A study on sulfuric acid attack on cement mortar with rice husk ash

B.C. Mondal
Department of Civil Engineering, Chittagong University of Engineering and Technology, Chittagong, Bangladesh

N. Uddin & I. Amin
Department of Civil Engineering, Chittagong University of Engineering and Technology, Chittagong, Bangladesh

ABSTRACT: A major consequence of environmental degradation is the adverse effect of pollution on building materials. With the growing contamination of water by industrial and domestic waste, building materials, especially concrete and mortar are becoming increasingly prone to aggressive chemical attack. The Rice Husk Ash (RHA) is an agricultural by-product that can be used as an admixture in concrete and mortar. The RHA used in this investigation was obtained from a controlled auto combustion chamber with controlled burning temperature and time. In this investigation, the mortar cubes of size 50mm were cast with the partial replacement of cement by 0%, 5%, 10%, 15% and 20% of RHA finer than 0.075mm and placed in two types of sulfuric acid environments with pH values ranging from 2.0 to 3.0 and in pure water. The compressive strengths of cube specimens were determined for different exposure periods viz. 3, 7, 28, 60 and 90 days. The strength of mortar decreases with age with increase in RHA in both acidic environments with lower decreasing rate in pH 3 than pH 2.

1 INTRODUCTION

Rice husks are a residue produced in significant quantities on a global basis. While they are utilized as a fuel in some regions, in other countries they are treated as waste, causing pollution and disposal problems. Due to growing environmental concern, and the need to conserve energy and resources, efforts have been made to burn the husks under controlled conditions and to utilize the resultant ash as a building material (Mehta 1994a, Zhang et al 1996 & Barkakati et al 1994).

Rice husk ash (RHA) is a highly reactive pozzolanic material suitable for use in lime-pozzolana mixes and forPortland cement replacement. RHA contains a high amount of silicon dioxide, and its reactivity towards lime depends on a combination of two factors, namely the non-crystalline silica content and its specific surface. The non-crystalline phase in RHA obtained from combustion at temperatures below 600°C consists primarily of a disordered Si-O structure which is the product of decomposition and sintering of opaline or hydrous silica without melting. Occasionally, a small amount of crystalline impurities may be present, including quartz, cristobalite and/or tridymite. When RHA is produced by uncontrolled combustion, the ash is generally crystalline and presents poor pozzolanic properties. However, by burning the rice husks under controlled temperature and atmosphere, a highly reactive RHA can be obtained (Cook 1986).

Over the past years, there has been an increase in the use of industrial, agricultural and thermoelectric plant residues in the production of concrete. Different materials with pozzolanic properties such as fly ash, condensed silica fume, blast-furnace slag and rice-husk ash have played an important part in the production of high-performance concrete. Thousands of tones of these residues and industrial byproducts are produced every year; therefore, the study of their characteristics and possible applications becomes a priority as their use brings benefits in technical, economic, power and environmental terms [Malhotra 1996].

Among the different existing residues and by-products, the possibility of using rice-husk ash (RHA) has attracted more attention of cement researchers than other crop residues. First, due to the overabundance of this residue, 100 million tonnes of husk are obtained from an annual world production of 500 million tones of rice, a huge quantity of residue that can only be consumed by the cement and concrete industries that use a wide range of by-products according Mehta (Mehta 1992). Secondly, rice-husk is not appropriate as feed for animals due to its few nutritional properties and its irregular abrasive surface is resistant to natural degradation, which poses serious accumulation problems. When it is incinerated, it produces a great quantity of ash. On average, each tonne of rice-husks, on complete combustion, produce 200 kg of RHA. No other crop residue generates a greater quantity of ash when it is burnt [Mehta 1992]. Thirdly, the use of RHA as a supplementary cementing material is of great interest to many developing countries where Portland cement is in short supply but rice production is in abundance.

Fly ash, iron blast-furnace slag, condensed silica fume and RHA were identified for the 73-SBC RILEM Committee (RILEM Committee 73-SBC) as the principal by-products that possess pozzolanic and/or cementitious properties. A tremendous amount of literature is available on concrete containing pozzolanic materials (Malhotra 1996), and different materials with pozzolanic properties such as fly ash, condensed silica fume and blast-furnace slag have played an important part in the production of high-performance concrete [Mehta 1998, Krishnamoorthy et al 2002, Swamy 1997 & Mehta 1994b]. Pozzolanic additions reduce the porosity of concrete especially at the interfaces between cement paste and aggregates, which are the weakest zones of the material. The development and use of rice-husk ash (RHA) is not new (Mehta 1992). Rice-husk ash is a mineral admixture for concrete (Mehta 1992, RILEM Committee 73-SBC), and much data has been published concerning its influence on the behavior of concrete. Results for concretes with a 10% substitution of Portland cement by RHA indicate excellent performance when compared to control concretes (Mehta 1977, James 1986, Mehta 1994, Zhang at al. 1996, Zhang & Malhotra 1996, de Sensale & Molin 2000, de Sensale 2006).

