

## INVESTIGATING THE REMOVAL OF DISSOLVED INORGANIC ELEMENTS FROM A GAS CONDENSATE STREAM AT SECUNDA SASOL SYNFUELS USING ALUMINA IN CONTINUOUS MODE

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### ABSTRACT

Raw gas condensate emanating from the Sasol Synfuels gasification plant contains trace amounts of silicon, iron, calcium and aluminium which can precipitate from the gas condensate in the form of scale in pipes and heat exchangers either during:

- Gas condensate transportation from the gasification process to the Phenosolvan plant or
- During the liquid-liquid extraction process at the Phenosolvan plant.

Preliminary experimental results showed that, within the experimental conditions investigated, a packed bed column with alumina reduced the silicon concentration in the gas condensate and with an increase in the residence time in the column; a higher overall removal of silicon is achieved as substantiated by removals of 66.4% and 19.1% for 60 minute and 6 minute residence times respectively. The system showed a positive and neutral effectiveness with regards to the removal of calcium and iron respectively. Conversely, the aluminium concentration in the gas condensate initially increased when passed through the alumina filled column and then stabilised at aluminium concentrations of 16.0ppm and 12.0ppm for residence times of 60 minutes and 6 minutes respectively. No further significant increases in the aluminium concentration in the gas condensate were observed subsequent to passing a cumulative volume of 6 litres of gas condensate through the column up to a total treated volume of 20 litres. Analysis of the scanning electron micrographs of the alumina before and after treatment showed strong evidence that the aluminium and silicon species in the gas condensate had reacted with the alumina samples suggesting a surface reaction. In conclusion, alumina exhibits good dissolved inorganic elements removal characteristics that have the potential to reduce the fouling of aluminium silicate in the heat exchangers and tubes during the liquid-liquid extraction process at the Phenosolvan plant

### 1. INTRODUCTION

Raw gas condensate (GC) emanating from the Sasol Synfuels gasification plant contains trace amounts of silicon, iron, calcium and aluminium which can precipitate from the

gas condensate as scale in pipes and heat exchanger plates either during:

- a. GC transportation from gasification to the Phenosolvan plant or
- b. During the liquid-liquid extraction process at the Phenosolvan plant.

Phenol is the major high value component of the GC and is selectively recovered by diisopropyl ether (DIPE) in a liquid-liquid extraction process. Preceding the extraction process, carbon dioxide is bubbled through the GC in order to reduce its pH from 9.5 to 8.6. In the extraction process, diisopropyl ether exhibits a high degree of selectivity for phenol against the metal ions from the GC. The recovery of phenol with DIPE takes place at 35 - 40°C and a pH of 8.6. Characterisation studies using ion chromatography (IC) and thermodynamic model identified metal ions such as aluminium, calcium, iron, magnesium, silicon and potassium in the GC samples analysed during this study. Major anions detected in the liquid samples were sulphate, fluoride, chloride, bicarbonate, carbonate and nitrate (Matjie and Engelbrecht, 2007). It was proposed that aluminium hydroxide with trace amounts of Fe, P, K and Ca, as well as the trace amount of K-Al-silicate present in the precipitate were most likely responsible for the formation of the scaling precipitate during the extraction of phenols from the GC (Matjie and Engelbrecht, 2007). This hypothesis was, in part, confirmed by an aqueous thermodynamic modelling study (Lewis, 2005). In that study, the dominant precipitates were found to be Al(OH)<sub>3</sub>, CaCO<sub>3</sub> and Fe(OH)<sub>3</sub> between pH 8 and pH 10 and a temperature of 40°C (Fig. 1).

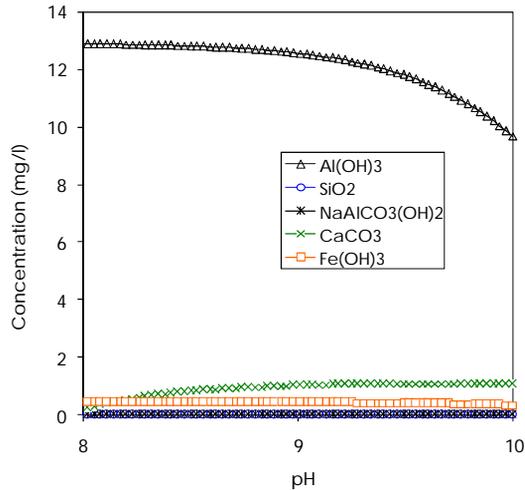


Fig. 1: Concentrations of dominant solids for the GC stream in the pH range 8 to 10

Subsequent to this initial thermodynamic modelling study, a feasibility study investigating the use of alumina, silica gel and anthracite under batch operating conditions for the selective removal of the scaling cationic species from the GC was carried out (Lewis and Nathoo, 2006). The batch adsorption isotherms were obtained by measuring the removal of the scaling species from 40ml of GC with increased dosages of alumina, silica gel and anthracite ranging from 0 – 300g/L of GC. Based on the results of these studies, it was found that alumina exhibited the best contaminant removal characteristics. The objective of this study was to evaluate specific critical operating parameters aimed at maximising the removal scaling species in an alumina filled packed bed column operated in continuous mode.

