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Utilising Fly Ash as a Salt Sinking Media Through Pasting with Industrial Brine

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Abstract - **SASOL is the largest producer of synthetic fuel from coal and natural gas in South Africa and due to its exothermal nature require the intake of water from natural resources. Large volumes of raw water are consumed and brines (saline/salty effluents) are produced as a consequence of re-use operations, many of which are currently disposed of in the fly ash system. South Africa is a water scarce country, therefore vigilant management of its water resources is vital and it was decided in the 1980's to design the largest SASOL facility in Secunda as a zero effluent discharge complex. This design philosophy and sequential process alterations gave rise to an accumulation of salts within the current fly ash disposal system, which in turn is posing significant environmental risks.**

Preliminary research in mixing fly ash with different process brines to a high solids paste illustrated that the mixture hardens over time and more importantly proved that the final hardened product presented very low water permeability. Leaching tests indicated that the final product will not allow excessive ingress of salts to the soil and surface water resources in close complex proximity. It is exactly these physical properties that make the material attractive as a capping media for existing fly ash dams while simultaneously providing a sustainable salt sinking media to the wider SASOL processes.

The work presented focuses on the process development aspect of the proposed process as the pasting of industrial brine and fly ash remains to be a novel concept. Attention was paid to the development of preliminary flow sheets, the selection of the more suitable flow scheme and appropriate methodology elaboration into the flow sheet selection. Finally an introduction to the pilot plant design is discussed and its role in advancing the technology to full scale implementation.

Key words: Industrial brine, paste, salt management, waste management.[1]

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I. Introduction

SASOL in Secunda (South Africa), as a 1980's commissioned inland site, faces considerable salt handling as well as waste management problems. This challenge is not SASOL specific and sustainable salt management is a global challenge [1, 2]. The accumulation of salts within the complex is a major contributor

to pipe scaling and other operational malfunctions, along with the introduction of environmental risks. The origin of these salts traces back to chemicals used for normal operation, whereas the majority of these salts come from the brines generated during desalination and raw water regeneration.

Currently, salts from the complex are disposed via a selection of systems, but the bulk is disposed in the ash system. The direction of salty water streams are mainly controlled by the Secunda zero liquid effluent discharge (ZLED) policy, which limits the discharge of liquid waste streams outside the complex boundaries. A ZLED policy was adopted due to the geographical placement of the site [3]. Following this type of policy comes water balance issues, marked by large positive balances (inflow >> outflow). Historically the positive water balances at the Secunda complex was accommodated in dams and water recovery processes. Some successes are gained by the water recovery units (Tubular Reverse Osmosis - TRO and Electrodialysis Reversal - EDR), but dams are not a sustainable practise and are raising questions regarding the environmental footprint associated with them. Subsequently, the recycling of water (and salts) within the ash system introduced an accumulation of salts. So much so that the water quality is approaching a level that is not suitable for use in most processes.

SASOL identified the opportunity for the co-disposal of industrial brines with fly ash by means of pasting [4]. Both fly ash as well as brine poses an environmental threat within the context of sustainable development which drives the need to develop an environmentally sound salt management process for the complex [5]. Laboratory scale research at the

SASOL facilities indicated that the salinity and chemical composition of different brines within the complex affects the transportability of fly ash and brine pastes (FABP). There also exists a significant time-dependence on paste transportability as FABP exhibited hardening effects [4]. The use of paste technology as a disposal method in mine tailings is not a new concept and is well documented in literature [6, 7, 8]. The existence of secondary minerals in dry fly ash mixed with water, observed by Bergeson et al. motivated the study as an opportunity exists to stabilise ionic compounds within the brine in the paste similar to mine tailing practises [9].

This paper therefore represents an attempt to explore the engineering possibilities to paste technology as an alternative salt management solution through the co-disposal of brines and fly ash for the SASOL Secunda complex. Results from laboratory experiments were used to develop two independent flow schemes whereas bench scale testing results eliminated the possibilities to a single flow scheme. Key bench scale work underway will produce a pilot scale design, from which the commercial scale unit will be sized.

