

# The Effect of Sulphuric Acid Concentration on the Removal of Reactive Aluminium from South African Coal Fly Ash

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## ABSTRACT

Comprehensive utilization of coal fly ash has environmental relevance in addition to its industrial interest and thus can serve as a good alternative to its disposal, achieving significant economic benefits. South African coal fly ash contains considerable amounts of aluminium and silicon in the amorphous glass phase, forming the main composition of fly ash. Silicon and aluminium are primary constituents in the production of zeolites and the synthesis of mesoporous silica materials. The extraction of these elements from the fly ash glassy phase and conversion thereof into productive and environmentally friendly materials is of interest in this study.

The extraction of silicon from fly ash, the resulting formation of silicon-rich solutions, and its degree of purity would benefit from the pre-removal of aluminium from the fly ash glass matrix. For this reason, this report will focus on the removal of aluminium from the glass phase, while subsequent studies will investigate the potential of extracting silicon selectively.

Our study reports on the selective extraction of aluminium from a South African ultra-fine coal fly ash sample, using sulphuric acid as extracting reagent with minimum loss of silicon. Our results show that leaching of coal fly ash using a sulphuric acid method for aluminium extraction results in a solid residue of which the main component is silicon. This solid residue can be further processed to produce commercial-grade silicon-containing products.

An optimum aluminium extraction of 80% from the amorphous glass phase was achieved at 95°C, using a 5M sulphuric acid solution under reflux conditions for 4 hours.

## INTRODUCTION

Coal fly ash (CFA) contains considerable amounts of aluminium and silicon as main elements. The composition of CFA typically ranges between 25-30% alumina and 40-60% silica<sup>1</sup>. Converting both alumina and silica, sequestered from CFA, into productive and environmentally friendly materials is of interest in this study.

Silicon and aluminium can be used as primary constituents during production of zeolites<sup>2</sup> and the synthesis of mesoporous silica materials<sup>3-5</sup>. A number of authors have reported on the extraction of aluminium and silicon from different materials considered to be solid by-products; these range from clays to other alumina and silica bearing minerals<sup>6-11</sup>. Sulphuric acid is often the preferred leaching agent for the recovery of metals from fly ash, particularly via the direct acid leaching process<sup>12</sup>. Direct acid leaching of CFA can be advantageous during the separation process of aluminium and silicon from the CFA matrix, because silica is insoluble in acidic media solutions<sup>13</sup>. The leaching of CFA using sulphuric acid results in a silicon-rich solid residue, which can be purified to produce silica or silica-related products. Extracting silicon from CFA for the synthesis of silica products of high purity will thus depend on prior removal of aluminium and other metals from the CFA matrix<sup>14</sup>.

Aluminium from the amorphous glass phase is expected to be reactive, while aluminium present in the crystalline mullite component may not be easily leachable<sup>15</sup>. These two phases (amorphous versus crystalline) play a key role in alumina dissolution from fly ash. The crystalline mullite phase is acid-insoluble and aluminium in this phase is not easily recovered, while only the metals in the amorphous phase are dissolved and extraction of aluminium is possible via direct acid leaching in this case. The alumina in the mullite phase can be extracted by methods of indirect leaching<sup>16</sup>. Direct acid leaching requires no intervention before the leaching process. However, indirect acid leaching requires some material pre-conditioning (such as sintering a mixture of CFA and calcium sulphate, which convert alumina into an acid-soluble form) prior to leaching<sup>17</sup>. The pre-conditioning step helps to achieve modification of some chemical characteristics of the CFA alumina species in order to make it more responsive to the leaching process.

The success of aluminium extraction from coal fly ash largely depends on the selection of suitable leaching process parameters (coal fly ash particle size, leaching temperature and time, solid to liquid ratio, extracting reagent concentration, etc.) at which the extraction efficiency is optimal. Other authors have reported leaching temperature and time to be the main contributing factors influencing the extraction rate of aluminium from CFA suspended in sulphuric acid solutions<sup>18</sup>.

