Ammonium sulphate and/or ammonium bisulphate as extracting agents for the recovery of aluminium from ultrafine coal fly ash

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Highlights

• Aluminium was extracted from an ultrafine coal fly ash
• Ammonium sulphate and ammonium bisulphate were used as extracting agents
• A process of thermochemical treatment followed by aqueous leaching was employed
• A maximum non-selective recovery of 46.6% aluminium was obtained
• Selective extraction of aluminium (37.3%) over silicon and iron was achieved

Abstract

We recently showed that the selective extraction of aluminium from the amorphous phase of a South African ultrafine coal fly ash can be achieved via thermochemical treatment with ammonium sulphate for 1h followed by aqueous dissolution, as an alternative to conventional hydrometallurgical processes. In this study, insight gained from the previous work was applied to investigate and compare total vs selective aluminium extraction efficiencies using ammonium sulphate or ammonium bisulphate either on its own, or as a mixture of the two salts as extracting agents during a 2h thermal treatment process. The effects of (i) ash-to-extractant mass ratio and (ii) temperature during thermal treatment on extraction efficiency was investigated. While a maximum, but non-selective, recovery of 46.6% total aluminium was achieved using ammonium bisulphate at 400 °C, the most technically appropriate results for selective recovery yielded 37.3% aluminium, with only 0.3% silicon, 0.1% titanium and 3.9% iron having been co-extracted when using ammonium sulphate at a processing temperature of 600°C. Extraction of most of the calcium and magnesium could not be prevented. Using mixtures of ammonium salts as extracting agents during
Thermochemical treatment may however introduce technical difficulties on large scale. Our results indicate that any of the two ammonium salts could be used on their own during thermochemical treatment. Thermochemical treatment of coal fly ash using ammonium salts may therefore represent a promising technology for extracting aluminium from South African coal fly ash.

**Keywords:** coal fly ash; thermochemical processing; aluminium extraction; ammonium sulphate; ammonium bisulphate

1. Introduction

The recovery of aluminium (Al) from coal fly ash (CFA) is of particular relevance to South Africa because the country has no economically viable bauxite deposits. Although South Africa has been actively involved in CFA beneficiation and/or utilisation research, the recovery of alumina as the precursor for aluminium production has not been widely pursued (Matjie et al., 2005; Shemi et al., 2012; Shemi et al., 2014; Shemi et al., 2015). This is rather surprising since the alumina content of domestic fly ashes generally exceeds 30%.

Due to the long distance between the power stations and the industrial hub of the country it is customary in South Africa to process and beneficiate CFA at source prior to being transported to the market. Air-classification is used to extract the particular size fractions required by the market. One of these is a commercial-grade, ultra-fine fly ash that is used as a high-performance pozzolan in the cement industry and as a filler for polymers (plastics). This fraction of ash was used in the present study because it is slightly higher in alumina than other South African coal ash resources, and has an elevated amorphous content and a high specific surface area.

The pioneering work by Grzymek (Grzymek, 1976), demonstrating that alumina could be recovered from CFA, provided the mineralogy was altered by high temperature sintering, precipitated extensive research into the efficacy of various sintering agents in forming soluble aluminium compounds. In particular, lime sinter, lime soda sinter, and Calsinter (Egan, 1980) processes, along with high temperature chlorination, received global attention. Acid leach methodologies were shown to be less effective in selectively extracting aluminium (Yao et al., 2015; Yao et al., 2014).

Our recent study indicated that thermochemical treatment using ammonium sulphate \((\text{NH}_4)_2\text{SO}_4\) may represent a promising technology for extracting Al from fly ash (Doucet et al., 2016). One of the advantages of this process resides in the fact that \((\text{NH}_4)_2\text{SO}_4\) is widely available at low cost and can be easily recycled.
(Highfield et al., 2012). The most promising processing conditions were determined to be a temperature of 500 °C and a fly ash to (NH₄)₂SO₄ weight ratio of 2:6 when a reaction time of 1h was used (Doucet et al., 2016). It was also found that water leaching of the reaction products obtained under these conditions resulted in the selective recovery of 95.0% Al from the amorphous phase, with < 0.6% Si extracted. Results indicated that mullite (Al₆Si₂O₁₃) was unlikely to have reacted with the extracting agent when a reaction time of 1h was used.

