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Determination of amorphous silica in rice husk ash by a rapid analytical method

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Abstract

A rapid analytical method for evaluating amorphous silica in rice husk ash (RHA) is provided and therefore an assessment of its potential pozzolanic activity. The method is based on bringing the siliceous non-crystalline fraction of the pozzolan into solution as glycerosilicate by treating the test material with glycerol. The titration of the resulting solution is performed with an aqueous glycerol solution of barium hydroxide. Data are compared to those obtained using a standard method and a good concordance is achieved. It is demonstrated that the proposed method can be a useful tool for evaluating amorphous silica in RHA. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Amorphous material; Reaction; Pozzolan; Titration

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 [1–3].

Rice husk ash (RHA) is a highly reactive pozzolanic material suitable for use in lime–pozzolana mixes and for Portland 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 [4].

Thus, the reactivity of RHA as pozzolanic material depends on the crystalline/amorphous ratio. Therefore, for RHA characterization, the evaluation of the amount of amorphous silica becomes very important. For this purpose, there are some specific methods in the literature. One of them, proposed by Mehta [5], established that the degree of amorphousness of silica is estimated by the "silica activity index," which is determined by calculating the percentage of available silica that is dissolved in an excess of boiling 0.5 M sodium hydroxide in a 3-min extraction period. Another simpler method is to titrate a suspension containing 1 g of the ash in 25 ml of distilled water against methylene blue. The amount of methylene blue required to produce a color change could also be used as an index of the state of the silica in the ash [4].

Standard test methods for evaluating reactive silica (also called soluble silica) are somewhat tedious, since these include stages of filtration, calcination, etc.

Therefore, the interest in having rapid analytical methods that can provide a measure of the amount of amorphous silica in RHA (and in other pozzolans) is justified, mainly to provide an assessment of the pozzolanic activity of these materials.

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Kreshkov et al. [6] developed an analytical method for evaluating free amorphous silica (FAS) in clay, which is based on bringing it into solution as glycerosilicate by treating the test material with glycerol and titrating the glycerol solution obtained with an aqueous glycerol solution of barium hydroxide, using phenolphthalein or alizarin yellow as the indicator. The advantage of this titrimetric method is its speed, as it can be carried out in 35–50 min.

The main goal of this work is to provide a rapid analytical method for evaluating amorphous silica in RHA. We have used Kreshkov's method for the first time in determining the amorphous silica content in RHA. We compared the results of this determination with those provided by a standard method. We have demonstrated that the proposed titrimetric method, initially developed for determining free silica in silicates, is suitable for evaluating amorphous silica in RHA.

2. Experimental

2.1. Materials

Some RHAs studied in this research were from the Spanish enterprise Agrocítrica (Alzira, Valencia). These were obtained from rice husks burnt in an open chamber and from burning them as fuel in a furnace. In both cases, the combustion process occurred under uncontrolled conditions; but while in the open chamber, burning lasted some weeks, in the furnace it took only a few hours. Different samples were taken at random points from piles of ashes. These ashes were ground in a laboratory ball mill for 5 min until the mean particle diameter ranged between 10 and 17 μm. Then, they were dried at 120°C for at least 24 h. Additionally, RHA samples containing a high content of amorphous silica were obtained in a laboratory furnace at 600°C.

Chemical reagents, barium hydroxide, glycerol (1,2,3-propanetriol), phenolphthalein, were analytical grade reagents. To prepare standard amorphous silica, sodium silicate and sulfuric acid were used; the silica gel obtained was washed with a 5% solution of nitric acid containing a few drops of hydrogen peroxide. After washing, the product was dried at 120°C for at least 24 h. For the application of the standard method, hydrochloric acid, potassium hydroxide and silver nitrate solutions were used as reagents. Fine powdered quartz was also used as reference material.

2.2. Procedures

The proposed method consists of the following stages.

2.2.1. Preparation of titrant and indicator solutions

A 0.005 M aqueous glycerol solution of $Ba(OH)_2$ is prepared from a saturated aqueous solution of $Ba(OH)_2$ (the solubility of $Ba(OH)_2$ in water at 20°C is 3.89 g/100 ml), taking an appropriate volume after filtration (e.g., 10.4 ml of filtrate was taken to prepare 250 ml of solution) and mixing it with an aqueous glycerol solution, in which the water to glycerol ratio was 1:1. The resulting solution must be protected from atmospheric CO_2. An alcoholic solution of phenolphthalein (covering the pH range 8.1–9.8) was used as indicator.

