

Kinetic and thermodynamic parameters of silica leaching from Camden power station fly ash

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Abstract: - Fly ash from a South African power station ash dam was used. The fly ash approximated Class F fly ash but had a loss on ignition greater than 6%. The leaching parameters investigated were leaching time, KOH concentration, agitation speed, fly ash particle size, leaching temperature and liquid solid ratio (L/S). It was found that the optimum leaching conditions were leaching time of 6 h, 3M KOH, 500 rpm agitation speed, 25 L/S ratio, leaching temperature of 100°C. Silica leaching followed a modified Jander equation kinetics with an N value of 1.48 and an activation energy of 5.9 kJ/mol.

Key-Words: - Fly ash, Leaching, Potassium silicate,

1 Introduction

The increase in the human population and industrialization has led to the need to generate more electrical energy. Coal, being a relatively cheap resource, has led to the increase in its use for power generation, inevitably leading to huge amounts of fly ash (FA) being produced. FA is a micro spherical particulate waste gathered from flue gases during coal combustion for electricity generation. South Africa has the largest dependence on coal for electricity production in the world [1] South Africa's electricity generation utility, ESKOM, consumes 70% of the domestic coal supply accounting for 93 % of South Africa's power generation through coal fired thermal plants [2]. In 2010 Eskom generated 36 million tons of fly ash of which about 95% was disposed of in ash dams and dumps [3]. There are a number of problems associated with FA handling and disposal. These include that FA is a very difficult material to handle in a dry state because it is very fine and readily air borne even in mild wind. Long exposure to FA through inhalation causes fibrosis of lungs, silicosis and pneumonitis bronchitis [4, 5]. The heavy metals in FA can cause cancer and nervous system impacts such as cognitive deficits, developmental delays and behavioral problems [6]. People who live near unlined wet FA ponds and who get their drinking water from wells, have as high as 1 in 50 chance of getting cancer from drinking arsenic-contaminated water [7]. The dumping of FA in ash dams is a very costly exercise, leading to loss of arable land, impacting negatively on the environment, causing air and water pollution [8]. Though a pollutant, FA can be considered as the world's fifth largest raw

material resource [9]. Most research FA has focused on the use of FA as a construction material, alumina extraction, as an adsorbent for heavy metals, soil ameliorant and as a catalyst [9-15]. Silica extraction research has mainly focused on behavior of different fly ashes to leaching conditions using NaOH [16,17], but none of this research has come up with the thermodynamic and kinetic parameters of silica leaching from FA. Most of the research has focussed on classified FA which satisfy the ASTM C 618 [18] standard. This paper therefore seeks to establish the kinetic and thermodynamic parameters of silica leaching from FA and the mechanism of leaching. This paper also uses the FA which is being dumped in FA dams which is not being used in the construction industry (the 95%). The idea is to use for material which currently is being dumped and contributing to pollution of the environment. The research deliberately uses KOH as a leachant due to several possible favourable uses of potassium silicates. Potassium silicates produce a violet flame colour making them ideal for high-temperature welding with carbon arc electrodes, coatings of potassium silicates do not effloresce on exposure to the atmosphere, making them a preferred choice for decorative coatings, paints, and ceramic binders.

2 Materials and Methods

The FA was collected from Camden power station ash dam. KOH was supplied by Rochelle Chemicals. A 1000 ppm Si standard was supplied by Sigma Aldrich.

2.1 Equipment

Silica analysis was done using an Atomic Absorption Spectrometer (AAS) (Thermo scientific ICE 3000 Series). A Rigaku ZSX Primus II XRF was used for FA chemical content determination. Mineralogical content analysis was done using a Rigaku Ultima IV diffractometer. An Eriez Magnetics rotatory riffler was used for sample splitting.