## 2. EXPERIMENTAL EQUIPMENT AND METHODS

The continuous mode adsorption studies using alumina were performed in a jacketed glass column. Fig. 2 represents a schematic diagram of the column set up, which had an internal diameter of 76mm and a height of 700mm.

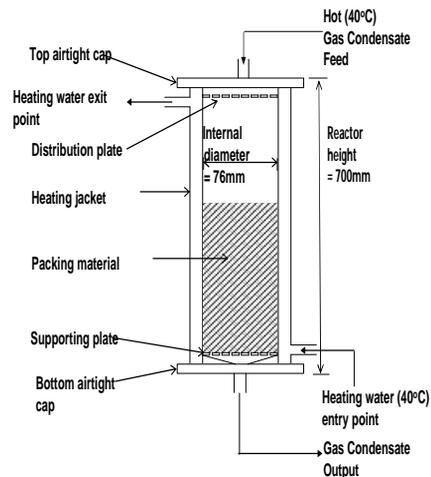


Fig. 2: Schematic diagram of the packed bed column used in the continuous mode experiments

For the experiments being reported, unless otherwise stated, the column was packed with the 200g of Selexsorb<sup>®</sup> alumina (spherical and extrudate materials produced by BASF Chemical Company, Germany). 860g of a commercial Filtrilur<sup>®</sup>, used as a sand filter material was packed above the alumina. The feed GC was preheated and maintained in feed tank at a temperature ensuring 40°C during feeding. The GC was then pumped into the column at a predetermined fixed flow rate using a Matson Marlow 505S peristaltic pump. Heated water from a temperature controlled water bath was constantly circulated through the jacket of the glass column so as to keep the adsorption temperature within the column at a constant temperature of 40°C. The exiting GC stream from the column was connected to a Watson Marlow 505S peristaltic pump ensuring sufficient back pressure to compensate for any fluctuations in the flow rate resulting from the hydraulic head pressure. This was to ensure that the overall flow rate and consequently the residence time in the column was maintained at required residence times. Two residence times were investigated i.e. 6 minutes (a predetermined residence time which was based on the current GC residence time in the sand filter beds at the Phenosolvan plant) and 60 minutes for the experiments aimed at investigating the benefits of a longer residence time. For each experimental run a total volume of 20L of GC was treated. An initial sample of the feed stream and samples of the exiting stream were removed during the course of the experiment for analysis at predetermined cumulative volumes of GC passing through the column. The samples were filtered through a 0.45µm Millipore cellulose acetate filter and the filtrate analysed for Al, total iron (Fe<sub>T</sub>), Si and Ca concentrations using Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES).

The percentage removal of the individual species was calculated as follows:

$$\% \text{ removal of species} = \left( \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100 \right)$$

where  $C_{\text{initial}}$  and  $C_{\text{final}}$  are the initial and final concentrations of the individual species respectively.

Standard epoxy resin polished sections were made of samples of the unused Selexsorb<sup>®</sup> extrudate alumina, used Selexsorb<sup>®</sup> extrudate alumina, Selexsorb<sup>®</sup> spherical alumina, used Selexsorb<sup>®</sup> spherical alumina and commercial Filtrilur<sup>®</sup> for analysis using scanning electron microscopy utilising backscatter electron (BSE) imaging for an atomic weight contrast image where the grey level variation is a reflection of the atomic weight of the sample and energy dispersive spectrometry (EDS) for determining the elemental proportions.

### 3. RESULTS AND DISCUSSION

#### 3.1 Dissolved inorganic elements removal profiles with increasing cumulative volumes of GC treated for a residence time of 6 minutes

The relationship between the initial and final concentrations of the various scaling as a function of increasing cumulative volumes of the GC passing through the column are presented in Figs. 3 to 6 for a residence time of 6 minutes.

In each case, the top graph represents the actual concentration in ppm of the dissolved inorganic element exiting the column as a function of the cumulative volume of GC treated, with a line indicating the initial concentration of that particular species in the feed tank for comparison. The bottom graph represents the percentage removals of the respective species as a function of the cumulative volume of GC treated. A positive percentage removal indicates that the contaminant was removed from the GC by the alumina, whilst a negative percentage removal indicates that the species was leached into solution from the alumina.