The use of industrial or agricultural by-product substitutions for cement has greatly contributed to sustainable development practices. The joint use of chemical activators has produced improvements in the mechanical properties of concrete. The effects of chemical activators K_2SO_4, Na_2SO_4, Na_2SiO_3 on compressive strength, chloride penetration and carbonation of concrete mixtures with rice husk ash have been investigated (Gastaldini et al 2007). Results indicate that the use of these activators has beneficial effects on initial strength and reduces chloride penetration.

Mineral admixtures generally lead to a densification of the concrete internal structure. In this sense, the failure mechanism could be modified so that the concrete exhibits a more brittle behavior. The effects of rice-husk ash (RHA) additions to concrete, based on analyses of the mechanical behavior of normal and high-strength concrete has been done (Gaiccio et al 2007). It appears that the incorporation of RHA in concrete increases the strength, particularly for lower water/binder ratio concretes. The analysis of the failure mechanism indicates a tendency for more brittle failure behavior in RHA concretes. For the same strength level, however, the energy of fracture was reduced no more than 10%, which is much smaller than the variations that may be produced by a change in the type or size of coarse aggregate. Effect of polyvinyl alcohol (PVA) was studied on the hydration of ordinary Portland cement in the presence and absence of rice husk ash (RHA) by employing different techniques. The results have shown that PVA increases the strength and decreases the porosity. The increase in strength is due to the interaction of PVA with cement, forming some new compounds that fill the pores or improve the bond between the cement (Singh 2001). However, none of these studies investigated the acidic attack on mortar with rice husk ash.

2. EXPERIMENTAL PROGRAM

2.1 *Materials*

2.1.1 Sand

Mainly local sand was used in this experiment. Four types of sieves were used for casting of mortar samples. Sieves were #16, #30, #50 and #100. The ratios among #16 passing & #30 retain, #30 passing & #50 retain and #50 passing & #100 retain were 1:2:1. As #16 passing & #30 retain was not available in sufficient amount from local sand, so a small amount of Sylhet sand was used in the local sand.

2.1.2 Cement

The brand of the cement was used in the experiment was Aramit whose chemical composition has been given in the Table-1**.** The physical properties of cement are given in Table-2.

Table 1: Chemical Composition of Cement

Constituents	Amount (%)
CaO	65.20
SiO_2	20.88
Al_2O_3	6.92
Fe_2O_3	3.28
MgO	1.47
SO_3	1.61
Free lime	1.12
Insoluble residue	0.34
Loss on ignition	1.48
C_3S	50.90
C_2S	22.05
C_3A	12.80
C_4AF	9.97

Table 2: Physical Properties of Cement

Name of the Properties	Results
Normal Consistency (%)	26.00
Initial Setting Time (hour:minute:second)	02:26:00
Final Setting Time (hour:minute:second)	03:17:00
Soundness (mm)	4.90
Specific Surface Area (cm^2/gm)	3800

2.1.3 Acids

One type of acid HCl was used in the experiment. The pH value of each acid were 2 and 3.

2.1.4 Mix Proportion

To make the mortar cubes one type of cement sand ratio (c/s) 1:2.75 was used. The water cement ratio (w/c) was 0.45. There were five cement replacements by RHA levels which were 0%, 5%, 10%, 15% and 20% by weight of cement.

2.1.5 Cube size

The cube size was 50.5mm.

2.2 *Tests on Mortar Specimens*

2.2.1 Visual Inspection

The visual inspection of each specimen was done.

2.2.2 Compressive Strength

The compressive strength of cement mortar specimens were determined directly using compression testing machine as per I.S procedure. From the compression testing machine the total load to crush the cube specimens were measured. Then the compressive strengths were determined using the size of the specimen.

3. RESULTS AND DISCUSSION

Total 225 cubes were cast of which one third were placed in normal water, another one third were placed in H_2SO_4 solution with pH value of 2 and the last one third were placed in H_2SO_4 solution with pH value of 3. Three samples from each environment were tested at the age of 3, 7, 28, 60 and 90 days respectively. The results are presented graphically below.

