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Investigation of Corn Ash as a Supplementary Cementitious Material in Concrete

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ABSTRACT

This paper describes investigation into pozzolanicity of corn husk ashes as supplementary cementitious material in concrete. Two types of corn husks were studied, and four different ash production techniques were employed. XRD and XRF were used to quantify the chemical signatures and structure of the ashes, and SEM analysis was used to examine particle shapes. Pozzolanicity of the ashes was determined based on strength activities of mortar samples made with various rates of ash replacement for Portland cement. Thermogravimetric (TG) analysis was used to determine the level of cementitious material hydration. Results indicate that the chemical compositions of the high-silica corn ash (HSCA) and regular corn ash (RCA) are similar, and they both contain high levels of SiO_2 (35.6-38.3%) and K_2O (24.0-27.6%). The mortar samples containing HSCA displayed comparable strength to the samples made with 100% Portland cement and much higher strength than the samples containing RCA at later ages.

INTRODUCTION

As countries such as Indian and China continue to develop infrastructures and become economic powers in the world market, building materials are required such as cement to make concrete. The creation of better roads in Africa will allow better distribution of food, medicine, and overall lifestyle improvements. The demand for cement in the developed countries is ever-increasing, which has caused a deficiency of cement on the world market causing elevated prices [PCA 2004]. Meanwhile, cement production creates approximately 5% of the total worldwide CO_2 emissions which contributes to global warming.

In order to reduce greenhouse gases, cement companies have turned to the use of supplementary cementitious materials (SCMs). There are various SCMs used in concrete including commonly used fly ash, blast furnace slag, and silica fume, while other SCMs can be agricultural by-products such as rice husk ash. Since cement is the most expensive fraction in concrete and difficult to obtain for third-world countries, other ash materials have been used to help extend cement supplies and allow more development. The use of saw dust ash along with naturally occurring metakaolin type clay has shown promise for low-cost concrete production in Africa [Elinwa *et al.* 2005]. One study from Cuba used another waste material, this time from the burning of sugar cane husks leftover from sugar production. The results showed that sugar cane husks burned in the open-air produced a highly reactive pozzolanic material [Hernardez *et al.* 1998]. The use of corn ash as a SCM would allow corn growing areas of the world to increase their concrete building construction without adding to cement costs.

Agricultural seed producers have developed corn varieties that contain high levels of elemental silica deposited in the stalks and leaves. High silica levels contained in plant cell walls make those plants undesirable to foraging insects. The silica effectively makes the plant so difficult to digest that the insects find another source of food, thereby protecting the corn plant from infestation without the addition of insecticides [Buendgen *et al.* 1990]. Mature corn plants have been found to have the highest levels of silica of 7 to 11 percent [Lanning *et al.* 1980]. Since amorphous silica is the main component in SCMs that react with the calcium hydroxide released from the cement to form hydration products, using ash from a plant with naturally high levels of silica should produce an excellent material suitable for use as an SCM.

Utilization of high-silica corn husk ash (HSCA) as a SCM has the potential to benefit the environment, as well as corn and cement producers. Corn biomass normally left to degrade in the field can now become a commodity. Cellulose-based ethanol production facilities produce the bio-fuel from corn biomass without removing the silica necessary for use as a SCM. The current socio-economic climate in the world requires engineers to consider non-traditional materials to help minimize environmental impacts. Low-cost cementitious materials are necessary for improving the standard of living in sub-Saharan Africa and the utilization corn husk ash for extending the cement supply could be one solution.

Scope of Study

This study was performed to investigate the potential for utilizing ashes from both traditional corn husks and corn husks bred to contain higher silica levels as supplementary cementitious materials in concrete. Ash production methods were investigated to produce the highest reactivity as determined using compressive strength according to ASTM C1240. Chemical and thermal analysis determined the ash composition and the effect on cement hydration. The effect of replacement rate for cement determined the optimal content.

