Study on the Pozzolanic Properties of Silica Obtained from Rice Husk by Chemical and Thermal Process

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Received zzz, revised zzz, accepted zzz
Published online zzz

PACS 81.05.Mh, 81.05Rm

In this study, the effect of chemical and thermal treatment on the pozzolanic properties of rice husk ash (RHA) was investigated. The rice husks were subjected to chemical and thermal treatments. After the chemical treatment, the husks were burned under controlled conditions in order to obtain amorphous silica to be used as a pozzolanic material. Finally the ash obtained was milled in a ball mill to reduce the size of the particles. All the products obtained were characterized in terms of silica content, amorphous character, particle size distribution, and pozzolanic activity. The ash produced after an acid treatment with HCl to the husks produced a high percentage of ash with amorphous silica; high fineness, purity, and pozzolanic activity. The silica obtained was incorporated to cement pastes and concretes to evaluate the mechanical, rheological and durability properties.

1 Introduction

Rice Husks are the natural sheaths that form on rice grains during their growth. When is removed during the refining of rice [1], there are some problems with the disposal of this material, because it doesn't have commercial interest. Rice Husk is the most important agricultural residue in quantity (614 million tones per year) [2]. On average it accounts for 20% of the rice produced on weight basis, then, the world wide annual husk output is about 120 million tones [2], these problems are due to a great volume of waste and its local situation (limited geographic area). On the other hand, this waste is problematic during its handling and transportation due to low density. Actually the rice husk is uncontrolled burned at open air or used as fuel in the rice paddy milling process, which creates significant environmental problems as pollution and contamination of springs. As a result, the use of such ash has stimulated the development of research into the potentialities of this material.

Rice is one of the crops with highest silicate content, mainly in the husk [3-4]. When subjected to combustion, almost 20% of the husk becomes ash with a porous cellular structure, having a high specific surface (50 to 100 m^2/g). Such silica can react in the presence of water, with calcium hydroxide (lime), resulting in cementitious compounds [5], generating a highly reactive material suitable for use as a pozzolan in lime/pozzolan mixes and a supplementary cementing material. Cement has been partially replaced by active nanopowders or supplementary cementing materials, such as ground granulated blast furnace slag (GBFS), silica fume (SF), rice husk ash (RHA), metakaolin (MK) or fly ash (FA). These are examples of those new binders and constitute a significant contribution to the eco-efficiency of the

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global economy and a solution to problems related to the concrete durability and its corrosion control [6-11]. In this study, the effect of incorporation of different ashes obtained from rice husks in rheological properties of pastes and in the compressive strength and durability properties of concretes was investigated.

As result, it was found that treated rice husk ash is a very active pozzolanic material that enhances the mechanical and durability properties in concretes and similar rheological properties when compared with silica fume in pastes.

2 Experimental Program

2.1 Materials and Procedures

The binder materials used for the production of pastes and concretes were as follows:

Rice Husks (RH): The rice husks used in this project were obtained from a local rice mill. As received, the husks were washed and dried, and then subjected to different treatments. The first one consisted in a thermal treatment; rice husk ash (RHA) was obtained by burning dried rice husk under controlled temperature and a chemically treated Rice Husk Ash (ChRHA) which treatment consisted in a chemical treatment, by soaking the RH into a solution of HCl 5N at environment temperature. The husks were washed repeatedly with water until hydrochloric acid was undetected and then air-dried at room temperature. After that, husks were burned under the same conditions as for RHA; this product was white in colour, because of the iron oxides and other metallic traces were dissolved into the solution; these elements are responsible for the coloration of the ashes [12]. All the ashes obtained after thermal treatments were ground at different milling times in a ball mill, using ceramic balls. The chemical and physical properties of the obtained rice husk ashes (ChRHA and RHA) are presented in tables 1 and 2.

All the ashes showed in table 1 were used for the rheological study of cement pastes. Based on the ash properties, RHA-4 and ChTRHA-2 were selected to be used as replacement of portland cement in concrete mixes.

Silica fume (SF): a mineral admixture was used for comparison purposes in concrete mixtures, its physical and chemical characterization is presented in tables 1 to 3.

Cement: Colombian Type V Portland cement was used for all mixes, the chemical and physical properties of this cement are presented in table 4.

