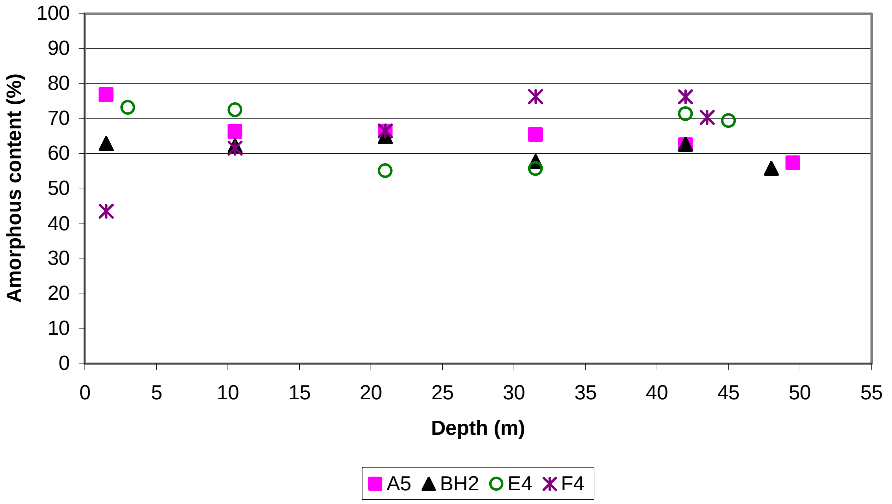

Figure B4.12 Behaviour of amorphous content by Lab B

B4.1 Major Minerals

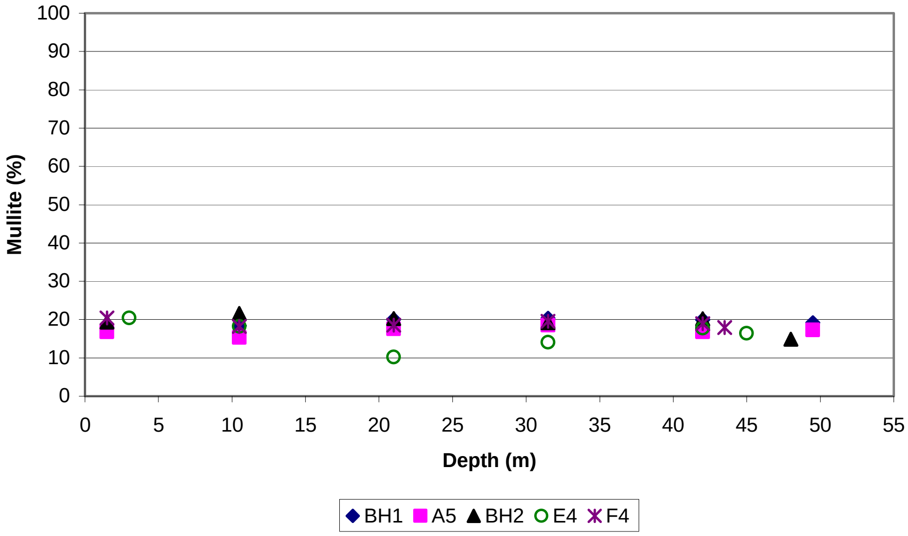

Figure B4.13 Behaviour of mullite in each borehole

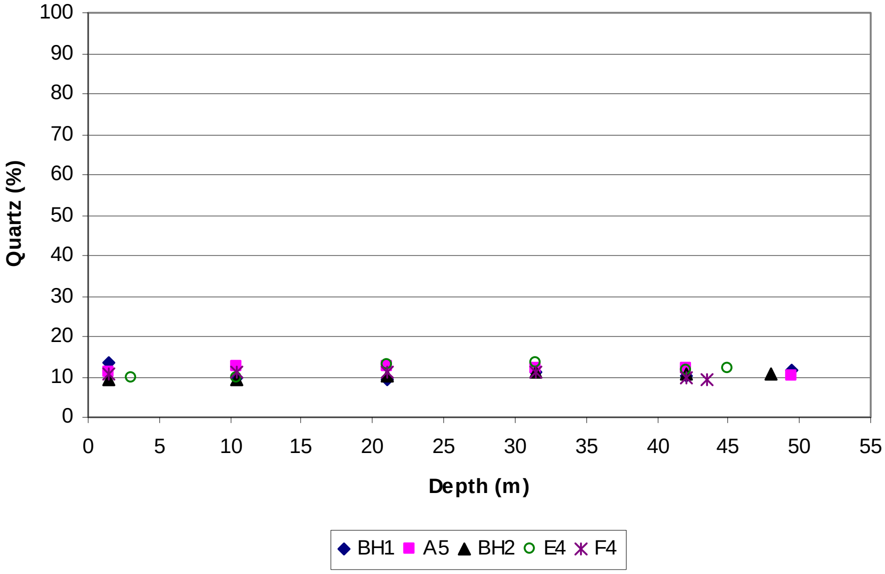

Figure B4.14 Behaviour of quartz in each borehole

B4.2 Minor Minerals

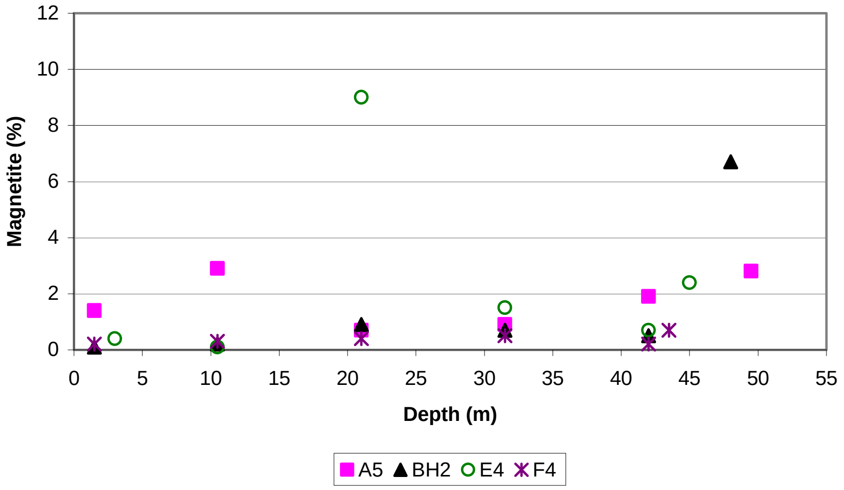

Figure B4.15 Behaviour of magnetite of WFA from Lab B

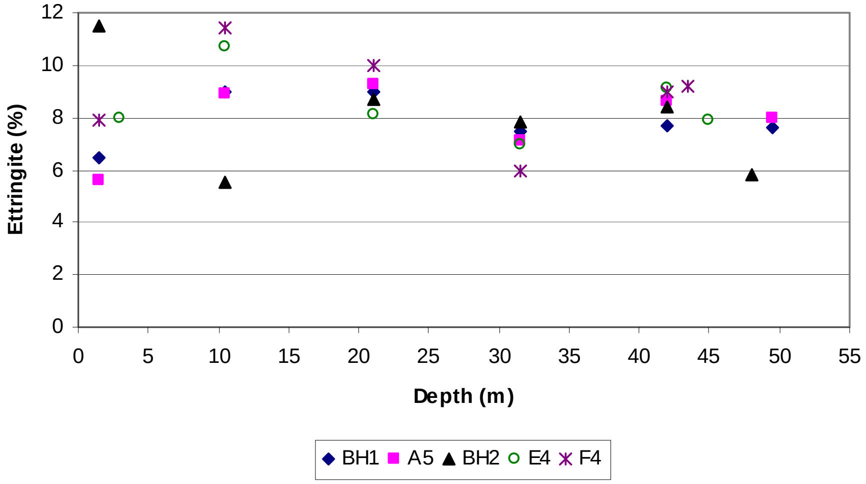

Figure B4.16 Behaviour of ettringite of WFA from Lab B

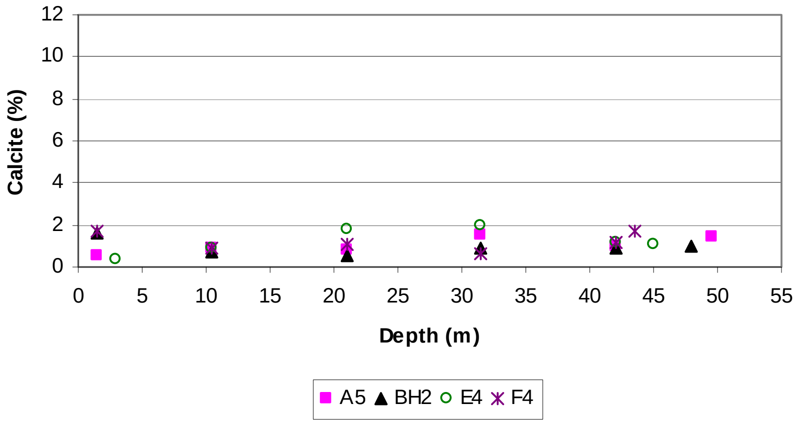

Figure B4.17 Behaviour of calcite of WFA from Lab B

Table B4.1 Variation of pyrrhotite in WFA

Depth (m)	**A5**	**BH2**	**F4**	**E4**
1.5	0.1	-	0.1	-
10.5	0.1	-	-	-
16.5	-	-	-	0.8
21	-	-	-	2.9
25.5	-	-	-	1.0
31.5	-	-	0.2	0.1
42	-	0.2	-	-
45	-	1	0.1	0.1

B5 DSC MICROGRAPHS

The DSC micrographs of fly ash and a typical weathered fine ash are presented in Figures B4.18 and B4.19. The main purpose of this work was to illustrate that additional secondary phases can be identified using thermal analysis which cannot be detected by XRD.

