



Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Thermochemical processing of a South African ultrafine coal fly ash using ammonium sulphate as extracting agent for aluminium extraction

Frédéric J. Doucet^{a,*}, Sameera Mohamed^{a,b}, Nicole Neyt^b, Barbara A. Castleman^b, Elizabet M. van der Merwe^{b,*}

^a Council for Geoscience, 280 Pretoria Street, Silverton, Pretoria 0001, South Africa

^b Department of Chemistry, University of Pretoria, Lynnwood Road, Pretoria 0002, South Africa

ARTICLE INFO

Article history:

Received 12 March 2016

Received in revised form 21 July 2016

Accepted 29 July 2016

Available online xxxx

Keywords:

Coal fly ash

Thermochemical processing

Aluminium extraction

Ammonium sulphate

ABSTRACT

South African coal fly ash represents an untapped secondary resource of aluminium. Continuous research is conducted to develop suitable chemical and/or geometallurgical processes for aluminium extraction, preferably accompanied by minimal silicon extraction. The thermochemical treatment of a South African ultrafine coal fly ash was investigated to test the feasibility of recovering aluminium using ammonium sulphate, a widely available, low-cost, recyclable chemical agent. The optimum processing conditions were determined to be a temperature of 500 °C and a fly ash to ammonium sulphate weight ratio of 2:6 when a reaction time of 1 h was used. Water leaching of the reaction product obtained under these conditions resulted in the selective recovery of 95.0% aluminium from the amorphous phase, with <0.6% Si extracted. Mullite was unlikely to have reacted with the extracting agent. Except for Si, the process was not element-selective, but the extraction of iron could be minimized by increasing the treatment temperature to 600 °C without compromising Al extraction. Thermochemical treatment using ammonium sulphate may therefore represent a promising technology for extracting aluminium from coal fly ash, which could be subsequently converted to value-added products such as alumina.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Coal fly ash (CFA) is a solid incombustible residue that is mainly produced during the combustion of pulverized coal in thermoelectric power stations. Eskom, the main power generator in South Africa, consumed 124.7 Mt of coal producing 36.2 Mt of CFA in 2011 (Eskom, 2011). Only about 5% of CFA is currently recycled, mostly in the form of building materials such as bricks and as a cement extender, while the unused CFA is disposed of either in dry or slurry form in ash-handling dams which require maintenance and eventual rehabilitation. SASOL Synfuels generates an additional 4 million tons per annum (Mahlaba et al., 2011).

Aluminium is typically the second most abundant element in CFA after silicon, which makes CFA a potential pre-mined substitute of bauxite for alumina production. This is of particular relevance to South Africa which has no mineable bauxite ore deposits, the raw material used to produce aluminium. The chemical extraction of aluminium from CFA has been well documented over the past 50 or so years, and the topic remains high on the R&D agenda (Guo et al., 2013; Li et al., 2014; Shemi et al., 2014; Yao et al., 2014; Zhu et al., 2015). It is generally performed using metallurgical methods, which can be categorized into three

types of processes: (i) acid leaching, (ii) sintering, and (iii) HiChlor (Yao et al., 2015). All the processes have their own advantages and drawbacks. Some of the processes are nevertheless in the early stages of commercialization, although they might not be currently economically viable in their own right. For this reason, researchers and companies are increasingly looking into aluminium recovery combined to potential additional revenue streams generated from the simultaneous recovery of other strategically-valuable elements (Tolhurst, 2015).

Although South Africa has been actively involved in research and development for CFA beneficiation and/or utilization (Mahlaba et al., 2011; Muriithi et al., 2011; Muriithi et al., 2013; Muriithi et al., 2014; Muriithi et al., 2015; Musyoka et al., 2014; van der Merwe et al., 2014a; Böke et al., 2015), research on the recovery of aluminium from South African CFA (Shemi et al., 2014; Matjie et al., 2005; Shemi et al., 2012; Shemi et al., 2015) is limited. It is also mostly restricted to acid leaching methods, which are unlikely to be adopted at large scale. The focus of our group was to identify and test a promising aluminium extraction process that makes use of a widely available, low-cost, recyclable extracting agent. Ammonium sulphate salt ((NH₄)₂SO₄) meets all three criteria (Highfield et al., 2012), and its thermal solid-solid reactions with silicate and oxide minerals for elemental extraction have been extensively studied (Bayer et al., 1982; Nagaishi et al., 1984; Abd-Elzaher, 1999; Mudher et al., 1999; Nduagu et al., 2012; Mohamed et al., 2016). Its reaction with CFA has also recently emerged as an area of great interest in China, owing to its advantages over acidic,

* Corresponding authors.