Since ammonium bisulphate (NH₄HSO₄) is known to yield better elemental extraction efficiencies from serpentine minerals than (NH₄)₂SO₄ (Romão et al., 2016), the present paper tested and compared, for the first time, the potential of these two agents, used either singularly or as mixtures in various mass ratios, for the extraction of Al from the same classified ultrafine South African CFA. The selectivity of these two extracting agents for Al vs other major elements has also not been previously examined. The second objective was therefore to compare the selectivity of these agents for Al recovery with minimal extraction of other major elements (i.e. Ca, Fe, Si, Ti and Mg). Thirdly, the duration of the thermochemical treatment was increased from 1h to 2h to examine the extent of reactivity between the mullite component of CFA and the two extracting agents. An outline of the multi-stage extraction process proposed is illustrated in Fig. 1. Potential chemical reactions taking place during the thermochemical treatment of CFA and the ammonium salts used in this study have already been described in the literature (Wang et al., 2014a; Wang et al., 2014b).

2. Experimental

2.1 Materials description and characterisation

A representative sample of an ultrafine siliceous coal fly ash (CFA) was obtained from the Ash Resources Pty Ltd.’s ash beneficiation site at Eskom’s Lethabo Thermal Power station, South Africa. This commercial-grade CFA is specified to have more than 90% of its particles with a diameter smaller than 11 µm (vol. %). Detailed surface and bulk characterization of the sample, which included XRF, XRD, PSD, FE-SEM, Raman, FTIR and XPS analyses, was reported elsewhere (van der Merwe et al., 2014). Briefly, the sample consisted of an amorphous glass phase (64.3%), which co-existed with two primary crystalline phases, mullite (Al₆Si₂O₁₃; 30.2%) and quartz (SiO₂; 5.5%). It was made up of six major chemical constituents (SiO₂, 52.9%; Al₂O₃, 33.5%; CaO, 5.0%; Fe₂O₃, 3.3%; TiO₂, 1.7%; MgO, 1.1%).
Reagent grade (99.5%, Merck) ammonium sulphate and ammonium bisulphate (hereafter referred to as “AS” and “ABS” respectively) were used in all experiments.

2.2 Thermochemical processing and aqueous dissolution

The first step of the staged process involved processing CFA by thermochemical treatment using either AS, ABS or a mixture of both in various mass ratios as extracting agents. CFA and the ammonium salts were thoroughly mixed in fused quartz crucibles at CFA:AS:ABS mass ratios of 2:6:0; 2:4:2; 2:3:3; 2:2:4; and 2:0:6. These ratios were chosen to give a stoichiometric excess of SO$_4$ over the total amount of extractable elements (e.g. Al, Ca, Fe), to ensure that the amount of the ammonium salt did not represent a limiting factor during extraction. The mixtures were thermally treated in a static muffle furnace at 400, 500 or 600°C for 2h. The reaction products (CFA$_{ctt}$) were then subjected to aqueous dissolution in deionised water. The chemical composition of the leachates was determined by ICP-MS, while that of CFA$_{ctt}$, and the filtered solid residues (CFA$_{res}$) were characterised by XRD and FE-SEM. The ICP data was used to calculate elemental extraction efficiencies, i.e. the mass fraction of elements extracted as sulphates into the aqueous solution,
was compared to the mass of these elements initially present in untreated CFA (determined by XRF). The procedures followed for dissolution experiments and solid residue characterisation were described previously (Doucet et al., 2016).