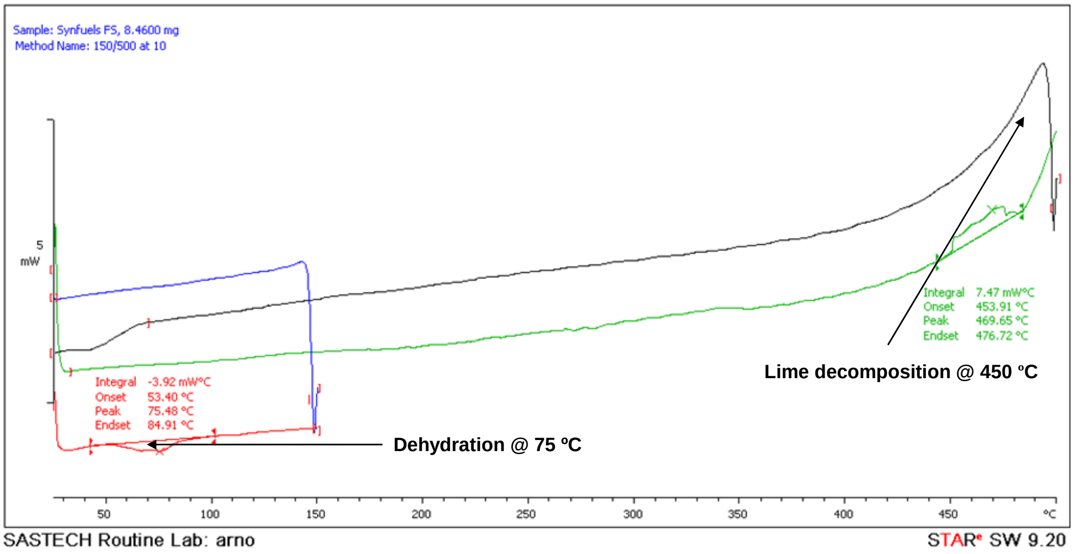

Figure B4.18 DSC graph of raw fly ash

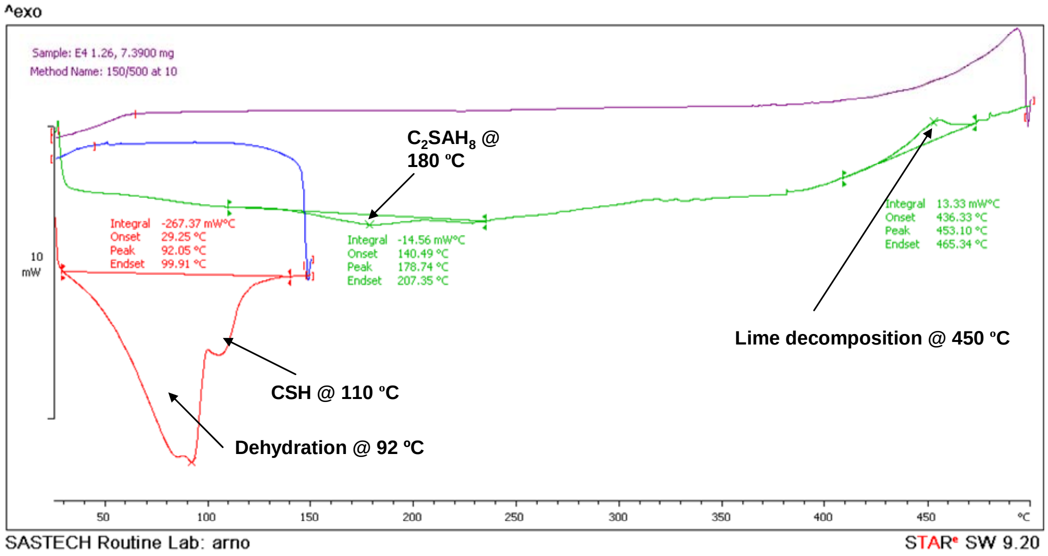

Figure B4.19 DSC graph of a typical WFA

B6 SEM MICROGRAPHS

Additional SEM images of WFA are presented in Figure B4.20.

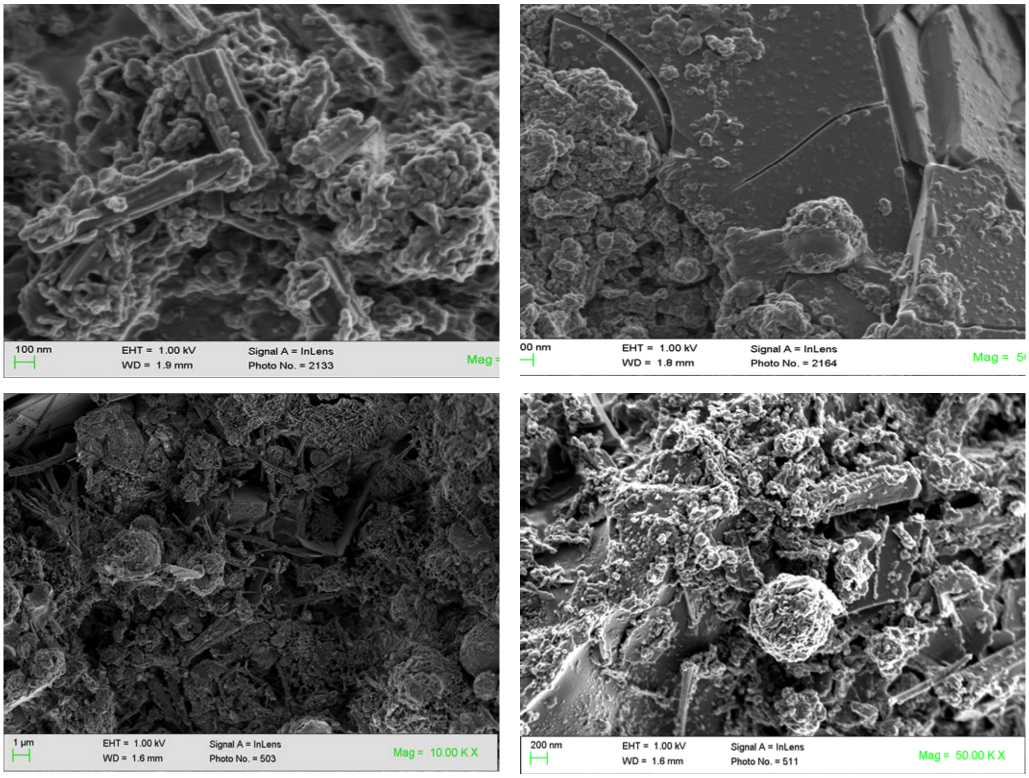

Figure B4.20 Additional FEG SEM images of WFA

B7 THE 8-MONTH OLD FINE ASH

The FEG SEM images of 8-month old FA are shown in Figure B4.21 where little existence of new phases is present.