II. Flow sheet development

The physical behaviour (particle size distribution) and chemical properties (reactive glassy phases) of fly ash make it an attractive material for pasting [10]. A great extent of research time has been devoted by a number of authors on the use of paste technology to dispose of mining tailings, through the dewatering of the slurry [11, 12, 13]. The formation of secondary hydration minerals upon mixing fly ash with water, along with literature on mine tailings served as the initial motivation to this investigation, where these secondary minerals largely contributes to the hardening of the paste. Transportability issues regarding this time dependant hardening of the paste are a major concern, therefore a modified slump test to the original ASTM C 143-90 was used to measure the slumping characteristics of the paste [14]. From these slumping tests it was found that a mixing ratio of *ca* 68wt % fly ash produces a paste which will allow adequate transportation times while producing as little bleed as possible [4].

Two flow sheet possibilities were identified, the first being a dry ash transportation scenario and the second developed as a wet ash transportation scheme. The difference between the two flow sheets will become apparent later in the text. The flow sheets for the two pasting scenarios were developed on basis of an additional 80 ton/day of salt encapsulation within the complex, while consuming *ca* 20wt % of the fresh fly ash production. The effect of introducing pasting on the current system was also considered and the total sinking capacity of the proposed system was aligned with the Secunda salt strategy.

If it is assumed that removal of 20% of the fresh fly ash production will not negatively influence the current ash system and its salt holding capacity, *ca* 66 ton/h of ash can effectively be redirected for use as a raw material in pasting. In-house results indicated that higher concentration brines delivered final hardened products with lower permeability values. This, along with the fact that fly ash becomes a limiting reagent if the brine is too diluted, lead to the inclusion of a concentration step to both flow schemes as presented in Figure I and Figure II [15].

A. Dry fly ash pasting scenario

Dry fly ash pasting relies on the principle where fly ash is collected from the hoppers in a dry state and pneumatically transported to a mixing vessel. Here, the fly as is mixed with the required amount of brine to produce a 68wt % paste and transported to the point of disposal or further use, Figure I.

If the regeneration brine stream is concentrated from *ca* 30 kg/m^3 to 160 kg/m^3, 81.3% of the water needs to be evaporated from the inflow, resulting in a distillate flow rate of *ca* 135.5 m^3/h. The latter can be reused elsewhere in the process (typically as boiler feed). The 31 m^3/h concentrated brine stream will then be used to paste 66 ton/h of fly ash, producing 97 ton/h paste product.

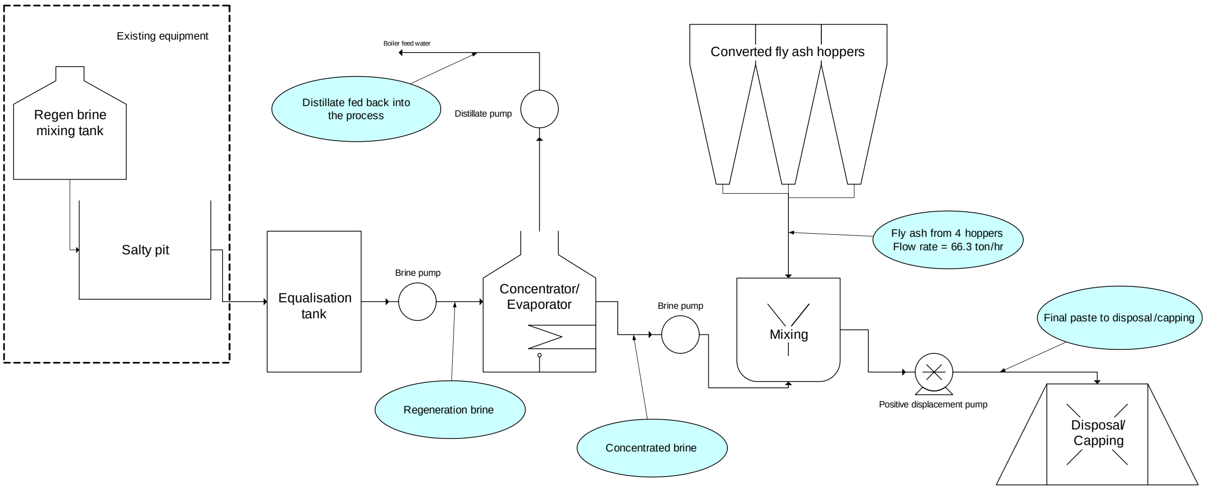

Figure I: Flow scheme for pasting fly ash with industrial brine by means of dry fly ash transportation.