EXPERIMENTAL METHODS

Ash Production Procedure

The method used to produce the corn ash went through successive iterations in order to improve the reactivity. At the completion of the growing season, corn stalks were hand-harvested by cutting the stalk approximately 15 cm (6 inches) above ground level and then cleaned to remove soil particles. The corn biomass, termed corn husk for the purpose of this paper, included everything but the corn cobs and kernels, so the material that would be left behind after harvesting the grain. The corn husks were then air dried and coarsely chopped before shipment to the lab, Figure 1a. Two varieties of corn material were investigated, one with typical silica levels as the Regular Corn Ash (RCA) and a second bred for high silica levels, termed the High-Silica Corn Ash (HSCA).

The corn ashes were produced at temperatures below 700ºC (1,292ºF) so as to maximize the content of amorphous silica [Chopra *et al.* 1981]. Simple open burn procedures typically occur between 500ºC (932ºF) and 600ºC (1,112ºF) [Nair *et al.* 2006]. Iterations used in the present study are listed as follows:

Procedure 1 (500ºC burning): The initial procedure followed that provided for laboratory production of rice husk ash [Nair *et al.* 2006]. With constant air supply, the dried corn husks were heated to 500ºC (932ºF) and maintained for 12 hours. Then, the oven was turned off and allowed to cool to ambient temperature for 24 hours.

Procedure 2 (600ºC burning): With constant air supply, the dried corn husks were heated to 600ºC (1,112ºF) and maintained for 12 hours. After the heating period the oven was turned off and allowed to cool to ambient temperature for 24 hours, Figure 1b.

Procedure 3 (Double burning with grinding): The material was first burned in a larger open reactor at an average temperature between 500ºC (932ºF) and 600ºC (1,112ºF) as taken at several points with an infrared thermometer. Then with constant air supply, the corn husk ashes were moved to a muffle furnace and heated to 600ºC (1,112ºF) and maintained for 12 hours. After the second heating, the oven was turned off and allowed to cool to ambient temperature for 24 hours. After cooling, the material was ground to homogenize the particle sizes and consistency, Figure 1c.

Procedure 4 (Triple burning with grinding): To further increase the reactivity, material created using procedure 3 was subjected to a second two complete cycle in the laboratory furnace at 600ºC (1,112ºF), followed by grinding.

(a) Initial Material **(b) After Furnace** **(c) After Grinding**

Fig. 1. Steps of Corn Ash Production

Ash Characterization Testing

Specific gravity of the ashes was measured using a helium pycnometer according to ASTM D5550. The chemical composition of the ashes was determined using a PHILIPS PW2404 X-ray fluorescence spectrometer (XRF). The mineral composition of the ashes was examined using a Siemens D500 x-ray diffractometer (XRD). The morphology of the gold-coated ashes was observed under a Hitachi S-2460N variable pressure scanning electron microscope (SEM).

Ash Reactivity Testing

The compressive strength cube samples were prepared according to ASTM C1240, Standard Specification for Use of Silica Fume as a Mineral Admixture in Hydraulic Cement Concrete, Mortar, and Grout. Samples were prepared with 10% by weight replacement of cement with corn husk ash and cured in a sealed moist container at 65ºC (149ºF) for 7-days. Selected mixtures were also tested at 28-days and 56-days. Compressive strength was tested on 5cm (2 in.) cubes according to ASTM C109.

Thermogravimetric (TG) analysis was performed to examine the $Ca(OH)_2$ reduction in pastes due to the pozzolonic reaction. A TA Instruments thermal analysis system sodium hydroxide filter at a rate of 10ºC/minute from ambient to 1,000ºC for powdered samples of pastes at 7, 28, and 56 days.

Mixture Proportions

The mortar mixture proportions used in the present study are listed in Table 1. The replacement of cement for ash varied from 0% to 10%. Water-to-cement ratio of the mortar was 0.48 and a binder to aggregate ratio was 0.36. A dry high-range water reducer was added to maintain mortar flow at 100% to 115% of the straight Portland Cement (PC) Control.

Table 1. Mixture Proportions

Mixture Identification	Cement (g)	Corn Ash (g)	Sand (g)	Water (g)
PC Control	500	0	1500	242
HSCA 1%	495	5	1500	242
HSCA 3%	485	15	1500	242
HSCA 5%	475	25	1500	242
HSCA 7%	465	35	1500	242
HSCA 10%	450	50	1500	242
RCA 10%	450	50	1500	242

RESULTS AND DISCUSSION

Bulk Ash Material Properties

The specific gravity was determined as 2.31 for the RCA sample and 2.50 for the HSCA sample. Surface area of the ashes were determined using Blaine tests, and it was 561 m^2/kg for RCA and 910 m^2/kg for HSCA samples.