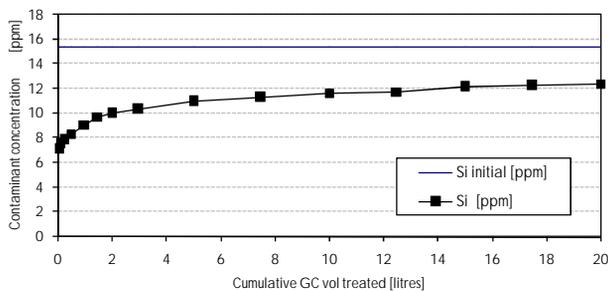


Fig. 3a: Si concentration in GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 6 minutes)

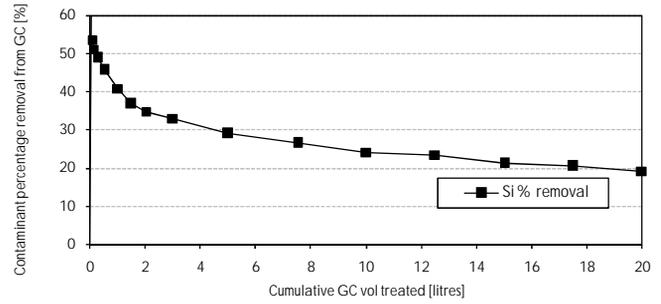


Fig. 3b: Percentage Si removed from GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 6 minutes)

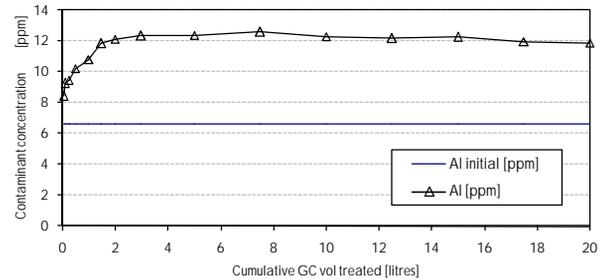


Fig. 4a: Al concentration in GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 6 minutes)

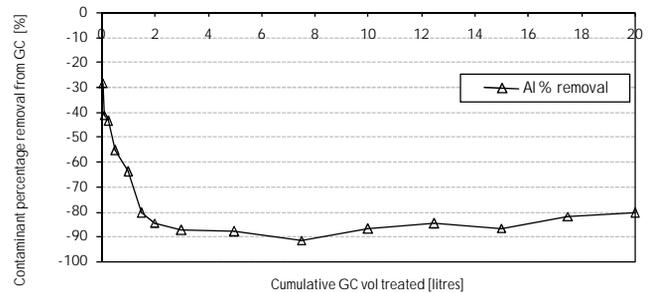


Fig. 4b: Percentage Al removed from GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 6 minutes)

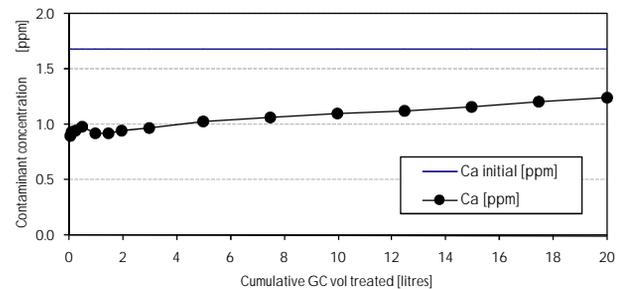


Fig. 5a: Ca concentration in GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 6 minutes)

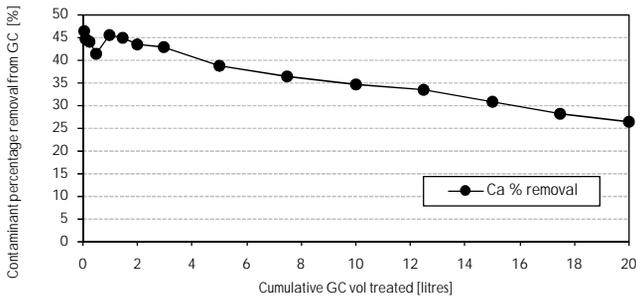


Fig. 5b: Percentage Ca removed from GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 6 minutes)

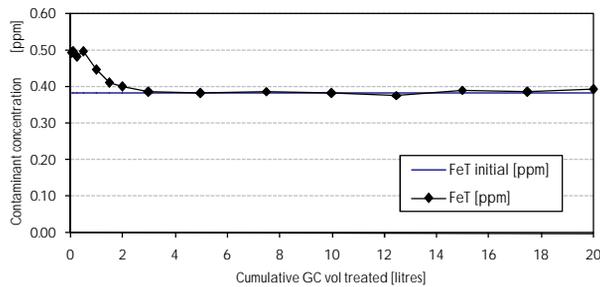


Fig. 6a: Fe<sub>T</sub> concentration in GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 6 minutes)

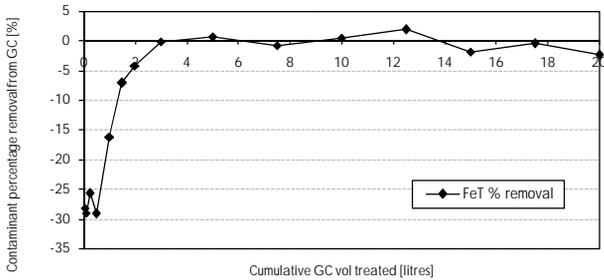


Fig. 6b: Percentage Fe<sub>T</sub> removed from GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 6 minutes)