The final destination of the paste will either be disposal on new sites or serve as a cap to existing dams, irrespective of pasting methodology. Ongoing leaching tests and results from EIA (environmental impact assessment) studies will determine the best suited disposal method complying with all appropriate environmental standards.

B. Wet fly ash pasting scenario

A thickening unit marks the difference between the wet and dry ash pasting scenarios. Dry fly ash from the hoppers is mixed with a brine stream at *ca* 30wt % fly ash concentration and transported to the thickening unit/train. This configuration simulates closely the current method of fly ash removal in Secunda and is considered due to the opportunity to incorporate existing equipment in the proposed configuration as illustrated in Figure II. The success of the wet ash system lies within the level of separation achievable by the deep cone (or other configuration) thickener and whether the thickener design will be able to produce a bottoms paste of *ca* 68wt %.

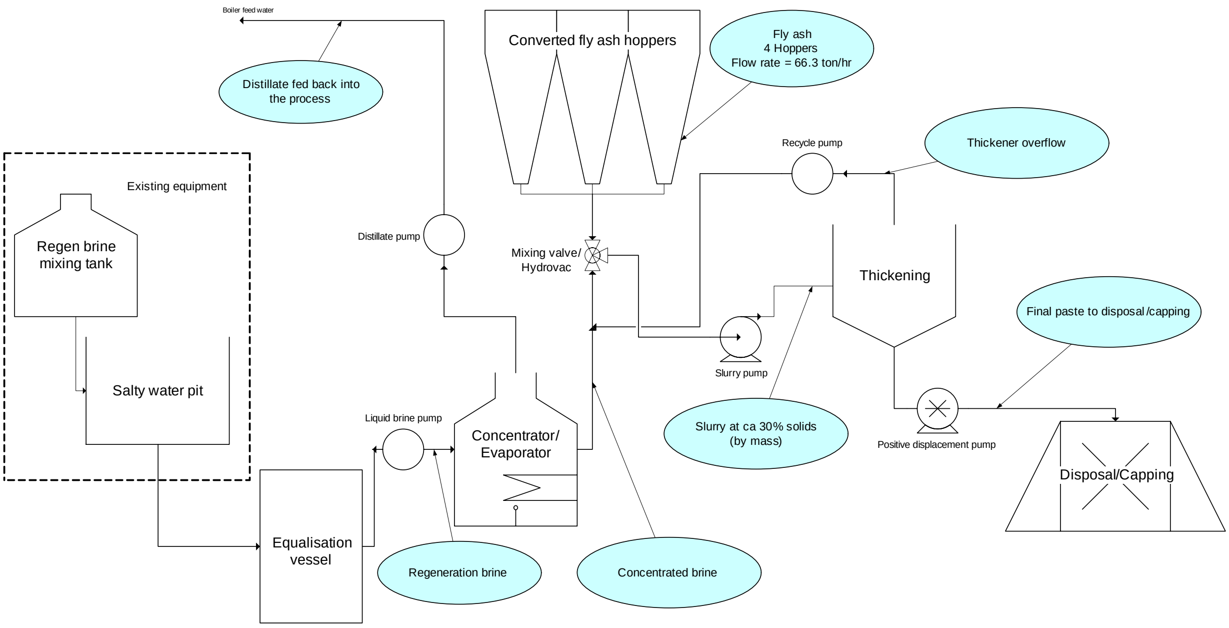

Figure II: Flow scheme for pasting fly ash with industrial brine by means of wet fly ash transportation.

Both flow sheets appear to be feasible based on mass balance considerations, but the feasibility in terms of physical implementation may differ significantly from this initial estimate. For this reason, Paterson & Cooke Consulting Engineers in South African was approached to complete the rheology characterisation of pastes produced by simulating each flow sheet in a bench-scale investigation.

III. Bench Scale Rheology Study – Flow Sheet Elimination

The study directed to Paterson & Cooke involved two different brines, the first in dilution form and a more concentrated sample. The two brines were tested over a range of fly ash concentrations (65wt % to 70wt% fly ash by mass), producing bench top thickening, mixing and viscometer test results to establish the paste rheology.