The bulk chemistry of the two ashes was similar as seen by XRF results shown in Table 2. The loss on ignition (LOI) was 5.3% for the HSCA sample and 11.4% for the RCA sample. The high LOI indicates high carbon content in the sample, which may have negative impact on effectiveness of admixtures used in the concrete and may increase the water demand of the corresponding concrete.

Although the HSCA was bred for higher silica levels, the XRF results show that the HSCA had similar amounts of silica (35.61%) to RCA (38.33%), and the total content of SiO_2, Al_2O_3, Fe_2O_3 as well as CaO content of the two ashes are also similar (approximate 45%). Typical fertilizer applied to corn is a combination of nitrogen (N), potassium (K_2O), and phosphate (P_2O_5), which would account for the higher levels of those minerals in the ashes.
Both ashes contain significant levels of alkalis, notably potassium (K) and phosphorus (P). Additional investigation is needed before any trial applications to determine the impacts these alkalis would have on durability. One other interesting chemical present is higher than anticipated levels of magnesium. Since levels are similar to those observed in Class C fly ash or blast furnace slag, the only concern is the potential for accelerated set with higher magnesium levels.

The X-ray diffraction results from the two ash samples are shown in Figure 2 for the HSCA sample and Figure 3for the RCA sample. Both samples had glass halos occurring between 28º to 30º two-theta which classifies the samples as high-calcium glass. XRD for both samples indicate significant levels of amorphous silica, which is desirable for the use of corn ash as a pozzolan. Both samples detected crystalline peaks of Sylvite, Quartz, and Periclase, which was anticipated from the chemical composition determined by XRF.

Table 2. XRF Chemical Analysis

Element	HSCA Conc. (%)	RCA Conc. (%)
SiO_2	35.61	38.33
K_2O	23.95	27.58
MgO	9.77	5.01
P_2O_5	9.27	4.53
CaO	8.99	7.83
SO_3	2.65	1.72
Cl	2.25	3.02
Fe_2O_3	0.35	0.47
Al_2O_3	0.29	0.22
LOI	5.3	11.4

