

Kinetic Mechanism of Desilicated Fly Ash Lime Consumption

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This paper presents study of the kinetic mechanism of lime consumption using desilicated fly ash (DFA). Desilicated fly ash (DFA) a residue from leaching of silica from fly ash was stabilised using lime at elevated temperatures. DFA and lime were mixed in different ratios at optimum moisture content and maximum dry density and then cured at 40 °C, 80 °C and 100 °C for 4 days. 80 °C was found to be the optimum curing temperature. The DFA: lime ratio of 70:30 was found to have an average UCS of 8.6 MPa. Lime consumption was found to follow modified Jander kinetics with activation energy of 16 kJ/mol and a reaction grade of 3 meaning that the reaction was controlled by diffusion of reactants through a dense layer of reaction products. The main hydration products were calcium silicate hydrate and tricalcium aluminate. Toxicity leaching tests showed a 79 % reduction in the leachability of trace and heavy metals. Therefore, DFA can successfully be stabilised using lime.

Keywords: desilicated fly ash, modified Jander kinetics, toxicity.

1. INTRODUCTION

Fly ash (FA) is the micro spherical particulate waste gathered from flue gases during coal combustion for electricity generation. South Africa uses low grade coal for power generation, which results in approximately 25 % or greater inorganic residue, remaining as waste. The major component of this waste is FA [1]. Metal or mineral recovery from FA is one of the numerous ways to use FA as a resource. Elements such as titanium, germanium, silica, aluminium, cadmium, calcium and magnesium [2–4] have been recovered from FA. Silica recovery from FA has led to the synthesis of zeolites, nanosilica particles and xerogels for use as adsorbents [5, 6]. The residue (desilicated fly ash (DFA)) from silica extraction from FA has not received attention in research. Lime stabilisation of the desilicated fly ash is one of the alternative ways to make valuable civil engineering materials from DFA since lime has been used to stabilise high alumina low silica FA [7]. The kinetic mechanism of lime stabilisation of DFA needs therefore to be studied so that the mechanism is understood so as to make quality civil engineering materials. There are varying kinetic mechanism reported in literature by various researchers to explain lime consumption in FA and lime composites. These include pseudo first order [8, 9] and pseudo second order [10] modified second order [9]. The above kinetics and thermodynamic studies do not take into account the amount of FA used in hydration reaction. A quick survey on lime and FA hydration reaction shows that less than 40 % FA takes part in hydration reaction [11–13].

This necessitates the need for research in lime and DFA reactions where the amount of DFA that partakes in

the hydration reactions is accounted for in calculating thermodynamic and kinetic parameters. The influence of curing temperature and time on lime consumption by DFA were investigated in detail. In addition, series of tests on toxicity leachability using Toxicity Characteristic Leaching Procedure (TCLP) were conducted in to assess the in service pollution potential of the DFA composite.

2. EXPERIMENTAL METHODS

Oven dry DFA and lime were dry mixed at ratios of 90:10, 80:20, 70:30 and 60:40. Table 1 shows the X-ray Fluorescence (XRF) characterisation of DFA. The pH of DFA was found to be 12.28. The pH was higher than that typical FA because DFA has more basic oxides (especially K₂O) than FA which then contribute to the high alkalinity. DFA was also characterised by low silica content due to leaching of silica.

Water was then quantitatively added at the optimum moisture content (OMC) of each mix. The DFA-lime – water mixture was then mixed thoroughly to uniformly spread the moisture amongst the dry solids. The calculated weight of water added was done after lime had slaked. For each mix ratio at a particular water content, three moulds were prepared. The mixed DFA-lime –water mixture was then cast into a 100x100x100 mm³ mould and pressure molded from one end using a moulding load of 5 kN. The moulding was done at maximum dry densities for each particular ratio of DFA: lime. When the mould had obtained sufficient strength, it was demoulded and subsequently sealed in a plastic. Casts which showed uneven surfaces due to demoulding or pressure casting were rejected. The above procedure was repeated with as received FA for comparison. The casts were then cured for 96 h at 80 °C. After 96 h the cast were removed from the oven and allowed to cool to room temperature.