Aggregates: A crushed limestone and a silicious river sand were used in this study as aggregates for the concrete mixes. The maximum size of coarse aggregate was 19 mm and for of fine aggregate was 4.75 mm. A naphthalene formaldehyde-based superplasticizer (SP) was also used as liquid chemical admixture. Normal tap water was used as mixing water and for curing. The physical properties of coarse and fine aggregates are shown in Table 5.

Table 1 Characteristics of the Pozzolanic Materials

Mineral Admixture	Blaine Fineness (m^2/kg.)	Amorphous Silica %	Average Particle Size (μm)
RHA-1	424	32.3	41.51
RHA-2	1091	32.3	6.82
RHA-3	1018	87.4	34.31
RHA-4	1587	87.4	8.99
ChRHA-1	1197	94.1	36.48
ChRHA-2	1963	94.1	8.95
SF	945	--	21.34

Table 2 Physical Properties of the mineral admixtures.

Physical Properties	SF	ChRHA2	RHA4
Specific Gravity (kg/m^3)	2230	2080	2160
Nitrogen Absorption (m^2/g)	27	274	24
Color	Dark Gray	White	Pink
Silica Activity Index (%)	-	99.4	89.5
Pozzolanic Activity Index (ASTM C618)	123	125	95

Table 3. Chemical properties of Portland Cement and Mineral Admixtures.

Compound [wt, %]	SF	ChRHA-2	RHA-4	Compound [wt, %]	SF	ChRHA-2	RHA-4
SiO_2	90	99	90	TiO_2	0.02	0.02	0.04
Al_2O_3	0.46	< 0.01	0.68	P_2O_5	0.06	0.11	0.68
Fe_2O_3	4.57	0.13	0.42	MnO	0.16	0.02	0.19
K_2O	1.69	0.06	2.80	P.F (%)	0.54	0.16	0.13
CaO	0.49	0.49	1.23	Ba (ppm)	10	20	10
MgO	0.68	< 0.07	0.35	Sr (ppm)	100	40	40
Na_2O	0.05	< 0.32	< 0.32	Zr (ppm)	10	10	10

Table 4 Chemical, Potential Composition and Physical Properties of Type V Portland Cement

Chemical Composition, %									
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI	SO_3	Free CaO
21.27	4.63	3.96	63.05	1.56	0.16	0.18	2.25	1.75	0.54

Potential Composition, %				Density	Blaine Fineness	Compressive Strength (MPa)			
C_3S	C_2S	C_4AF	C_3A	kg/m^3	m^2/kg	1 day	3 days	7 days	28 days
53.29	20.79	12.05	5.56	3050	377	10.1	23.3	36.0	46.7

Table 5 Physical properties of fine and coarse aggregates

Property	Fine Aggregate	Coarse Aggregate
Specific gravity, kg/m^3	2570	2690
Water absorption, %	1.78	1.36
Fineness modulus	3.05	-
Type	Natural river sand	Crushed Limestone

2.2 Mixes Design and Samples Preparation

2.2.1. Paste mixtures

Type V portland cement was used for the paste mixes with a water/binder ratio of 0.35. Pozzolanic materials (RHA, ChRHA and SF) were used in a percentage of 10% as replacement of portland cement, and the superplasticizer (SP) was 0.4% by weight of the cementitious material.

2.2.2 Concrete Mixture Proportions

All the concrete mixes were proportioned to have the same total cementitious material content of 440 kg/m^3. The mixture proportions are given in Table 6, and described as follows:

Control Mix: This was the reference mixture, containing 440 kg/m^3 of Colombian Type V portland cement only.

RHA Mix, ChRHA Mix, and SF Mix: These mixtures incorporated 396 kg/m^3 of Colombian Type V portland cement, and 44 kg/m^3 of thermal treated rice husk ash or Chemical-thermal treated rice husk ash or Silica Fume, respectively, this proportion of addition is equivalent to 10% of the total cementitious material.

