

# Extraction of Aluminum and other Strategic Metals from Coal Fly Ash using a Novel Process and Low-cost Recoverable Reagent

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## ABSTRACT

Aluminum extraction from coal fly ash is generally performed using metallurgical methods such as strong acid leaching and soda-lime sintering. In this study, aluminum was extracted using a novel roasting process with a low-cost recoverable reagent (ammonium sulfate;  $(\text{NH}_4)_2\text{SO}_4$ ) combined to aqueous leaching. The results showed that the procedure could be successfully applied to recover aluminum and other strategic metals (e.g. vanadium) from their amorphous silicate matrix. The percentage recovery from the amorphous phase ranged from over 95% for aluminum to over 75% for vanadium. The recovery of the metals depended on the solid-solid ratio and the roasting temperature. In addition to making use of a low-cost and widely-available, recoverable reagent, this process yields a significant amount of aluminum-depleted residue rich in silica, which could be used as raw material for  $\text{SiO}_2$  recovery.

## INTRODUCTION

Fly ash is considered as a potential source of aluminum and other strategic metals. Aluminum extraction from coal fly ash is generally performed using metallurgical methods such as strong acid leaching and soda-lime sintering. Although many studies were already performed in the 1980s, aluminum extraction remains an area of strong interest, and the range of methods available has recently been the subject of a detailed review<sup>1</sup>. However, many of these methods are unlikely to be adopted at commercial scale in South Africa.

This study investigates the potential of using ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$ , as a chemical activator under thermal conditions to extract aluminum from the glass phase of coal fly ash (CFA), in combination with an aqueous leaching step where the formed aluminum-based salts can be solubilized for further processing.

## **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 ammonium sulphate  $((\text{NH}_4)_2\text{SO}_4)$  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>4</sup>). Field emission scanning electron microscope (FESEM) was used under dry high-vacuum condition to observe differences in morphology of the CFA particles before and after treatment.

The concentrations of dissolved aluminum, silicon and other elements were determined by ICP-OES.

### **Extraction of aluminum**

The first step of the staged process involved the activation of CFA by thermochemical treatment using  $(\text{NH}_4)_2\text{SO}_4$  as an activating agent. CFA and  $(\text{NH}_4)_2\text{SO}_4$  salt were thoroughly mixed at two mass ratios (2:3 and 2:6) in a quartz crucible. The mixtures were subsequently inserted in a static muffle furnace operating at different reaction temperatures (400, 500 and 600  $^\circ\text{C}$ ) for 1h. The products of the reactions, which either had an appearance of sintered solid or were free-flowing powders (depending on the reaction temperature) were then subjected to a leaching procedure for Al extraction. Thermochemically-treated CFA was analysed by XRD.

Chemical extraction of Al and other value-added elements from untreated and thermochemically-activated CFA was investigated in ultrapure water (3g/300ml) at 22  $^\circ\text{C}$ . The pH, electrical conductivity and temperature of the suspension were logged using a multiparameter logger at 30 s intervals to collect time-series data on the dynamics of the system. The reaction was terminated when the pH and electrical conductivity remained unchanged for 10–15 min. At completion of the dissolution experiment, the leachant was filtered under reduced pressure. The concentrations of dissolved Al and other elements were determined by ICP-MS and the composition of the non-dissolved residues was determined by XRF and XRD.