3. Results and discussion

3.1 Structural changes following thermochemical treatment and subsequent leaching of CFA

Characterization of all CFA\textsubscript{tct} and CFA\textsubscript{res} samples was performed by XRD and FE-SEM in order to better understand the effect of the ammonium salts on CFA. Previous work (Doucet et al., 2016) reported that the surface topography of untreated CFA spheres was relatively smooth at the scale of observation allowed by the FE-SEM, regardless of the particle size, and that CFA\textsubscript{tct} generated using (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} consisted of spherical particles surrounded by newly-formed, sub-10 µm hexagonal structures that were mostly interlocked to form clusters of varying sizes. We have now observed that the hexagonal structures which formed when using ABS as extracting agent were substantially smaller (sub-µm) than those formed when AS was used (results not shown).

The occurrence of new mineral phases during one-hour thermochemical treatment of CFA with (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} was examined previously using XRD (Doucet et al., 2016). The amorphous silica alumina glass phase content of untreated and thermochemically-treated CFA was determined by addition of silicon as internal standard and the relative phase amounts were estimated using the Rietveld method, as described before (van der Merwe et al., 2014). The current results, which were obtained after 2h thermochemical treatment, confirmed that Al was extracted from CFA primary phases to form either millosevichite (Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}) only (at 600°C), or co-existing millosevichite and godovikovite (NH\textsubscript{4}Al(SO\textsubscript{4})\textsubscript{2}) (at both 400 and 500°C) (Fig. 2); two Al and SO\textsubscript{4}-containing minerals which were previously found to exhibit varying solubility properties (Doucet et al., 2016). Ca was extracted from the amorphous phase and reacted with the extracting agent to form anhydrite (CaSO\textsubscript{4}). The same mineral phases were formed in CFA\textsubscript{tct} at the same temperatures, regardless of the ammonium salt or ratio of the two salts used. For this reason, only an example of the XRD patterns of CFA, CFA\textsubscript{tct} thermochemically treated for 2 h at a CFA:AS:ABS mass ratio of 2:3:3 at 400°C, 500°C and 600°C; and that of the corresponding CFA\textsubscript{res} samples obtained following elemental extraction from CFA\textsubscript{tct} is given (Supplementary Figure SF1).
Figure 2: Quantitative XRD analysis of CFA and CFA<sub>tct</sub> (A, C and E) thermochemically treated for 2 h at 400°C (A), 500°C (C) and 600°C (E); and that of CFA and CFA<sub>res</sub> (B, D and F) obtained from CFA<sub>tct</sub> treated at 400°C (B), 500°C (D) and 600°C (F).

Quantitative XRD analysis (Fig. 2) furthermore confirmed that the proportional ratios at which the sulphate mineral phases formed during thermochemical treatment was relatively independent of the type of ammonium salt or ratios used, but varied substantially with the thermochemical treatment temperature.
This was an indication that the thermochemical treatment temperature, rather than the ratio between activators used, had affected the specific phases produced. Millosevichite was observed in the products, but its content differed considerably upon varying the thermochemical treatment temperature, with 30% formed at 600°C, between 12-23% at 500°C and only 2% at 400°C. Godovikovite was predominantly formed at lower temperatures (14-30% at 500°C and 17-32% at 400°C), and was not observed in the products formed at 600°C. Similar amounts of anhydrite (3-4%) were formed upon thermochemical treatment at 500 and 600°C, but the phase was absent in the products obtained at 400°C. Significant amounts of unreacted reactant (ABS) and decomposition products of the reactants AS and ABS (letovicite, (NH₄)₃H(SO₄)₂ and ABS) were observed in all samples thermochemically treated at 400°C.