E-mail addresses: fdoucet@geoscience.org.za (F.J. Doucet), liezel.vandermerwe@up.ac.za (E.M. van der Merwe).

alkali, and acid-alkali methods (Li et al., 2012; Wang et al., 2014; Wu et al., 2014). Al extraction efficiencies >85% were obtained from Chinese CFA, with Al being extracted from both the amorphous phase and the mullite component of CFA.

The primary objective of this paper was to demonstrate the usefulness of thermochemical solid–solid treatment of a South African classified CFA with $(\text{NH}_4)_2\text{SO}_4$, coupled to aqueous dissolution, for the selective extraction of aluminium from the amorphous glass phase. A secondary objective was to test the selectivity of $(\text{NH}_4)_2\text{SO}_4$ for the preferential extraction of aluminium over silicon, since the latter is undesirable for high-purity alumina synthesis.

2. Experimental

2.1. Materials description, preparation and characterization

A representative sample of a classified, ultrafine Class-F coal fly ash (CFA) was obtained from the Ash Resources Pty Ltd.'s ash beneficiation site at Eskom's Lethabo Thermal Power station, which is located between Vereeniging and Sasolburg in the Free State province of South Africa. This commercial-grade CFA is air-classified on site and is specified to have a mean particle size between 3.9 and 5.0 μm , with >90% of the volume distribution of its particles having a diameter smaller than 11 μm . After classification it is marketed as a very fine, spherical, pozzolanic, and highly reactive aluminosilicate with low carbon content. The product currently finds application in the construction industry, but is also used in small quantities in the rubber and polymer industries.

Homogeneous sub-samples of the prepared batches were obtained with a sample splitter for future experiments. Particle size distribution (PSD) was obtained by laser diffraction (Malvern Mastersizer, 2000 fitted with a Hydro 2000G dispersion unit, Malvern Instrument Ltd. Worcester, UK) to confirm the fineness of the ash particles. Scattered light data were recorded from 2000 to 5000 snapshots of 10 μs . A poly-disperse mode of analysis and a refractive index of 1.533 with an adsorption of 0.1 were chosen. Size data collection was performed at constant obscuration in the range 15–20%.

The elemental and mineralogical compositions of the ash were analysed using XRF (ARL9400XP + XRF spectrometer, Thermo ARL, Switzerland) and XRD (PANalytical X'Pert PRO X-ray diffractometer), respectively. Detailed description of these analyses was given elsewhere (van der Merwe et al., 2014b).

A Zeiss Ultra SS field emission scanning electron microscope (FESEM), operated at an acceleration voltage of 1 kV, was used under dry high-vacuum condition to observe differences in morphology of the CFA particles before and after treatment. For this purpose, the powder was mounted on a double-sided carbon tape by dipping carbon stubs into the samples. Excess material was removed by gentle blowing with compressed nitrogen. The sample was then sputter-coated with carbon in an Emitech K550X (Ashford, England).

Ammonium sulphate (reagent grade, 99.5%, Merck, South Africa), $(\text{NH}_4)_2\text{SO}_4$, was used as supplied in all experiments.