## RESULTS AND DISCUSSIONS

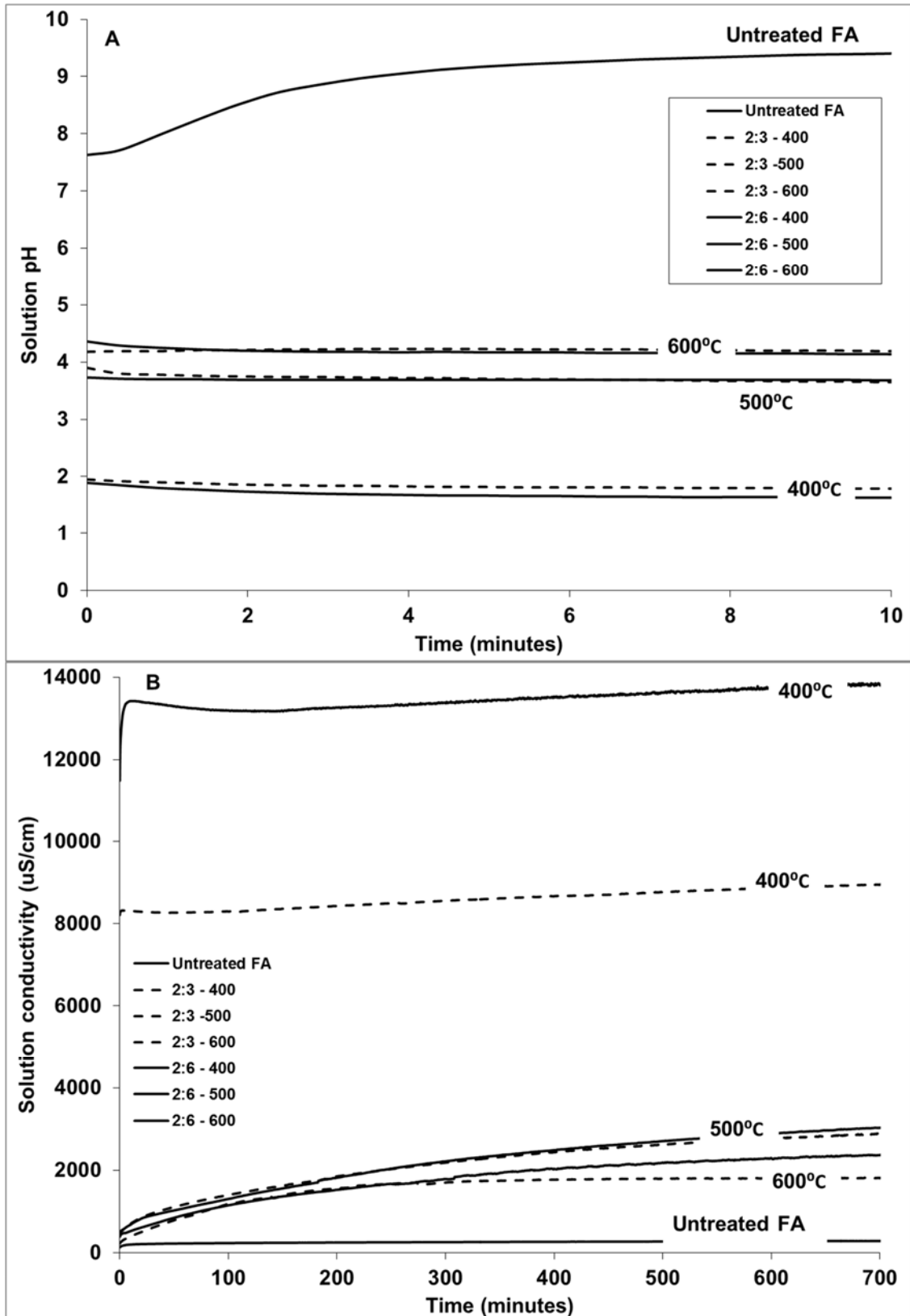
### Materials characterization

A detailed surface and bulk characterization of the classified, ultrafine Class-F coal fly ash (CFA) used in this study was performed and was reported elsewhere<sup>4</sup>. Briefly, CFA contained mainly Al<sub>2</sub>O<sub>3</sub> (33%), SiO<sub>2</sub> (51%), CaO (5%), Fe<sub>2</sub>O<sub>3</sub> (3%), TiO<sub>2</sub> (2%) and MgO (1%). Its mineralogy predominantly consisted of an amorphous alumina silica glass phase (64.2%), and two crystalline phases, i.e. mullite (28.5%) and quartz (7.2%).

### Effect of activation on aluminum extraction

The chemical extraction of Al from untreated and thermochemically-activated CFA dispersed in ultra-pure water (i.e. under uncontrolled pH conditions) was investigated by initially monitoring the profile of two solution parameters over time: pH and conductivity (Figure 1). For untreated CFA, solution pH increased rapidly before progressively plateauing and stabilizing at 9.61. This was accompanied by a slight increase in solution conductivity (ca. 290 μS/cm).

