

Leachate Characteristics of Ash Residues from a Laboratory-Scale Brine Encapsulation Simulation Process

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ABSTRACT

Sasol, a global petrochemical player uses large quantities of coal, steam and oxygen as feedstock for the production of fuels and chemicals. Inevitably, large amounts of waste products are generated such as coal combustion residues (ash) via coal gasification as well as brines via demineralization, desalination and evaporation processes. Sasol Technology Research and Development is currently investigating the concept of brine (high strength inorganic salt solutions) encapsulation with the use of coal gasification ash. The process will involve reacting inorganic salts with the coal mineral matter under thermal conditions to form stable compounds, potentially resulting in an environmentally safe brine disposal option. Laboratory-scale experiments investigated brine addition at 3.5% (m/m) and 29% (m/m) to coarse gasification coal ash (with and without CaO addition). These samples were sintered at 700 °C for 30 or 60 mins. Selected ash residues from laboratory-scale brine gasification simulations were subjected to water leaching tests to determine the leachate properties, the extent of salt stabilisation achieved as well as the influence that CaO addition on inorganic salts encapsulation. The results of this study indicated that some of the ionic species in the brine were encapsulated and the addition of CaO improved stabilization.

INTRODUCTION

Sasol, a global petrochemical player uses large quantities of coal, steam and oxygen as feedstock for the production of fuels and chemicals. Inevitably, large amounts of waste products are generated such as coal combustion residues (ash) via coal gasification as well as brines via demineralization, desalination and evaporation processes. A brief discussion on the origin of gasification ash and brines at the Sasol Synfuels Plant in Secunda is discussed in below.

Approximately 28 million tons of low-grade coal is utilised annually by the gasification process employed at Sasol Synfuels in Secunda South Africa, producing 7 million tons of gasification ash (GA). The remaining fraction of coal, a finer coal fraction, is combusted to produce steam and electricity required for various processes. Coal ash generated through the gasification process termed 'coarse ash', is a combination of red and white to grey fused clinkers with heterogeneous texture varying from fine material to large irregularly shaped aggregates of sizes ranging from 4mm to 75mm². This ash comprises predominantly of an assemblage of major oxides (quartz, mullite, anorthite) and minor oxides (diopside, hematite, cristobalite) and anhydrite. These materials contain a small percentage of unburnt carbon-containing coal minerals and trace quantities of trace elements².

Brines on the other hand are generated at Sasol Synfuels, Secunda South Africa from various processes that are currently employed for maximum utilization, up-grading and re-use of various industrial effluents, such as desalination, evaporation, softening and ion exchange. Typical saline brines (Br) that occur at Sasol Synfuels contain the following components: Na (2% – 4.4%), Cl (5%), SO₄ (5%), Ca (0.12%), K (0.38%), Mg (0.059%) ions and trace elements such as Fe, Mn, Cr, V, Ti, P, Si and Al.

Accumulation of inorganic salts on the Sasol Synfuels Plant is a major challenge that is not only unique to Sasol but is also relevant to many other inland industries including mining operating in water short areas where water re-use and recycling is a necessity. At the Sasol Synfuels Plant, accumulation of inorganic salts has occurred since commissioning of the Secunda Complex. This is a challenge considering future plans to expand the complex. Many brine handling techniques require further expensive treatment options or disposal into lined dams to minimise environmental impacts. These treatment options are generally capital intensive and have high operating costs.

During this study, the possibility of encapsulating brine species in the coal ash was investigated. During this process, concentrated inorganic salts such as desalination and evaporation brines would be contacted with coal ash, possibly resulting in the irreversible retention of the brine species into the coal ash mineral matter during the thermal process, resulting in an environmentally safe brine disposal option. This process is attractive because the ash produced

during coal gasification contains high concentrations of coal mineral matter that would enhance the reaction between brine species and the coal inorganic minerals. In order to determine the extent of brine species stabilization during this process a water leach test was conducted on the resulting ash.

The objectives of the study were thus to firstly evaluate the degree of salt stabilization achieved during the simulation of a brine gasification process and to determine the influence of CaO addition on salt stability. Standard water leach tests (DIN 38414-T4) were used to evaluate responses. In addition the effect of time and the amount of brine addition on the overall salt stabilization process was also investigated.

