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Featured Article:

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A Study on the Pozzolanic Properties of Pennisetum Purpureum Ash

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Abstract

Pozzolanic properties of Pennisetum purpureum grass ash were tested on Portland cement. Results show that the ash can be blended with cements without compromising binding strength of the cement. It was found that Portland cement could be blended with Pennisetum purpureum up to a ratio of 3:2 compromising compressive strength of mortar.Mortar with lower cement replacement took longer to set as evidenced by lower compressive strength within the 28-day aging time. Mortar with higher cement replacement had lower water absorption capacity, an indication that the test pozzolan was of smaller particulate size. XRF analysis and the FTIR spectrum showed that the ash has a higher content of silica. The XRD pattern of the ash showed that the ash was predominantly amorphous. SEM images showed that the ash produced at 600°C had residual carbon material.

1 Introduction

Reports in the literature suggest that global cement manufacturing contributes about 5% anthropogenic carbon dioxide emissions (Huntzinger and Eaton, 2009; Worrell et al., 2001). Carbon dioxide is one of the greenhouse gases responsible for the increase in global warming. The debate on reduction of green gases has been going on for more than 20 years and has been subject of discussion at major international conferences, e.g. The Kyoto Protocol.To mitigate against release of huge volumes of carbon dioxide in cement manufacture, a number of pozzolans are being developed as substitutes in the cement manufacture. Pozzolans are inexpensive, naturally occurring and man-made siliceous materials that can be used as cement substitutes in mortar or concrete mixtures. They participate in a cementitious reaction with calcium hydroxide (lime) and other alkalis.

The major sources of pozzolans suitable for various applications include, ash-like deposits from volcanic activity, fired and crashed clay, furnace slag from industrial processes and organic ash from burning coal. A number of researchers have reported on potential pozzolanicmaterials and these include rice husk ash (Habeeb and Fayyadh, 2009; Salas et al., 2009), zeolites (Madandoust et al., 2013), metakaolin (Courard et al., 2003), silica fumes (Wong and Razak, 2005), coalfly ash (Kiattikomol et al., 2001) and slag. Use of such material in cement manufacture contribute towards reduction of energy consumption and release of carbon dioxide.

We report a potential application of *Pennisetum purpureum* ash, better known as elephant grass ash as a pozzolan in cement production. The grass grows to a height of up to 2 metres and is found in many parts of Africa inclusive of Zimbabwe (Figure 1). It is mostly used as thatching grass, although most of it is burnt out during land clearance and cut to improve visibility along roadsides.

Figure 1: Picture of *Pennisetum purpureum*

2 Experimental

Elephant grass was harvested from the Scientific and Industrial Research and Development Centre farm, in Harare. The grass was sun dried and pulverized in a laboratory mill. The pulverized sample was acid leached in a 2 M HCl solution. The acid leached sample initially burnt out to remove most of the carbonaceous material before being ignited in a muffle furnace at 650°C for one hour to get rid of any residual carbon material. The resultant white ash sample was characterized as explained below.

A Thermo Fisher Scientific Nicolet iS5 MIR FTIR spectrophotometer equipped with an ATR iD7 accessory and OMNIC software was used to record spectra of ash samples. A GBC Quantima 120 ICP-AES was used in the determination of cation exchange capacity as described below. A Pananalytical Laboratory Axious 172 Series wavelength dispersive XRFspectrophotometer was used to determine the elemental composition of the *Pennisetum purpureum* ash. A Joel JSM 6510 microscope was used to record SEM images of ash samples. Ash samples were prepared on sample powder holder.

For the determination of pozzolanic properties, Portland cement samples were first blended with *Pennisetum purpureum* ash in the ratios of 4:1, 18:7, and 3:2 as summarized in Table 1. Selected pozzolanic properties of the ash samples which included cation exchange capacity, compressive strength, strength activity index, electrical conductivity, lime absorption and water absorption were determined as described below.