Dispersing thermochemically-activated CFA in ultra-pure water introduced very distinct temporal changes to the pH and conductivity of the solution when compared to those observed with untreated CFA. For instance, the rapid decrease of the solution pH below 4 immediately upon addition of all treated CFA was the first indication that CFA had undergone significant structural changes. The ash:activator ratio had little effect on solution pH under the experimental conditions tested (Figure 1A). In contrast, the activation temperature played a significant role (Figure 1A), with a temperature of 400°C promoting a lower pH (1.61-1.74) than elevated temperatures (2.91-2.95 at 500°C; 3.31-3.49 at 600°C). In a similar manner, leaching of CFA activated at 400°C resulted in higher solution conductivity (> 8000 μS/cm) than for CFA treated at higher temperatures (3157-3430 μS/cm at 500°C; 1822-2470 μS/cm at 600°C). In addition, greater ash-activator ratios led to higher conductivity values (Figure 1B). This observation was particularly dominant at 400°C, which indicated that an excess of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> had been used at this temperature and was still present in the activated material because it had most probably not fully reacted with CFA and it had not fully decomposed into volatile gases. No (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or similar derivative species was expected to be present in the solids generated at higher temperatures. As a result, the difference in solution conductivity observed between the two ash-activator ratios experiments can most likely be explained in terms of differences in dissolved Al and other metals. In particular, the positive effect of increased ash-activator ratio on the extent of Al (and/or other metals) extraction appeared to be greater at 600°C than at 500°C.