The preliminary analysis of the results for the continuous mode operation for a residence time of 6 minutes in a packed column with 200g of alumina shows that:

1. **Si removal:** When operated in continuous mode, the system is capable of reducing the initial 15.3ppm Si concentration in the GC feed to 7.1ppm, a percentage removal of 54% (Fig. 3a and Fig. 3b). This removal efficiency progressively dropped off with an increase in the cumulative volume of GC treated, approaching steady state at a percentage removal of 19.1 % (exiting Si concentration of 12.4ppm) after treating 20L of GC. Importantly, even after treating a total GC volume of 20L, the Si percentage removal for a alumina dosage of 200g did not reach the breakthrough volume for a system in which the breakthrough volume is defined as

the maximum cumulative volume of GC that can be treated before the concentration of Si in the exiting stream equals that in the feed stream i.e. the alumina has no purification effect on the feed stream.

2. **Al removal:** As is consistent with previous research findings (Lewis and Nathoo, 2006), the Al species appear to be leached into the GC solution from the alumina. However, for an initial Al feed stream concentration of 6.6ppm, the negative percentage removal trend rapidly approaches a steady state value after treating 2L of GC. This indicates that the percentage removal levels off between -80% to -90% (exiting Al concentration of ~12.0ppm) after treating 2L of GC, despite an increase in the cumulative volume of GC treated (Fig. 4a and Fig. 4b).
3. **Ca and Fe<sub>T</sub> removals:** The concentrations of the Ca (1.7ppm) and Fe<sub>T</sub> (0.4ppm) are low to start with in the GC feed stream remain fairly unchanged relative to changes in the Al and Si species.

### 3.2 Dissolved inorganic elements removal profiles with increasing cumulative volumes of GC treated for a residence time of 60 minutes

This investigation was carried out to establish the benefits of a significant increase in the residence time within the column on the removal of scaling species. The initial and final concentrations of species in the GC after exiting the column for increasing cumulative volumes of the GC passing through the column are presented in Fig. 7 to 10 for a residence time of 60 minutes.

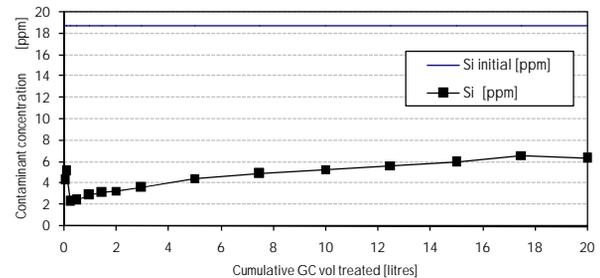


Fig. 7a: Si concentration in GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 60 minutes)

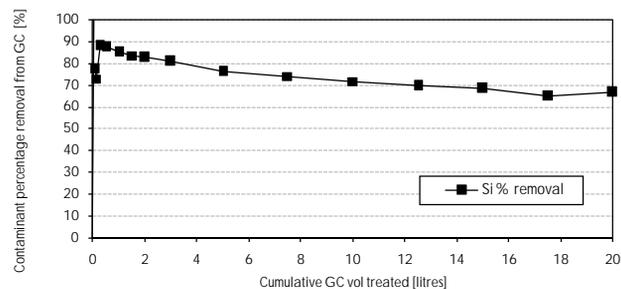


Fig. 7b: Percentage Si removed from GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 60 minutes)

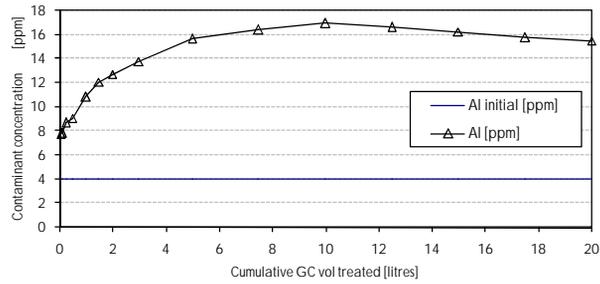


Fig. 8a: Al concentration in GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 60 minutes)

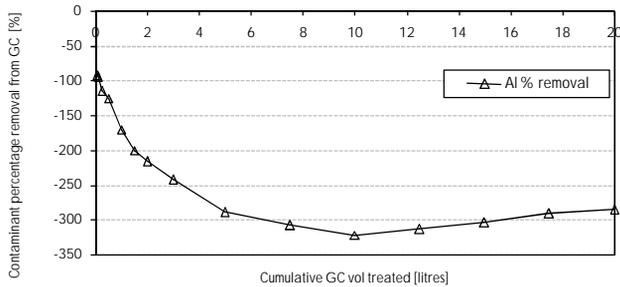


Fig. 8b: Percentage Al removed from GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 60 minutes)

