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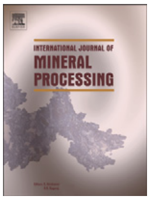

Extraction of aluminium from coal fly ash: Identification and optimization of influential factors using statistical design of experiments

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ABSTRACT

In this study, a statistical Design of Experiments (DOE) method combined with response surface methodology (RSM) was used for identification and optimization of factors influencing the extraction of aluminium from coal fly ash (CFA). The factors investigated included: acid concentration, leaching time, temperature and solid to liquid ratio. The significance of each factor and associated interactive effects were evaluated using a two-level factorial statistical design (2^4) in conjunction with statistical software based on quadratic programming. Results showed temperature and time to be statistically significant; other factors and interactive effects were found to be insignificant. Optimization of the two significant factors was achieved by employing the second order quadratic regression model in combination with the central composite rotatable design (CCRD).

From the prediction model, an optimal aluminium extraction efficiency of 23.95% was obtained at optimal values of 82 °C temperature and 10.2 h leaching time. A confirmatory test showed an aluminium extraction efficiency of 24.8%, giving an error margin of 3.4%, with a linear correlation coefficient of 97.8%, hence verifying the fitness of the model and experimental data. The 24.8% extraction efficiency represents 89.3% aluminium extraction from the amorphous phase of CFA.

1. Introduction

CFA typically contains 26–31% alumina whereas Bauxite, a naturally occurring alumina ore, contains about 30–60% alumina (Authier-Martin et al., 2001) and is the main source of aluminium metal in the world. CFA is formed when pulverized coal is combusted in power stations to heat boilers, which in turn drive generators to produce electricity. Most of the CFA produced from South African power stations is disposed of as waste and very little is re-used for productive purposes (Landman, 2003). CFA contains metal constituents and is capable of becoming a secondary source of strategic metals thus serving as a national resource and alleviating the waste-disposal problem (Murtha and Burnet, 1983). This would unlock large tonnage of previously unavailable raw material as feedstock for production of aluminium metal. Finding innovative and economically competitive methods of CFA utilization is therefore imperative.

Based on its amphoteric properties, alumina is capable of dissolution in either acidic or alkaline media and is therefore recoverable by chemical and hydrometallurgical means. However, CFA phase mineralogy is such that it consists of two alumina phases, the amorphous phase and the mullite phase (Nayak and Panda, 2009; Matjie et al., 2005). The two phases play a key role in alumina dissolution. The crystalline mullite phase is acid-insoluble and aluminium in this phase cannot easily be recovered while the non-crystalline amorphous phase is acid-soluble and aluminium can thus easily be recovered by direct acid leaching (Nayak and Panda, 2009; Kelmers et al., 1982). While direct acid leaching is targeted at the acid-soluble amorphous phase, the alumina in the mullite phase can only be leached indirectly. Indirect acid leaching involves intervention measures such as sintering of material, at temperatures typically in excess of 1000 °C, to allow for mullite phase transformation prior to leaching.

The direct acid leaching method, though low on aluminium extraction efficiencies, has advantages of low cost, mild process conditions and low energy demand. On the other hand, indirect acid leaching, though high on energy requirements, has an advantage of very high aluminum extraction efficiencies. This study was primarily concerned with the direct acid leaching of CFA.

Previous research work on CFA leaching is available in extant literature and most of this work is inclined towards acidic leaching methods (Seidel et al., 2001; Murtha and Burnet, 1983; Kelmers et al., 1982; Matjie et al., 2005; Shcherban et al., 1995; Nayak and Panda, 2009; Nehari et al., 1999; Seidel and Zimmels, 1998; Gilliam et al., 1982; Phillips and Wills, 1982; Jinping et al., 2007; Padilla and Sohn, 1985). This inclination is probably due to the high silica content of CFA and the advantage that silica is substantially insoluble in acidic media unlike alkaline solutions (Nayak and Panda, 2009; Shcherban et al., 1995). Among the acidic lixiviants mostly used, sulphuric acid has been particularly preferred because of its stability, ease of use, low cost and ability to allow for good solubilization of alumina (Shcherban et al., 1995; Nayak and Panda, 2009). Direct leaching of CFA using an inorganic acid such as sulphuric acid is achieved by proton attack. The hydronium

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ion displaces the metal cation (Eq. (1.1)) from the ash particle matrix, thus inducing the dissolution of metals.

$$CaO + Al_2O_{3(s)} + 8H^+{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} \rightarrow 2Al^{3+}{}_{(aq)} + CaSO_{4(s)} + 4H_2O_{(l)} \tag{1.1}$$

The non-acid soluble phases of the ash plus calcium sulphate precipitate are retained as residue and the resultant aluminium sulphate leach liquor is set aside for purification and recovery of alumina by processes such as solvent extraction, precipitation and re-crystallization. The success of aluminium extraction from CFA largely depends on the selection of suitable process parameters at which the measured response is optimum. Experimental strategies for obtaining optimum results entail the use of a combination of factorial designs and a response surface methodology (RSM). RSM is a famous technique used to find optimal conditions by using a quadratic polynomial regression model and is applied after diagnostic factorial experiments (Box et al., 1978).