Characterisation of the non-dissolved residues (CFAₗₚₙ) indicated that two of the newly formed sulphate phases (i.e. godovikovite and millosevichite) had not, or only partially, dissolved during leaching. Leaching conditions were not effective in dissolving all the millosevichite (Al₃(SO₄)₃), especially for samples thermochemically treated at 600°C where between 1-8% Al₃(SO₄)₃ remained in the undissolved residues. Most of the Al₃(SO₄)₃ formed at 500°C dissolved, indicating that the leaching conditions need to be optimised for samples with higher Al₃(SO₄)₃ content. Between 12-26% godovikovite remained in the non-dissolved residues of samples which contained this phase before leaching. Anhydrite, letovicite and ammonium bisulphate dissolved completely during leaching of CFAₗₚₙ. Compared to the amorphous content of untreated CFA, the amount of amorphous phase remained relatively constant for CFAₗₚₙ obtained from CFAₗₚₙ at 400°C, with the exception of the sample treated with ABS for which it increased from 64% in CFA to 89% in CFAₗₚₙ. CFAₗₚₙ obtained from thermochemical treatment of CFA at both 500°C and 600°C showed a similar increase in the amorphous phase (avg. 13%).

Contrary to previous results (Doucet et al., 2016), mullite seems to have reacted under the thermochemical conditions used in this study. Previous results had shown no evidence of mullite reactivity with AS after 1h of thermochemical treatment, and we subsequently concluded that Al was mostly extracted from the amorphous phase. By increasing the thermochemical treatment time from 1h to 2h, a further increase in Al extraction efficiency was observed, which strongly suggested reactivity between mullite and the ammonium salts studied. Mullite was not observed in many of the samples obtained from thermochemical treatment of CFA at 400 and 500°C (Fig. 2A and 2C), but then occurred in the non-dissolved residues following leaching of the same samples. The formation of a significant amount of new crystalline phases during thermochemical treatment may have diluted the mullite content to such a degree that it was not observed in CFAₗₚₙ (Fig. 2A and 2C), but then observed again in the corresponding CFAₗₚₙ upon dissolution of the soluble sulphate phases (Fig. 2B and 2D). Quartz has no known reactivity with AS or ABS, and therefore the relative proportion of
mullite to quartz, obtained from quantitative XRD measurements, should remain constant if the two phases did not react with the ammonium salts during the thermochemical treatment process (Fig. 3). In comparison to untreated CFA, the mullite to quartz content of CFA_{res} decreased with decreasing thermochemical treatment temperature (Fig. 3). Addition of ABS as reactant also seemed to promote mullite reactivity, compared to CFA_{res} resulting from thermochemical treatment with AS, especially for CFA_{res} obtained from CFA\textsubscript{tct} treated at 400°C. Mullite reactivity was only observed when increasing the duration of thermochemical treatment experiments, and therefore our latest results indicated faster kinetics for Al extraction from the amorphous phase than from the mullite phase.

![Figure 3: Comparison of the mullite/quartz weight ratio of CFA and CFA\textsubscript{res}. Mass ratios in the legends refer to mass of CFA:AS:ABS.](image)

3.2 Effect of thermochemical processing of coal fly ash on elemental extraction

Extraction efficiencies of the main elements (Al, Si, Ca, Fe, Mg and Ti) from untreated CFA and CFA_{tct} were evaluated (Fig. 4). Dissolution of untreated CFA in ultra-pure water was minimal (Al, Fe, Ti and Si ≤ 0.2%), except for Ca and Mg which were partially extracted (21.6% and 10.3% respectively). The extent of Al extraction improved substantially following thermochemical treatment. Different combinations of CFA:AS:ABS ratios and processing temperatures resulted in varying concentrations of Al in the filtrates. For the duration of the thermochemical processing step used in this study (i.e. 2h), the highest Al extraction efficiency (46.6%) was achieved with a CFA:AS:ABS ratio of 2:0:6 and a temperature of 400°C. The least amount of Al (21.5%) was extracted using a CFA:AS:ABS ratio of 2:6:0 and a temperature of 400°C. This observation indicated that the decomposition step of AS to ABS during thermal treatment may be a limiting
step for Al extraction, a phenomenon that was previously seen with serpentine (Romão et al., 2016). Using AS at 500°C during 2h yielded a maximum extraction of 38.9% of Al, which was about 8% greater than for a reaction time of 1h (Doucet et al., 2016). Previous work (Doucet et al., 2016) eluded to the fact that mullite had probably not reacted, or very slightly, under this condition. The observed increase in extraction efficiency when using a longer thermochemical treatment further confirmed our previous suggestion that mullite had reacted under the present conditions, and that the kinetics of the sulphate-forming reactions between the amorphous phase and AS and/or ABS during thermochemical treatment is faster than the corresponding reactions between mullite and the respective ammonium salts.