The purpose of this project is to selectively remove aluminium from the amorphous phase of CFA, using sulphuric acid as the leaching agent. The effects of varying acid concentration and leaching time on the extraction rate of aluminium and the amount of silicon lost during aluminium extraction were investigated.

## EXPERIMENTAL

### Starting materials and chemical reagents

A representative sample of a classified, ultrafine CFA sample was obtained from Ash Resources (Pty) Ltd's ash beneficiation site at Eskom's Lethabo Thermal Power station. This commercial-grade CFA is air-classified on site and is specified to have a mean particle size between 3.9 and 5.0  $\mu\text{m}$ , with more than 90% of the volume distribution of its particles having a diameter smaller than 11  $\mu\text{m}$ . The CFA samples were first sub-divided using a rotary splitter to obtain representative sub-samples. Deionised water and analytical grade sulphuric acid (98% w/w), obtained from Merck, were used in the experiments.

### Analytical methods

The elemental composition of the CFA sample was determined by X-ray fluorescence (XRF) fused bead analysis while the mineralogy of the CFA sample was determined by X-ray diffraction (XRD). The particle size distribution of the sample was obtained by laser diffraction. Additional details regarding the methods and analytical techniques used for the detailed characterisation of the sample are reported elsewhere (van der Merwe et al<sup>19</sup>). The concentrations of dissolved aluminium, silicon and other elements were determined by ICP-OES.

### Alumina extraction

10g of CFA was dispersed in 100 ml of water (control) or  $\text{H}_2\text{SO}_4$  of varying concentrations (1; 3; 5; 8 and 10 M). The suspensions were heated to  $95 \pm 3$  °C in a silicon oil bath, while stirring constantly using a magnetic stirrer. The reaction mixture was refluxed for different durations ranging between 30 and 480 minutes. At completion of the experiments, the suspensions were centrifuged, the supernatants were stored at 4 °C before being analysed using ICP, and the undissolved solids were rinsed thoroughly with deionised water and dried at 60 °C up to constant weight, before being characterized by XRD.

## RESULTS AND DISCUSSIONS

The results obtained for characterization and leaching of CFA in sulphuric acid are summarized in Figures 1-3 and Table 1.

### Characterization of the fly ash sample

A detailed surface and bulk characterization of the CFA sample used in this study was performed and reported elsewhere<sup>19</sup>. Briefly, CFA contained mainly  $\text{Al}_2\text{O}_3$  (33%),  $\text{SiO}_2$  (51%),  $\text{CaO}$  (5%),  $\text{Fe}_2\text{O}_3$  (3%),  $\text{TiO}_2$  (2%) and  $\text{MgO}$  (1%). Its mineralogy predominantly consisted of an amorphous alumina silica glass phase (64.2%), and two crystalline phases; mullite (28.5%) and quartz (7.2%).