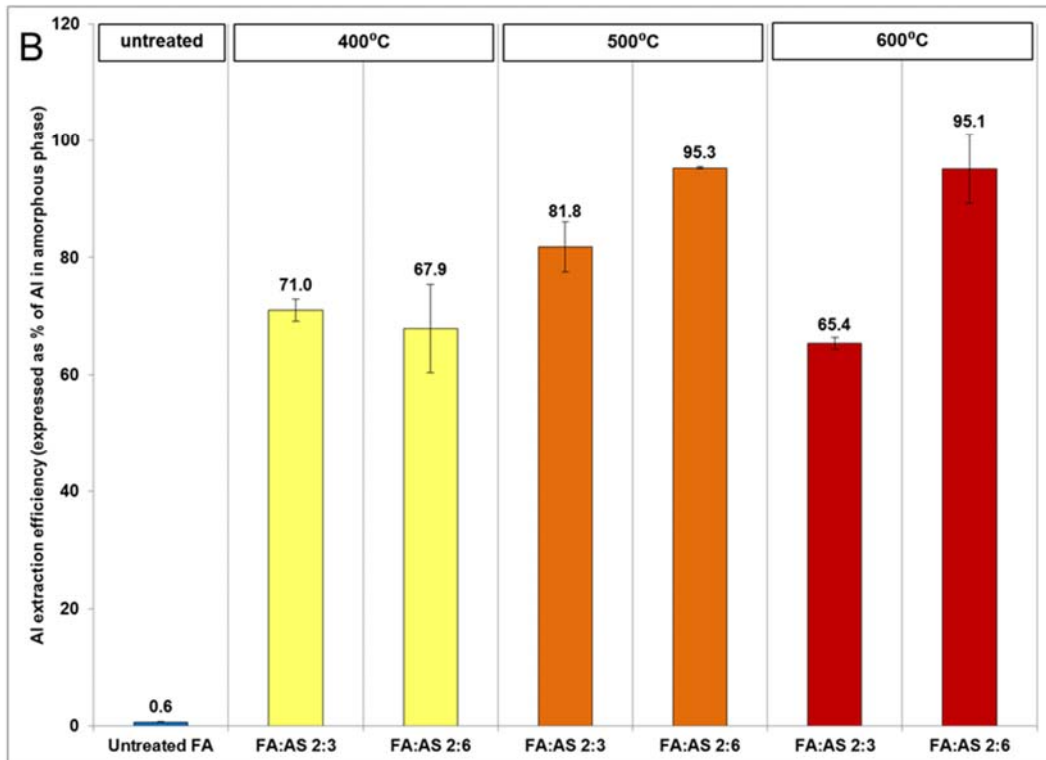
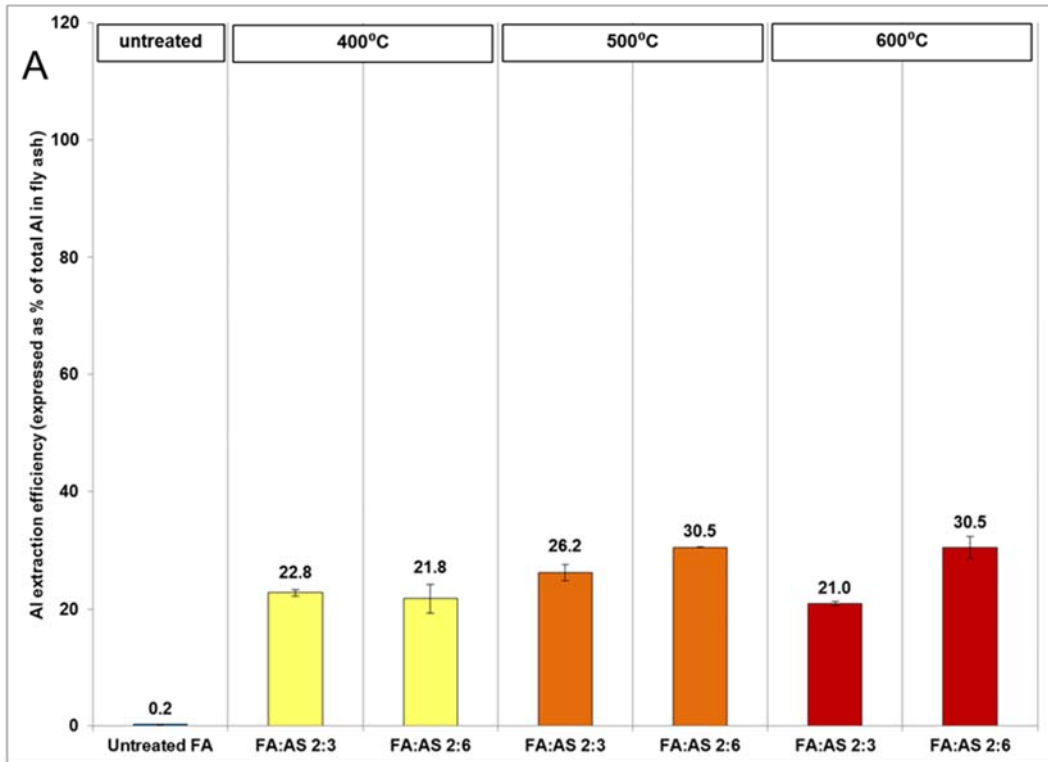


**Figure 1** - Solution pH (a) and conductivity (b) profiles for the leaching of untreated and thermochemically-activated South African ultrafine coal fly ash.

Extraction of Al from untreated and thermochemically-activated CFA was also evaluated. The total content of Al in as-received, untreated CFA was 34.0% (expressed as  $\text{Al}_2\text{O}_3$ ), which corresponds to 17.99g Al/100g CFA. The speciation of Al in CFA was two-fold. CFA contained a crystalline mullite phase ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ; 31.8%), which is theoretically composed of 38% of Al, and a glass phase which comprised the remaining Al. This implied that 11.47g of Al was trapped in the potentially unreactive mullite fraction and 6.52g of Al was distributed in the structure of the presumably more reactive glass phase. It was anticipated that Al present in the glass phase would react more extensively with  $(\text{NH}_4)_2\text{SO}_4$  and/or its derived species generated during its thermal decomposition (e.g.  $\text{NH}_4\text{HSO}_4$ ,  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_7$ ) than the Al confined in the mullite component. For this reason, Al extraction efficiency was calculated both as a percentage of total Al ( $\text{Al}_{\text{tot}}$ ) present in CFA (Figure 2A) and as a percentage of Al present in the amorphous phase ( $\text{Al}_{\text{glass}}$ ; Figure 2B).