2.2. Methods and processes

2.2.1. Thermochemical processing of coal fly ash

The first step of the staged process involved the processing of CFA by thermochemical treatment using $(\text{NH}_4)_2\text{SO}_4$ as extracting agent. $(\text{NH}_4)_2\text{SO}_4$ is widely available at low-cost and offers the added advantage of being recyclable (Highfield et al., 2012), in comparison to other activating agents such as NaOH and Na_2CO_3 . Insight on the thermal decomposition of pure $(\text{NH}_4)_2\text{SO}_4$ over the temperature range studied was provided elsewhere (Mohamed et al., 2016). CFA and $(\text{NH}_4)_2\text{SO}_4$ salt were thoroughly mixed at two mass ratios (2:3 and 2:6 m/m) in a fused quartz crucible. It was important to use a CFA: $(\text{NH}_4)_2\text{SO}_4$ mass ratio which gave a slight excess of SO_4 over Al (mole:mole), so that the amount of $(\text{NH}_4)_2\text{SO}_4$ did not represent a limiting factor for Al

extraction. The 2:3 and 2:6 m/m ratios of CFA: $(\text{NH}_4)_2\text{SO}_4$ were equivalent to SO_4 :Al mole ratios of 1.73 (SO_4 in slight excess over Al) and 3.47 (SO_4 in large excess over Al, to circumvent the fact that some SO_4 reacts with other elements contained in CFA (e.g. Ca, Fe, Ti)) respectively. The mixtures were subsequently inserted in a static muffle furnace operating at different reaction temperatures (400, 500 and 600 °C) for 1 h. The products of the reactions, which either had the appearance of sintered solid or were free-flowing powders (depending on the reaction temperature) were then subjected to a dissolution procedure for Al extraction.

2.2.2. Dissolution experiments

Chemical extraction of Al and other major elements from untreated and thermochemically-treated CFA was investigated in ultrapure water (3 g/300 ml) at 22 °C. All treatment solutions were continuously stirred to maintain treated CFA particles in suspension throughout the experiment. The pH, electrical conductivity and temperature of the suspension were logged using a Hanna HI 2829 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 leachate was filtered under reduced pressure through 0.4 μm membranes filters (Whatman Nucleopore® Track-Etched polycarbonate, Whatman UK Ltd.) in closed polycarbonate filtration vessels (Sterifil, 47 mm Millipore). The concentrations of dissolved Al and other elements were determined by ICP-OES at an accredited laboratory (Waterlab Pty Ltd., Pretoria, South Africa). These ICP data were used to calculate elemental extraction efficiencies, i.e. the mass fraction of elements extracted as sulphates from the mass of these elements present in CFA, by combining them to the XRF data of untreated CFA (for aluminium, iron, calcium and titanium), and the estimated aluminium content of the mullite and amorphous phases (in the case of Al) in untreated CFA. The non-dissolved residues (CFA_{res}) were rinsed thoroughly with ultra-pure water, oven-dried at 40 °C up to constant weight. Their chemical and mineralogical compositions were also determined by XRF and XRD respectively.

3. Results and discussion

3.1. 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 (van der Merwe et al., 2014b). Briefly, the XRD pattern of CFA (Fig. 1) demonstrated that the sample was predominantly composed of an amorphous alumina silica glass phase (62.1%), which co-existed with the two primary crystalline phases, mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$; 31.8%) and quartz (SiO_2 ; 6.1%). This mineralogy was confirmed by the XRF data, which indicated the presence of six major chemical constituents (SiO_2 , 49.3%; Al_2O_3 , 34.0%; Fe_2O_3 , 5.8%; CaO, 5.1%; TiO_2 , 2.0%; MgO, 1.0%). Additional features of the sample included a low total alkaline content ($\text{Na}_2\text{O} + \text{K}_2\text{O} < 1\%$), a low total concentration of alkaline earth metals ($\text{CaO} + \text{MgO} < 6\%$), and a low loss on ignition (LOI of 0.52%). The latter indicated a low percentage of moisture, sulphur, unburned carbon, carbonates and hydroxides.

3.2. Structural changes during thermochemical treatment of coal fly ash

Characterization of thermochemically-treated CFA using XRD, and FE-SEM was carried out in order to better understand the effect of $(\text{NH}_4)_2\text{SO}_4$ on CFA.

3.2.1. Mineralogical characterization

Fig. 1 and Tables 1 to 3 report the crystalline phases present in CFA thermochemically-treated at 600 °C, 500 °C and 400 °C respectively, where their amounts were normalized to 100%. The reasons for

Download English Version:

<https://daneshyari.com/en/article/4769058>

Download Persian Version:

<https://daneshyari.com/article/4769058>

[Daneshyari.com](https://daneshyari.com)