A. Dry fly ash pasting scenario

Bench top mixing simulating post concentration process steps (Figure I) illustrated that both brines could be mixed above the desired solids concentration and up to 72wt % fly ash could successfully be achieved.

B. Wet fly ash pasting scenario

Bench top thickening was performed with both brine mixtures and it was concluded that it is not possible to produce a thickened underflow material above 50wt % fly ash concentration. A wide range of flocculants were also tested with little to no progress in the obtained underflow solids concentration. This finding automatically eliminates one of the proposed flow schemes. Future attention will only be paid to the dry fly ash pasting flow schemes as the desired salt retaining will not be achieved by this lowered solids concentration paste.

1. Time dependence of paste

The time-dependant hardening of the FABP may possibly influence the transportability of the paste [4]. Consequently, Paterson & Cooke was tasked to investigate this phenomenon over the presented brine to fly ash concentration range.

The time dependant behaviour was investigated by continuously shearing the paste for 60 minutes at a rate of 168 s^{-1}, therefore simulating the upper extreme conditions expected in large scale applications. Shear stress vs. time plots at the constant shear rate was established for both flow schemes at the specified 68wt % fly ash concentrations, mixed with each brine individually. Figure III shows the dry ash flow sheet representation; noting that no considerable change in the paste behaviour could be recorded, therefore suggesting the paste will not pose significant difficulties in plant transportation.

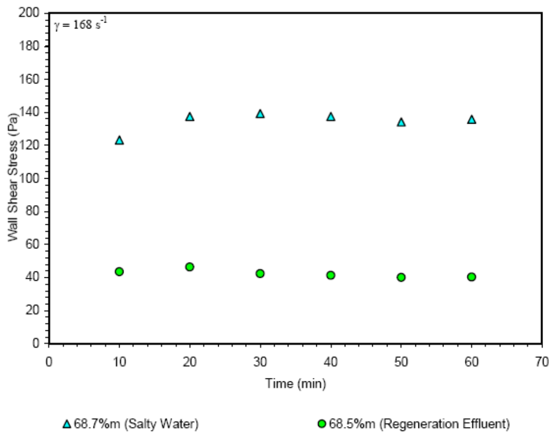

Figure III: Time dependent hardening behaviour of the paste from the dry ash pasting scenario.

The wet ash flow sheet representation shows a decrease in wall shear stress over time (Figure IV). This phenomenon may largely be contributed to the disintegration of flocculant structure with the continuous sheering of the material. This, along with the inability of the thickener to produce the required underflow solids concentration, adds to the elimination of the wet ash flow sheet from current considerations.

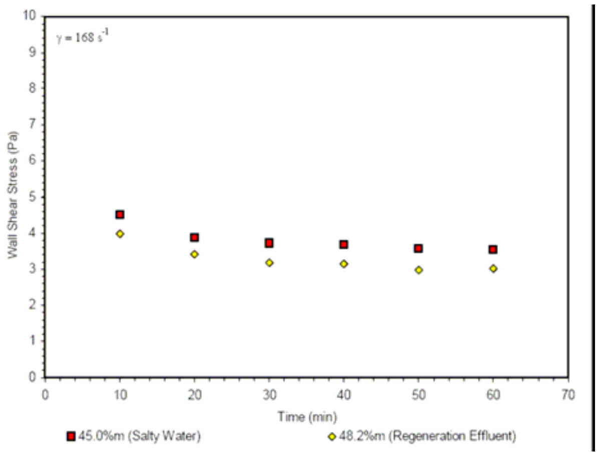

Figure IV: Time dependent hardening behaviour of the paste simulating the wet ash pasting scenario. The thickener underflow could not achieve 68wt % solids concentration, therefore the paste concentrations used for this test were introduced at *ca* 45 – 48wt % fly ash.

C. Paste rheological characterisation

Seeing that the dry ash pasting scenario will be the likely option pursued in future study, the rheology of the wet ash pasting flow sheet will not be discussed here. The fly ash and brine samples produced from the dry ash pasting flow sheet could be characterised as viscous

Newtonian fluids, where the rheological parameters could be defined by using the Newtonian viscosity, μ.