MATERIALS AND METHODS

Various laboratory-scale brine encapsulation experiments were conducted simulating the addition of brine (at 3.5 and 29%) at the bottom of a gasifier (ash-bed) at 700°C for 30 and 60 min period. The influence of CaO addition during gasification on the degree of stability of the brine species was also investigated. Ash residues produced during the gasification simulation experiments were submitted to a standard water leaching tests to determine the leachate properties as well as the degree of salt stabilisation achieved during the gasification.

Encapsulation experiments

The sample preparation matrix for the encapsulation experiments is summarised in Table 1a and 1b. However, a detailed account of this is presented elsewhere.³ All the brine encapsulation simulation experiments were conducted at 700°C in the presence of air.

The brine and the gasification ash (GA) samples used during the experiments were obtained from Salty Effluent Dam 3 and the Gasification Plant in Sasol Synfuels, Secunda (South Africa), respectively.

Table 1a: Summary of the brine encapsulation simulation studies (3.5% brine addition)

Sample ID	Mass of GA (g)	Mass of Brine (g)	Mass of Lime (g)	Sintering time (min)
1	100	0	0	30
2	100	0	0	60
3	100	3.5	0	30
4	100	3.5	0	60
5	100	0	1.5	30
6	100	0	1.5	60
7	100	3.5	1.5	60
8	100	3.5	1.5	30

Note: ID- sample identity
GA: Gasification ash

Table 1b: Summary of the brine encapsulation simulation studies (29% brine addition)

Sample ID	Mass of GA (g)	Mass of Brine (g)	Mass of Lime (g)	Sintering time (min)
1	1300	0	0	30
2	1300	0	0	60
3	1300	377	0	30
4	1300	377	0	60
5	1300	0	42	30
6	1300	0	42	60
7	1300	377	42	30
8	1300	377	42	60

Note: ID- sample identity
GA: Gasification ash

Water leaching experiments

The ash residues obtained from the encapsulation simulation experiments were subsequently subjected to a standard water leaching test (DIN 38414-T4) to determine the degree of salt (brine species) stabilization. This allowed for the comparison of leachate qualities for samples with and without brine and/or lime addition.

During the water leaching test, a 100g of ash of finely ground ash residue material was added to a beaker and leached on a rotating shaker with 1000ml of distilled water for 24hr. The leaching solution was separated from the leached ash residue by filtration (GFA filter paper) and sent to the Institute for Soil Climate and Water (ISCW) Pretoria, South Africa for the following analyses: Na, K, Ca, Mg, B, F, Cl, NO₂, NO₃, PO₄, HCO₃, CO₃, SO₄, pH, electrical conductivity (EC) and total dissolved solids (TDS).

Calculation for the determination of the mass of salt stabilized

The following method was adopted as a rough calculation to determine the degree of salt stabilization:

A: Quantity of salt added (known from the brine)

B: Quantity of salt leached from untreated ash (measured)

C: Quantity of salt leached from brine treated ash (measured)

D = C – B: Quantity of salt leached (not retained) attributed to the added brine

E = A – D: Quantity of salt retained

(E/A)*100: Percent salt stabilization

Example of stabilization calculation:

An example calculation using the Na leachate data from Appendix A4 is given below:

A = Quantity of Na added to coarse ash prior to sintering
377g brine added to 1300g ash or 29 g/100 g (29% Brine) at 44000 mg/l Na
= 1276.0 mg Na/ 100 g Ash

B = Quantity of Na leached from untreated ash
5.6 mg/l or **5.6 mg/100 g Ash**

C = Quantity of salt leached from brine treated ash
735.3 mg/l or **735.3 mg/100 g Ash**

D = C – B: Quantity of salt leached that was added
 $735.3 - 5.6 = \mathbf{729.7 \text{ mg/100 g Ash}}$

E = A – D: Quantity of salt retained
 $1276 - 730 = \mathbf{546 \text{ mg/100 g Ash}}$

Percent salt stabilisation $= (E/A) * 100$
 $= (546/1276) * 100$
 = 43% Na stabilisation