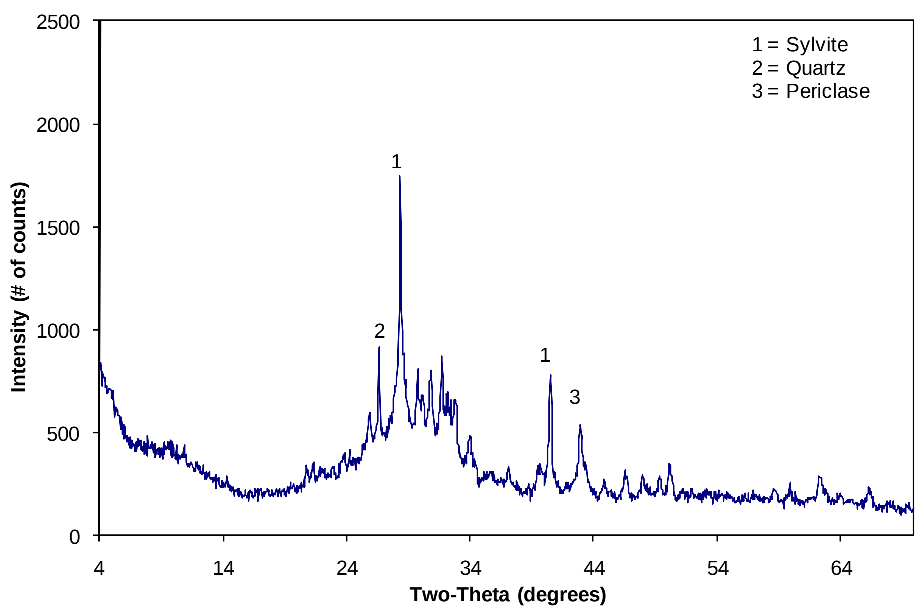

Fig. 2. XRD Results for HSCA Sample

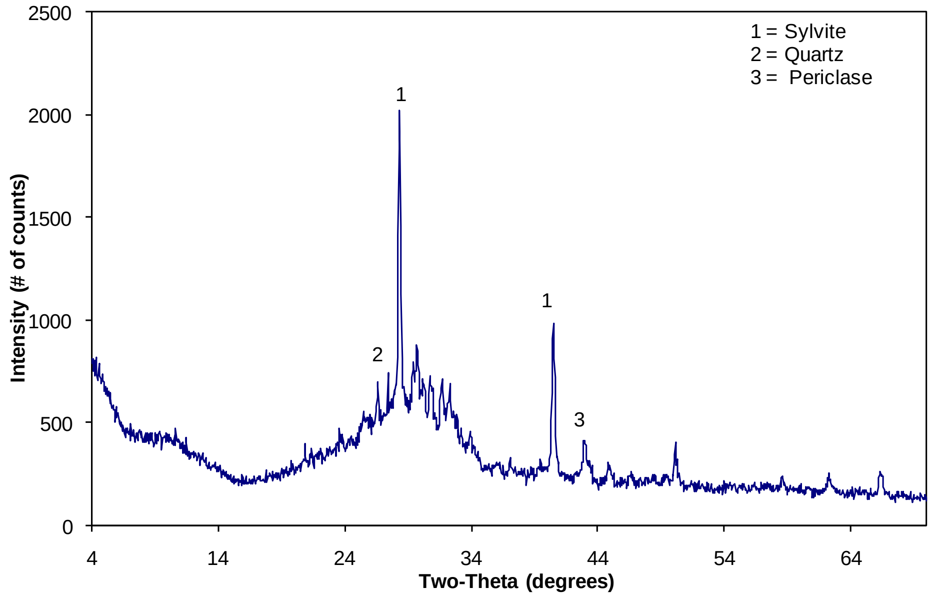

Fig. 3. XRD Results for RCA Sample

SEM micrographs of the RCA at 10,000X magnification are shown in Figure 4 for samples produced using procedure 4. The images show a variety of angular particles sizes that are slightly smaller for the HSCA versus the RCA.

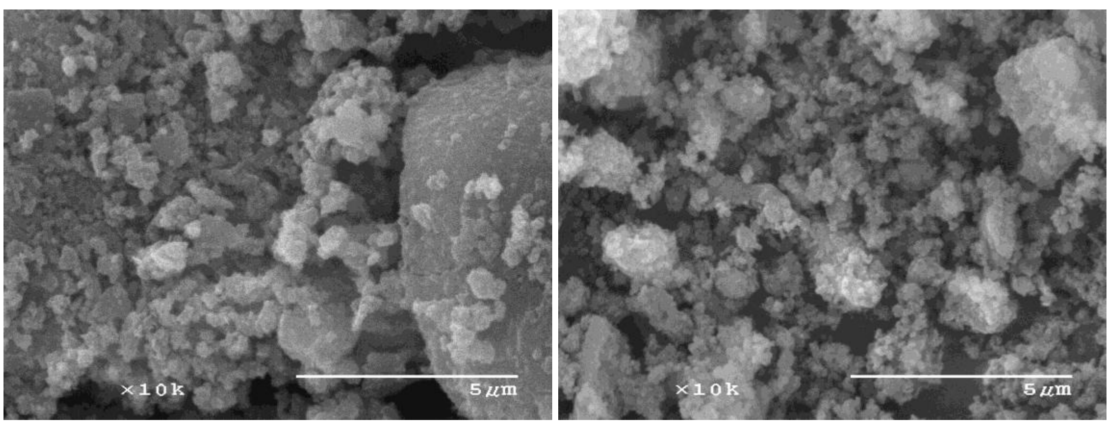

Fig. 4. SEM Micrographs of (a) RCA Sample and (b) HSCA Sample

Results of Ash Production Trials

The compressive strength results from the various production methods are shown in Table 3. No clear trend was observed from the RCA with additional processing, with the highest compressive strength occurring using production procedure 3. The reactivity of the HSCA was not significantly impacted between the two production temperatures, but compressive strength increased with grinding and burning a second time. Consequently, samples produced to determine strength development with time used ash produced using procedure 4.