Fig.1 to Fig.5 represent the compressive strength of mortar specimens with cement replacement level by 0%, 5%, 10%, 15% and 20% by RHA respectively cured in normal water and in H_2SO_4 solution with pH value ranging from 2 to 3. From all figures it is seen that the compressive strength of mortar specimen decreases with age in acidic environments. It is similar to other author (Bakharev 2005). This reduction in strength in acidic environments is due to the fact that the sulfate ions tend to initiate the sulfate attack, in addition to the dissolution process caused by the hydrogen ions. The corrosion of mortar by sulfuric acid consists of two stages. In the first stage, the sulfuric acid chemically reacts with hydration products such as calcium hydroxide (CH) and calcium silicate hydrates (C-S-H) to form gypsum ($CaSO4 \cdot 2H_2O$). In the second stage, gypsum reacts with hydrated tricalcium aluminates (C_3A) to form ettringite ($C_6AS_3H_{32}$) and its analogs. The process is described by the following equations (Monteny et al. 2000):

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O \quad (1)$$

$$CaO \cdot SiO_2 \cdot 2H_2O + H_2SO_4 \rightarrow CaSO_4 + Si(OH)_4 + H_2O \quad (2)$$

$$3CaO \cdot Al_2O_3 \cdot 12H_2O + 3(CaSO_4 \cdot 2H_2O) + 14H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \quad (3)$$

Both gypsum and ettringite have very low structural stability in comparison to the reactants they replace. They are also believed to cause expansion, which initiates cracks in the structure, leading to reduced structural capacity (Stark 2002).The compressive strengths of mortar specimens decrease in acidic environments with the increasing of RHA in the mortar. It may be due to less amount of CaO in RAH (Giaccio et al 2007) resulting less amount of C-S-H. So, more RAH leads to less CaO as well as less C-S-H i.e. less compressive strength. The mortar specimen in acidic environments gain the maximum strength within three days of curing then it decreases gradually with age of mortar. At the early age of curing the acid attack may not be sufficient to cause the decrease in strength. The penetration of acid in the mortar specimen may be less at the early age. The depth of acid penetration becomes more and more with age. So the CH and C-S-H produced by the hydration may be converted into gypsum and ettringite completely. Besides this the less expansion may be occurred at the early age of curing (Stark 2002) although it should be investigated later. So the strength may become less with age of curing. The strength is higher in pH 3 than pH 2 for all cases. The strength should be more when the pH value is less (Islander et al. 1991). The strength decreasing rate is more at the early age of mortar (up to 28 days) and it becomes lower at the greater age.

At the later age (over 90 days) of mortar the strength of mortar becomes more or less same in both acidic environments. It may be due to the finishing of calcium hydroxide (CH) and calcium silicate hydrates (C-S-H) to form gypsum ($CaSO4 \cdot 2H_2O$) and hence ettringite ($C_6AS_3H_{32}$). The maximum strength decreasing rates in pH 2 acidic environment corresponding to 0%, 5%, 10%, 15% and 20% RHA are 12.45%, 11.72%, 11.17%, 11.23% and 9.36% respectively and that of in pH 3 acidic environment are 10%, 13.62%, 12.91%, 13.31% and 10.67% respectively. It is observed from the figures that after the age of 90 days the strength decreasing rate is very small (maximum 8%).

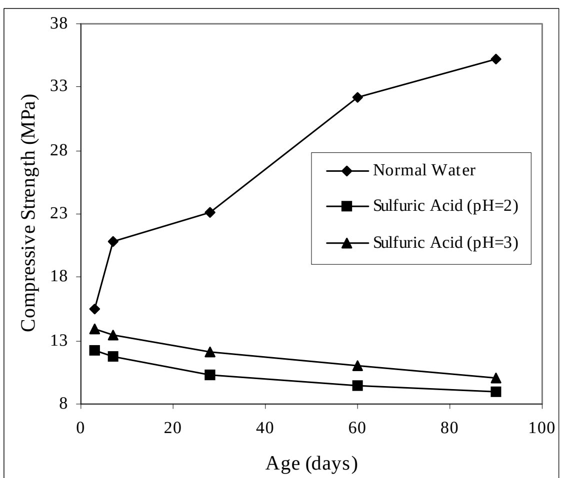

Figure-1: Compressive Strength vs Age (Cement:RHA=100:00)