Dissolution of untreated CFA in ultra-pure water was minimal. In particular, little Al (0.2% of  $\text{Al}_{\text{tot}}$ ; 0.6% of  $\text{Al}_{\text{glass}}$ ) had been released to solution; this was in agreement with the low electrical conductivity value measured (ca. 290  $\mu\text{S}/\text{cm}$ ). The extent of aqueous Al extraction from CFA improved substantially following its thermochemical activation using  $(\text{NH}_4)_2\text{SO}_4$  and was greater than 21.0% of  $\text{Al}_{\text{tot}}$  or 65.4% of  $\text{Al}_{\text{glass}}$  for all experimental conditions studied (Figure 2). Different combinations of activation temperature and ash:activator ratio resulted in varying concentrations of Al in the leachates. For the duration of the activation step used in this study (i.e. 1h) and at an ash:activator ratio of 2:6, an improvement in Al extraction efficiency was observed when the temperature of activation had been increased from 400 $^{\circ}\text{C}$  (21.8% of  $\text{Al}_{\text{tot}}$ ; 67.9% of  $\text{Al}_{\text{glass}}$ ) to 500 $^{\circ}\text{C}$  (30.5% of  $\text{Al}_{\text{tot}}$ ; 95.3% of  $\text{Al}_{\text{glass}}$ ). A further increase to 600 $^{\circ}\text{C}$  did not increase the extent of Al extraction (30.5% of  $\text{Al}_{\text{tot}}$ ; 95.1% of  $\text{Al}_{\text{glass}}$ ). Reducing the ash:activator ratio from 2:6 to 2:3 had no effect on the concentration of dissolved Al for CFA activated at 400 $^{\circ}\text{C}$ . This was a strong indication that the activator was present in excess for the two investigated conditions. Since less Al was extracted at this temperature than at 500/600 $^{\circ}\text{C}$  and no other easily leachable elements were present in sufficiently large quantity in CFA, the higher solution conductivity measured for the 400 $^{\circ}\text{C}$  treatment was most probably generated by the release of  $\text{SO}_4^{2-}$  ions from unreacted water-soluble  $(\text{NH}_4)_2\text{SO}_4$  and/or its derived species generated during its thermal decomposition after the 1h activation step. Reducing the ash:activator ratio from 2:6 to 2:3 had a measurable negative effect on the concentration of dissolved Al for CFA activated at 500 $^{\circ}\text{C}$  and 600 $^{\circ}\text{C}$ . The lower extraction of Al for CFA treated at 600 $^{\circ}\text{C}$  compared to that treated at 500 $^{\circ}\text{C}$  suggested that at an ash:activator of 2:3 the kinetics of thermal decomposition and volatilisation of  $(\text{NH}_4)_2\text{SO}_4$  at 600 $^{\circ}\text{C}$  had been more rapid than the rate of reaction between the activator and CFA.

An ash:activator of 2:6 at 500 $^{\circ}\text{C}$  over a 1h-period was the optimal condition for the extraction of Al from the amorphous phase of CFA. Significant extraction of Al from the mullite component appeared unlikely at this stage.