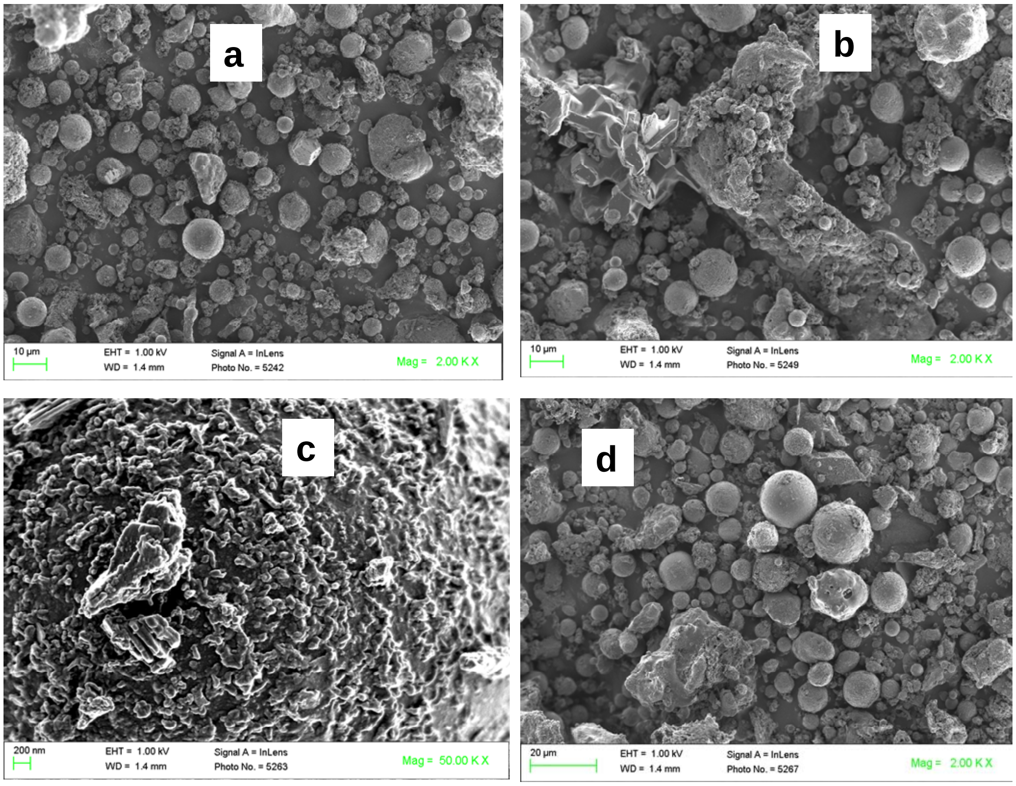

Figure B4.21 Morphological presentation of 8-month old fine ash

APPENDIX C

ADDITIONAL DATA FROM EXPERIMENTAL WORK

C1 WORKABILITY DATA

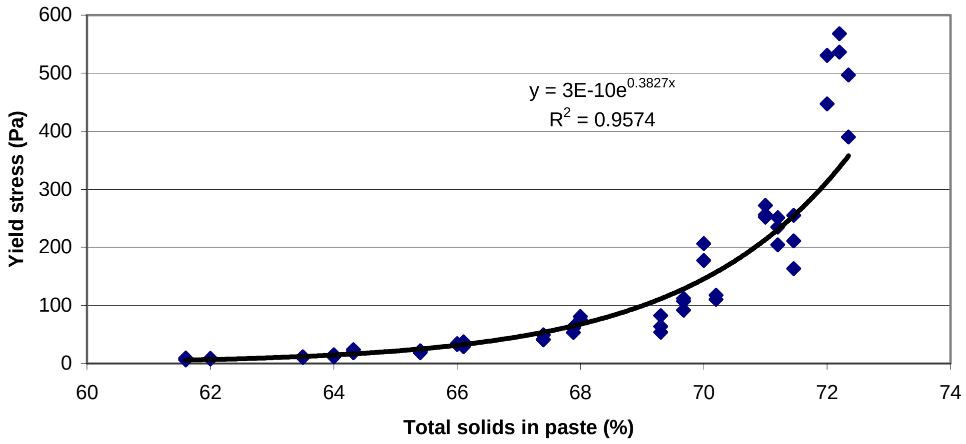

Figure C5.1 Equation to predict yield stress of pastes with Synfuels fly ash

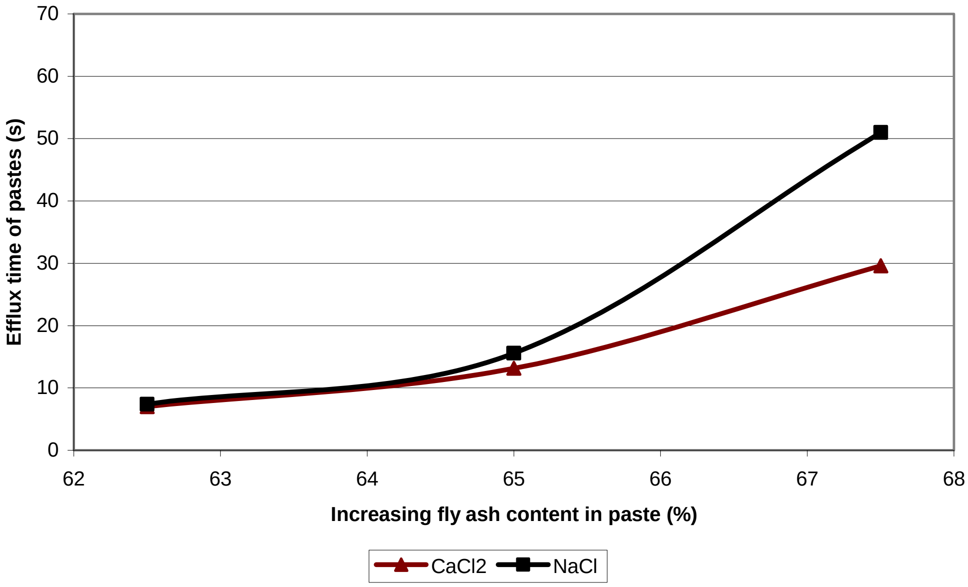

Figure C5.2 The effect of NaCl and $CaCl_2$ solutions on efflux times of paste

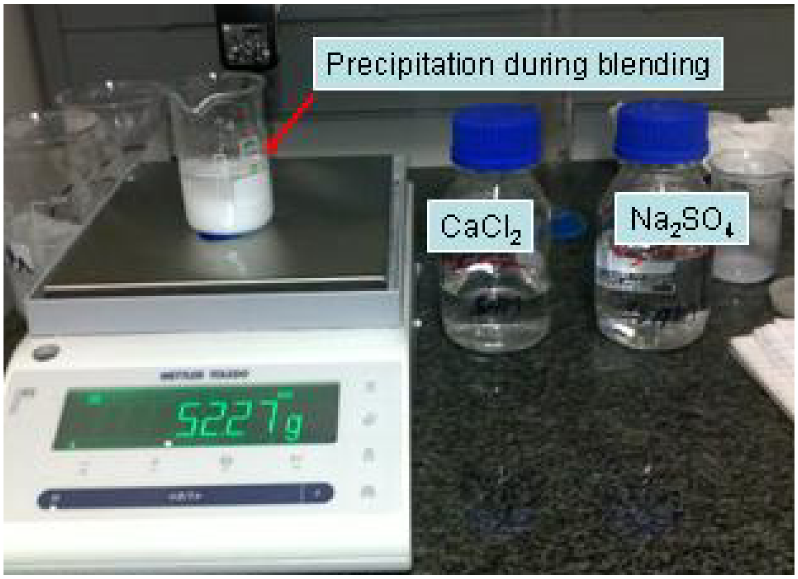

Figure C5.3 Illustration of precipitation during blending Na_2SO_4 and $CaCl_2$ solutions

Table C5.1 Statistical analysis of yield stress using different brine sets

	Variable 1	**Variable 2**
Mean	72.95	62.87
Variance	886.84	467.48
Observations	30	30
Pooled Variance	677.16	
Hypothesized Mean Difference	0	
df	58	
t Stat	1.50	