Table 6 Mixture Proportions of Concrete

Material W [Kg/m³]	Control	RHA-4	ChRHA-2	SF
Cement	440	396	396	396
RHA	0	44		0
TRHA	0	0	44	0
SF	0	0		44
Water (W)	198	198	198	198
Fine aggregate	731	724	723	725
Coarse aggregate	930	921	920	923
Plasticizer (ml/kg of cement)	-	0.92	0.95	0.8
W/Cementitious Material	0.45	0.45	0.45	0.45

2.3 Testing

2.3.1 Rheological properties of Pastes

The effects of treated rice husk ashes (RHA) and silica fume admixtures upon the rheological behavior of cementitious mixes were investigated. The measurement of the viscosity was done using Brookfield DV-II + Pro equipment that recorded the viscosity (cP) and the shear rate (rpm). The viscosity of the samples was measured starting at time 4 minutes each running was repeated five times discarding the first measurement. In the study of the rheological properties, the water/cementitious ratio was 0.35 for all pastes tested.

2.3.2 Compressive Strength

Five cylinders (100 mm x 200 mm) were cast for each age of curing in all concrete mixes. Specimens of each mix were cured continuously at 100 percent of relative humidity until test ages of 7, 28, 56 and 90 days.

2.3.3 Durability Tests

Tests such as Resistance to chloride ion penetration and absorption of concrete mixes were realized. The chloride ion permeability was performed following the ASTM C1202 (Rapid Determination of the Chloride Permeability of Concrete), and the density and Absorption test was performed following the ASTM C 642 (Standard Test Method for Density, Absorption and Voids in Hardened Concrete). Cylinders of 75mm in diameter and 50 mm length were used to determine the durability properties.

3 Results and Discussion

3.1 Rheological Properties of Mortars

Rheological characterization of the pastes was done using a Brookfield DV-II+Pro viscosimeter and a spindle Nº 2.The viscosity of the samples was measured starting at time 4 minutes each running was repeated five times discarding the first measurement.

Figure 1 shows the changes in the shear rate-viscosity for portland cement slurries containing the mineral admixtures, it can be observed a lower viscosity and shear rate when a crystalline ash is incorporated to the pastes and in less proportion; this behavior is observed with the mixes with size reduced particle were blended, contrarily to the expected results[13-15].

According to the results showed in figure 1, the mixes (ChRHA-1 and ChRHA-2) with addition of HCl treated RHA reported high viscosity at very low shear rates. This is really thickening effects of the HCl treated RHA particles on the viscosity. This augment in viscosity could be explained by the fact, observed in table 1 that the treated RHA particles presented an amorphous microstructure (amorphous silica greater than 94%) due probably to the negative increment of the zeta potential or electro kinetic potential – the electrical potential at the hydrodynamic plane of slippage that exists in the double layer across the interface of all solids and liquids during flow of a suspension - that should have a marked effect upon the stability of the smaller particles or interaction between them[16-17].

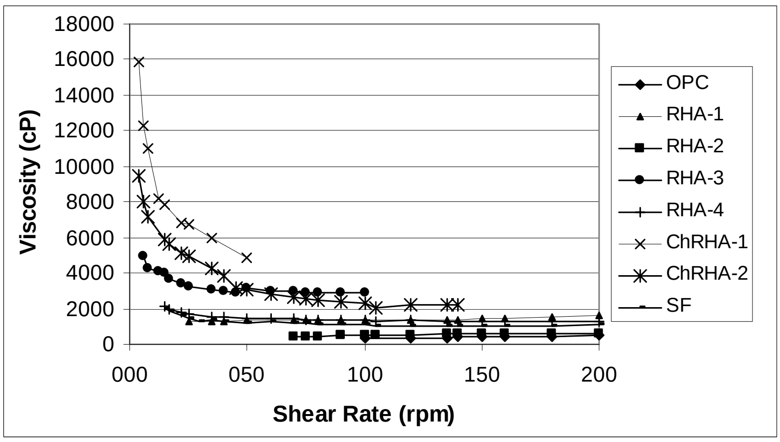

Fig. 1 Changes in the Viscosity of Pastes with different Pozzolanic Materials.

On the contrary, particles with high crystallinity did not increase markedly the viscosity of the cementicius slurries (RHA-1 and RHA-2). However all the added slurries tend to present constant viscosities in the high shear-rate region which is in accord to the Bingham behavior that is characteristic of cementicius slurries. The RHA-1 and RHA-2 mixes exhibited strong thinning or pseudoplastic behavior in the low shear rate region.