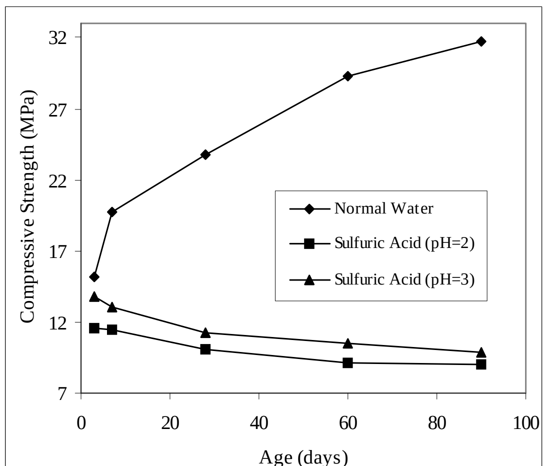

Figure-2: Compressive Strength vs Age (Cement:RHA=95:05)

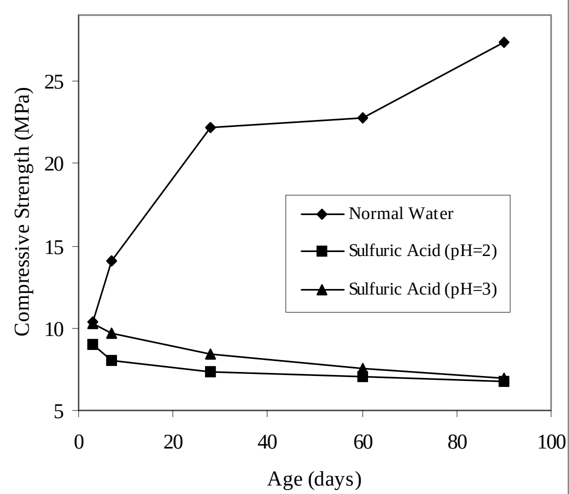

Figure-3: Compressive Strength vs Age (Cement:RHA=90:10)

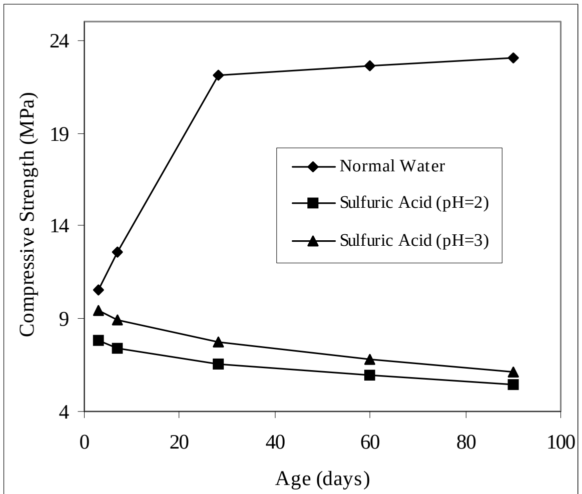

Figure-4: Compressive Strength vs Age (Cement:RHA=85:15)

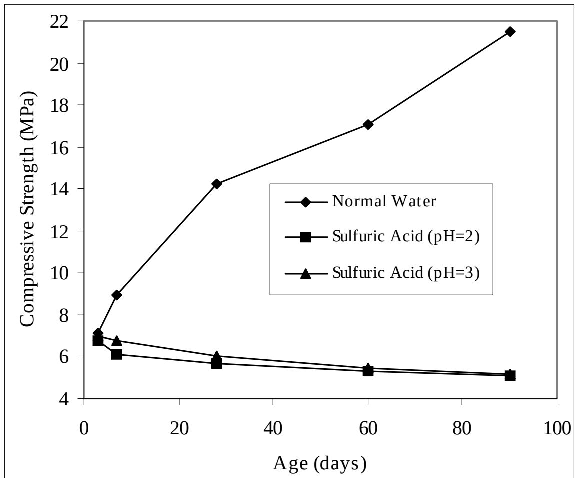

Figure-5: Compressive Strength vs Age (Cement:RHA=80:20)

4. CONCLUSION

This paper analysis the strength behavior of mortar with RHA in sulfuric acid environments where pH ranging from 2 to 3. The main conclusions of the research are as follows: The compressive strength of mortar with RHA is less in sulfuric acid environments compared to that of in normal water. The strength decreases in acidic environments with age of mortar also with increasing of RHA content in mortar where as the strength is less in pH 2 than in pH 3. And in case of normal water the compressive strength of mortar increases with age of mortar. But the strength value decreases with increasing of RHA. After 90 days of age, the compressive strength attains more or less a uniform value in all acidic environments. The mortar gains the maximum compressive strength within 3 days of curing period. Maximum 10% RHA addition level and pH value of 3 may be acceptable on the basis of strength. Because the ultimate compressive strength remains a reasonable value up to 10% cement replacement levels.