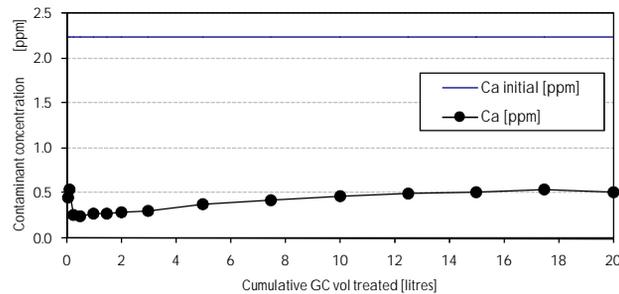


Fig. 9a: Ca concentration in GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 60 minutes)

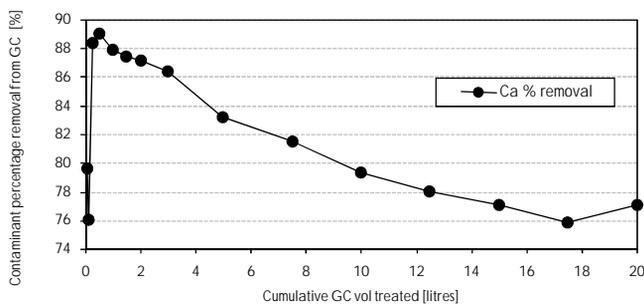


Fig. 9b: Percentage Ca removed from GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 60 minutes)

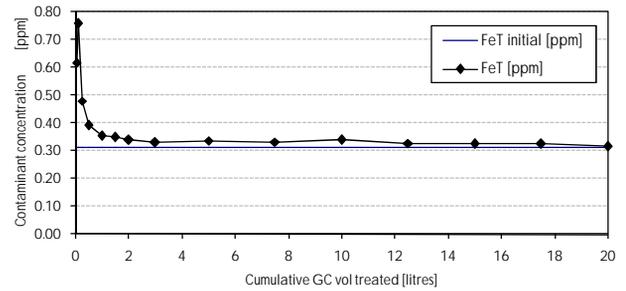


Fig. 10a:  $Fe_T$  concentration in GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 60 minutes)

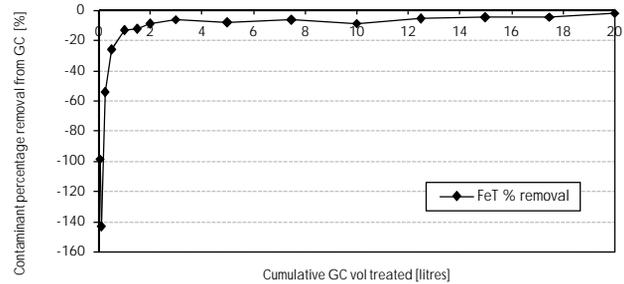


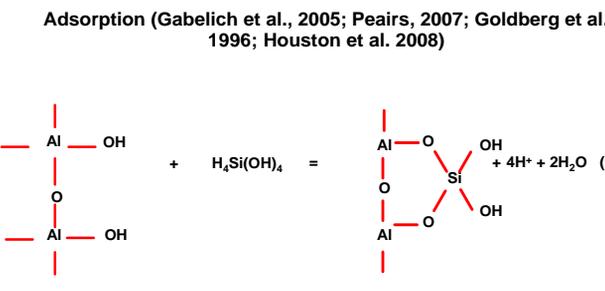
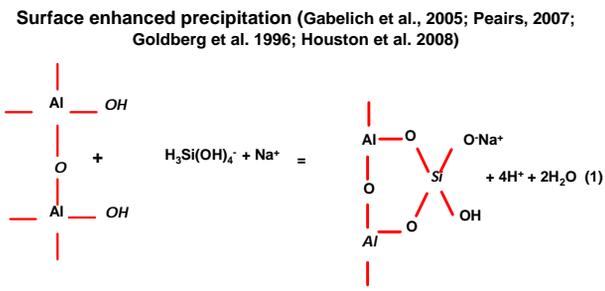
Fig. 10b: Percentage  $Fe_T$  removed from GC with increasing volumes of GC treated (Mass of alumina: 200g; Residence Time: 60 minutes)

The analysis of the results for the continuous operating mode for a residence time of 60 minutes in the packed column with 200g of alumina shows that:

1. **Si removal:** The system is capable of reducing the initial 18.8ppm Si concentration in the GC feed to 2.3ppm, a percentage removal of 87.7% after treating 0.25L of GC (Fig. 7a and Fig. 7b). This removal efficiency progressively dropped off with an increase in the cumulative volume of GC treated, approaching steady state at a percentage removal of 66.4% (exiting Si concentration of 6.3ppm) after treating 20L of GC. Importantly, even after treating a total GC volume of 20L, the Si percentage removal for an alumina dosage of 200g did not reach the breakthrough volume.
2. **Al removal:** Consistent with the findings from the preceding phases of this research project (Lewis and Nathoo, 2006), as well as the results for the 6 minute experiments; Al species appear to be leached into the GC solution from the alumina. For a 60 minutes residence time and an initial Al feed stream concentration of 4.0ppm, the negative percentage removal trend approaches a steady state value of between -300% to -320% (exiting Al concentration of ~16.0ppm) after treating 6l of GC, without any further significant increase despite an increase in the cumulative volume of GC treated (Fig. 8a and Fig. 8b).
3. **Ca and  $Fe_T$  removals:** As can be expected, the concentrations of the Ca (2.3ppm) and  $Fe_T$

(0.3ppm) are low to start with in the GC feed stream remain fairly unchanged relative to changes in the Al and Si species.

4. **Chemical reactions between the dissolved Si and Ca and the  $\gamma$ -alumina pellets:** The significant removal of the dissolved Si and Ca (Fig.3a, Fig. 3b, Fig. 7a, Fig. 7b, Fig. 5a, Fig. 5b, Fig. 9a and Fig. 9b) can be attributed to the surface precipitation and adsorption of both Si and Ca species from gas condensate on the hydroxylated or hydrated  $\gamma$ -alumina [Gabelich et al. 2005; Peairs, 2007]. The following possible reactions occur at alkaline pH values during precipitation and adsorption of Si and Ca species from GC:



**3.3 Establishing the GC breakthrough volumes for a fixed mass of alumina for a residence time of 6 minutes**

This experiment was carried out to obtain an indication of the total volume of GC that could be treated for a fixed mass of alumina before reaching the breakthrough volume. Hence

From the previous results, it was apparent that the total cumulative volume of GC treated would need to be

significantly higher than 20L to obtain the breakthrough volume. However, due to the limited volumes of GC available for these experiments, the total mass of alumina packed into the column and the corresponding mass of commercial filtrilur was reduced to a third of the normal 200g of alumina and 860g of commercial filtrilur. Thus, a mass of 66.7g of alumina was used to treat 20L, which is equivalent to treating to 60L of GC with 200g of alumina.

The relationship between the initial concentration of each individual dissolved inorganic element in the GC feed tank and final concentrations in the GC exiting the column for increasing cumulative volumes of the GC passing through the column, are presented in Fig. 11a, Fig. 11b, Fig. 12a, Fig. 12b, for the Si, and Al respectively for a residence time of 6 minutes. The cumulative volume of GC has been normalised to a per-kg-of-alumina unit in order to obtain an operational value for the breakthrough volume that can be directly used on the plant. The outlier at a GC cumulative volume of 30L/kg alumina in Fig. 11a, Fig. 11b, Fig. 12a and Fig. 12b, is as a result of the feed pump having to be momentarily shut down and restarted due to a minor unexpected experimental anomaly.

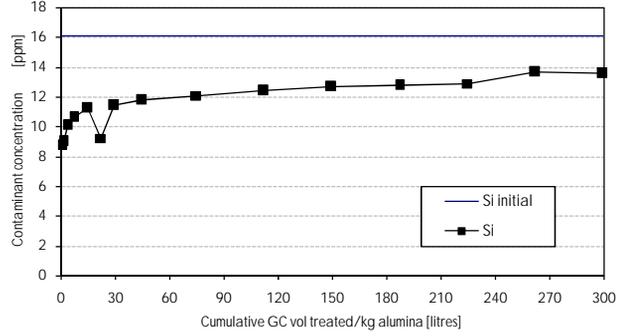


Fig. 11a: Si concentration in GC with increasing volumes of GC treated (Mass of alumina: 66.7g; Residence Time: 6 minutes)

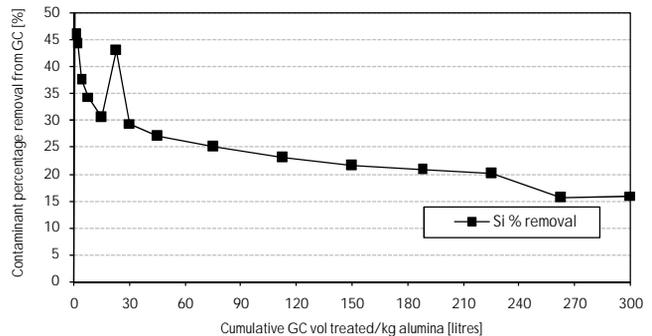


Fig. 11b: Percentage Si removed from GC with increasing volumes of GC treated (Mass of alumina: 66.7g; Residence Time: 6 minutes)