Figure 4: (A) Al, (B) Fe, (C) Ca, (D) Si, (E) Mg and (F) Ti extraction efficiencies for CFA thermochemically treated at different CFA:AS:ABS ratios and temperatures (light grey: 400°C, dark grey: 500°C, black: 600°C) for 2 h (n=2).
The amounts of Fe and Ti extracted was marginally affected by the ratio of extracting agents tested but it could be controlled and substantially limited (Fe: 2.6%; Ti: 0.2%) by increasing the treatment temperature from 500°C to 600°C, with minimal negative impact on Al extraction (Fig. 4B). Under these conditions, Ca and Mg extraction ranged between 30 - 40%. Under all conditions tested, the process permitted to selectively extract Al over Si, with Si extraction being < 2% under all conditions. The best thermochemical treatment conditions for selective extraction of Al (37.1%) over Si (0.2%), Ti (0.2%) and Fe (2.6%) were found to be a CFA:AS:ABS ratio of 2:4:2 at a processing temperature of 600°C. However, using mixtures of AS and ABS may not be practical to apply on large scale unless a significant increase in extraction efficiency and/or selective extraction of the element of interest can be obtained. Employing AS as the sole extracting agent at a processing temperature of 600°C produced similar results, with 37.3% of Al being extracted, with co-extraction of Ca (39.0%), Mg (39.0%), Fe (3.9%) and almost no Si (0.3%) and Ti (0.1%). Upon decreasing the thermochemical treatment temperature to 500°C, the process with AS was able to extract slightly more Al (38.9%), reduced amounts of Ca (35.7%) and Mg (26.7%), with the disadvantage of increased amounts of Fe (9.6%) and Ti (1.7%) being co-extracted.

4. Conclusions

The potential for selectively extracting Al over Si, Fe and Ti from an ultra-fine coal fly ash was demonstrated in this study, with Al extraction efficiencies of up to 46.6% being achieved. The process was not selective with regard to Ca and Mg extraction, whereas varying the extracting agent and treatment temperature permitted the selective extraction of Al over Si, Fe and Ti.

Both AS and ABS were found to be suitable chemical agents to facilitate the extraction of Al from CFA, although not under the same reaction conditions. ABS promoted better elemental efficiencies at lower temperatures used during thermochemical treatment, which presented the advantage of lower energy consumption and probably minimal loss of the reagent for subsequent ABS recycling. The penalty was co-extraction of Fe and Ti, and the fact that recycling of ABS is more complex, more costly, and requires higher water consumption. Thermochemical treatment at higher temperatures, with the resulting energy penalty, was required to obtain comparable extraction efficiencies using AS as extracting agent. The use of higher temperatures during thermochemical treatment is unfavourable for industrial application due to a significant loss of sulphur, in the form of SOx gas, due to thermal AS decomposition (Highfield et al., 2012). Mullite reactivity was promoted by the presence of ABS, whereas thermochemical treatment using AS required increased temperatures and duration of the thermochemical step to overcome the slow kinetics of the
reaction between AS and the mullite component of CFA. Ultimately, the use of AS is preferred over ABS, given that AS is a readily-available, low-cost and easily recyclable reagent.

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Supplementary Figure SF1: XRD patterns of CFA, CFA_{tct} after 2 h thermochemical treatment at a CFA:AS:ABS mass ratio of 2:3:3 at 400°C (A), 500°C (B) and 600°C (C); and that of the corresponding CFA_{res} samples obtained following elemental extraction from CFA_{tct}. 