RESULTS AND DISCUSSION

The results obtained during the water leaching of the residual ash produced when sintering brine-gasification ash mixtures at elevated temperatures are presented below. In general, the analyses of leachates produced during water leaching of ash residues clearly indicate that the brine treated sintered residues have elevated leachate electrical conductivity (EC) and Na, K, Ca, Cl and SO₄ concentrations compared to the non-brine treated sintered ash residues. This increase is attributed to the applied brine. The higher brine (29%) addition in most cases produced a significantly inferior leachate quality when compared to the lower brine (3.5%) addition and therefore only the results obtained for the 3.5% brine addition will be discussed. Furthermore the 3.5% brine addition represented a more realistic scenario for full-scale application. The results obtained from the leachate analyses of the GA treated with 3.5% brine with and without CaO addition are presented and summarised in Tables 2a & 2b.

Table 2a: Summary of leachate analyses showing the effect of brine (3.5%) and CaO (1.5%) addition on leachate quality at 30 min sintering (700°C)

Parameter	GA	GA + Brine	GA + CaO	GA + CaO + Brine
EC (µS/cm)	710.0	960.0	1290.0	1530.0
TDS (mg/L)	418.9	572.8	689.2	797.7
Na (mg/L)	5.2	38.7	9.4	64.0
Cl (mg/L)	1.7	79.4	2.3	100.4
SO ₄ (mg/L)	87.3	126.5	32.2	36.6

The results presented in Tables 2a & b indicate that all of the monitored parameters in the leachate increased with the addition of brine to the GA but decreased significantly (with the exception of Cl) when CaO was added to the brine and ash mixture. For example the leachate SO₄ concentrations given in Table 2a increased from 87.3 mg/L with no brine addition to 126.5 mg/L upon brine addition but significantly decreased to 36.6 mg/L when CaO was added with the brine. This clearly suggests CaO addition to have significantly increased the quantity of SO₄ stabilised.

Table 2b: Summary of leachate analyses showing the effect of brine (3.5%) and CaO (1.5%) addition on leachate quality at 60 min sintering (700°C)

Parameter	GA	GA + Brine	GA + CaO	GA + CaO + Brine
EC (µS/cm)	820.0	1010.0	3030.0	1460.0
TDS (mg/L)	445.4	1012.8	1494.0	825.9
Na (mg/L)	4.6	39.7	9.6	27.7
Cl (mg/L)	1.2	101.5	111.5	96.3
SO ₄ (mg/L)	97.7	150.4	126.0	41.8

It should be noted that the measured parameters on the leachate obtained for the sintered GA+CaO mixture gave slightly higher results (more especially for the sulphate and chloride) than was expected and this was probably due to

possible contamination. Although this is the case the result in Table 2b gave a similar trend that was also observed for the 30 min sintering time.

The effect of adding CaO clearly improved the leachate quality in terms of the overall TDS as well as all the measured parameters as seen in both Tables 2a and 2b. These results suggest that the decrease in the leachate SO₄ concentrations could be explained by a possible reaction that takes place between the added lime and the sulphate species present in the brine at elevated temperatures to form insoluble CaSO₄. This reaction consumes the SO₄ thus reducing the labile form of SO₄ species (e.g. Na₂SO₄) in the brine.

Calculation of the percentage salt stabilisation achieved may be an appropriate way of showing the benefits of this concept. It should be noted that the salt stabilisation calculation does not take into account the loss of ions by gaseous release. This is currently being investigated and initial indications are that this is not a significant pathway. Nevertheless, it is important to cautiously utilise the salt stabilization data to observe trends rather than to measure qualitative rates of salt stabilization. The calculated percentage salt stabilisation values are given in Figure 1 and Table 3. The results in Figure 1 and Table 3 also allow for the comparison between the salt stabilization achieved at 30 min and 60 min sintering periods and also show the effects of the addition of CaO on the degree of stabilisation.