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Unconfined Compressive Strength (UCS) was determined in accordance with ASTM D2166. Free lime content was determined using the method proposed by Rao and Asha (2012) [8]. A standard solution of ammonium acetate was prepared by dissolving 1.6 g of ammonium acetate in 100 mL of ethanol using a 100 ml volumetric flask. 0.2 ml of phenolphthalein solution was added per every 100 ml of ethanol glycerol solvent (2:1). 1 g of finely ground composite sample was added to 60 ml of the ethanol-glycerol in a 250 ml round bottom flask to which 2 g of anhydrous strontium nitrate was added. The round bottom flask was then connected to a condenser and the mixture was brought to boil for 20 min. After 20 min boiling was stopped followed by filtration of the hot mixture. The filtrate was brought to boiling point and immediately titrated against the standard ammonium acetate solution to a colourless end point.

The percent free lime is calculated as:

$$\% \text{ free CH} = EV \times 100, \quad (1)$$

where E is the lime equivalent of the ammonium acetate solution (g/mL) and V = milliliters of ammonium acetate titre. An average of three casts within 10 % of each other was reported as the final result.

A modified picric acid methanol method was used [11] to determine reacted/hydrated DFA. 1 g of DFA: lime composite was accurately weighed into a teflon beaker. A picric acid-methanol solution (9 g : 60 ml) was added to the composite material. The mixture was stirred for 15 min and then subsequently 40 ml of deionised water was added and stirring was continued for another 45 min. The mixture was immediately filtered using ashless filter paper. The ash-less filter paper and the residue were washed with methanol until the filtrate appeared colourless and then they were further washed with 300 ml of deionized water at 60 °C. The residue and ash-less filter paper were ignited in an electric furnace at 950 °C for 60 min. The % reacted DFA was calculated using:

$$Y = \left(1 - \left(\frac{S}{P_f F} \right) \right) * 100, \quad (2)$$

where S is the residue per gram of the composite, P_f is the % DFA in the composite, F is the residue for pure DFA.

Table 1. XRF analysis of FA and DFA

Parameter	FA, % m/m	DFA, % m/m
Na ₂ O	0.0658	0.0658
MgO	0.585	0.485
Al ₂ O ₃	23.8	38.7
SiO ₂	45.06	19.6
P ₂ O ₅	0.63	0.84
SO ₃	1.250	0.613
K ₂ O	1.2	25.2
CaO	6.82	4.25
TiO ₂	2.54	2.55
Fe ₂ O ₃	9.4	4.25
LOI	7.9	2.5
pH	10.69	12.28

3. RESULTS AND DISCUSSION

3.1. Variation of UCS with DFA content

Fig. 1 shows the variation of UCS with lime composite.

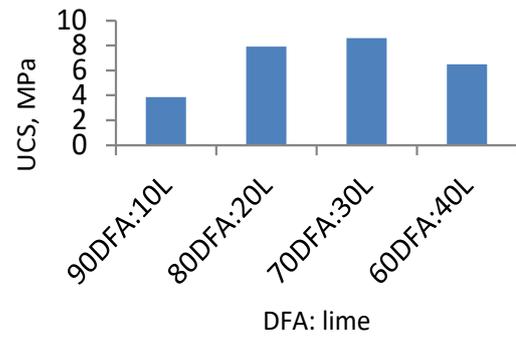


Fig. 1. Variation in UCS composites with lime content after curing at 80 °C for 96 h

The 70:30 DFA:Lime composite had the highest UCS of 8.57 MPa. After 24 h of soaking in water the composite had a UCS of 6.5 MPa and water absorption of 17.3 %. This composite met the minimum requirements of the ASTM C34-13 and was therefore taken for further test work.

3.2. Effect of curing temperature

Fig. 2 shows the variation of UCS with temperature.

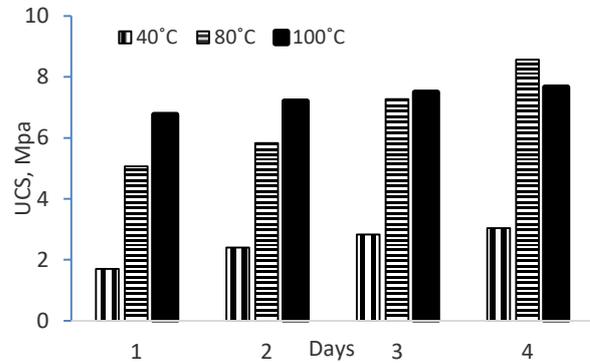


Fig. 2. Variation in UCS with curing temperature and curing time of the 70:30 DFA:lime composite

A change in temperature from 40 °C to 80 °C brought about at least 140 % increase in UCS in DFA:lime composites showing that the initial temperature increase accelerated pozzolanic/hydration reaction. The increase from 80 °C to 100 °C brought about a 33 % increase in UCS only after 24 h, there after the increase in UCS was not significant with the difference at 3 days being 3 %. After 4 days the UCS of composites cured at 80 °C were higher than the one at 100 °C. This can be explained using SEM (Fig. 3) micrographs of the 70:30 DFA: Lime composites cured at 80 °C and 100 °C.

