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## Co-Disposal of Dry FGD By-product with Coal Gasification Ash and Inorganic Brines

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### ABSTRACT

There is a growing pressure from the environmental authorities and public bodies to reduce anthropogenic pollution. Stringent environmental legislation is being implemented for industries around the world, even more so for coal consuming industries. Control of gaseous emissions is one of the areas that are receiving considerable attention towards sustainable development. Coal combustion in coal-fired power utilities emits  $SO_x$  to the atmosphere. Dry flue gas desulphurisation (FGD) is a well known technology often used to mitigate sulphur emissions in coal-fired power utilities. It traditionally uses lime to neutralise  $SO_x$ , and forms a mixture of anhydrite ( $CaSO_4$ ), and calcium sulphite ( $CaSO_3$ ). Several options are reported in literature for the utilisation and management of FGD by-product. However, this paper reports on the preliminary findings of the option where excess FGD by-product is co-disposed with gasification/bottom ash and brines. The study examined the influence of moisture content, chemistry of the liquid medium, and ratio of FGD by-product to gasification ash on the physical and chemical properties of the cured mix. The results demonstrate that the chemistry of raw materials influences the final properties of the resultant product.

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### 1. Introduction

Coal continues to be the dominant source of energy worldwide (van Dyk et al., 2008; Jorgenson et al., 2006; Litto et al., 2007; van Dyk et al., 2006; Auner and Holl, 2006; Younger, 2004) but is the most polluting of the fossil fuels. The major by-products of coal combustion are coal ashes, wastewater, and gaseous emissions to the atmosphere (Bealey et al., 2007; Auner and Holl, 2006). Sulphur ( $SO_x$ ) and nitrogen ( $NO_x$ ) emissions from coal combustion pose a ubiquitous environmental concern since they contribute to acid-rain formation and ozone depletion. Conversely, the scarcity of water drives the recovery of usable water from various sources including industrial effluents via desalination technologies which inevitably produce brines which require acceptable disposal

(Mahlaba and Pretorius, 2006; Ravizky and Nadav, 2007; Swift et al., 2002).

Control of gaseous emissions is one of the areas that are receiving considerable attention in support of sustainable development (Shin et al., 2007; Bealey et al., 2007; Dong et al., 2009; Smodiš, 2007; Jollands et al., 2007; Zheng et al., 2007). Flue gas desulphurisation (FGD) is a well known technology often used to mitigate  $SO_x$ 's in coal-fired power utilities, by traditionally using lime to neutralise them. Dry FGD technology yields approximately a 50:50 mixture of calcium sulphite ( $CaSO_3$ ) and anhydrite ( $CaSO_4$ ) as by-product whereas wet FGD process yields high purity gypsum with better applications e.g. wallboards, agriculture, and cement making (Clark et al., 2001; Butalia et al., 2001) but plant equipment and water requirements usually override the benefits.

A by-product from a dry FGD process on the other hand is less attractive commercially, hence, a co-disposal with brines was investigated during a feasibility study. Several options exist for

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individually managing these materials (brines, coarse ash and FGD by-product) but this manuscript reports on the findings where FGD by-product is co-disposed with coarse ash and brines. A scenario is presented where three different types of industrial by-products can be co-disposed in a potentially environmentally sound manner.

## 2. Materials and Methods

### 2.1 Materials

The sample of FGD sample was obtained from a paper company in South Africa. This material is believed to closely represent the expected FGD material that will be produced upon implementation of the project. A proactive study was initiated to investigate acceptable options for handling such a by-product. A characteristic dry FGD material was evaluated for potential co-disposal with coarse ash and brines. Coarse ash is a combination of gasification ash particles > 250 µm and bottom ash from the gasification and steam generation processes, respectively. The ratio of gasification ash to bottom ash is approx. 4:1 in a typical coarse ash sample. The chemical composition of FGD by-product used is predominantly composed of gypsum (50%), hemihydrate (13%), hannebachite (34%), and calcite (3%). Characterisation using CCSEM and XRD showed that gasification ash is principally composed of aluminosilicate (34.1%), anorthite (8.7%), mullite (2.8%), quartz (11.7%), kaolinite (27%), pyrrhotite (3.5%), oxides (1.4%), char (3.2%), and other (7.6%) (Matjie and van Alphen, 2008). The chemical compositions of the two inorganic brines used in the investigation are illustrated in Table 1.