The ash content was determined by igniting a dried grass sample at 700°C and calculated as shown in equation 1.

$$\% - ash = \frac{m_{ash}}{m_{biomass}} 100 \qquad (1)$$

The bulk density of sample that was sieved through 250-nm sieve was determined using a method described in the Indian Standards and was calculated using equation 2.

$$\rho_{bulk} = \frac{m_{ash}}{v_{ash}} \qquad (2)$$

The method for loss on ignition (LOI) was adapted from Poon et al. (1999). An elephant grass ash sample (2 g) dried at 105°C to a constant mass was ignited at 775°C for 1 hour. Equation 3 was used to calculate loss on ignition of the cooled sample.

$$LOI = \frac{m_1 - m_2}{m_2}100 \quad (3)$$

The cation exchange capacity was determined in order to determine the amount of exchangeable Na, K and Mg. The method was adapted from Musyoka et al. (2009). *Pennisetum purpureum* ash (0.5 g) was stirred in 25 ml 0.1 M ammonium acetate solution of pH 2 for 1 hour. The ash was filtered off. The filtrate was filled to the 100-mm mark of a volumetric flask. The concentrations of exchangeable cations were determined using an ICP-AES instrument.

A commercially available Portland cement equivalent to ASTM Type I was used in this study. Formulations were adapted from Amudhavalli and Mathew (2012) and are summarized in Table 1.

Table 1: Formulations of mortar and *Pennisetum purpureum* ash

Ingredient	Control mortar	Mortar with 4:1 Cement: Ash blending ratio	Mortar with 18:7 Cement: Ash blending ratio	Mortar with 3:2 Cement: Ash blending ratio
Portland cement (g)	500	400	360	300
Graded standard sand (g)	1375	1375	1375	1375
Distilled water (ml)	242	242	242	242
Pennisetum purpureum ash (g)	nil	100	140	200

Compressive strength is the ability of a material to resist applied force. When the compressive strength limit is reached the material simply breaks up. Concrete cubes were cured at 27°C over a total setting period of 28 days. Cube specimen (150 mm) of each concrete mixture were tested of their compressive strength on 2000 kN hydraulic press at a loading rate of 0.18 N/mm^2/s after 3, 7 and 28 days of setting time. The compressive strength was calculated as shown in equation 4.

$$c = \frac{AL}{A} \quad (4)$$

where c is the compressive strength (kN/mm^2), *AL* the applied load in Newtons and *A* the cross sectional area in mm^2.

A Chappelle test method adapted from Perraki et al. (2012) was used to determine pozzolanic activity. To anash sample (0.5 g) suspended in 200 ml distilled water, calcium hydroxide (1.0 g) was added. The suspension was refluxed for 16 hours. The solution was then filtered and titrated with 0.1 M HCl. A control mixture with calcium hydroxide only was also prepared. To this mixture of sugars (60 g) were added to dissolve calcium hydroxide. The pozzolanic activities were calculated as shown in equation 5.

$$mgCaO = 2 \times \frac{(v_2 - v_1)}{v_2} \times \frac{74}{56} \times 1000 \quad (5)$$

Where v_1 is the titration volume of the pozzolanic mixture (CaO and pozzolan), v_2 the titration volume of the control mixture CaO.

The method for strength activity index (SAI) was determined as reported by Papadakis et al. (2002) and was calculated as shown in equation 6.

$$SAI = \frac{A}{B} \times 100 \quad (6)$$

Where A is the unconfined compressive strength of the test pozzolan specimen in MPa and B is the compressive strength of the control mortar.

A method for water absorption was adapted from Ahmadi and Shekarchi (2010). Concrete cores of 75 mm in diameter and 130 mm in height obtained from 200 mm-concrete cubes blended with pozzolan and standard brick were cured for 14 days. The cured concrete cores were oven dried at 110°C for 72 hrs and percentage weight gain calculated.