3.2 Concrete Properties

3.2.1 Fresh Concrete

Fresh properties of all mixes are shown in Table 7. The mixes with both of the rice husks exhibited higher requirements of superplastizicer than the control and SF mixes to reach the same level of workability. It could be attributed to the high specific surface area caused by the mesopore structure of the rice husk ashes [18].

Table 7 Characteristics of fresh concrete

Characteristics	Control	RHA-2	ChRHA-4	SF
Superplasticizer, %	0	0.35	0.38	0.20
Slump (mm)	191	127	102	102
Density, kg/m^3	2425	2400	2403	2405
Workability	Good	Good	Good	Good

3.2.2 Hardened Concrete

Mechanical properties as compressive strength were evaluated at 7, 28, 56 and 90 days of curing and durability properties as absorption and chloride permeability were evaluated at 56 days.

The compressive strength development of the concrete mixes with and without mineral admixtures is shown in Fig. 2. The compressive strength of the concrete added with ChRHA is significantly higher when compared with ordinary portland cement mix (100% Portland cement), and is similar to the behavior of silica fume mix. These results show that ChRHA has a similar reactivity than silica fume [19] in spite of its high particle size. This high reactivity can be explained by its extremely high porosity that is represented by the high specific surface and its high content of pure amorphous silica.

The resistance to the penetration of chloride ions was measured following the ASTM C1202 “Standard Test Method for Electrical Indication of Concrete’s ability to resist Chloride Penetration” as the charge passed through the concrete under the application of an external electrical field (60V) during a period of six hours. The test was carried out on cylindrical specimens of 50 mm thick after 56 days of curing. This test, called rapid chloride permeability test (RCPT), is essentially a measurement of electrical conductivity which depends on both the pore structure and the chemistry of pore solution. The results are shown in Table 8.

The incorporation of ChRHA in concretes enhances it’s durability properties, by reducing the concrete permeability and the results are comparable with the results obtained with SF, a very effective pozzolana, with finer particles than many cementitious materials that makes pore structure of concrete denser [17,18]. Because of this, the incorporation of ChRHA into concrete mixes plays its major role in properties related to permeability and durability properties.

The water absorption was evaluated by ASTM C642. In general the results obtained in the absorption test (Table 9) shown that concretes with addition of RHA with and without chemical treatment exhibited a least permeability than the mixes with SF and the mix without mineral admixture; fact coherent with the compressive strength reported by these materials; the total absorption and porosity values, lower than 3 and 10% respectively, are considered acceptable as parameters of compaction and durability. These results permit to catalogue the concretes incorporated with ChRHA as durable material, due to comply with this criterion.