*Ash-transport water* is brine resulting from the wet ash removal system containing 6.5% salts while *salty water* is a resultant residue from the thermal water recovery process containing 10–12% dissolved salts. Both brines have high concentrations of sodium, chloride, sulphate, calcium, magnesium, potassium, and total organic carbon (TOC).

### 2.2 Methods

The investigation was divided into three separate sections of research to address specific aspects of the problem. These sections are combined at the end of the manuscript to provide a holistic view of the proposed solution.

#### 2.2.1 Effect of moisture content on cementation

It is generally known that most reactions require a liquid medium to occur (Jozic and Zelic, 2006). This is essential for hydration reactions because compounds should dissolve and form new species (Ćojbašić et al., 2005; Gabrovšek et al., 2006). It is, however, critical not to add too much water since it can leak to the environment. Varied amounts of ash-transport water were added to equivalent mixtures of coarse ash and FGD by-product. A large batch of coarse ash was thoroughly mixed with 0.5% FGD by-product (w/w) before splitting into three equivalent portions. Varied amounts of ash-transport water (corresponding to 18%, 26%, and 32% (w/w) of the solid content) were then dispensed to the solid mixtures. Values were arbitrarily chosen based on previous experience.

#### 2.2.2 Influence of the liquid medium on binding

Mahlaba and Pretorius (2006) reported that brine chemistry affects the cementation of ash-based-mixtures. It was justified to

**Table 1**  
Typical compositions of the industrial brines

Component	Units	Ash transport water	Salty water
pH	-	12.1	8.8
P-Alkal	mg/l as CaCO <sub>3</sub>	1270	370
M-Alkal	mg/l as CaCO <sub>3</sub>	1382	920
Cl	mg/l	930	24300
F	mg/l	27	40
SO <sub>4</sub> <sup>2-</sup>	mg/l	2 500	15200
PO <sub>4</sub> <sup>3-</sup>	mg/l	<0.2	5
Ca	mg/l	450	2100
Fe	mg/l	0.2	0.5
K	mg/l	130	1300
Mg	mg/l	3	1500
Mn	mg/l	<0.1	5
Na	mg/l	1 150	21000
Sr	mg/l	30	30
Si	mg/l	5	N/A
<sup>1</sup> TOC	mg/l	80	700
<sup>2</sup> TDS	mg/l	6 500	110000

<sup>1</sup> TOC = total organic carbon

<sup>2</sup> TDS = total dissolved solids

investigate the validity of their finding in the proposed co-disposal method and this would enable the selection of the appropriate brine(s). A mixture of coarse ash and 0.5% FGD by-product was prepared and split into three portions as in section 2.2.1. Equivalent volumes (contributing 30% moisture in the mixture by weight) of distilled water, ash-transport water, and salty water were added into separate solid mixtures.

#### 2.2.3 Influence of varied ratios of coarse ash to FGD by-product

This section was aimed to determine the optimum dosage of FGD by-product that should be added to coarse ash and achieve cementation with minimal environmental impact. Varied amounts of FGD by-product were added (0%, 0.1%, 0.5%, 1%, 2.5%, 5%, 10%, and 20%) to coarse ash in separate vessels. This was followed by the addition of 30% by weight of ash-transport water to each vessel.

## 3. Results and Discussion

The physiochemical properties investigated are moisture content, water quality, quantity of FGD by-product, hydraulic conductivity, and unconfined compressive strength.

### 3.1 Effect of Moisture Content

The samples with higher moisture content were visually homogeneous and felt stronger than those with less moisture content. Figure 1 shows the improvement in homogeneity in the samples according to increased moisture content. The moisture content increases from left to right; where the lowest moisture content (18%) is heterogeneous and the 32% is homogeneous.

The homogeneity is believed to be caused by the reactions between individual components while a heterogeneous nature indicates that less or no reactions occurred. This is confirmed by the detection of traces of ettringite on the sample containing 32% moisture content while no difference was found on gypsum and calcite concentrations after five weeks of curing. It is nevertheless

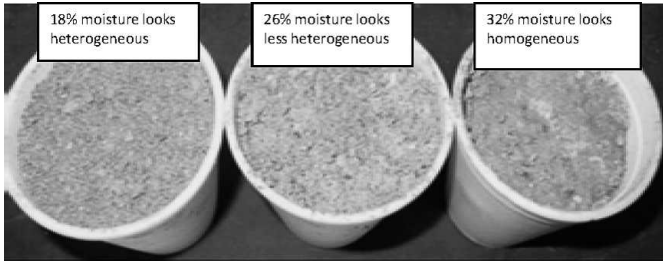


Fig. 1. Improvement in homogeneity with increased moisture content.

concluded that approx. 32% moisture content is essential for the proposed co-disposal.