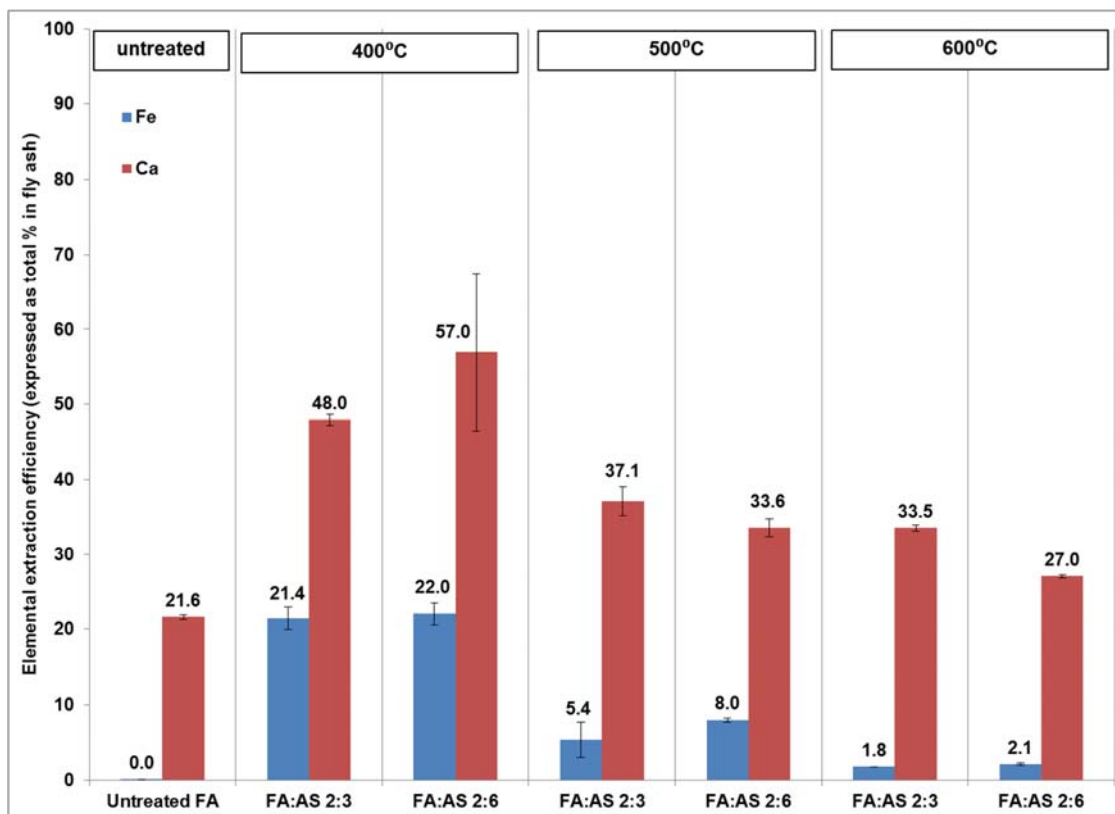


**Figure 2** Aluminum extraction efficiency (A. expressed as % of total aluminium in CFA; B. expressed as % of Al in amorphous phase) at two different ash:activator ratios (2:3 and 2:6) and three activation temperatures (400°C, 500°C, 600°C) (FA:AS is the fly ash to activator ratio;  $n = 2$ ).

## Effect of activation on other strategic metals extraction

Extraction of other strategic elements from untreated and thermochemically-activated CFA was also evaluated. The treatment did not improve significantly Si extraction (< 0.5% of total Si) when compared to that from untreated fly ash (0.0% of total Si). This confirmed that the activation process under development can selectively extract aluminum over silicon.

The extent of calcium extraction was much greater than that for iron. For both elements, the extraction appeared to be favored at lower temperature (i.e. 400°C), which is opposite to what was found for aluminum. This occurrence is beneficial if the selective extraction of aluminum over calcium and iron is preferred.



**Figure 4** Iron and calcium extraction efficiency (expressed as % of total element in CFA) at two different ash:activator ratios (2:3 and 2:6) and three activation temperatures (400°C, 500°C, 600°C) (FA:AS is the ash to activator ratio;  $n = 2$ ).

## Characterization of CFA treated at 600°C

Characterization of CFA thermochemically-treated at 600°C was carried out using XRD, TGA, FE-SEM and SEM-EDS in order to better understand the activation effect of  $(\text{NH}_4)_2\text{SO}_4$  on CFA at this temperature. Table 1 reports the crystalline phases present in activated CFA, where their amounts were normalized to 100%. For comparison purpose, the crystalline phases of untreated fly ash consisted of mullite (84.3%), quartz (15.5%) and a very small amount of lime (0.2%). Lime was