### Extraction of Aluminium from fly ash

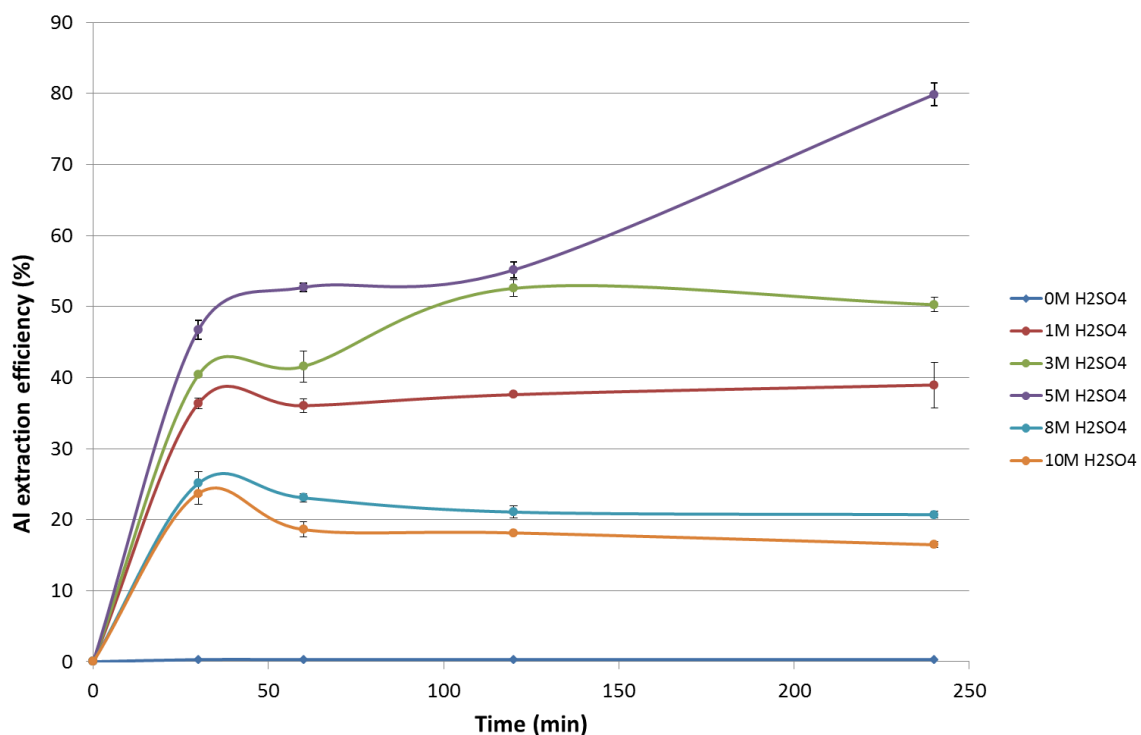
Table 1 shows the results of the extraction efficiency of silicon and aluminium from the CFA sample, performed at a low sulphuric acid concentration (1.0 M).

**Table 1. Effect of reaction time on Si and Al extraction efficiency from fly ash at low H<sub>2</sub>SO<sub>4</sub> concentration (1M)**

Time (min)	Total Si extraction (%)	Total Al extraction (%)	Al extraction from glass phase (%)
30	8.3	14.2	36.4
60	7.7	14.1	36.0
120	7.3	14.7	37.6
240	6.7	15.2	38.7

It was apparent that under these experimental conditions silicon and aluminium were extracted simultaneously. About 8% of silicon was extracted after 30 minutes, with no further extraction being observed with increasing reaction time, while the total extraction efficiency of aluminium was around 14%; corresponding to 37% extraction from the amorphous phase. Co-dissolution of silicon and aluminium under weak acidic conditions was already reported elsewhere<sup>20,21</sup>. The reason for the low extraction rate of aluminium under these conditions can be ascribed to a low proton activity<sup>22</sup>.

Figure 1 shows the extraction efficiency of aluminium from the amorphous phase, with different H<sub>2</sub>SO<sub>4</sub> concentrations as a function of time.