3.2 Influence of Water Quality

Samples prepared with distilled water were the weakest while those with salty water were the strongest. The strength of samples according to liquid medium can be ranked as follows: distilled water << ash-transport water << << salty water. It was particularly encouraging to note that high salt retention was achieved with ash-transport water and salty water while distilled water induced leaching (Table 2).

Leaching trends of conductivity illustrated in Figure 2 also confirm the salts retention in mixtures prepared with brines. However, salty water showed the highest salt retention while

Table 2 Summarised results on leachate per liquid medium

Water sample	TDS of brine (g/l)	TDS of leachate (g/l)	Retained Salts (%)
Distilled water	0.50	0.88	-76
Ash transport water	6.48	1.32	80
Salty water	110	7.05	94

samples prepared with distilled water mobilised salts from the solid materials (Table 2). These observations support those made by Mahlaba and Pretorius (2006) that brine chemistry affects cementation.

The use of various liquid media has a huge impact on the resultant properties of solid mixture. However, the mixing of FGD by-product with coarse ash and sufficient moisture reduces the mobility of contaminants. Approx. 6% of secondary minerals were formed with ash-transport water and salty water while less than 5% formed with distilled water.

3.3 Effect of FGD by-product content

The leaching results demonstrated that increased amounts of FGD additions gave high leachate concentrations. The leaching of untreated FGD by-product gave the highest release of salts than blended mixtures probably because of large surface area. Figure 3

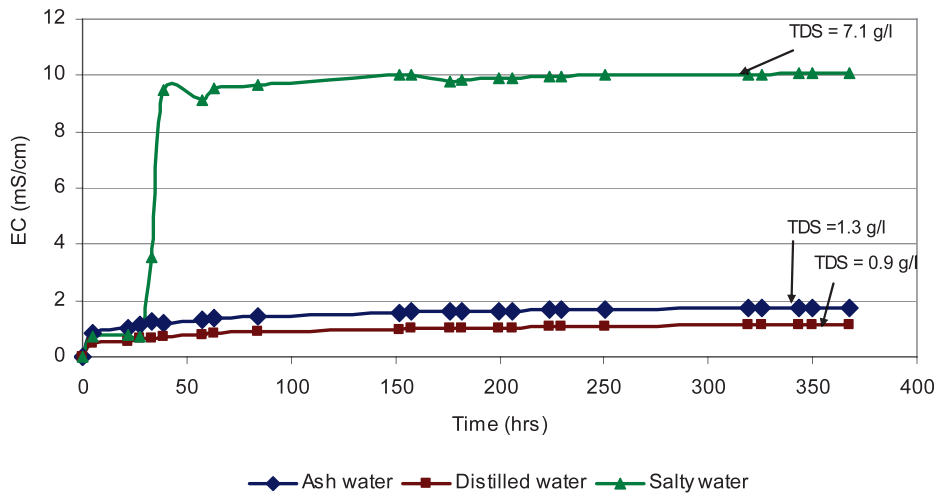


Fig. 2. Leachate trend on samples from different liquid media.

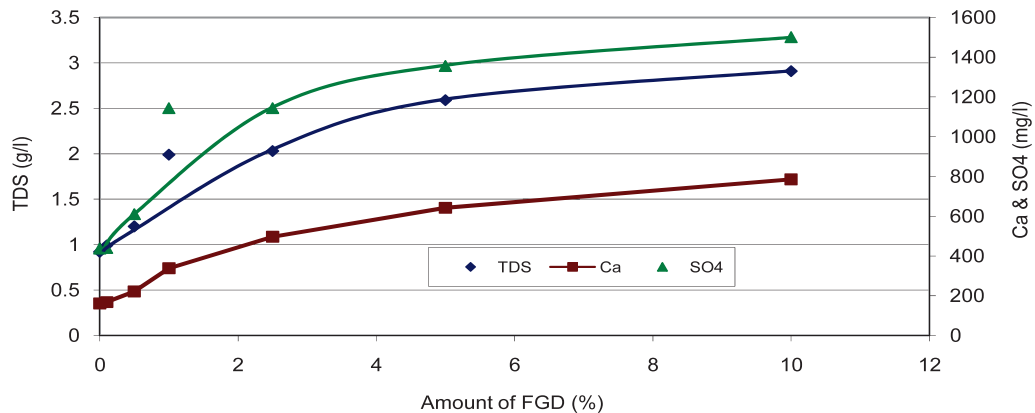


Fig. 3. Leachate results with increased FGD.