Table 3: Calculated percentage salt stabilisation for GA treated with 3.5% brine, 1.5% CaO at 30 and 60 min sintering times

Parameter	30 min		60 min	
	(without CaO)	(with CaO)	(without CaO)	(with CaO)
TDS	67	77	-23	245
Na	78	65	77	88
Cl	49	35	34	110
SO ₄	75	97	67	153

The results given in Table 3 are graphically represented in Figure 1 to allow for ease of comparison of the % stabilization results achieved under various experimental conditions. The results in Figure 1 and Table 3 indicate that the overall TDS stabilization increased for both 30 and 60 min sintering periods upon the addition of CaO. The results further indicate that the % salt stabilization (measures as TDS) with the addition of CaO at 30 min increased from 77% to 245 % at 60 min. A stabilization figure > 100% denotes that additional stabilization is achieved in addition to the added brine species while a negative figure implies the opposite.

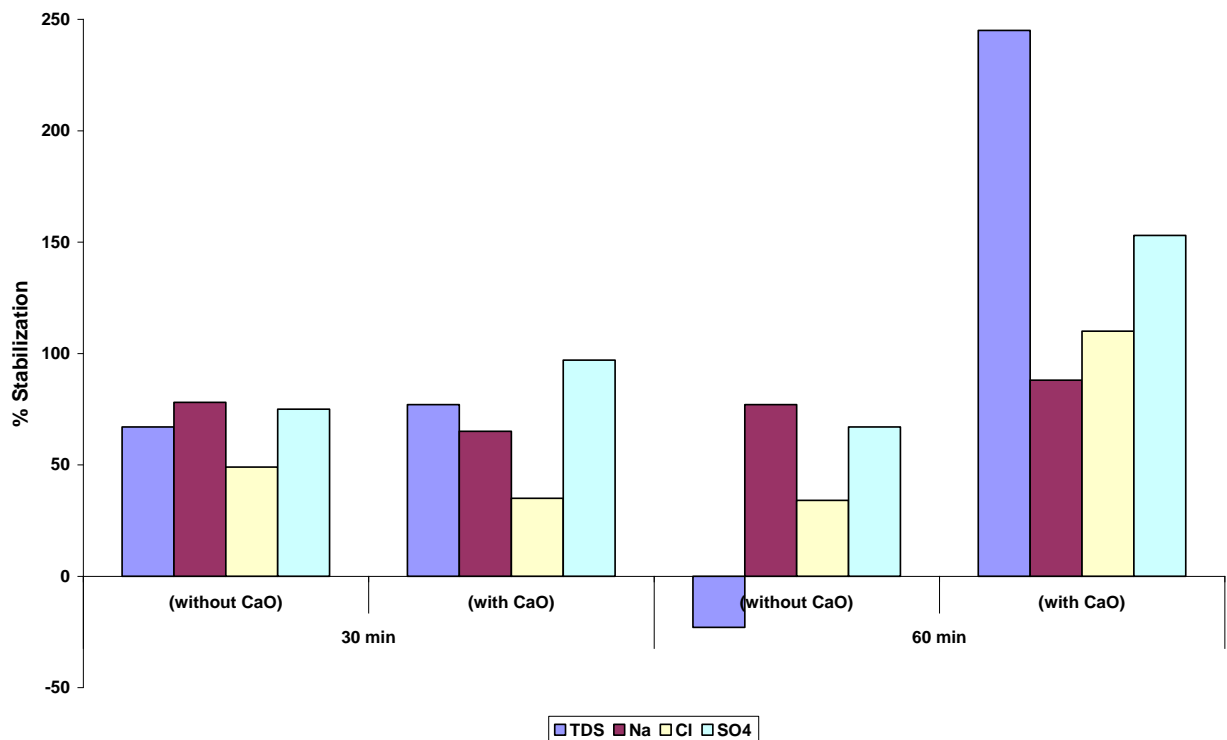


Figure 1: Calculated percentage salt stabilisation for GA treated with 3.5% brine, 1.5% CaO after 30 and 60 minutes sintering

The stabilization of Na species at 30 min decreased slightly upon addition of CaO (from 78% to 65%). However, at 60 min an increase from 77% to 88% in the stabilization was observed upon lime addition. This observation probably suggests that the stabilization of Na was more favourable at longer sintering periods. The influence of CaO on the stabilization for this species was not clear from the above results. A possible mechanism accounting for the observed stabilization for sodium species could be the formation of anorthite [(Na, Ca) $AlSi_3O_8$] from the reaction of Na with coal mineral matter.