The extensive covering of DFA particles with lime and hydration products after 1 day of curing for the composite cured at 100 °C would be the reason for the early development of high strength as compared to the one cured at 80 °C (Fig. 3 a and b respectively). The extensive covering also acts as a barrier for the further hydration of DFA particles as by the third day DFA particles were completely covered by hydration products (Fig. 3 c). The composite cured at 80 °C was still fairly covered by hydration products at day four allowing for further hydration to take place.

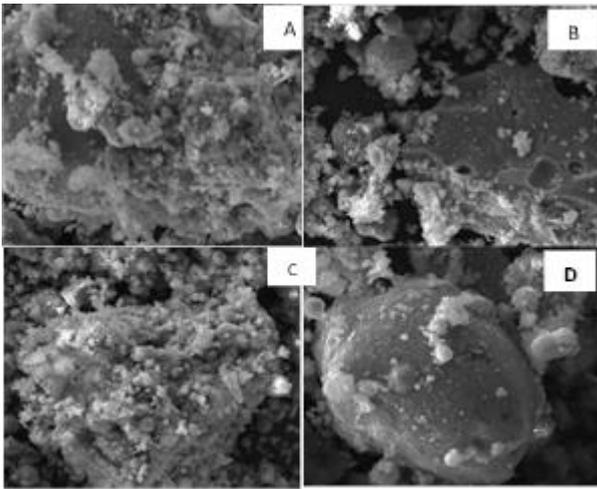


Fig. 3. SEM micrographs of 70: 30 DFA: lime composite: a–100 °C after 1 day; b–80 °C after 1 day; c–100 ° after 3 days; d–80 °C after 4 days

3.3. Kinetics of lime consumption

Fig. 4 shows the variation in lime consumption with time and curing time.

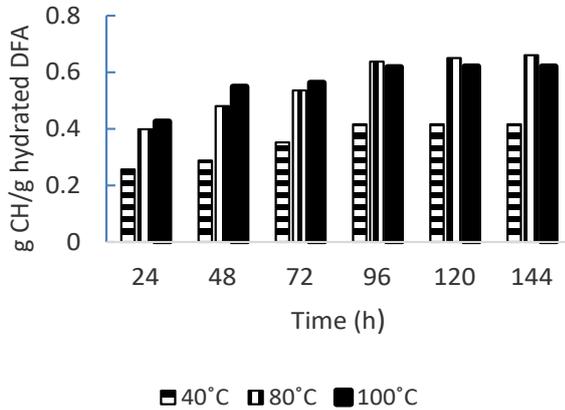


Fig. 4. Lime consumption at various temperatures over 96 h using DFA: Lime (70:30) composite

The highest consumption was at 100 °C up to 72 h. The high temperature provides enough thermal energy for hydration to take place. After 24 h lime consumption is about 61, 69 and 69 % of the 96 h consumption for composites cured at 40 °C, 80 °C and 100 °C. From 96 h to 144 h the consumption of lime at 80 °C was higher than that at 100 °C. This is due to extensive encapsulation of DFA particles at 100 °C hindering further hydration (Fig. 4).

Second order kinetic model and modified Jander kinetic model were tested to see if lime consumption fitted these models. Second order was chosen because previous FA lime consumption reaction have been modelled as second order [8, 11]. Fig. 5 and Fig. 6 show the plots of the modified Jander and second order kinetics respectively.

The modified Jander plot had a better fit as it had R^2 valued greater than 0.92. Furthermore, the k values obtained from the second order plot could not be used to calculate activation energy as the Arrhenius plot had a R^2 value of 0.00528. Therefore, the modified Jander equation was chosen to describe lime consumption by DFA. One of the assumptions of the modified Jander kinetics is that for

diffusion-controlled mass transfer spherical particles could be treated as flat slabs [14].