2.2 Procedure

Silica extraction was achieved using a reflux reactor at various temperatures using a silicon oil bath coupled to a magnetic stirrer. The effects of leaching time, liquid solid loading (L/S), concentration of KOH, fly ash particle size, agitation speed and leaching temperature on the leaching of silica from Camden power station FA was investigated separately. The silica yield was obtained by analysis of leachate solution using an AAS with the incorporation of volume change as given in equation 1[19]

$$\%SiO_2 = \frac{\left(V_0 - \sum_{i=1}^{i-1} V_i \right) C_{SiO_2} + \sum_{i=1}^{i-1} V_i C_{SiO_2,i}}{m \left(\frac{C_{SiO_2}}{100} \right)} \quad (1)$$

2.3 Characterisation of Camden power station FA

Various techniques were used to characterise FA.

2.3.1 XRF

10 g of Camden power station FA dried at 100°C for one hour was mixed with 3 g of Sasol wax. The two were then thoroughly mixed using a mortar and pestle. The mixture was then quantitatively transferred into a pellet container and pelletised at 795 MPa pressure. The pellet made was then ready for XRF analysis.

2.3.1 XRD

Finely ground Camden power station FA was put into an XRD sample container and run on an XRD machine.

2.3.1 Loss on Ignition(LOI)

1.0 g of Camden power station FA was measured into a crucible. The FA was then ignited at 750°C

for 1 h. The loss in weight as a percentage was taken LOI.

2.4 Leaching Procedure

Various parameters were investigated to determine the optimum leaching conditions.

2.4.1 Effect of leaching time

A dry composite sample of FA was used to determine the silica leaching characteristics. The leaching was carried out for 6 h using the following conditions: L/S ratio of 20, 2 M KOH, agitation speed of 500 rpm, FA particle size as received. Sampling was done at 1 h intervals. The leachate was subsequently filtered and analysed on the AAS.

2.4.2 Effect of Liquid solid (L/S) ratio

Silica leaching was carried out under the following conditions: time 6 h, 2M KOH, agitation speed of 500 rpm, FA particle size as received. L/S ratio was varied from 15 to 30. Sampling was done at 1 h intervals for each L/S ratio. The leachate was subsequently filtered and analysed on the AAS.

2.4.3 Effect of KOH concentration

Silica leaching was carried out under the following conditions: time 6 h, L/S of 25, agitation speed of 500 rpm, FA particle size as received. KOH concentration was varied from 1 to 4 M. Sampling was done at 1 h intervals for each KOH concentration. The leachate was subsequently filtered and analysed on the AAS.

2.4.4 Effect of FA particle size

Silica leaching was carried out under the following conditions: time 6 h, L/S of 25, agitation speed of 500 rpm, KOH concentration of 3M. FA particle size was varied as follows -75, +75-106, +106-300 μm and as received. Sampling was done at 1 h intervals for each particle size. The leachate was subsequently filtered and analysed on the AAS.

2.4.5 Effect of agitation speed

Silica leaching was carried out under the following conditions: time 6 h, L/S of 25, agitation speed of 500 rpm, KOH concentration of 3M and FA particle size as received. Agitation speed was varied as follows 250, 500 and 750 rpm. Sampling was done

at 1 h intervals for each agitation speed. The leachate was subsequently filtered and analysed on the AAS.

2.4.6 Effect of leaching temperature

Silica leaching was carried out under the following conditions: time 6 h, L/S of 25, agitation speed of 500 rpm, KOH concentration of 3M and FA particle size as received. Temperature was varied as follows 80, 90, 100 and 110°C. Sampling was done at 1 h intervals. The leachate was subsequently filtered and analysed on the AAS.

2.5 Statistical Analysis

All experiments were carried out in duplicate with the average results of two outcomes within 5% of each other reported. ANOVA was employed to check the significance of variation of results.

3 Results and Discussion

3.1 Composition of Camden FA

Table 1 shows the oxide content (% w/w) of major elements and LOI for the Camden power station FA.

Table 1: Composition of Camden FA

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	LOI
47.8	28	5.1	7.3

Silica was the major component followed by alumina. The loss on ignition was high showing the % unburnt carbon.

3.1 Effect of leaching time

Fig. 1 shows the effect of leaching time.