3 Results and Discussion

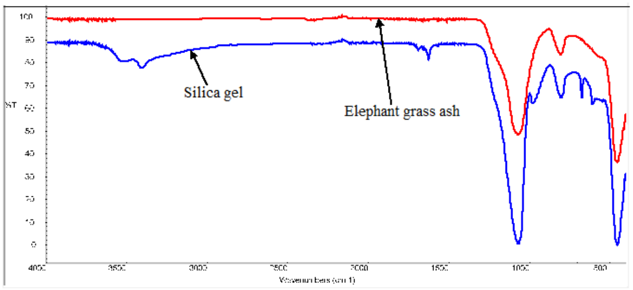
3.1 Proximate Analysis

Table 1 shows proximate analytical data and chemical composition of *Pennisetum purpureum* ashes determined using an XRF instrument. The ash content of the dried dead mass was found to be 6.3%. This is close to what has been reported by Río et al. (2012). The elemental composition shows that the ash has a high silica content of 81.09% which can slightly be increased by acid leaching. This is comparable with the content rice husk ashes and sugarcane bagasse ashes that have also been tested as potential pozzolanic material (Ugheoke and Mamat, 2012; Teixeira, 2010). The loss on ignition for the untreated ash and leached ash were 5.3% and 4.04% respectively and this may be due to unburnt carbon material.

Table 2: Ash characteristics and elemental composition

	Raw ash	Acid leached ash
Grass ash content	6.3 ±0.001	-
Bulk density (g·cm^{-3})	0.27	0.27
Loss on ignition	5.3	4.04
	Percentage compositions	
SiO_2	81.09	82.92
Al_2O_3	0.89	0.88
MgO	2.32	2.28
CaO	2.99	2.88
SO_3	2.08	2.06
TiO_2	0.05	0.05
Fe_2O_3	1.85	1.64
Mn_2O_3	0.09	0.08
P_2O_5	1.10	1.18
Na_2O	0.32	0.23
K_2O	1.80	1.71

Figure 2: FTIR spectra of raw and acid leached *Pennisetum purpureum* ash

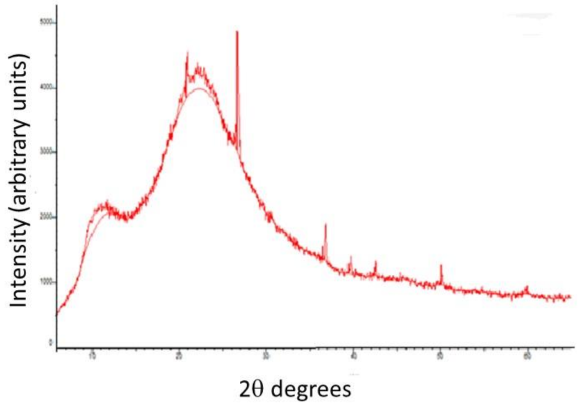


3.2 FTIR and Morphological Characterization

FTIR spectra of raw and acid leached *Pennisetum purpureum* ash are shown in the Figure 2. It can be concluded from intensity of typical absorption bands that the ash has high silica gel content. The strong absorption band at 1065 cm^{-1} can be attributed to asymmetric Si-O-Si stretching vibration while the band at stretching vibration. Such IR absorption bands 960 cm^{-1} related to Si-O stretching mode. The have been observed for silica and ash samples band at 810 cm^{-1} is due to a symmetric (Essien et al., 2012; Singh et al., 2012; Nayak and Bera, 2009).

An XRD pattern for purpureum ash produced at confirmed by absence of ordered crystalline 600°C is shown in Figure 3. It can be observed structure. The diffractogram has similarities to from the XRD pattern that *Pennisetum* those reported for pure silica (Adam and Chew, 2011; Essien et al., 2011).

Figure 3: XRD spectrum of acid leached *Pennisetum purpureum* ash



The SEM images of *Pennisetum purpureum* ash some evidence biomaterial despite having is shown in Figure 4. The micrograph show ignited the samples at 600°C.

3.3 Cation Exchange Capacities

The cation exchange capacities (CEC) of blended cement samples are shown in Table 3. The results show a decrease in exchangeable Mg^{++} and Ca^{++} with increase in added pozzolan.

3.4 Compressive Strength

The effect of amount of pozzolan added on the increase in the percentage of the pozzolan with compressive strength is illustrated in Figure 5 that compressive strength increases with 4:1 blending ratios having a compressive below. From the diagram it can be concluded strength comparable to the control of sample that had been aged for 28 days.