P(T<=t) one-tail	0.07	
t Critical one-tail	1.67	
P(T<=t) two-tail	0.14	
t Critical two-tail	2.00	

Table C5.2 Basic properties of brines used to calibrate the model

Component	**Salty water**	**#acidic synbrine**	***synbrine**
pH	8.8	0.3	10.0
EC (mS/cm)	124	93	181
Na	21.0	21.0	36.9
Ca	2.1	2.1	2.1
Cl	34.3	34.3	34.3
SO_4^{2-}	15.2	15.2	15.2
OH^-	-	-	11.7
TDS	108.0	72.6	100.2

#acidic synbrine = simulated industrial brine which is acidic
*****synbrine = simulated industrial brine after pH adjustment

C2 ADDITIONAL DATA OF PASTES

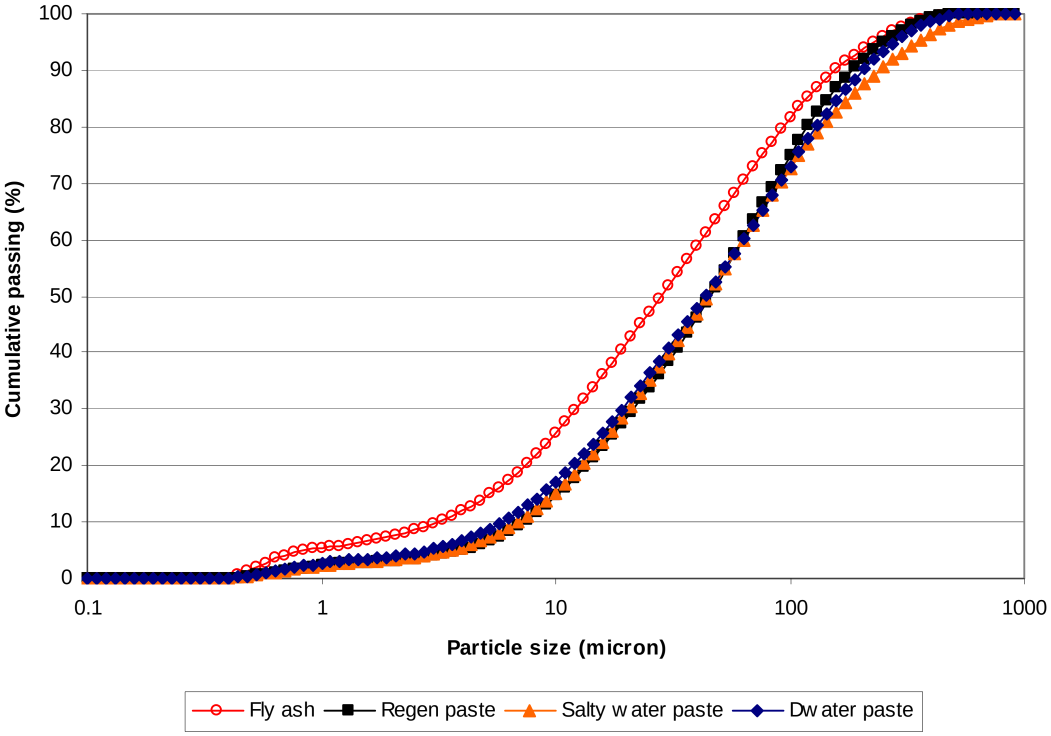

Figure C5.4 Particle size distributions of pastes and fly ash

Extra FEG SEM images for 18-month old pastes are depicted in Figures C5.5 – C5.7, illustrating similarity with fly ash particles as well as evidence of secondary phases.