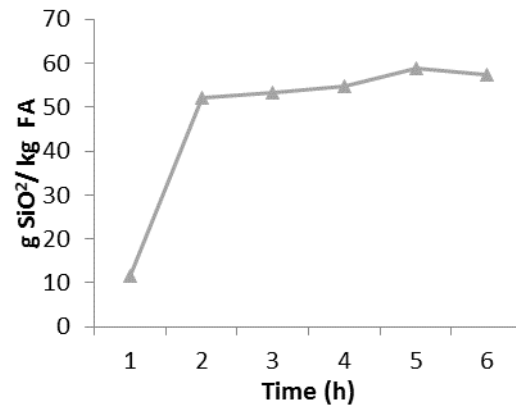


Fig. 1: Variation in silica yield with time (L/S ratio of 20, 2 M KOH, agitation speed of 500 rpm, FA particle size as received, Temperature 90°C)

The leaching of silica proceeds via a very fast reaction during the first hour and then stabilizes from then onwards. The difference in yield between 5 and 6 h was not statistically different so 6 h was taken as the leaching time.

3.2 Effect of L/S ratio

Fig. 2 the variation silica yield with solid loading

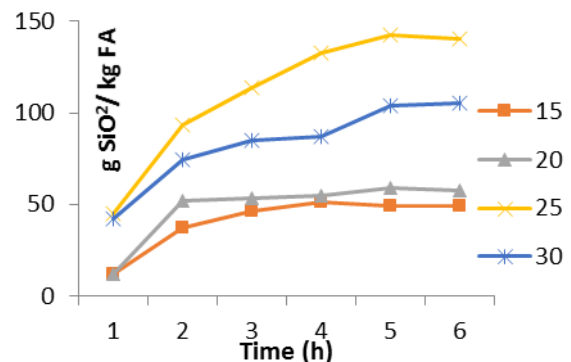


Figure 2: Variation of silica yield with L/S ratio (time 6 h, 2M KOH, agitation speed of 500 rpm, FA particle size as received, Temperature 90°C)

Fig. 2 shows that a reduction of L/S ratio from 20 to 15 resulted in the decrease in silica yield to about 48.97 g SiO₂/kg of FA. This is due to increased solid loading which results in the reduction of efficient mass transfer [20]. Low L/S ratios are also associated with geo-polymerisation as opposed to dissolution. Geo-polymerisation results in the consumption of dissolved silica thereby reducing the amount of silica extracted. The maximum yield of 140.32 g SiO₂/kg of FA was achieved at an L/S of

25. An L/S of 30 resulted in a 25% decrease in silica yield relative to the one at an L/S of 25. This can be attributed to a decrease in the amount of solid per amount of reagent in the reaction mixture. Therefore an L/S of 25 was used for subsequent experiments.

3.3 Effect of KOH concentration

Fig. 3 shows the variation in silica yield with concentration of KOH

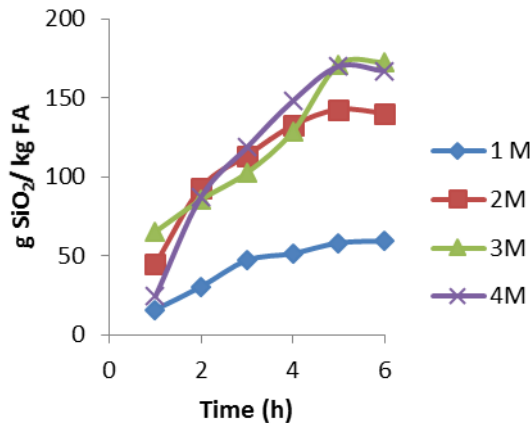


Fig. 3: Variation of silica yield with concentration of KOH (time 6 h, agitation speed of 500 rpm, L/S 25, ash particle size as received, Temperature 90°C)

There was an increase in silica yield with increase in KOH concentration. This is due to an increase in the available OH⁻ anion for leaching. An increase of KOH concentration from 3M to 4M resulted in a slight decrease on the yield of silica. This is due to the fact that a high concentration of KOH results in the co dissolution of alumina which then reacts with silica to precipitate as sodalite or cancrinite [21]

3.4 Effect of PSD

Fig. 4 shows the variation in silica yield with PSD.