3.5 Strength activity index

The effect of the amount of pozzolan added on strength activity index is illustrated in Figure 6. From the diagram,

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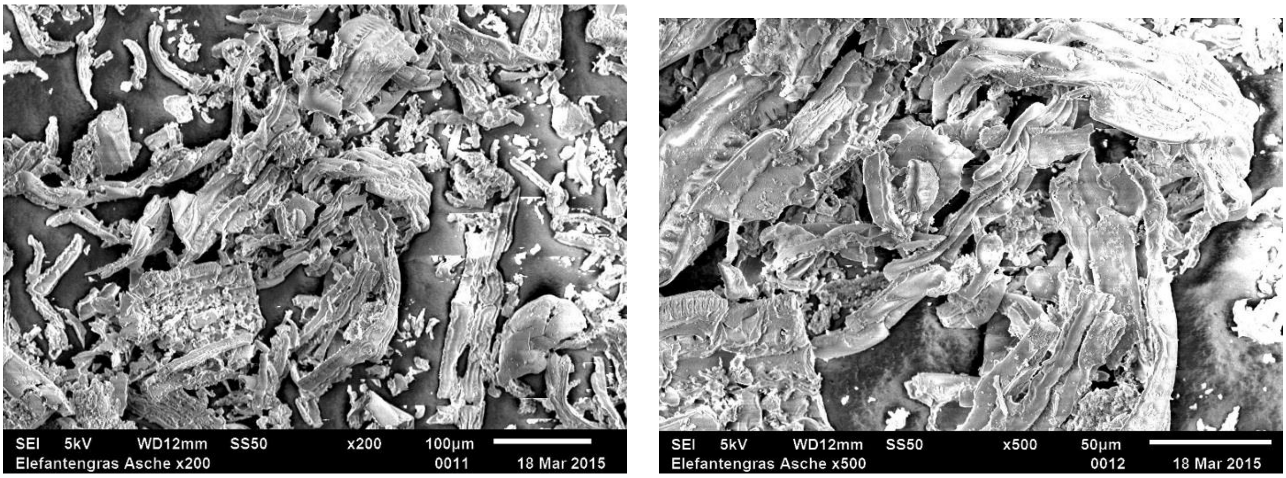
Figure 4: SEM Images of acid leached *Pennisetum purpureum* ash sample



A B

Table 3: Values for cation exchange capacities for blended cements in ppm

		Cement type			
Ion type	Ash	Unblended cement	With 4:1 Cement: Ash ratio	With 18:7 Cement: Ash ratio	With 3:2 Cement: Ash ratio
Na^{+}	4.60	4.60	4.50	4.60	4.68
K^{+}	4.60	12.24	19.78	12.12	11.59
Mg^{++}	12.24	25.37	12.02	12.02	9.87
Ca^{++}	16.60	321.00	225.01	195.01	167.07
Total	39.94	362.78	261.31	253.75	241.20

Figure 5: Effect of compressive strength on aging times

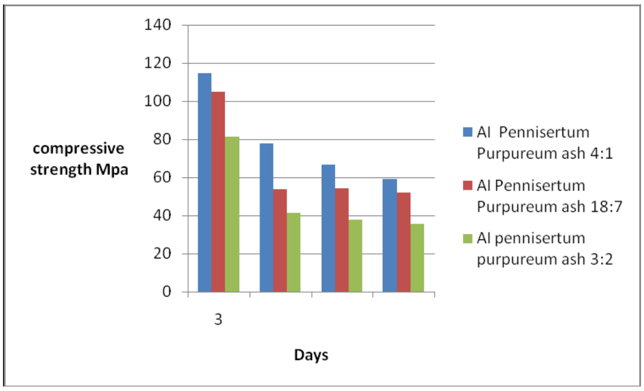
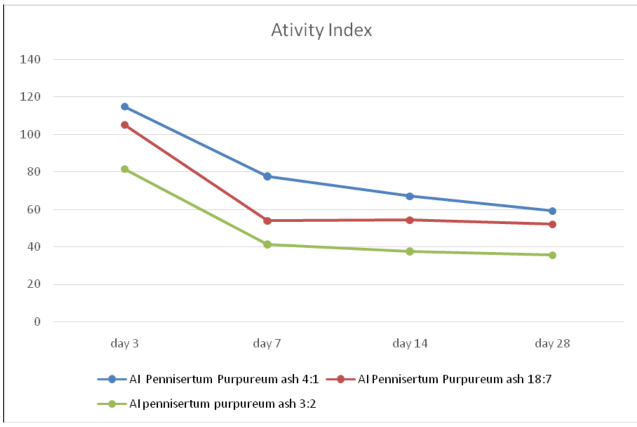