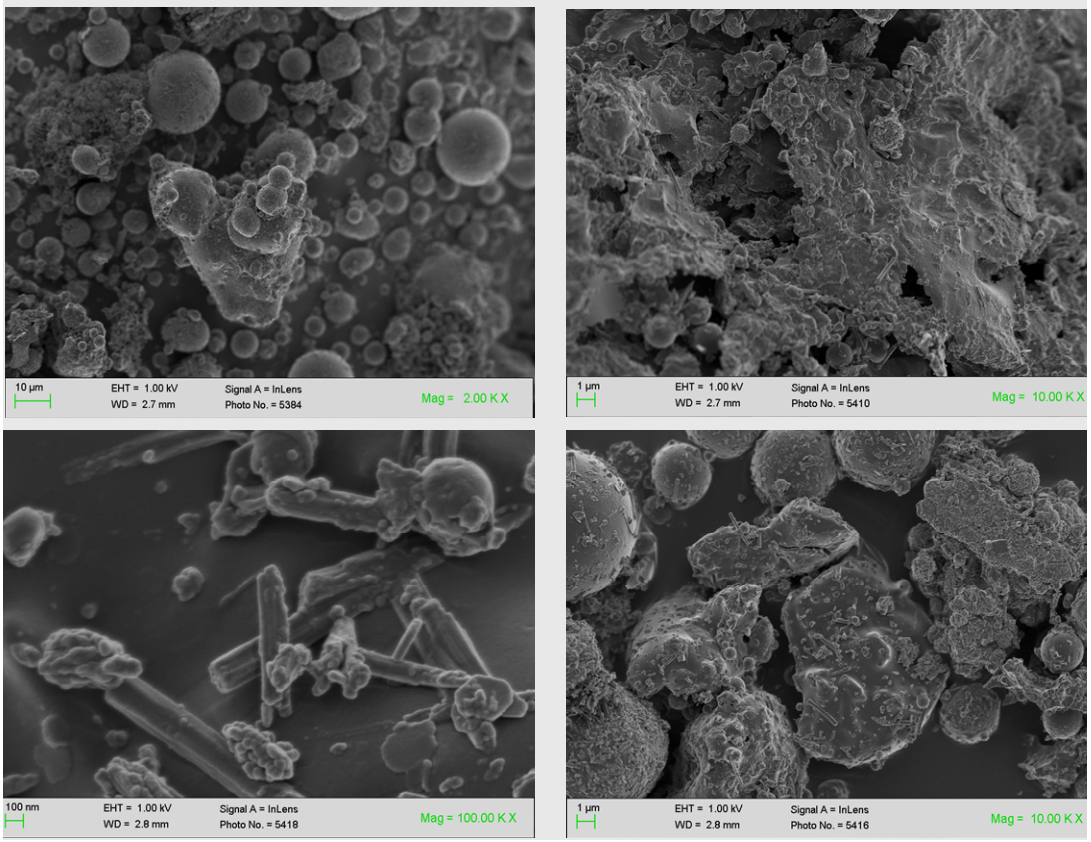

Figure C5.5 FEG SEM images of deionised water bearing paste

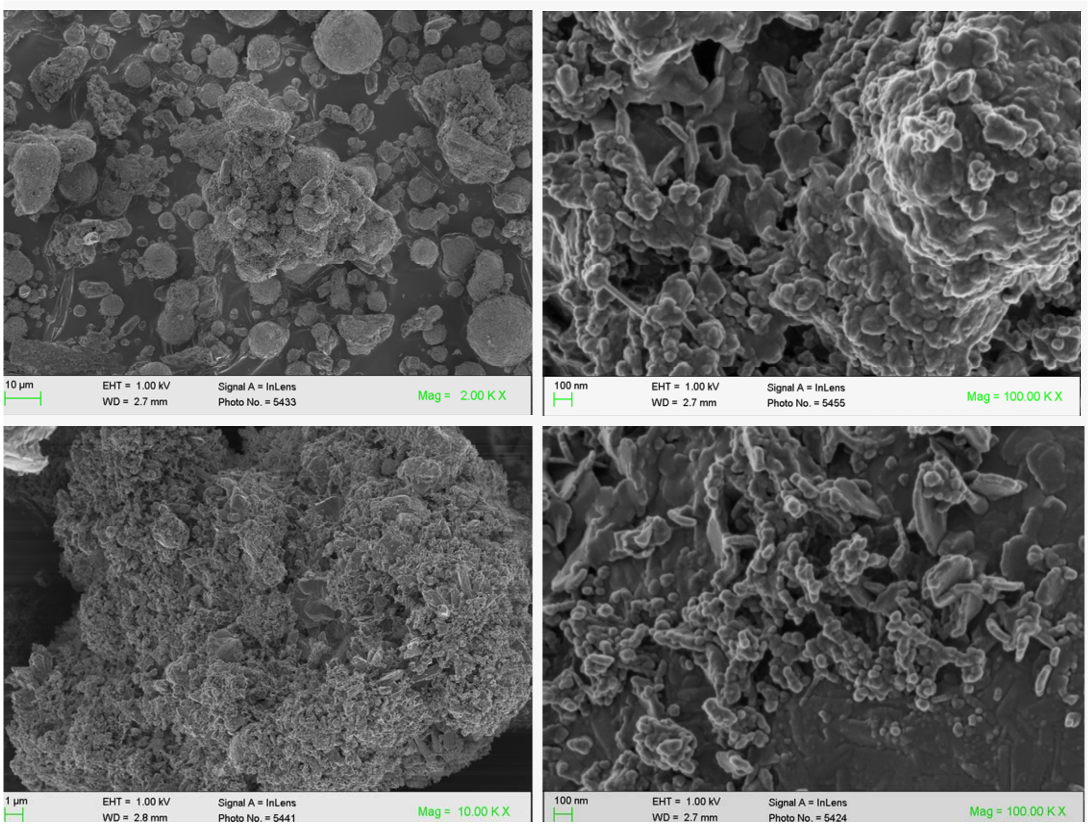

Figure C5.6 FEG SEM images of regen brine bearing paste

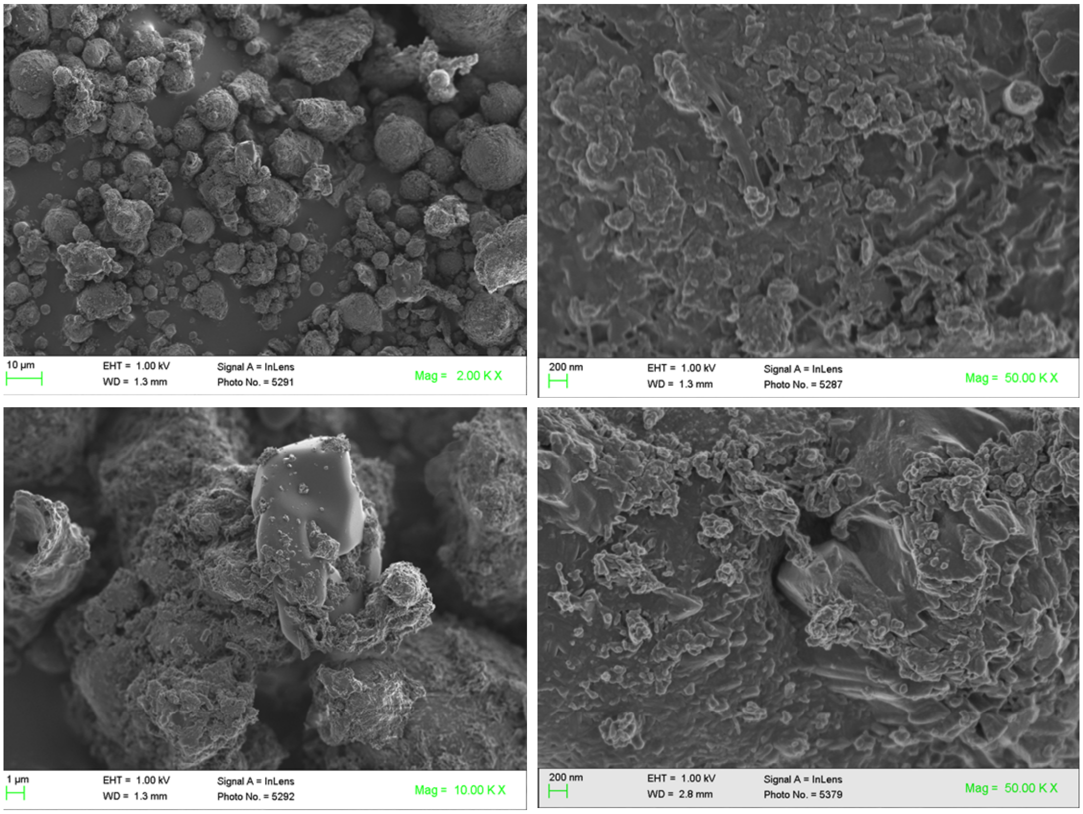

Figure C5.7 FEG SEM images of salty water bearing paste

Table C5.3 Detailed XRF data of 18-month old pastes

Component (%)	**Synfuels fly ash**	**Dwater paste**	**Regen paste**	**Salty water paste**
SiO_2	47.92	49.71	47.31	44.99
TiO_2	1.63	1.56	1.60	1.60
Al_2O_3	32.78	33.43	31.75	30.63
Fe_2O_3	2.05	1.70	1.94	1.98
MnO	0.05	0.04	0.05	0.04
MgO	1.18	1.37	1.66	1.68
CaO	9.48	8.44	8.89	8.77
Na_2O	0.67	0.73	2.35	3.43
K_2O	0.92	0.95	0.98	1.07
P_2O_5	1.07	1.22	1.20	0.94
Cr_2O_3	0.03	0.02	0.03	0.02
NiO	0.01	*<0.01*	*<0.01*	0.01
V_2O_5	0.03	0.03	0.03	0.03
ZrO_2	0.10	0.03	0.06	0.09
SO_3	0.51	0.39	0.81	1.58
BaO	0.77	0.12	0.28	0.48
Y_2O_3	0.01	0.01	0.01	0.01
SrO	0.57	0.19	0.39	0.52

