Durability of desilicated fly ash lime composites

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Abstract. Remediation of residual fly ash from coal fired electric power plants is beneficial to the environment. The chemical, physical, geotechnical and radiological properties of desilicated fly ash (DFA) were investigated. The DFA: lime ratio of 70:30 composite was found to have an average UCS of 8.8 MPa showing 19.5% water absorption after a 24 h soak with a corresponding 23.5% reduction in UCS. The composite was found to meet the minimum UCS requirements after 8 wet and dry cycles but with failure at 10 cycles. The composite was found not to be resistant to acid attack at pH 2 and hence could not be used in the vicinity where landfill leachate may come into contact with the composite. The composite had relative stability against acid rain and normal rain. The composite met the minimum requirement of ASTM C34-13, and thus provide an opportunity for high volume utilization of the residual ash for construction of load bearing walls.

1. Introduction
Fly ash (FA) is a residue from the combustion of coal for electricity generation. FA is a well-known pollutant as long term exposure to FA through inhalation causes fibrosis of lungs, silicosis and pneumonitis bronchitis [1, 2]. The increase in the need for silica has led to the use of FA as a source of silica [3, 4]. The leaching of silica from fly ash is a well-studied topic [3, 4]. Silica leaching is achieved using either KOH or NaOH. The leached silica can then be used to produce zeolites, coatings and mesoporous silica adsorbents [5-7]. Not much attention has been given to the residue of silica leaching from FA. If the silica leaching residue, desilicated fly ash (DFA), is not utilised then it becomes a secondary pollutant whose effect on the environment are unknown.

DFA has been shown to be alkaline with a pH of 12.28 [8]. The alkaline pH is due to basic oxides (especially K2O) it contains. DFA is characterised by low silica to alumina ratio of 0.51 due to removal of silica during leaching. One research has shown that DFA mixed with lime can be used to stabilise expansive soils [8]. This study therefore seeks to explore the durability of the DFA: lime composite with regards to its potential application in masonry. The most competent DFA: lime composite was found to be the one with a ratio of DFA: lime of 70:30 wt respectively [8]. This composite was then subjected to wet unconfined compressive strength (UCS) tests, alternate wet and dry cycles tests and exposure to different acidic media. The criterion for determination of durability was UCS using ASTM standards. The research also focused on the use of microstructure to explain physical properties of the composite.

2. Materials and Methods
2.1 Materials
FA was supplied by Camden power station in South Africa. DFA was obtained through leaching of silica from FA.
2.2 Equipment
Mineralogical analysis was done using a Rigaku Ultima IV difractometer. Unconfined compressive strength (UCS) was tested on all samples using a Cyber plus evolution compression machine at 0.25 MPa/s [9]. The reported UCS was an average of 3 samples.

2.3 Methods
The cured DFA: lime (70:30) composite was subjected to a variety of tests to determine durability. ASTM D559- (ASTM, 2015) [10] was used to determine the variation of UCS with alternate wet and dry cycles. The cured composites were also immersed for a period of 28 days in various acidic conditions. A pH of 2, 4.88 and 6 were chosen. The solution were synthesised by mixing 1 M citric acid and 1 M sodium citrate until the required pH was attained. pH 2 represented the landfill leachate pH, pH 4.88 represented acidic rain and pH 6 represented normal rain [11]. Water absorption of the cured composites was determined using ASTM C373 (ASTM 2014) [12].

2.4 Background
Previous studies by the authors [8] have shown that a DFA: lime (70:30) cured at 80º C for 96 h produced the most competent composite with a UCS of 8.8 MPa. The composite had an optimum moisture content of 30%. An increase in lime content to 40% was accompanied with a 24.4% drop in UCS. The environmental footprint of the composite was assessed using Toxicity Characteristic leaching Procedure (TCLP) and the results are shown in Table 1.

![Table 1. TCLP analysis if the DFA: lime composite](image)

The composite was shown not to be toxic as all analysed elements were within the TCLP limits. Of interest too was that the curing of the composite was accompanied with the reduction in leachability of metals. This showed that the DFA: lime composite was capable of immobilising metals in its structure. The XRD analysis of the DFA: lime composite is shown in Figure 1.
Figure 1. XRD analysis of DFA and DFA:lime composite (cured at 80°C for 4 P: Philipsite K, M: Mullite, Q: Quartz, L: CaO, CS: Calcium silicate hydrate, CA: tri-calcium aluminate hydrate)

The obtaining hydration products of the DFA: lime composite were calcium silicate hydrate and tri-calcium aluminate hydrate, which were responsible for the strength gain at the end of the curing period.