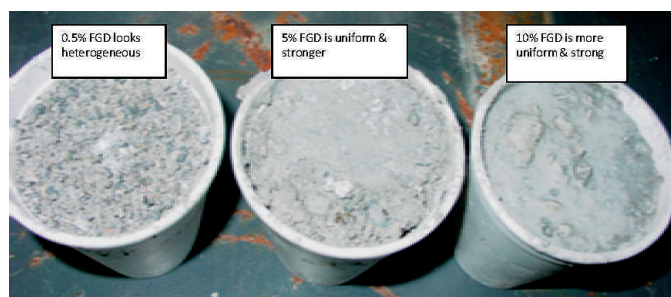


Fig. 4. Illustration of binding by increased FGD by-product additions.

shows that there was no significant difference between 5% and 10% FGD additions in terms of leachate qualities. This material will give a leachate which is 50% less concentrated than ash-transport water, which can improve the desalination of ash-transport water and membrane lifespan. However, an increase in calcium and a decrease in sulphate were observed.

It is important to note that solid-phase analysis confirmed the presence of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ ), and calcite ( $\text{CaCO}_3$ ). This evidence serves as a strong indication that the proposed co-disposal is possible although gypsum was in relatively large quantities than ettringite and calcite in addition to original mullite, anorthite, and quartz. The increased addition of FGD by-product resulted in more secondary phases, for instance 2.5% FGD by-product gave 10.2% gypsum, 2.2% ettringite, and 2.5% calcite while 10% FGD by-product gave 20.8% gypsum, 5.2% ettringite, and 10.3% calcite.

However, it goes further than leachate quality when physical phenomena are taken into consideration. Figure 4 illustrates the improvement in cementation by virtue of increased FGD by-product additions based on visual observations.

It was not possible to determine the unconfined compressive strength (UCS) value of the control (i.e. 0% FGD) after 14 days because the sample was too brittle. Nevertheless, the results of compressive strength indicate that there was an increase in UCS with increased amounts of FGD by-product for both 14- and 28-day cured samples, illustrating that FGD by-product increases the stability and structural integrity of the mixture while achieving co-disposal of these materials. This is prominent for the 28-day old samples containing 10% to 20% FGD by-product where UCS almost doubled from 1.5 kN to 3 kN, which is higher than a minimum strength of 1 kN for stabilised by-products (Laugesen and Eriksson, 2006), indicating that higher additions of FGD by-product could provide even more stability based on UCS results.

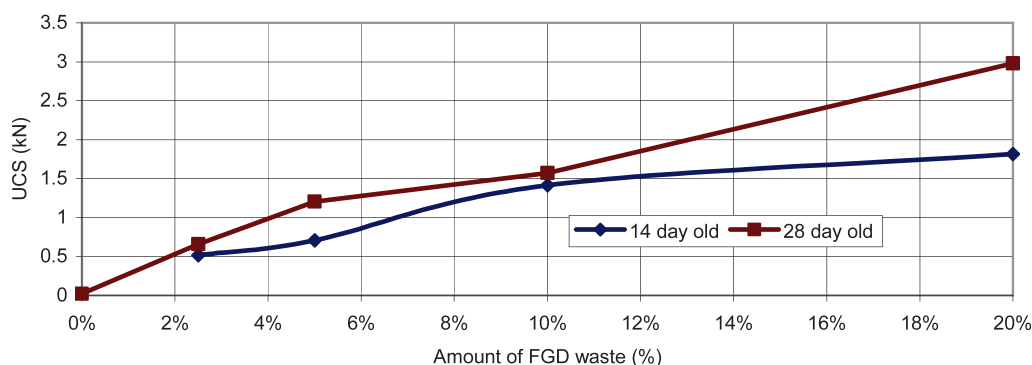


Fig. 5. Compressive strength results.

Furthermore, it is shown in Figure 5 that curing is important for strength development.