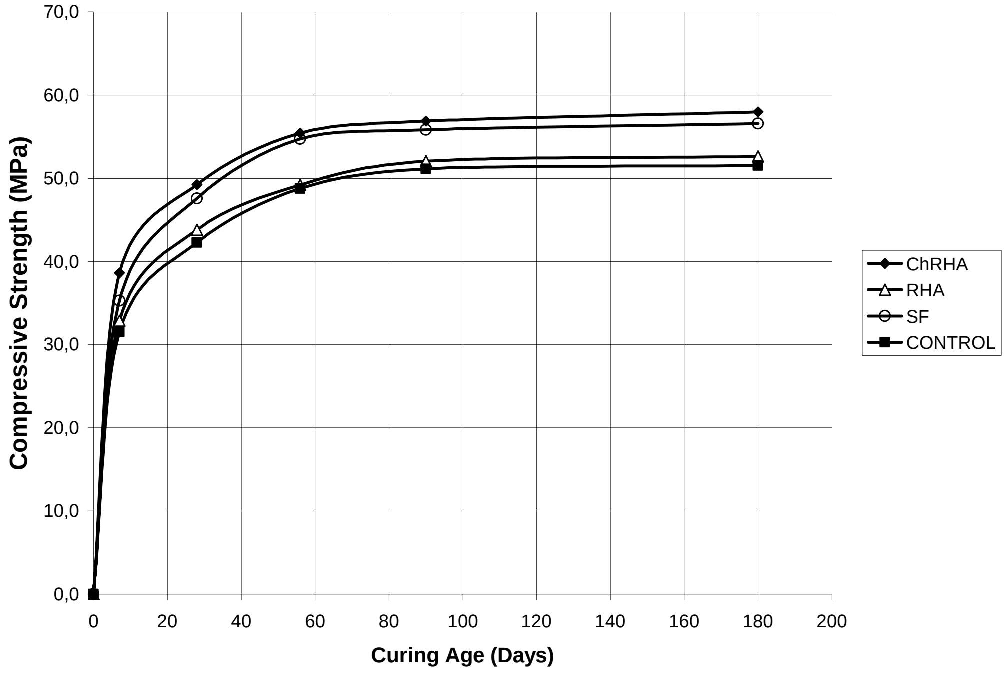

Fig. 2 Compressive Strength of Concrete mixes

Table 8 Chloride Ion permeability of concrete Mixes

Mix	Transferred Charge (Coulombs)		Resistivity ρ (Kohms.cm)
CTRL	3529	Moderate	6.25
RHA	1413	Low	14.9
SF	970	Very Low	22.0
ChRHA	960	Very Low	22.2

Table 9 Density, Absorption and Voids in Hardened Concrete

Mix	Abs. After Immersion (%)	Apparent Density, kg/m^3	Vol. Permeable Pores %
CTRL	4.63	2700	11.22
SF	3.77	2640	10.15
RHA	4.26	2640	10.68
ChRHA	3.61	2650	9.82

4 Conclusions

Based on the experimental results, the following conclusions can be drawn:

- The increase in the amorphicity of the silica in the RHA increases the viscosity of the cement pastes.
- Depending on the type of the ChRHA or RHA, is possible to obtain similar values in the viscosity than that obtained with SF.
- Because of the high of amorphous SiO_2 content in ChRHA with high activity, a significant increase in the compressive strength of concretes is observed compared with the strength of control concrete and that made with RHA.
- Incorporation of ChRHA in normal concretes enhances durability properties by refining its pore structure, these results are similar than that obtaining by using Silica fume.
- Finally, it is possible to produce High Performance Concretes using ChRHA as supplementary cementing material.

Acknowledgements The authors wish to thank the University of Valle (Colombia), the Colombian Institute to Development of Science and Technology "Francisco José de Caldas" (COLCIENCIAS) and the Excellence Center for Novel Materials (CENM) for the support in the development of this study.

References

[1] C. Real et al., Journal of American Ceramic Society **79**, **8**, 2012 (1996).
[2] FAOSTAT Database, FAO, Rome. IRRI World Rice Statistics. http://www.irri.org/science/ricestat/ .
[3] B. D. Park et al., Biomass and Bioenergy **25**, 319 (2003).
[4] P. Stroeven et al., Fuel **78**, 153 (1999).
[5] V. Ajiwe et al., Bioresurce Technology **73**, 37 (2000).
[6] T. Kuennen, Road Science, July 2004, pp. 21-28.
[7] V. Bonavetti et al., Cement and Concrete Research **33**, 865 (2003).
[8] R. Mejía de Gutiérrez et al., Journal of Solid Waste Technology and Management **23**, **3**, 144 (1996).
[9] R. Mejía de Gutiérrez et al., Materiales de Construcción **54**, **274**, 65 (2004).
[10] J. F. Martirena et al., Cement and Concrete Research **28**, **11**, 1525 (1998)
[11] R. Mejía de Gutiérrez et al., The Journal of Resource Management and Technology **22**, 3 (1994).
[12] R. Mejía de Gutierrez et al., in: Proceedings of the 20th International Conference on Solid Waste Technology and Management, Chester, PA, 2005, pp. 80-90.
[13] J. Sousa, Cement & Concrete Composites **25**, 51 (2003).
[14] G. Rodríguez, Cement & Concrete Composites **28**, 158 (2006).
[15] F. Chiara et al., Cement and Concrete Research **31**, 245 (2001).
[16] R. Flatt, Cement and Concrete Research **34**, 399 (2004).
[17] F. Qingge et al., Cement and Concrete Research **34**, 521 (2004).
[18] D. Bui, Rice Husk Ash as a Mineral Admixture for High Performance Concrete, Technische Univ. Delft (Netherlands), 2001, 138p.
[19] F. Zain et al., Cement and Concrete Research **30**, 1501 (2000).