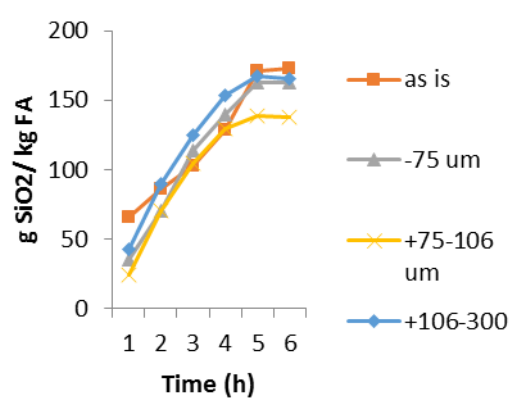


Fig. 4: Variation of silica yield with PSD (time 6 h, agitation speed of 500 rpm, L/S 25, KOH 3M, Temperature 90°C)

There was no significant difference in silica yield with variation in PSD as the difference in yield. This can be due to that over 85% of Camden power station fly ash was below 400 um with over 50% being less than 75 µm.

3.5 Effect of agitation speed

Fig. 5 shows the variation in silica yield with agitation speed.

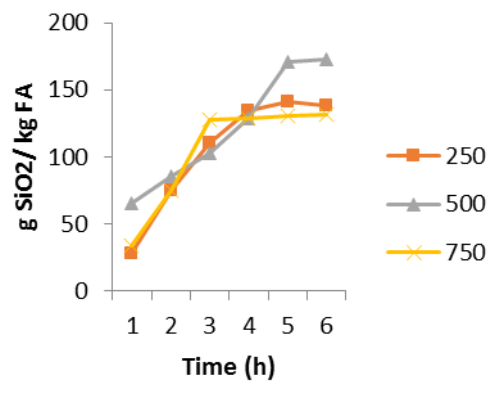


Fig. 5: Variation of silica yield with agitation speed (time 6 h, PSD as received, L/S 25, KOH 3M, FA particle size as received).

Increase in agitation from 250 to 500 rpm resulted in an increase in silica as this resulted in an increased contact between KOH and Camden ash. An interesting and odd result was found at 750 rpm where there was a 24% decrease in silica yield as compared to the yield at 500 rpm. The reason was that, for the leaching vessel used, agitation at 750 rpm resulted in spattering of Camden power station fly ash on the vessel walls due to high speeds resulting in a decrease in contact time between KOH and spattered ash leading to decrease in silica yield.

3.6 Effect of Temperature

Fig. 6 shows the variation of silica yield with temperature.

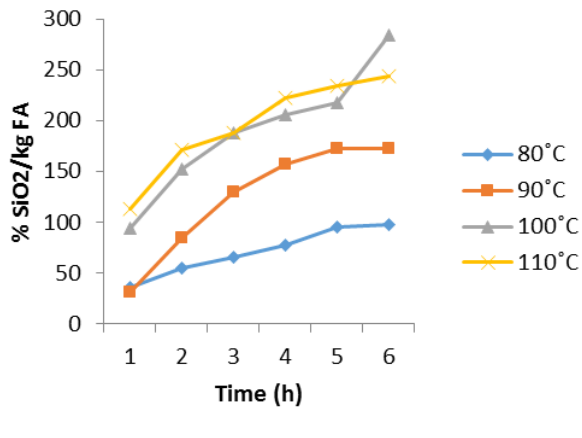


Fig. 6: Variation of silica yield with temperature (time 6 h, FA particle size as received, L/S 25, KOH 3M, agitation speed 500 rpm)

There was an increase in silica yield with an increase in temperature up to 100°C (Figure 9). An increase in temperature from 100°C to 110°C resulted in a decrease in silica yield from 283.7 g SiO₂/kg FA to 243.2 g SiO₂/kg FA. This is because higher temperatures promote co-dissolution of alumina which leads to high zeolite formation.