Table 2. Ash Production Results

Production Procedure	Ash Type	7-day Compressive Strength, Mpa (psi)	7-day SAI (%)
1 (500^{o}C burning)	CCA	24.0 (3,485)	76
	HSCA	26.0 (3,769)	82
2 (600^{o}C burning)	CCA	21.3 (3,090)	67
	HSCA	26.5 (3,847)	83
3 (Double burning w/ grinding)	CCA	25.3 (3,668)	79
	HSCA	29.3 (4,248)	92
4 (Triple burning w/ grinding)	CCA	29.6 (4,287)	72
	HSCA	39.6 (5,750)	96

Strength Development with Time

The compressive strength results of the various addition rates are shown in Table 4 for ashes produced using procedure 4. For the standard ASTM C1240 replacement of 10%, at 7-days the HSCA compressive strength was 96% of the PC control and the RCA was 79%. The SAI decreased slightly over time and at 56-days the SAI indices were 94% and 74%, respectively. At 7-days the highest relative compressive strength occurred at the 10% rate, at the later ages the lower replacement rates (7% to 1%) had the greatest effect. At all ages and replacement rates, the HSCA samples produced higher compressive strength than the RCA samples at 10% replacement.

Table 4. Strength Development with Time for Various Replacement Rates

Replacement Rates	7-day Compressive	7-day SAI (%)	Compressive Strength,	28-day SAI (%)	Compressive Strength,	56-day SAI (%)
HSCA 1%	38.9 (5,638)	94	47.1 (6,830)	109	47.5 (6,894)	103
HSCA 3%	34.5 (5,005)	84	41.3 (5,998)	95	45.6 (6,621)	99
HSCA 5%	29.9 (4,345)	73	44.6 (6,467)	103	44.5 (6,457)	96
HSCA 7%	33.6 (4,889)	82	41.4 (6,012)	96	46.5 (6,753)	101
HSCA 10%	39.6 (5,750)	96	41.3 (5,994)	95	43.6 (6,319)	94
RCA 10%	29.6 (4,287)	79	31.7 (4,593)	73	34.5 (5,000)	74

The compressive strength development with time is shown in Figure 5 for four selected HSCA addition levels, along with the PC control and the RCA control. The variability in the spread of compressive strength values was highest at 7-days and become less so with increased time. The PC control and all of the HSCA samples had similar compressive strengths at 56-days, while the RCA sample was less. However, all samples had compressive strength greater than that required for either ASTM type M or type S masonry mortars of 20 MPa and 15 MPa, respectively.

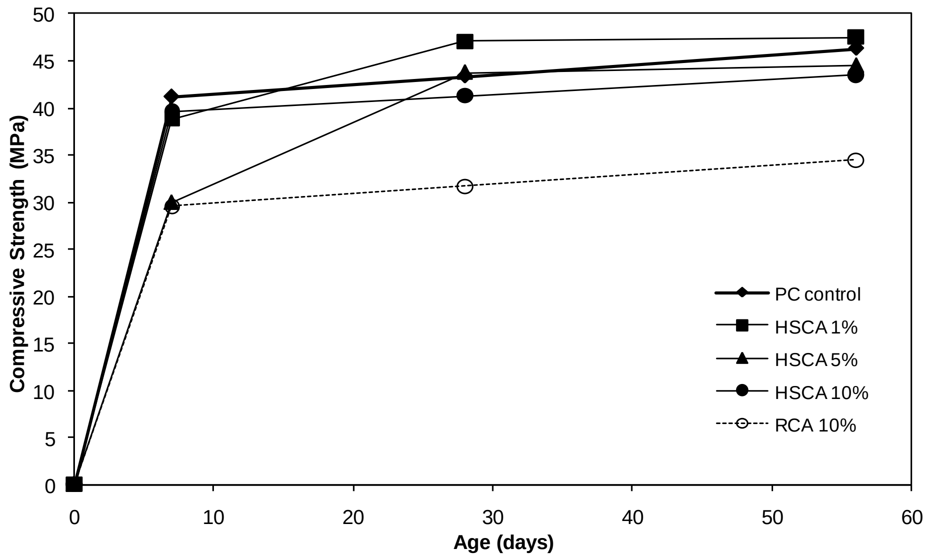

Fig. 5. Long-term Compressive Strength

TG Analysis Results

The TG analysis results for the 7-day samples are shown in Figure 6. The upper curves are both the HSCA and the RCA and show a reduction in calcium hydroxide content versus the bottom control (PC) curve. For both 28 and 56-day samples, the ash samples followed a similar trend of close TGA response and greater calcium hydroxide utilization.