Despite extensive previous works on acid leaching of CFA, information is scarce regarding CFA leaching models that are specific to the extraction of alumina from CFA using sulphuric acid. This study focuses on using a combination of the full factorial design and the RSM in conjunction with the CCRD to identify and optimize factors that influence the direct leaching of CFA using sulphuric acid.

2. Materials and methods

2.1. Coal fly ash

The CFA sample used in the study was obtained from Kendal Power Plant, a division of Eskom (RSA). The sample was characterized by investigating the surface morphology, phase mineralogy, particle size and chemical analysis. The phase mineralogy and chemical composition of CFA are summarized in Tables 1 and 2 respectively. The particle size analysis was done by physically screening the samples using test sieves (Fritsch, Germany) of various screen sizes within the range of −38 μm and +212 μm. The CFA surface morphology analysis was carried out using a Scanning Electron Microscope (Model: Quanta-400F, FEI, USA). The CFA phase mineralogy analysis was carried out using an X-ray diffractometer (Model: X'Pert, PANalytical, Netherlands) operated with Co-Kα radiation generated at 40 kV and 50 mA. The chemical composition analysis was carried out using a Wavelength Dispersive X-ray fluorescence (XRF) spectrometer (Model: Axios, PANalytical, Netherlands) operated with a Rhodium tube excitation source. Filtrates were analyzed for aluminium using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analyzer (Model: SPECTRO GENESIS, Spectro Analytical Instruments, Germany). All reagents used in this study were of analytical grade. The reagents were all purchased from Merck and Sigma Aldrich and were used as received without further purification. Distilled water and analytical grade sulphuric acid (98% w/w) were used in the experiments.

Table 1
Mineralogical analysis of Eskom CFA.

CFA	Phase	Al_2O_3
	wt.%	wt.%
Amorphous	52.9	27.8
Hematite	0.8	–
Magnetite	1.65	–
Mullite	30.68	72.2
Quartz	13.97	–

2.2. Experimental design

2.2.1. Factorial design

Statistical Design of Experiments (DOE) was employed to study the leaching behaviour of CFA using a 2^4 full factorial design. In this study, the choice of factors and levels was based on past CFA leaching experience. Experimental design factors were classified as controlled factors and held constant factors. The controlled factors, presented in Table 3, were the factors selected for investigation. The held constant factor such as agitation rate is a factor that may have an influence on the response but is of no particular interest in the current study so it was held constant at 150 rpm.

2.2.2. Methodology for data analysis

2.2.2.1. Normal probability plot of effects. In the assessment of effects from unreplicated factorials, occasionally real and meaningful higher order interactions occur and therefore it is necessary to allow for selection. A normal probability plot method (Daniel, 1959) by which effects are plotted was used to provide an effective way of helping with selection.

2.2.3. Response surface methodology and central composite rotatable design

Response Surface Methodology (RSM) was used in this study. The main objective of employing RSM is to optimize the response surface that is significantly influenced by various process variables (Tripathy and Murthy, 2012). The design procedure for RSM used in this study had three stages as follows: (i) Designing and conducting of experiments (ii) Deriving and developing a mathematical model and (iii) Finding the stationary points or optimal set of experimental parameters.

The data for fitting the second order response was collected by using the central composite rotatable design (CCRD). The experimental results were analyzed statistically by using the analysis of variance (ANOVA) using Fisher's ratio test; standard errors of model coefficient (*t*-test) and the coefficient of determination (R^2).

For the two variables under consideration, a second order polynomial regression model was proposed as follows:

$$y = \beta_o + \sum_{i=1}^{2} \beta_i x_i + \sum_{i=1}^{2} \beta_{ii} x_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{2} \beta_{ij} x_i x_j + \varepsilon \tag{2.1}$$

where,y is the predicted response, β_o is the coefficient for intercept, β_i is the coefficient of linear effect, β_{ii} is the coefficient of quadratic effect, β_{ij} is the coefficient of interaction effect, ε is a term that represents other sources of variability not accounted for by the response function; x_i and x_j are coded predictor variables for the independent factors. The coefficients of the regression model were estimated by fitting the experimental results using Design Expert® 6 software.

2.3. Experimental

The sulphuric acid leaching experiment consisted of a 500 ml volumetric flask, a thermal reciprocal shaking bath and a filter funnel fitted with a filter paper. The filter funnel was mounted on the 1000 ml Erlenmeyer flask. Leaching experiments comprised of adding a weighted CFA sample, typically 50 g, to the volumetric flask containing sulphuric acid then agitating the resulting slurry in a constant temperature reciprocal shaking bath. Separate samples were used for each allotted leaching condition. The leaching was conducted at a constant agitation rate of 150 rpm. After leaching, the leached residual CFA was separated from the solution by filtration. Distilled water was used to remove the residual liquor that was absorbed by the leached ash. Subsequently, the leach liquor and wash solution were combined to produce the final leach liquor. The total volume of the final leach liquor was recorded. The dry residual CFA was analyzed by X-ray fluorescence