A significant stabilization of the sulphate species was observed for both 30 and 60 min sintering times and as expected this stabilization improved significantly upon the addition of CaO. The stabilization of SO_4 was most likely also due to the formation of $CaSO_4$, as mentioned earlier.

The results indicate that Cl stabilization decreased from 49% to 35% upon CaO addition at 30 min sintering time. At 60 min sintering time the opposite trend was observed with increased Cl stabilization (from 34% to 110%) upon CaO addition. These trends are rather difficult to explain but could suggest greater sensitivity to the calculation by the results where ash chemical composition has a significant influence. However, the observed Cl stabilization could be due to its encapsulation in a water insoluble mineral, although, it is unclear at this stage which minerals this may be. Further investigation into the identification of the possible Cl-containing minerals should be conducted.

As already shown salt retention is specific to the individual ions present in the brine. Addition of lime can also significantly improve salt stabilisation rates. The presence of carbonaceous matter (unburnt carbon) can also result in to poor stabilization, especially for Cl and SO₄ species.

CONCLUSIONS AND RECOMMENDATIONS

The analysis of ash residue leachate obtained during this study clearly indicate that the ash residues produced during the sintering of the mixture of brine and gasification ash have elevated leachate electrical conductivity and Na, K, Ca, Cl and SO₄ concentrations compared to the gasification ash not treated with the brine. As would be expected, the addition of CaO significantly increased the leachate electrical conductivity and Ca ion concentration. The lower brine addition resulted in a relatively larger salt stabilization capacity compared to the higher brine addition.

Sintered ash residues treated with brine and CaO generally exhibited improved leachate properties compared to the treatment with brine only. Most of the brine species (Na, Cl and SO₄) were successfully stabilized within the ash matrix. Preliminary results indicate that the longer sintering time resulted in higher sodium stabilisation, which did not improve significantly with CaO addition.

A possible stabilisation mechanism for sodium species is the formation of anorthite [(Na,Ca)Al Si₃O₈] during the high temperature reaction of sodium with coal mineral matter and the added brine solution. 77% of the added sodium species was retained during ash-brine sintering. This increased to 88% upon CaO addition.

Sulphate stabilization was significantly improved by the addition of CaO at both 30 min and 60 min sintering periods. The stabilisation of this species could possibly be attributed to the formation of insoluble CaSO₄. More than 65% stabilisation of the sulphate was achieved under all experimental conditions.

The results of the study also indicated that the at least 34% of the Cl species present in the brine were stabilised under all experimental conditions. The stabilization of this species was not expected since most known Cl minerals are soluble.

In conclusion, the results of the preliminary study show that significant salt stabilisation was achieved during laboratory-scale brine encapsulation process and that the application of this technology may result in an environmentally sustainable way of handling brines. At this stage it is inappropriate to directly relate these findings to what might be expected in a full-scale brine encapsulation process. The findings do, however, suggest that mineral studies are required to identify and characterize the sodium-anorthite and the as yet unknown Cl-containing minerals that formed during ash-brine sintering.

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APPENDICES

Appendix A1. Water leachate chemical analysis of coarse coal ash sintered residues (30 min) for the brine, lime and brine + lime treatment (3.5% brine, 1.5% CaO)

Parameter	GA	GA + Brine	GA + CaO	GA + CaO + Brine
pH	10.7	10.9	10.8	10.9
SAR	0.2	1.1	0.2	1.1
EC	(μ S/cm) 710.0	960.0	1290.0	1530.0
TDS	mg/l 418.9	572.8	689.2	797.7
Na	mg/l 5.2	38.7	9.4	64.0
K	mg/l 5.4	4.1	10.1	4.7
Ca	mg/l 78.2	101.7	290.6	246.7
Mg	mg/l 1.0	0.9	0.9	0.8
B	mg/l 0.2	0.0	0.0	0.0
F	mg/l 1.5	3.2	2.4	4.7
NO ₂	mg/l 0.0	0.0	0.0	0.0
NO ₃	mg/l 0.1	1.0	0.0	0.5
Cl	mg/l 1.7	79.4	2.3	100.4
SO ₄	mg/l 87.3	126.5	32.2	36.6
PO ₄	mg/l 2.4	0.0	0.0	0.0
CO ₃	mg/l 76.5	84.0	168.0	138.0
HCO ₃	mg/l 320.3	268.4	347.7	402.6