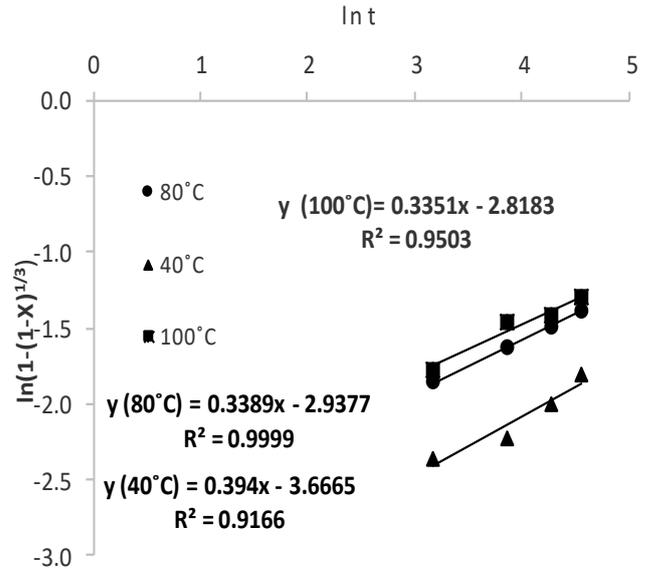


Fig. 5. Modified Jander plot at various temperatures of the 70:30 DFA:lime composite cured at 80 °C for 96 h (X is the fraction of lime consumed and t is temperature in Kelvin)

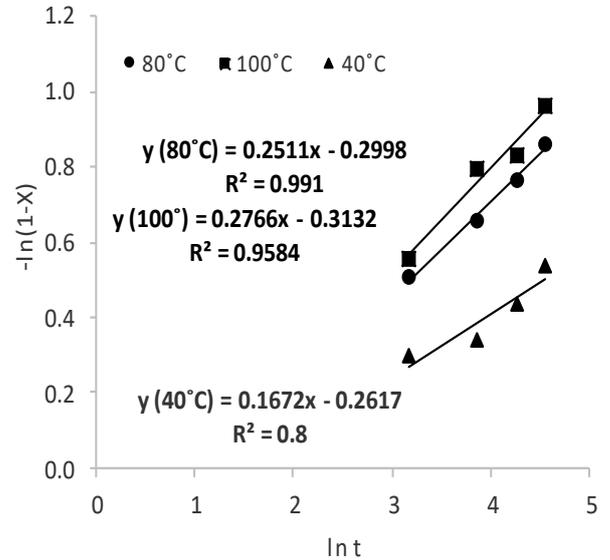


Fig. 6. Second order plot at various temperatures 70:30 DFA:lime composite cured at 80 °C for 96 h (X is the fraction of lime consumed and t is temperature in Kelvin)

The appearance of flat slabs in the SEM micrographs (Fig. 3) further validates the validity of the use of modified Jander equation to explain the kinetics of lime consumption by DFA. The original Jander equation was modified by incorporation of the term N (reaction grade) so that it can apply to broad reactions including consecutive and overlapping reactions [15]. This then suits hydration reaction of DFA since dissolution and hydration reactions are involved. The calculated N values at 40 °C, 80 °C and 100 °C were 2.6, 3.0 and 3.0 respectively. This therefore means that lime consumption by DFA is controlled by diffusion of reactants through a dense layer of reaction products [15]. This was also supported by the SEM micrograph analysis of DFA-lime composites (Fig. 3). The consumption of lime is greatly reduced once hydration products form around DFA particles (Fig. 3 and Fig. 4).

3.4. Activation energy

Fig. 7 shows the Arrhenius plot of lime consumption using DFA.

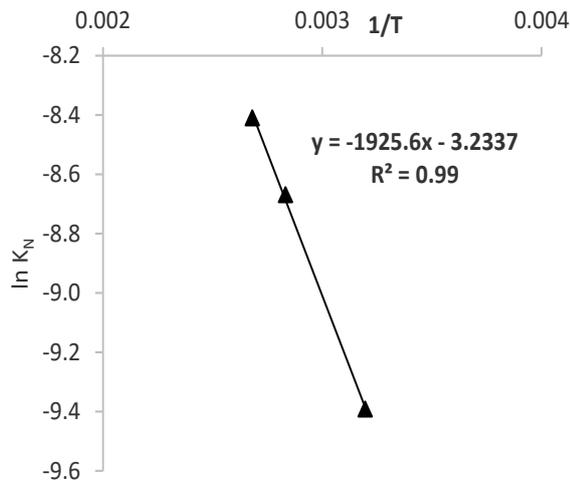


Fig. 7. Arrhenius plot of lime consumption by DFA (Where K_N is the slope of the Modified Jander plots Fig. 5 and T is the temperature in Kelvins)

The activation energy was calculated as 16 kJ/mol. Previous FA research has given figures of 47.3–63.1 kJ/mol [9] using modified second order and 1.6–30.7 kJ/mol [10]. The major difference is that the amount of DFA that reacted or participated in hydration reaction is quantified in this research. A quick survey of literature shows that only a small quantity of FA takes part in hydration reaction (below 40 %) [11–13]. Therefore, it was imperative to include the mass of reacted hydrated DFA in calculation of reaction extent rather than the whole DFA added to the composite.