very reactive and was not identified in any activated CFA samples, whereas mullite and quartz co-existed in all activated CFA, albeit representing a much smaller proportion of crystalline minerals (26.1-44.6% for mullite + quartz) than in untreated CFA (99.8%). CFA activated at 600°C exhibited the least complicated XRD patterns and quantification of the crystalline phases was possible. 100% of extracted Al crystallised in the form of water-soluble aluminium sulphate ( $\text{Al}_2(\text{SO}_4)_3$ ), also called millosevichite, which represented 46.1% and 67.0% of activated CFA for ash:activator ratios of 2:3 and 2:6 respectively. Calcium (Ca) was also extracted in significant amount, and crystallised in the form of anhydrous calcium sulphate ( $\text{CaSO}_4$ ), also called anhydrite. Since very little Ca was present in mineral forms in untreated CFA, it can be argued that most of the reacted Ca originated from the amorphous phase. The glassy phase had therefore been very reactive at this temperature. This strongly suggested that most, if not all, Al which had been converted to  $\text{Al}_2(\text{SO}_4)_3$  also originated from the amorphous phase. At this point, there is no evidence that mullite had reacted with the activator under the experimented conditions used in this study.

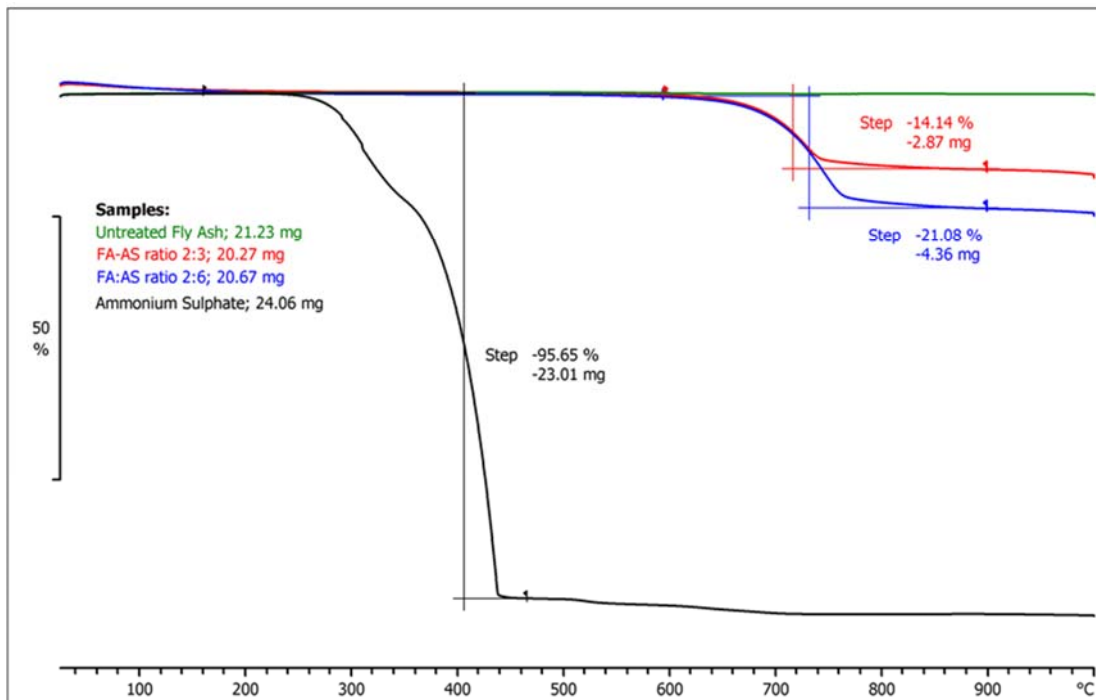
The TGA profiles of untreated fly ash, ammonium sulphate and thermochemically-activated fly ash for treatments performed at 600°C for 1h shows distinct differences between the thermal behaviour of these samples (Figure 5). The TGA experiments were performed up to 1000°C. Composition of the crystalline phases of these samples was determined by XRD (Table 1). Mullite, quartz and lime will show no change in weight upon heating and anhydrite will decompose at temperatures above 1000°C, which means that TGA can only report on the decomposition of  $\text{Al}_2(\text{SO}_4)_3$ . No  $(\text{NH}_4)\text{Al}(\text{SO}_4)_2$  was detected in the products obtained from thermochemical treatment at 600°C. Using the theoretical weight loss for the decomposition of  $\text{Al}_2(\text{SO}_4)_3$ , TGA identified mass losses for this mineral which corresponded to 20% and 30% for ash:activator ratios of 2:3 and 2:6 respectively. While XRD and TGA did not report the same phases, the ratio of the same mineral phase (i.e.  $\text{Al}_2(\text{SO}_4)_3$ ) between the two ash:activator ratios as reported by XRD and TGA were in agreement ( $67.0/46.1=1.45$  and  $30/20=1.5$  for XRD and TGA respectively).