Table C5.3 Detailed XRF data of 18-month old pastes (continued)

Component (ppm)	**Synfuels fly ash**	**Dwater paste**	**Regen paste**	**Salty water paste**
As	3.00	3.00	3.00	3.00
Cu	36.51	9.21	16.08	23.92
Ga	27.04	4.95	12.17	18.41
Mo	1.00	1.00	1.00	1.00
Nb	13.12	2.00	2.00	2.00
Ni	37.47	3.35	11.24	20.20
Pb	24.72	3.00	3.07	14.12
Rb	14.47	2.00	2.00	2.00
Sr	2370.86	237.39	798.11	1460.33
Th	5.00	3.00	3.00	3.00
U	3.00	3.00	3.00	3.00
W*	6.00	6.00	6.00	6.00
Y	48.00	3.00	9.73	22.58
Zn	50.58	38.27	41.51	45.32
Zr	236.77	23.65	71.20	132.45
Cl*	7.58	7.58	3779.42	12875.69
Co	10.90	7.28	8.28	9.47
Cr	168.70	142.65	164.22	184.54
F*	7352.71	7166.25	7849.66	8119.08
S*	778.96	371.80	1029.59	2349.16
Sc	27.28	28.97	29.78	29.84
V	152.81	132.78	138.74	144.77
Cs	11.70	9.43	15.98	13.27
Ba	2447.31	2349.27	2330.49	2224.63
La	93.86	94.86	85.77	88.29
Ce	234.45	181.26	201.49	207.57

NB: Results for elements indicated with an * should be considered semi-quantitative.

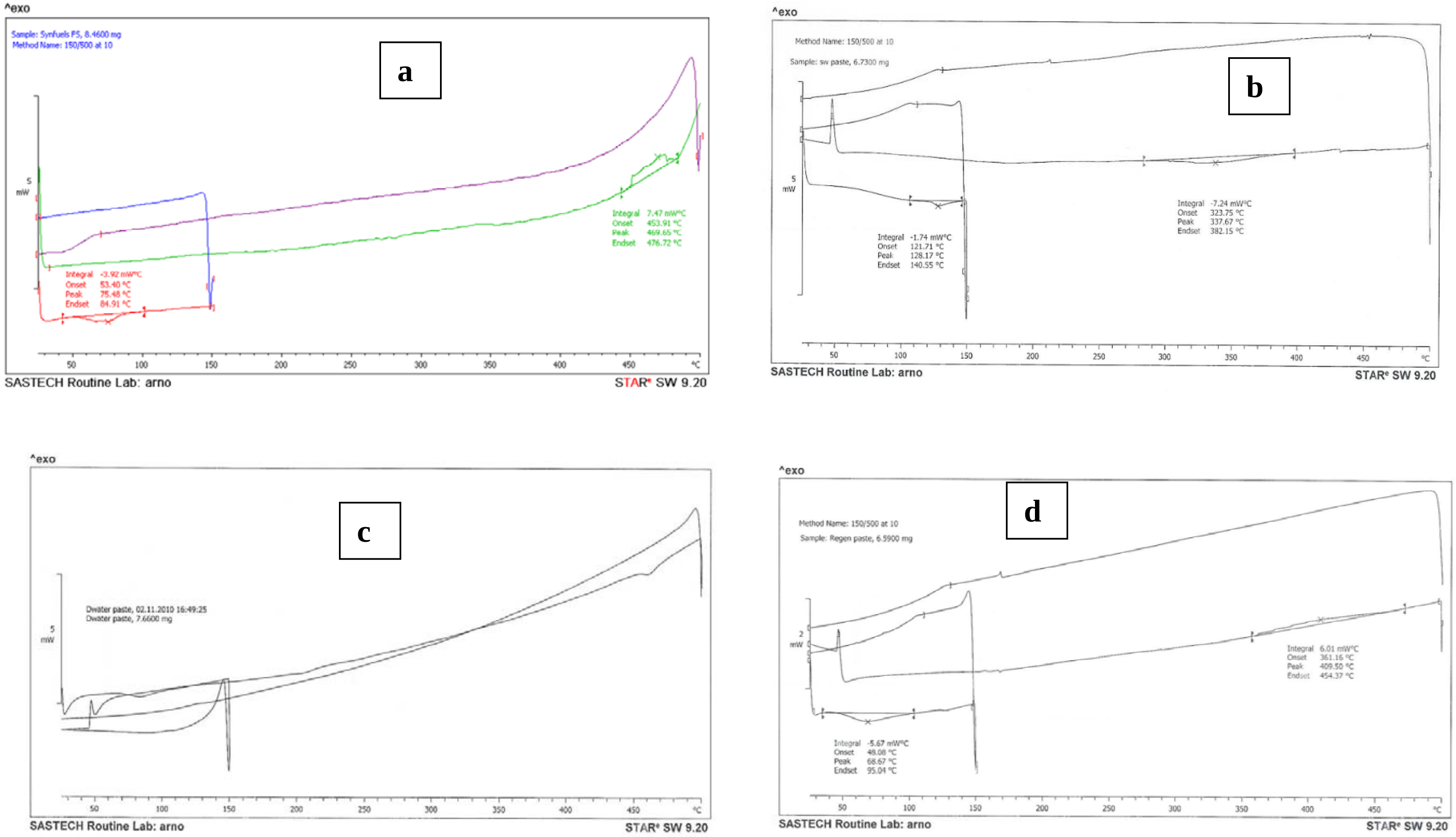

Figure C5.8 DSC micrographs (a) fly ash (b) salty water paste (c) Deionised water paste (d) regen brine paste