3.7 Kinetic modelling

Silica extraction was then done using the following condition: time 6 h, FA PSD as received, L/S 25, KOH 3M, Temperature 100°C and agitation speed at 500 rpm. The yield results were then fitted 21 kinetic models with the correlation coefficient being the determining factor for a best fit. The fitting of leaching results are shown in Table 2.

Table 2: The correlation coefficient of silica yield with various kinetic models

Type	R ²
Ginstling-Brounshtein	0.856
Zhuravlev, Lesokhin and Templeman	0.678
Anti-Jander (three-dimensional)	0.910
Kroger and Ziegler	0.7023
Jander (cylindrical diffusion)	0.8501
Anti-Jander (cylindrical diffusion)	0.902
Avrami-Erofeev	0.919
Avrami-Erofeev	0.922
Avrami-Erofeev	0.921
Avrami-Erofeev	0.916
Avrami-Erofeev	0.919
Zero order	0.9018
First order	0.848
Second order	0.849
Interface (contracting area)	0.918
Interface (contracting volume)	0.914
Interface	0.922
Prout-Tompkins	0.9168
SCM diffusion through inert/ash layer controls	0.853
SCM surface chemical reaction	0.924
Modified Jander Equation	0.982

From Table 2 only the modified Jander equation gave the best fit to the leaching data as it had a correlation coefficient of 0.982. The linearised version of the modified Jander is given in equation 2

$$\ln(1 - (1 - X))^{1/3} = \frac{1}{N} \ln K_N + \frac{1}{N} \ln t \quad (2)$$

Where t is the leaching time, X is the fraction of silica leached, K_N has the dimensions of a diffusion coefficient. The value of N is explained as follows [22] $N \leq 1$: The process is controlled by a chemical reaction at the surface or by dissolution of reactants or precipitation of reaction products, $1 < N \leq 2$, the process is controlled by diffusion of reactants through a porous layer of reaction products and $N > 2$, the process is controlled by diffusion of reactants through a dense layer of reaction products. Fig. 7 shows the plot of the modified Jander equation.

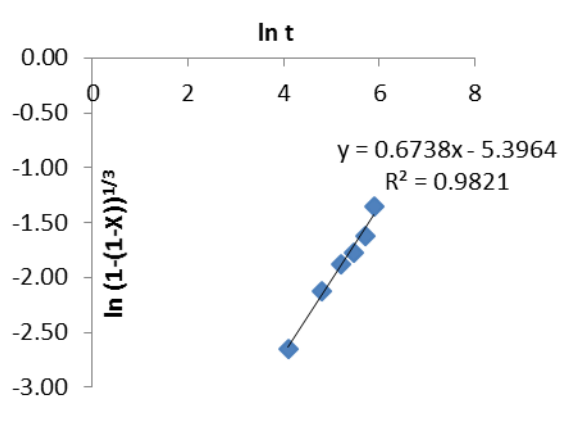


Fig 7: the plot of the modified Jander equation (Temperature 100°C, time 6 h, FA particle size as received, L/S 25, KOH 3M, agitation speed 500 rpm)

From Fig. 7 14 the value of N was calculated to 1.48. This therefore implies that the leaching of silica from ash within the first 6 h is controlled by diffusion of reactants through a porous layer of reaction products. To test the validity of the above, the plots were done at 80°C and 90°C. Figure 15 shows the plots at 80°C and 90°C.

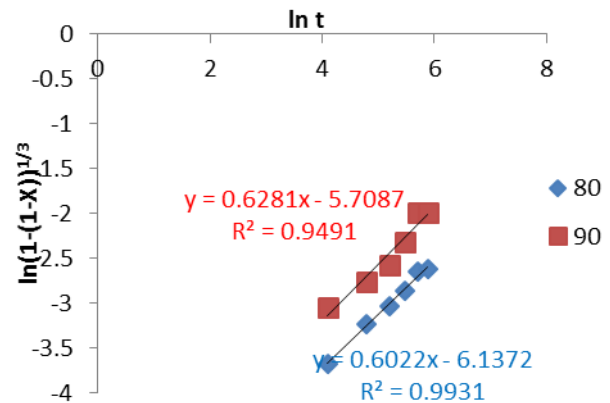


Fig. 8: the plot of the modified Jander equation at 80°C and 90°C (time 6 h, FA particle size as received, L/S 25, KOH 3M, agitation speed 500 rpm)