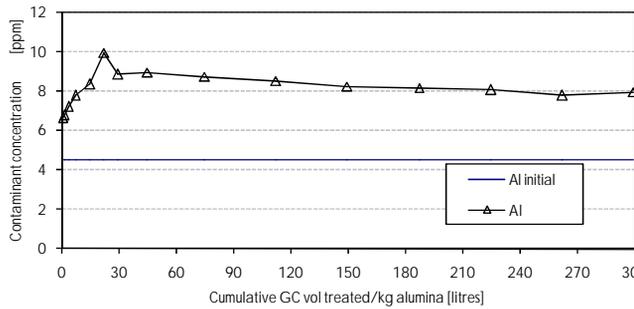


Fig. 12a: Al concentration in GC with increasing volumes of GC treated (Mass of alumina: 66.7g; Residence Time: 6 minutes)

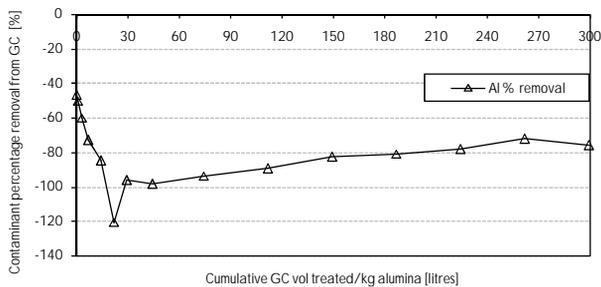


Fig. 12b: Percentage Al removed from GC with increasing volumes of GC treated (Mass of alumina: 66.7g; Residence Time: 6 minutes)

The analysis of the results for the continuous operating mode for a residence time of 6 minutes in the packed column with 66.7g of alumina shows that:

1. **Si removal:** As expected, the system shows a similar removal trend to that in Fig. 3a and Fig. 3b. The results show that under the experimental conditions investigated, after treating 300L of GC per kg of alumina, the Si concentration is still below that of the incoming feed stream. Hence, the breakthrough volume has not yet been achieved in accordance with the definition above and suggests that the alumina is still not fully loaded (Fig. 11a and Fig. 11b).
2. **Al removal:** Consistent with the findings from the preceding phases of this research project (Lewis and Nathoo, 2006), as well as, the results for the 6 minutes and 60 minutes experiments; Al species appear to be leached into the GC solution from the alumina (Fig. 12a and Fig. 12b). This levels off at a value of approximately 8.0ppm Al, which is 3.5ppm above the incoming Al concentration for a total cumulative volume of 300L of GC/kg alumina.

### 3.4 SEM characterisation of the used and unused alumina and used commercial Filtrilur®

An X-ray spectrum (SEM-EDS analysis) was acquired for each sample at comparatively low magnification (<100X). This semi-quantitative technique highlights the

relative variations in elemental proportions (Table 1). Based on results shown in Table 1 there is no notable concentration of inorganic elements from the alumina dissolved in the GC during the removal of contaminants from this condensate.

Table 1: Semi-quantitative elemental proportions

Elemental proportions (%)	Unused extrudate alumina	Used extrudate alumina	Unused spherical alumina	Used Spherical alumina
Magnification	66X	92X	44X	82X
O	51.75	48.75	54.39	54.39
Al	47.17	49.68	44.04	44.06
Si	0.33	0.53	0.54	0.46
P	0.28	0.20	0.42	0.33
S		0.13		
Cl	0.22	0.36	0.28	0.26
Ca	0.11	0.19	0.30	0.28
Ti		0.14		
Total	99.86	99.98	99.97	99.78

The dark edges of the unused alumina have elevated concentrations of carbon and chlorine (Fig. 13 and Fig.14). It is probable that the epoxy resin has reacted with the alumina beads. The Si and Al concentrations have increased along the edge relative to the centre (Fig. 15 and Fig. 16). This is noted in the activated Selexsorb® spherical alumina and extrudate alumina beads exposed to the GC. These variations were not evident in the fresh alumina samples. There is no obvious surface contamination on the alumina and the commercial Filtrilur® by organically bound sulphur (<1.5 mass-%) which is present in commercial Filtrilur®. A few commercial Filtrilur® particles were in the used alumina sample. Cl (<2 mass-%) is a contaminant in the fresh alumina particles. Energy dispersive spectrometry was used to determine the elemental proportions in the new and used alumina. Trace proportions (<0.2 mass-%) of Si, S, K, Ca and Ti were detected in the used alumina. It is possible that the sulphur could be derived from the commercial Filtrilur®. No elements other than S, C and O were detected in the used commercial Filtrilur®. The proportions of S, C and O were similar in the raw and used commercial Filtrilur®. A characteristic darker rim is notable in the samples examined (Fig. 13).