A good correlation of hydraulic conductivity data for duplicate samples was obtained (Figure 6). The hydraulic conductivity of the material decreases dramatically with an increase in the content of FGD by-product. The samples which contained 10% FGD by-product and higher showed hydraulic conductivities that were approx. 40-times less than that of the control ( $1.8 \times 10^{-3}$  cm/s). Addition of FGD by-product beyond 10% did not achieve hydraulic conductivity below  $4 \times 10^{-5}$  cm/s. This could be due to chemical reactions that have exhausted the lime since physical blocking of pores would still be detectable in these levels.

Good cementation reduces porosity and hence the ability of water to leach retained constituents is low (Jozic and Zelic, 2006; Asavapisit and Cosanavit, 2004; Li et al., 2001). Current data indicate that higher FGD by-product additions (typically 5% to 10%) to coarse ash will provide an environmentally sound management of FGD by-product. The reduction in hydraulic conductivity and an increase in compressive strength are in line with the requirements of United States Environmental Protection Agency (US EPA) in terms of stability and minimisation of infiltration (Laugesen and Eriksson, 2006; Paria and Yuet, 2006).

#### 4. Conclusions

- The optimum moisture content was found to be approx. 30% of the total solid content to get effective cementation of salts.
- Leach tests showed that the type of brine or liquid medium is important in the co-disposal of FGD by-product with gasification ash. Salty water provided best results in terms of salts retention and strength development which contribute towards minimisation of environmental impact. The use of clean water as liquid medium induces mobility of contaminants from the cured mixture.
- The addition of increasing amounts of FGD by-product and highly saline brines gave a couple of benefits in this study. The strength development was found to increase with curing time since 28-day old samples consistently gave higher UCS values than 14-day old samples.
- The presence of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ ), and calcite ( $\text{CaCO}_3$ ) after five weeks of curing indicates that hydration reactions occurred in the cured mixtures. The concentration of gypsum was in relatively large quantities than ettringite and calcite in addition to previously present mullite, anorthite, and quartz. The increased addition of

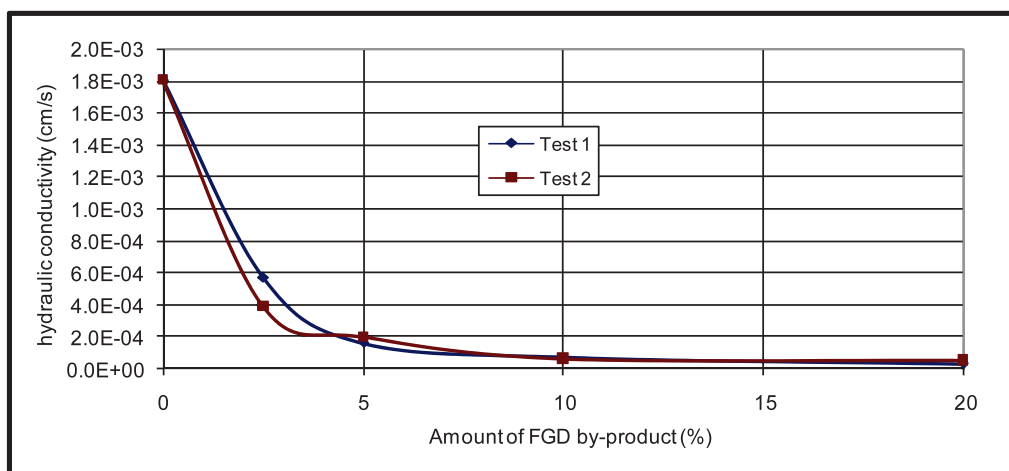


Fig. 6. Trend of hydraulic conductivity against increased FGD additions.

FGD by-product resulted in more secondary phases, for example 2.5% FGD by-product mixture gave 10.2% gypsum, 2.2% ettringite, and 2.5% calcite while 10% FGD by-product mixture gave 20.8% gypsum, 5.2% ettringite, and 10.3% calcite.

- The examination of physical and chemical aspects demonstrated the potential of mitigating the environmental footprint from a coal processing facility to co-dispose of FGD by-product with coarse ash and brines.

## 5. Recommendations

Considerable effort should be put towards simulating the expected leaching environment of the co-disposed material by using standard protocols such as synthetic precipitation leaching procedure (SPLP) and monolithic leach test. Optimisation of FGD by-product to coarse ash ratio requires consideration of both physical and chemical properties of the resultant by-product. Advanced analytical techniques, such as energy dispersive spectroscopy (EDS), and scanning electron microscopy (SEM), must be employed to obtain better understanding of the transformation occurring after hydration.

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