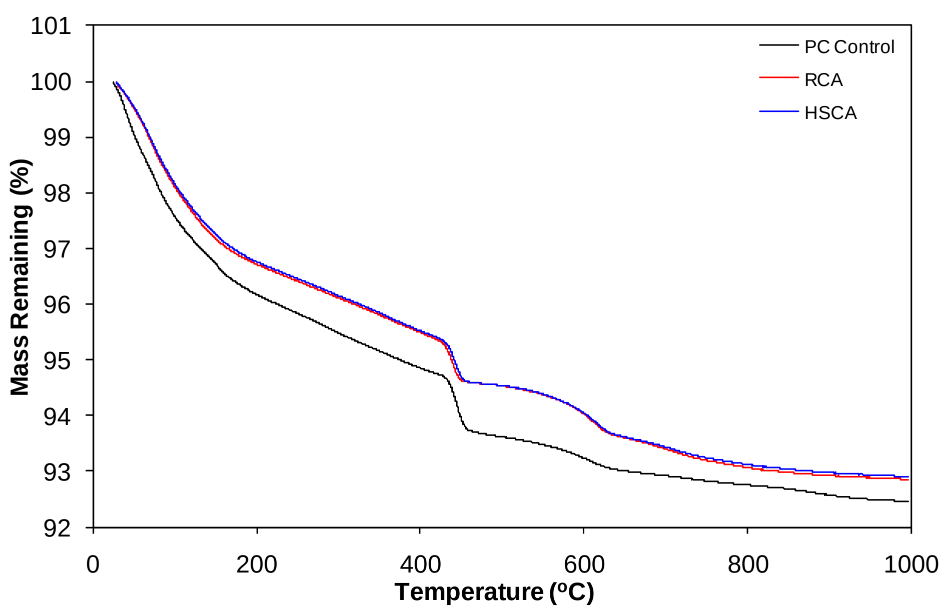

Fig. 6. TGA Results at 7-days

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn from this study:

- The chemical compositions of the high-silica corn ash (HSCA) and regular corn ash (RCA) are similar, and they both contain high levels of SiO_2 (35.6% and 38.3%) and K_2O (24.0% and 27.6%, respectively). However, the loss of ignition of HSCA is less than 50% of that of RCA, which may result in less negative impact on the effectiveness of admixtures in concrete.
- The reactivity of the high-silica corn ash (HSCA) increased with additional burning and grinding, but the regular corn ash did not show significant improved reactivity with additional processing.
- The mortar with up to 10% HSCA replacement for Portland cement produced comparative compressive strength values to mortar made with 100% Portland Cement and significantly higher compressive strength values (~20%) than samples produced using the regular corn ash (RCA).
- The increase in compressive strength between the HSCA and the RCA can be attributed to smaller particle size of the HSCA. The chemical analysis also indicated a higher level of Mg in the HSCA which could also contribute to higher compressive strength.
- Corn ash may have the potential for application in third-world countries to extend their cement supply.

As bio-energy research progresses, the proliferation of cellulose-based ethanol production facilities and collection equipment is streamlining the collection of the post grain corn biomass. Since the corn biomass in this study was first burned to remove the cellulose and to produce the amorphous silica, the cellulose-based ethanol waste may be more appropriate for reduction and incorporation into concrete. The ethanol process removes the cellulose without affecting the mineral components which will allow further utilization of the leftover ethanol waste by burning to create the amorphous silica then incorporation into concrete.

More research is required to evaluate the long-term durability and applicability of corn ash for extending cement supplies in developing countries and to investigate the potential of using corn ashes left over from ethanol production.

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