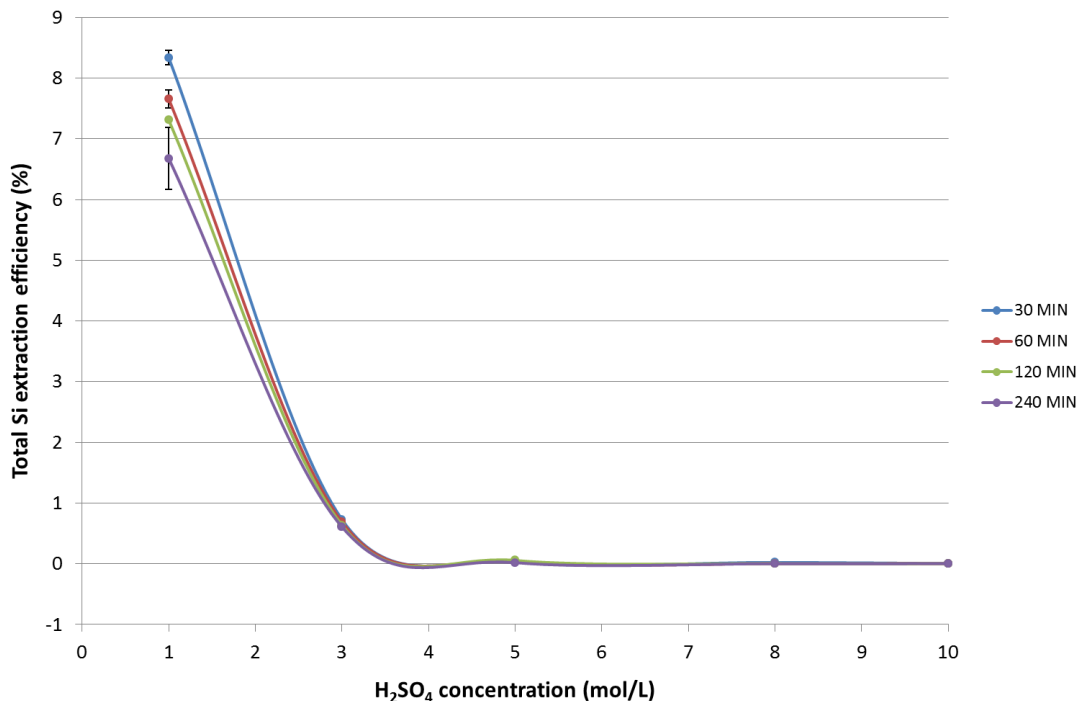
**Figure. 1 Extraction of aluminium from the glass phase of CFA as a function of H<sub>2</sub>SO<sub>4</sub> concentration and reaction time**

An increase in the amount of aluminium being extracted with increase in leaching time was observed for leaching experiments performed in 3 M and 5 M H<sub>2</sub>SO<sub>4</sub>, while the aluminium extraction rate levels off after 60 minutes for leaching experiments performed in 8 M and 10 M H<sub>2</sub>SO<sub>4</sub>. Decreased amounts of aluminium were extracted

using 8 M and 10 M  $H_2SO_4$  as leachates, and almost no aluminium was extracted from leaching in deionized water. The most favorable conditions for aluminium extraction (80% from the amorphous phase) could be achieved using 5 M sulphuric acid and a leaching time of 240 minutes. Lai-shi et al<sup>23</sup> also indicated that the extraction rate of aluminium increases with leaching time under the same temperature conditions, the same volume ratio of acid to ash and the same stirring speed.

The results in Figure 1 also indicate that an increase in proton activity (i.e. increase in acidity) results in higher dissolution of aluminium from the amorphous phase up to a sulphuric acid concentration of 5 M. Increasing the sulphuric acid concentration beyond 5 M yielded lower concentrations of dissolved aluminium, possibly due to the formation of an aluminium sulphate precipitate at the surface of CFA<sup>24</sup>. Increasing the acid concentrations increases the hydronium ions, which enhances the extraction rates of aluminium. On the other hand, the increase in the concentration of sulphate and dissolved aluminum ions intensifies the formation of aluminum sulphate, which hinders mass transfer across the ash particle. This effect is seen for sulphuric acid concentrations between 8 M and 10 M.