From Fig. 8 it can be seen the modified Jander equation fit the leaching data well, better than most kinetic models in Table 3. This therefore validated the diffusion model for the leaching of silica from FA. Leaching of silica at 80°C had the highest value of the correlation coefficient (0.9931). Lower leaching temperatures result in delayed formation of zeolites [23]. The delayed formation of zeolites mean that the impediment to silica diffusion is then reduced hence a higher correlation vale. A plot of the natural logarithm of the apparent constant against the inverse of temperature was then performed to calculate the activation energy of silica leaching.

3.8 Thermodynamics

Fig. 9 shows the Arrhenius plot for silica leaching.

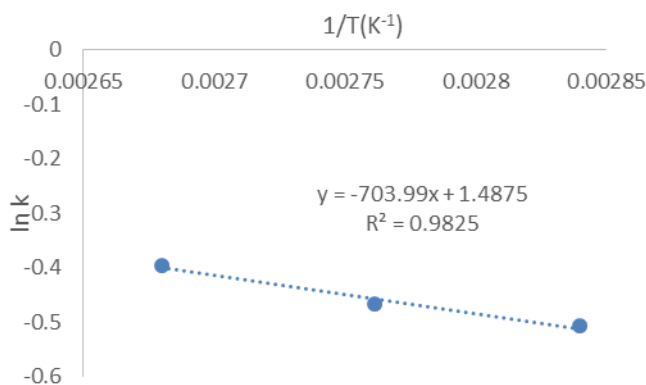


Fig 9: The Arrhenius plot for silica leaching from Camden power station FA

The correlation coefficient of 0.98 was seen as a good fit. The calculated activation energy was 5.9 kJ/mol. The low activation energy is agreement with diffusion controlled leaching and is very close with the activation energy obtained by Pietersen [24], (1993) for the dissolution of fly ash (6.5 – 9.2 kJ·mol⁻¹). This therefore validates that the modified Jander equation can be used as a kinetic model for the leaching of silica from Camden power station FA under alkaline conditions.

4 Conclusion

Camden power station FA can be used a source of silica. The best leaching parameters were 3M KOH, leaching temperature of 100°C, L/S ratio of 25, particle size as received from the power station, agitation speed of 500 rpm and a leaching time of 6 h. The leaching of silica is controlled by diffusion of reactants through a porous layer of reaction products as the leaching had an *N* value of 1.48 of the modified Jander equation kinetics. The yield was 283.7 g of silica per kg of FA. It is therefore recommended method to increase the yield by calcination of FA. It is also recommended to find use for the desilicated FA so as to achieve a zero waste discharge.

Acknowledgemnts

The authors would like to thank the University Research Council of the University of Johannesburg for their financial support. The authors are also

thankful to The National Research Foundation of South Africa for providing a bursary for the student.

References:

- [1] International Energy Agency, *Key world energy statistics*, Vol. 25, 2009.
- [2] Eberhard A, The Future of South African Coal: Market, investment, and Policy challenges, *Working Paper* 100 (2011).
- [3] Eskom Integrated Report 2011. Available online: www.eskom.co.za/annreport11/ (accessed on 26/10/2014.)
- [4] Schilling CJ, Davison AG, Durham S and Newman TAG, Asthma caused by pulverized fuel ash. *British Medical Journal*, Vol 292, 1986, pp. 156.
- [5] Cho K, Cho YJ, Shrivastara DK and Kapre S, Acute lung disease after exposure to fly ash, *Chest*, Vol. 106, 1994, pp. 309-311.
- [6] U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Office of Resource Conservation and Recovery. Human and Ecological Risk Assessment of Coal Combustion Wastes." Draft EPA, 2-4 (2010).
- [7] U.S. Environmental Protection Agency (EPA) Human and Ecological Risk Assessment of Coal Combustion Wastes" (draft). (Released as part of a Notice of Data Availability) (2007).
- [8] Carlson CL and Adriano DC, Environmental impacts of coal combustion residues, *Journal of Environmental Quality* Vol. 22, 1993, pp. 227-247.
- [9] Mukherjee AB, Zevenhoven R, Bhattacharya P, Sajwan KS, Kikuchi R, Mercury flow via coal and coal utilization by-products: a global perspective, *Resources Conservation and Recycling* Vol. 52, 2008, pp. 571-591.
- [10] Potgieter JH, Kabemba MA, Teodorovic A, Potgieter-Vermaak, SS and Augustyn WG, An investigation into the feasibility of recovering valuable metals from solid oxide compounds by gas phase extraction in a fluidized bed, *Minerals Engineering*, Vol 19, 2006, pp. 140-146.
- [11] Gitari WM, Petrik LF, Etchebers O, Key DL and Okujeni C, Utilization of fly ash for treatment of coal mines wastewater: Solubility controls on major inorganic contaminants, *Fuel*, Vol 87, 2008, pp. 2450-2462.