REFERENCES

Bakharev, T. 2005. Resistance of geopolymer materials to acid attack. Cem Concr Res 35: 658-670.

Barkakati, P. Bordoloi, D. Borthakur, P.C. 1994. Paddy husk as raw material and fuel for making Portland cement, Cem. Concr. Res. 24(4); 613- 620.

Cook, D.J. 1986. Rice husk ash, in: R.N. Swamy (Ed.), Concrete Technology and Design, Cement Replacement Materials, vol. 3, Surrey University Press, London, pp. 171- 196.

de Sensale, G.R. Dal Molin, D.C.C. 2000. Study of high performance concrete, regarding the effects of rice-husk ash substitution. In: Precast/Prestressed Concrete Institute, editor. Proceedings of the PCI/FHWA/FIB international symposium on high performance concrete pp. 135–144.

de Sensale, G.R. 2006. Strength development of concrete with rice-husk ash. Cem Concr Compos 28(2):158-160.

Gastaldini , A.L.G. Isaia, G.C. Gomes, N.S. Sperb, J.E.K. 2007. Chloride penetration and carbonation in concrete with rice husk ash and chemical activators, Cem Concr Compos 29(1):176-180.

Giaccio, G. ´guez de Sensale, G.R. Zerbino, R. 2007. Failure mechanism of normal and high-strength concrete with rice-husk ash, Cem Concr Compos 29(4):566-574.

Islander, R. L. Devinny, J. S. Mansfeld, F. Postyn, A.and Shih, H. 1991. Microbial ecology of crown corrosion in sewers, J. Environ. Eng., 117(6), 751–770.

James, J. Rao, M.S. 1986. Reactivity of rice husk ash. Cem Concr Res 16:296–302.

Krishnamoorthy, T.S. Gopalakrishnan, S. Balasubramanian, K. Bharatkumar, B.H. Rama P. Moan Rao, 2002. Investigations on the cementitious grout containing supplementary cementitious materials. Cem Concr Res 32(9):1345–14405.

Malhotra, V.M. Mehta, P.K. 1996.Pozzolanic and cementitious materials. Advances in concrete technology, vol. 1. Canada: Gordon and Breach Publishing.

Mehta, P.K. Pitt, N. 1977. A new process of rice husk utilization. In: International conference on the utilization of rice by-products, 1974 Valencia: IATA; p. 45–58.

Mehta, P.K. 1992. Rice husk ash – a unique supplementary cementing material. In: Proceedings of the CANMET/ACI international conference on advances in concrete technology. Canada: CANMET; p. 419–443.

Mehta, P.K. 1994. Highly durable cement products containing siliceous ashes. US Patent 5,346,548; 15 pp.

Mehta, P.K. 1994a. Rice husk ash - a unique supplementary cementing aterial, in: V.M. Malhotra (Ed.), Adv. Concr. Technol., Proc. CANMET, pp. 419- 444 (MSL Report, 94-1(R)).

Mehta, P.K. 1994b. Concrete technology at the cross-roads-problems and opportunities. In: ACI, vol. SP-144; p. 1–30.

Mehta, P.K. 1998. Role of pozzolanic and cementitious materials in sustainable development of the concrete industry. In: ACI, vol. SP- 179; p. 1–20.

Monteny, J. Vinke, E. Beeldens, A. DeBelie, N. Taerwe, L. Van Gemert, D.and Verstraete, W. 2000. Chemical, microbiological, and in situ methods for biogenic sulfuric acid corrosion of concrete, Cem. Concr. Res., 30(4), 623–634.

RILEM Committee 73-SBC. Final report: siliceous by-products for use in concrete. Mater Struct 1988;21(121):69–80.

Singh, N.B. Rai, S. 2001. Effect of polyvinyl alcohol on the hydration of cement with rice husk ash, Cem Concr Res 31(2): 239-243.

Stark, D. 2002.Performance of concrete in sulfate environments, RD 129, Portland Cement Association, Skokie, Ill

Swamy, R.N. 1997. Design for durability and strength through the use of fly ash and slag in concrete. In: ACI, vol. SP-171; p. 1–72.

Zhang, M.H. Malhotra, V.M. 1996. High-performance concrete incorporating RHA as a supplementary cementing material. ACI Mater J 93(6):629–636.

Zhang, M.H. Lastra, R. Malhotra, V.M. 1996. Rice-husk ash past and concrete: some aspects of hydration and the microstructure of the interfacial zone between the aggregate and paste. Cem Concr Res 26(6):963–977.