The Newtonian model is described as:

$$\tau_0 = \mu \cdot \gamma \tag{1}$$

Where τ_0 = wall shear stress (Pa)
μ = Newtonian viscosity (Pa.s)
γ = shear rate (s^{-1})

Figure V presents a good relationship between the model curve fit, according to the Newtonian model (1), and the laboratory established viscosity data. Also, both brines exhibited Newtonian behaviour, suggesting the use of any brine concentration between these two samples will follow similar trends.

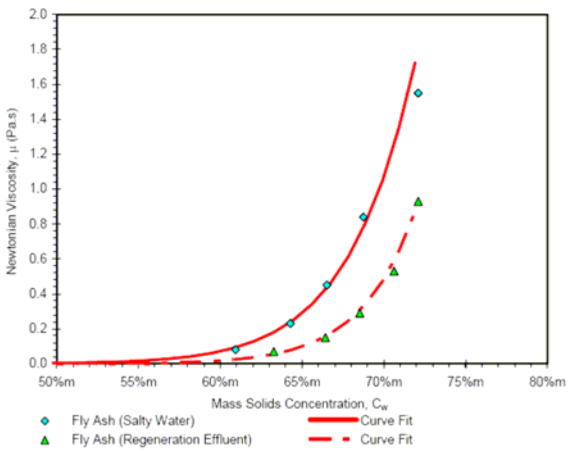

Figure V: Fly ash and brine Newtonian viscosity presented as a function of mass solids concentrations.

IV. Progression to Pilot Plant Design

On completion of the initial rheological characterisation of the paste, along with the elimination of one of the flow schemes, it is now possible to progress towards a pilot plant design. Paste systems are known to be complex and a flow loop study will be commenced shortly in order to gather all the necessary information required to adequately size the pilot plant as well as selecting the appropriate equipment. The flow loop tests are designed to determine the pumping characteristics of the paste product at various concentrations. The test rig is set up with a 43 mm internal diameter pipe loop, clear viewing sections, variable speed pumps or progressive cavity pumps, heat exchangers, manometer board, instrumentation and a computer-based data acquisition system.

Rheology tests will continue throughout the flow loop tests in order to corroborate the data with those gathered during the bench scale mixing of the materials. Ultimately this will ensure that the mixture properties remain similar and therefore introduce a wider area of certainty when selecting materials of construction, the general arrangement of the pilot plant as well as the overall equipment selection.

V. Conclusions

SASOL, as an inland petrochemical site, faces significant salt management challenges and consequently identified the opportunity to develop a co-disposal process for fly ash and industrial brines in an environmentally acceptable manner. In-house research revealed that fly ash mixed with highly saline industrial brine hardens over time and exhibits low leaching characteristics due to its impermeable nature. Ongoing research focuses on the understanding of the salt encapsulation mechanism(s) found when pasting fly ash and saline industrial brines. Structural development studies, leaching as well as strength correlations are being investigated as these properties will enable the broader understanding of the footprint expected from this product.

The work presented here directs the reader to the parallel development of a paste plant enabling 80 ton/day additional salt encapsulation for the SASOL Secunda complex in South Africa. From the two possible pasting scenarios the wet ash pasting scenario was eliminated on grounds of thickening difficulties. Bench scale investigations revealed that the required paste underflow of 68wt % solids concentration could not be reached, even with the introduction of large amounts of flocculants. Acknowledging that a pilot scale unit with mud bed heights comparable with full scale implementation may conclusively determine if the target underflow can be achieved, it is likely that future studies will only direct towards dry ash pasting. The latter could effectively be pasted up to 72wt % fly ash solids concentration.

Rheology results for the simulated dry fly ash transportation scenario showed that the brine and fly ash paste exhibited Newtonian fluid behaviour. This was true for fly ash pastes with diluted- as well as highly saline brines. Brines of different salinity values are found within the Secunda complex and the mutually

Newtonian behaviour exhibited by the test series introduces a new set of opportunities to further integrate site waste management. The elimination of a concentration step to the original flow scheme will greatly aid preliminary process economics as well as eliminating operatibility concerns of the full scale unit.

The study will now progress to a comprehensive flow loop study through which valuable data will be collected in order to determine the pumping characteristics of the paste product at the specified solids concentrations. Focus will remain on the dry ash pasting scenario and the parameters will be applied to size a pilot scale test facility and consequently gather enough data to progress towards the commercial scale plant.

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