3. Results and Discussion

3.1 Durability using wet compressive strength
Table 2 shows the variation in wet compressive strength of the composite with soaking over a period of 24 h. The composite showed a low water absorption rate of 17%. This is within the acceptable limits ATMM C34-13 where the maximum water absorption should be less than 25%. The low water absorption rates can be attributed to increase in crystalline structure of the composite as compared to DFA as shown in the XRD analysis (Figure 1).

Table 2. Wet compressive strength of the DFA: lime composite

| Composite (DFA:Lime) | 70:30 |
|---------------------|-------|
| Mass of cast (g)    | 1504.83 |
| Mass of cast after 24 h soak (g) | 1765.25 |
| UCS before soaking (MPa) | 8.6 |
| UCS after soaking (MPa) | 6.5 |
| % water absorption | 17.3 |
| % reduction in UCS | 24.4 |

3.2 Durability using wet and dry cycles
Figure 2 shows the change in UCS with wet and dry cycles
Figure 2. Variation in UCS with number of wet and dry cycles for the 70:30 DFA: lime composite.

The DFA: lime composite was resistant to alternate wet and dry cycles of up to 8 cycles. The initial increase in UCS from cycle 1 to cycle 3 may be due to availability of moisture during soaking which then allows hydration to take place during the drying part of a cycle. The composite fails after 8 cycles as the UCS drops to below 3.5 MPa. This is the minimum UCS allowed by the South African Building council for non-facing plastered brick (SANS 227:2007). The decrease in UCS is due to an increase in average porosity of the composite as is shown in Table 3. Figure 3 also shows the microstructural change that happen during the wet and dry cycles. It is important to note that there is a reduction in the intensity of the lime (CaO) peak after 8 cycles. Lime is weak filler and is therefore dissolved by water during the cycles due to water ingress into the composite. During the dry phase of the cycle, voids are left where lime unoccupied space leading to reduction of UCS.

Figure 3. Variation in UCS with soaking days and pH for the DFA: lime composite (70:30)
Table 3. Variation in porosity with number of wet and dry cycles

| Cycle | Average porosity |
|-------|------------------|
| 0     | 0.25             |
| 1     | 0.24             |
| 2     | 0.27             |
| 3     | 0.27             |
| 10    | 0.29             |

3.3 Durability using various acidic environments

Figure 4 shows the variation of UCS with exposure to different acidic environments.

There was an 87% reduction in UCS with a 28 day exposure to simulated landfill conditions. This therefore meant that the composite is not suitable for building near landfill sites where there might be a risk of exposure to landfill leachate runoff. The 28 day exposure to simulated acid rain resulted in a 30% reduction in UCS. Simulated normal rain showed a UCS reduction of 18%. The UCS reduction was also accompanied with weight loss of the composite. Figure 5 shows the microstructural changes after 28 days of immersion in different acidic conditions.

Figure 5. Change in microstructure of the DFA: lime composite with 28 days of immersion in various acidic solutions
There was a reduction in the intensity of all peaks with immersion in acidic media. There was significant reduction of the tri-calcium aluminate hydrate and calcium silicate hydrate for the composite immersed in pH 2 solution. This would explain the 87% reduction in UCS. The reduction for the respective peaks in the composite immersed in pH 6 solution was not significant and hence the less than 20% reduction in UCS.

4. Conclusion
The following conclusion can be derived from this work: Calcium Silicate hydrates and tricalcium aluminate hydrates are responsible for UCS growth in DFA lime composites. The presence of lime as a weak filler in the composite is responsible for the loss of UCS during 24 h soak and wet and dry cycles. The average porosity increase due to dissolution of lime also leads to UCS decrease. The consumption of calcium silicate and tricalcium aluminate hydrate during acid soak is responsible for the reduction of UCS on exposure to acidic environments. The DFA lime composite can be used in areas where acidic rain is experienced and not where landfill leachates can be experienced. This study provides opportunities for use of waste in the construction industry thereby reducing environmental impact of the waste. The DFA lime composite met the minimum requirements of ASTM C34-13[13].

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