Appendix A2. Water leachate chemical analysis of coarse coal ash sintered residues (60 min) for the brine, lime and brine + lime treatment (3.5% brine, 1.5% CaO)

Parameter	GA	GA + Brine	GA + CaO	GA + CaO + Brine
pH	10.8	10.9	10.9	10.9
SAR	0.1	0.5	0.1	0.4
EC	820.0	1010.0	3030.0	1460.0
TDS	445.4	1012.8	1494.0	825.9
Na	4.6	39.7	9.6	27.7
K	5.0	2.9	7.3	3.5
Ca	96.9	446.1	646.9	330.5
Mg	0.9	0.9	0.9	0.9
B	0.2	0.0	0.0	0.0
F	1.3	4.0	5.8	3.2
NO ₂	0.0	0.0	0.0	0.0
NO ₃	0.1	0.7	3.1	1.3
Cl	1.2	101.5	111.5	96.3
SO ₄	97.7	150.4	126.0	41.8
PO ₄	0.0	0.0	1.5	0.0
CO ₃	79.5	72.0	396.0	129.0
HCO ₃	317.2	390.4	372.1	384.3

Appendix A3. Water leachate chemical analysis of coarse coal ash sintered residues (30 minutes) for the brine, lime, brine + lime treatment (29% brine, 3.2% CaO)

Parameter		GA	GA + Brine	GA + CaO	GA + CaO + Brine
pH		10.7	11.1	11.3	11.4
SAR		0.1	8.9	0.1	1.9
EC	μS/cm	970.0	4170.0	7850.0	3640.0
TDS	mg/l	369.3	3432.6	3042.5	3093.8
Na	mg/l	5.6	735.3	6.6	204.8
K	mg/l	3.6	27.5	1.9	39.7
Ca	mg/l	119.7	510.9	1492.2	909.4
Mg	mg/l	1.5	2.2	1.4	1.6
B	mg/l	0.0	0.1	0.0	0.0
F	mg/l	2.7	0.0	0.0	0.0
NO ₂	mg/l	0.0	0.0	0.0	0.0
NO ₃	mg/l	0.3	5.0	7.6	0.9
Cl	mg/l	1.1	916.3	135.9	1047.8
SO ₄	mg/l	40.9	1181.7	164.2	787.5
PO ₄	mg/l	1.7	0.0	23.9	0.0
CO ₃	mg/l	150.0	30.0	1176.0	87.0
HCO ₃	mg/l	85.4	48.8	67.1	30.5

Appendix A4. Water leachate chemical analysis of coarse coal ash sintered residues (60 minutes) for the brine, lime, brine + lime treatment (29% brine, 3.2% CaO)

Parameter		GA	GA + Brine	GA + CaO	GA + CaO + Brine
pH		10.7	11.0	11.5	11.4
SAR		0.1	2.7	0.1	2.3
EC	μS/cm	1860.0	3780.0	7630.0	3220.0
TDS	mg/l	719.7	3352.7	2791.5	2875.7
Na	mg/l	8.5	282.4	8.4	249.2
K	mg/l	5.3	29.9	1.6	37.3
Ca	mg/l	378.0	857.4	1467.3	887.5
Mg	mg/l	1.5	1.9	1.5	1.6
B	mg/l	0.0	0.1	0.0	0.1
F	mg/l	3.8	0.0	0.0	4.5
NO ₂	mg/l	0.0	0.0	0.0	0.0
NO ₃	mg/l	0.0	0.7	5.0	0.7
Cl	mg/l	2.1	892.6	23.0	932.9
SO ₄	mg/l	48.4	1230.6	31.0	667.8
PO ₄	mg/l	2.0	2.8	29.4	1.3
CO ₃	mg/l	252.0	33.0	1191.0	75.0
HCO ₃	mg/l	36.6	42.7	67.1	36.6