3.5. Toxicity characteristic leaching procedure (TCLP)

Table 2 shows the leachability of metals from the 70:30 DFA: lime composite and the 80:20 FA:lime composite. The results are an average of three samples.

Table 2. TCLP results of the 70:30 DFA:lime composite

Element	DFA, ppm	70:30 composite, ppm	% reduction
Cr	0.116	0.028	75.8
Mn	0.388	0.015	96.1
Fe	5.98	1.25	79.1
Ni	0.215	0.022	89.8
Cu	0.315	0.035	88.9
Zn	0.125	0.001	99.2
Ba	10.3	0.821	92
Pb	0.286	0.0141	95.1

Stabilisation of DFA with lime using a ratio of 70:30 DFA: lime reduced the leachable heavy and trace metals by over 79 % (Table 5). An interesting point is that no new crystalline structure was formed which incorporated the heavy and trace metals in Table 2 (Fig. 8) yet their leachability was reduced in the composite. The explanation for this is that the covering/encapsulation of DFA particles with hydration products forms a barrier thereby preventing the leaching of heavy and trace metals (Fig. 5 and Fig. 6).

3.6. Development of hydration products

Fig. 8 shows the hydration products of the composite

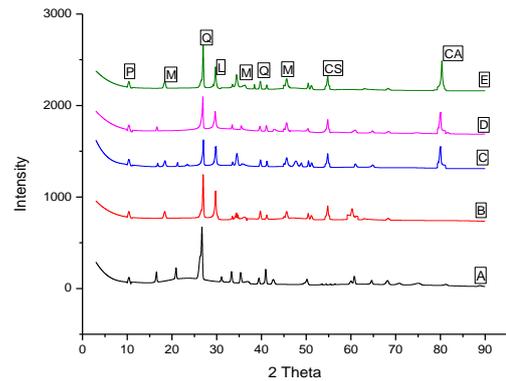


Fig. 8. XRD patterns of DFA (A) and DFA:lime composites (70:30) cured at 80 °C for 1, 2, 3, and 4 days (B, C, D, E respectively). P: Philipsite K, M: Mullite, Q: Quartz, L: CaO, CS: Calcium silicate hydrate, CA: tri-calcium aluminate hydrate

The major difference between DFA and the DFA:lime composite is the presence of hydration products in the composite. The hydration products are calcium silicate hydrate (CSH) at about 55° and tri-calcium aluminate hydrate (C_3AH) hydrate at about 80°. Though the CSH peak is normally at 29° and 50°, the peak at 55° can also be attributed to CSH [16]. Basal shift if calcium hydrates at low Si/Ca is highly likely due to low silica content in DFA [17]. The presence of tricalcium aluminate has also been reported in low silica FA hydration [18].

One interesting phenomenon is the appearance of C_3AH only after 48 h of curing whilst CSH appears after 24 h of curing. This is due to the fact that the solubility constant for CSH is lower than that of C_3AH [19] and hence CSH forms faster than C_3AH . There was also a corresponding decrease in the intensity of the lime spectra with increase in curing period as lime is being consumed. The presence of typical DFA phases (Mullite and Quartz) in the composites is further evidence of the presence of DFA which had not gone through hydration. The relative peak intensity of the CSH was 75 % less than that of C_3AH further proving that Al was more dominant than Si in the starting material.

4. CONCLUSION

DFA can be stabilised with lime resulting in a composite which can be used for masonry as the 70:30 DFA:lime composite met the minimum requirements for load bearing non exposed masonry and load bearing exposed side construction masonry (ASTM C34-13). The optimum curing temperature was 80 °C for 96 h. Lime consumption by DFA follows modified Jander Kinetics with an activation energy of 16 kJ/mol. DFA lime pozzolanic reaction are fast (69 % lime consumed within 24 h) as compared to FA lime reactions. Curing of DFA:lime composites at temperatures higher than 80 °C result in lowering of late stages strength due to encapsulation of DFA particles with hydration products. The 70:30 composite can be used safely in the environment

as 75%. The research therefore provides a way to deal with waste from silica leaching of fly ash thereby proving a zero waste process.

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