Figure 6: Effect of compressive strength on aging times

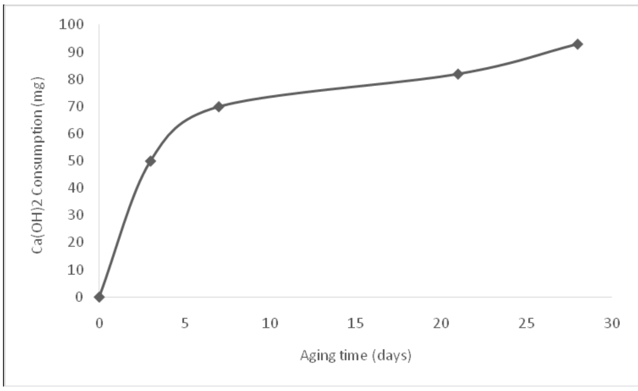


it can be concluded that strength activity index remained high with slight fluctuation for mortar mixtures blended with 3:2 cement: *Pennisetum purpureum* ash ratio over 28-days aging period.

3.6 Chappelle Test

The pozzolanic reactivity of a material is measured by the amount of fixed quantity of calcium hydroxide in pozzolanic materials. This was determined by lime consumption after *Pennisetumpurpureum* ash was reacted with CaO suspended in water. The effect of lime consumption by *Pennisetum purpureum* over 28 days of setting period is illustrated in Figure 7. From the graph it can be observed that lime consumption was high in the first 7 days of aging and increased gradually over the remainder of the period.

Figure 7: Lime consumption of *Pennisetum purpureum* ash



3.7 Water absorption tests

Water absorption is the weight of moisture in the pores to the weight of the mortar cubes. The effect of blending on water absorption is shown in Table 4 below. From the table it can be observed that there was a decrease in water absorption with increase in the percentage of the pozzolan.

This may be attributed to decrease in the porosity of the mortar cubes due to the small particulate nature of the added pozzolan. The average particle sizes was 26 μm and the distribution ranged from 2 mm to 100 μm (Figure 8).

Figure 8: Particle size distribution of *Pennisetum purpureum* ash

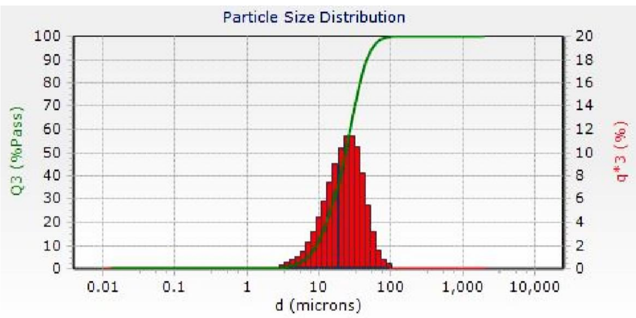


Table 4: Effect of blending on water absorption

Type of concrete block	% water absorption
Control	2.8
4:1 Cement:Ash ratio	2.5
18:7 Cement:Ash ratio	2.1
3:2 Cement:Ash ratio	2.0

4 Conclusion

The study showed that *Pennisetum purpureum grass* ash has good pozzolanic properties and hence can be used as a cement replacement. Portland cement with a blending ratio of 3:2 showed good binding properties comparable to Portland cement Type I. Cement mortar with lower replacements tended to age slowly and failed to reach the compressive strength of the control in 28 days of aging. Given the abundant nature of elephant grass, it can be concluded that elephant grass ash is a viable renewable pozzolanic material.

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