**Table 1** Rietveld quantitative phase analysis of untreated fly ash and fly ash thermochemically-activated at ash:activator ratios of 2:3 and 2:6 and at a temperature of 600°C (Reaction time: 1h; Activator used:  $(\text{NH}_4)_2\text{SO}_4$ ; only the crystalline phases are reported and were normalized to 100%).

Minerals	Chemical formula	Untreated fly ash	ash:activator ratio 2:3	ash:activator ratio 2:6
Mullite	$\text{Al}_6\text{Si}_2\text{O}_{13}$	84.3	33.2	16.3
Quartz	$\text{SiO}_2$	15.5	11.4	9.8
Lime	$\text{CaO}$	0.2	n.d.	n.d.
Anhydrite	$\text{CaSO}_4$	n.d.	9.3	6.9
Millosevichite	$\text{Al}_2(\text{SO}_4)_3$	n.d.	46.1	67.0

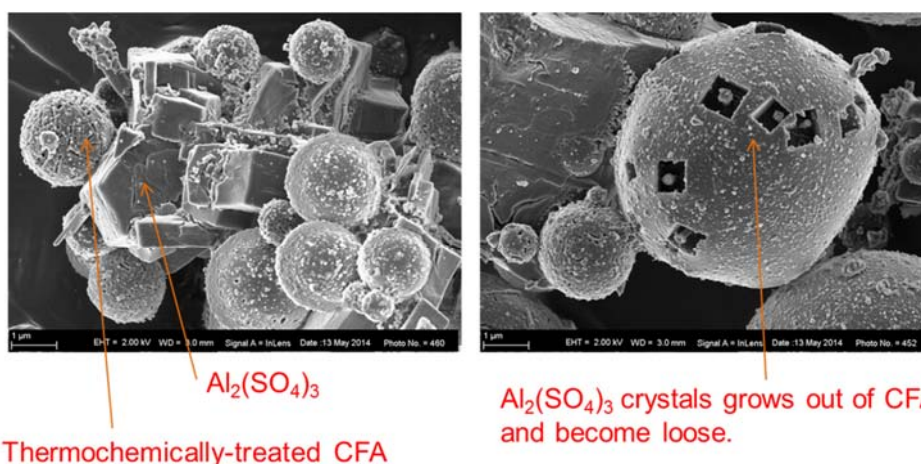
n.d.: not detected





**Figure 5** TGA profiles of untreated fly ash (green), ammonium sulphate (black) and thermochemically-activated fly ash at FA:AS ratios of 2:3 (red) and 2:6 (blue); Thermochemical treatment performed at 600°C for 1h.

The sample of CFA which was activated at 600°C using an ash:activator ratio of 2:6 exhibited well-shaped hexagonal crystals which were mostly composed of Al, S and O (as revealed by SEM-EDS; results not shown) and which were ascribed to  $\text{Al}_2(\text{SO}_4)_3$  (Figure 6). Most fly ash particles had retained their spherical morphology, and numerous particles featured square and/or rectangular cavities that strongly suggested the formation and growth of  $\text{Al}_2(\text{SO}_4)_3$  crystals at the surface of CFA which then became loose.



**Figure 6** FE-SEM micrographs depicting specific features of fly ash thermochemically-activated at a FA:AS ratio of 2:6 and at a temperature of 600°C (reaction time: 1h; acceleration voltage: 2kV; magnification: 30000x).

## **CONCLUSIONS**

This study demonstrated the usefulness in using  $(\text{NH}_4)_2\text{SO}_4$  as a chemical activator to facilitate the extraction of aluminum from the glass phase of CFA. Water leaching of the reaction product obtained under the experimental conditions tested resulted in the recovery of up to 95.0% aluminum from the amorphous phase. The process was also successful in co-extracting other potentially strategic metals.

## **ACKNOWLEDGEMENTS**

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