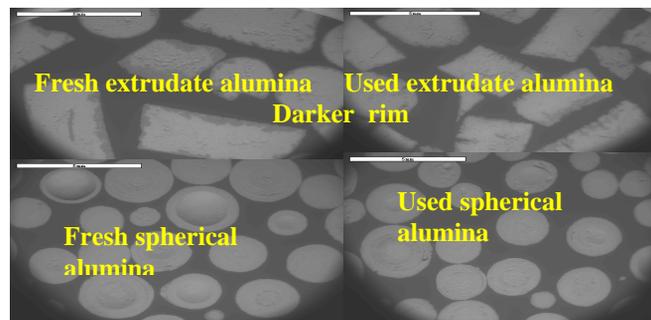


Fig. 13: Backscattered electron images of fresh extrudate alumina, used extrudate alumina, fresh spherical alumina and used spherical alumina analysed. Scale bar is 5mm

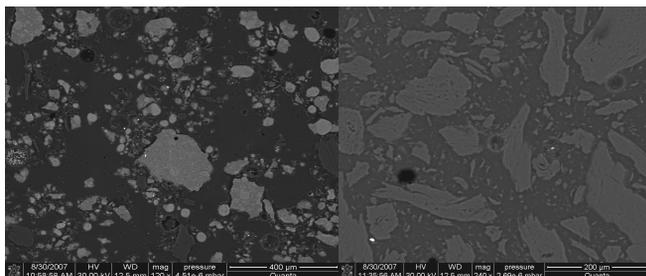


Fig. 14: Backscattered electron images of used extrudate alumina and commercial Filtrilur® (right)

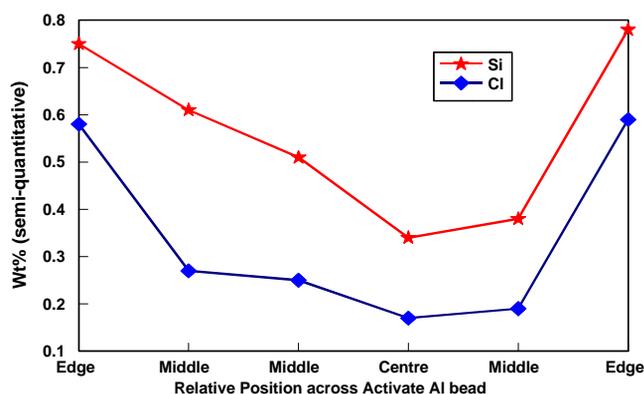


Fig. 15: Relative SiO<sub>2</sub> and Cl concentrations across spherical alumina (activate Al bead) exposed to the gas condensate.

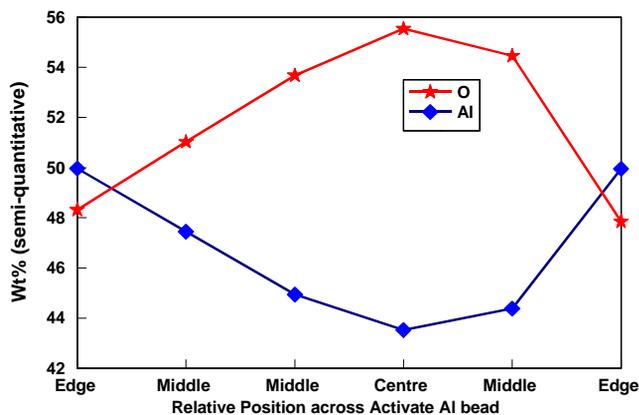


Fig. 16: Variation in Al and O concentrations across spherical alumina (activate Al bead) exposed to the gas condensate

The results of the SEM analysis of the used and unused alumina samples show strong evidence of Si reacting with the alumina pointing to a surface reaction.

## 5. CONCLUSIONS

Based on the results of these studies, it was found that, within the experimental conditions investigated, alumina exhibits good dissolved inorganic elements removal characteristics that have the potential to reduce the scaling potential of the GC in pipes and heat exchanger plates. When comparing the negative Al removal trends between the two residence times, the Al concentration stabilises at 16.0ppm and 12.0ppm respectively for the 60 minutes and 6

minutes residence time experiments respectively after treating 6 litres of GC without any further significant increase despite an increase in the cumulative volume of GC treated. After treating 300L of GC per kg of alumina for a residence time of 6 minutes in order to establish the breakthrough volume, the Si and Ca concentrations are still below that in the incoming feed stream. Hence, the breakthrough volume has not yet been achieved in accordance with the definition above and suggests that the alumina is still not fully loaded. From the SEM analysis of alumina before and after treatment, there is strong evidence that the Al and Si in the gas condensate has reacted with the spherical and extrudate alumina samples pointing to a surface reaction.

## 6. ACKNOWLEDGMENTS

This paper was developed from a collaborative research program between Sasol Technology Research and Development, the Crystallization and Precipitation Unit at the University of Cape Town and van Alphen Consultancy. Assistance provided by the personnel of Sasol Technology's Syngas and Coal Technologies group, Phenosolvan group, OPI group and Gas Production group is also gratefully acknowledged. Thanks are expressed to the two anonymous reviewers, whose constructive comments helped to further improve the quality of the manuscript.

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