- [12] Somerset V, Petrik L and Iwuoha E, (2008). Alkaline hydrothermal conversion of fly ash precipitates into zeolites : the removal of mercury and lead ions from wastewater, *Journal of Environmental Management*, Vol. 87, 2008, pp. 125–131.
- [13] Babajide O, Petrik L, Musyoka N, Amigun B and Ameer F, Use of coal fly ash as a catalyst in the production of biodiesel, *Petroleum & Coal*, Vol.52, 2010, pp. 261 – 272 (2010).
- [14] Vadapalli VRK, Gitari WM, Ellendt A, Petrik, LF and Balfour G, Synthesis of zeolite-P from coal fly ash derivative and its utilisation in mine-water remediation, *South African Journal of Science*, Vol.106, 2010, pp. 1-7.
- [15] Reynolds K, Kruger R, Rethman N and Truter W, The production of an artificial soil from sewage sludge and fly-ash and the subsequent evaluation of growth enhancement, heavy metal translocation and leaching potential, in: *Water SA Special 1 Edition: WISA Proceedings* (2002).
- [16] Moreno N, Querol X, Andres JM, Lopez-Sole A, Stanton K, Towler M, Nugteren HW and Janssen M, Determining the Suitability of a Fly Ash for Silica Extraction and Zeolite Synthesis. *Journal of Chemical Technology and Biotechnology*, Vol.79, 2004, pp.1009–1018.
- [17] Font O, Moreno N, Díez S, Querol A, López-Soler A, Coca P, and García Pena F, Differential behaviour of combustion and gasification fly ash from Puertollano Power Plants (Spain) for the synthesis of zeolites and silica extraction, *Journal of Hazardous Materials*, Vol.166, 2009, pp. 94–102.
- [18] Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete, American Society for Testing and Materials C 618.
- [19] Georgiou D and Papangelakis VG, Sulphuric acid pressure leaching of a limonitic laterite: chemistry and kinetics, *Hydrometallurgy*, Vol.49, 1998, pp. 23–24.
- [20] Nosrati A, MacCarthy J and Addai-Mensah J, Acid Leaching and Rheological Behaviour of Siliceous Goethite Ni laterite Ore: Effect of Solid Loading and Temperature. *Proceedings of Chemeca* (2013).
- [21] Zeng R, Umana JC, Querol X, Lopez-Soler A, Plana F and Zhuang X, Zeolite synthesis from a high Si–Al fly ash from East China, *Journal of Chemical Technology and Biotechnology*, Vol.77, 2002, pp. 267-273.
- [22] Chen C, Gong W, Lutze W, Pegg IL and Zhai J, Kinetics of fly ash leaching in strongly alkaline solutions. *Journal of Material Science*, Vol.46, 2011, pp. 590–597.
- [23] Nugteren HW, Secondary industrial minerals from coal fly ash and aluminium anodising waste solutions, PhD thesis (2010).
- [24] Pietersen HS, Reactivity of fly ash and slag in cement. PhD Thesis Delft University of Technology (1993).