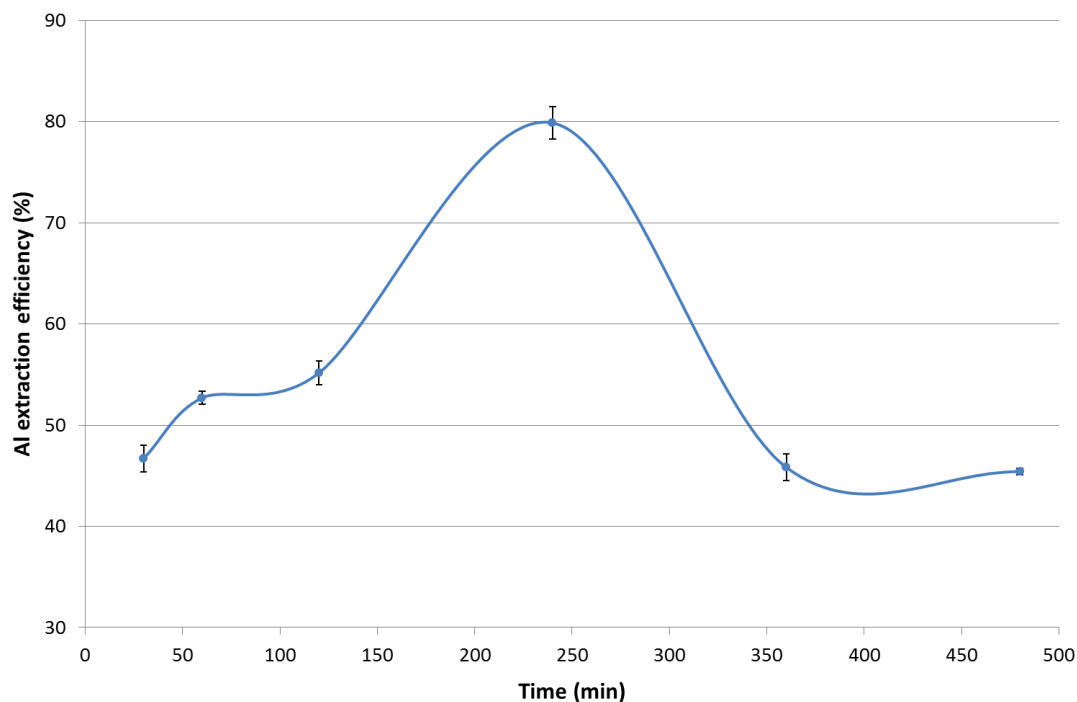
Figure 2 shows the extent of silicon extraction for experiments performed under varying conditions of sulphuric acid concentration and extraction time. Our results indicate that increasing the sulphuric acid concentration up to 5M and leaching time to 240min result not only in improved amounts of aluminium being extracted from CFA, but also in an improved amount of silicon being retained in the undissolved residue.



**Figure. 2 Total extraction efficiency of silicon as a function of  $H_2SO_4$  concentration (reaction temperature 95 °C) between 30 and 240 min**

Increasing the sulphuric acid concentration beyond 3M resulted in a decrease in the amount of silicon extracted from CFA. This can be attributed to the low solubility of silica under strong acid conditions.

Figure 3 shows the effect of increased leaching time on the extraction of aluminium from the amorphous phase using 5 M of sulphuric acid as leachate. By increasing the leaching time beyond 240 minutes under the same experimental conditions, a dramatic drop in the amount of aluminium extracted from the amorphous phase is observed. This result can be attributed to the fact that aluminium from CFA is no longer available for extraction, possibly due to precipitated aluminium sulphate that may form a layer on the surface of fly ash particles, and this encapsulates the unreacted core. Therefore the only available aluminium is that which is in solution; which can further react with excess sulphuric acid to increase the amount of precipitated aluminium sulphate, reducing the amount of aluminium in solution.



**Figure. 3 Extraction of Aluminium from the amorphous phase in 5M H<sub>2</sub>SO<sub>4</sub>**

## CONCLUSIONS

Leaching of CFA in low sulphuric acid concentrations (1M) resulted in simultaneous extraction of silicon and aluminium. Under these conditions, total extraction efficiency of 8% (silicon) and 14% (aluminium) was obtained. Simultaneous extraction of these elements is unfavourable for the purpose of this project. Increasing the sulphuric acid concentration beyond 3M resulted in increased amounts of silicon retained in the solid residue, and increased amounts of aluminium being extracted from the amorphous phase of CFA. Optimum results were obtained using 5 M sulphuric acid as leachate, and a leaching time of 240 minutes. By increasing the leaching time beyond 240 minutes using 5 M sulphuric acid, a dramatic decrease in the amount of aluminium being extracted from CFA was observed.

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