2.2.2. Determination of the amount of titrant equivalent to 5 ml of glycerol

A 5 ml volume of glycerol is measured out into a small beaker or a porcelain capsule (using a syringe) and slowly titrated with the aqueous glycerol $Ba(OH)_2$ solution, both being mixed with a magnetic stirrer. Due to the high viscosity of glycerol, the detection of the endpoint of the titration must be carried out externally of the titration receptacle. The color change of the solution is determined as follows: two drops of the indicator are placed on a porcelain plate and two drops of the solution being titrated added to it. The drops are mixed with a glass rod. This procedure is repeated after each addition of titrant. Titration is considered to be complete when the color of the mix solution indicator on the porcelain plate changes to rose. The amount of titrant used (V_2) is taken into account in subsequent calculation.

2.2.3. Determination of the amount of titrant used for titrating standard silica dissolved in glycerol

An amount of 10–30 mg of standard amorphous silica (previously prepared and finely dispersed in an agate mortar) is weighed (m_2) and placed in the porcelain capsule or beaker, covered with 5 ml of glycerol and the mixture ground together (with the aid of the magnet) and, after that, mixed with a magnetic stirrer for 20 min minimum. The mixture is then titrated as follows: $Ba(OH)_2$ solution in an amount equivalent to 5 ml of glycerol is added, the suspension mixed carefully for 10 min, and titration then carried out slowly, adding the titrant until reaching the endpoint, just as it has been explained in the second point. The volume of titrant used (V_1) is taken into account in subsequent calculation.

2.2.4. Determination of amorphous silica in RHA

An amount of 40–300 mg of sample is weighed (m_1) (the amount depends on the crystallinity or amorphousness of the sample) and placed in the porcelain capsule or beaker, covered with 5 ml of glycerol and the mixture ground together for 20 min. The mixture is then titrated as described above. The volume (V_3) of titrant used is noted.

2.2.5. Calculation of amorphous silica content in RHA

The percentage of FAS (FAS_{gly}) in the sample is then calculated by means of the formula [Eq. (1)]:

$$\%FAS_{gly} = \frac{m_2(V_3 - V_2)}{m_1(V_1 - V_2)} \times 100. \tag{1}$$

3. Results and discussion

The Spanish standard [7,8] specifies that the percentage of reactive silica contained in pozzolans is determined by the difference between the total amount of silica and the silica that remains unchanged as an insoluble residue following attack by hydrochloric acid and boiling 4 M potassium hydroxide in a 4-h extraction. However, work by the current authors has shown that this treatment is too drastic because it dissolves not only the amorphous silica, but also crystalline silica. Thus, the time of extractive treatment with 4 M KOH was varied. For this purpose, several 1-g samples of a fine powdered crystalline SiO_2 (quartz) were treated with a boiling solution of 4 M KOH for different times, and the amount of dissolved SiO_2 was established in each case. The results of this study are shown in Fig. 1.

At an extraction time below 3 min, the dissolved silica remains constant at 4%. This is interpreted as being due to dissolution of isolated surface SiO_4 groups. Chemical treatment over longer period results in the partial dissolution of highly crystalline matter, so that for 60-min treatment, 18% of the total silica content was dissolved. In contrast, a freshly prepared amorphous SiO_2 was found to fully dissolve after 3 min in boiling 4 M KOH solution. This suggests that 3 min is a suitable extraction time for total dissolution of vitreous SiO_2. This procedure was therefore adopted to determine the amount of amorphous silica in some samples of RHA. Percentages of amorphous SiO_2 are given in Table 1. RHA samples, which contained a wide range of amorphous matter (from 8% to 84%), were selected . Data for fine powdered quartz are also included.

Additionally, Kreshkov's method using glycerol was applied to RHA samples and fine powdered quartz. In this method, the amorphous SiO_2 fraction from RHA samples is dissolved in the glycerol media. Glycerol molecules, $OH{-}CH_2{-}CH(OH){-}CH_2OH$, work as coordination ligands towards silicon. Ligands could work as monodentate anion ligands $(OH{-}CH_2{-}CH(OH){-}CH_2O)^-$, as bidentate dianion ligands $(O{-}CH_2{-}CH(OH){-}CH_2O)^{2-}$ or as tridentate trianion ligands $(O{-}CH_2{-}CHO{-}CH_2O)^{3-}$. These anionic ligands L^{q-} ($q = -1, -2, -3$) coordinate silicon, yielding a glycerosilicate complex according to the following equation [Eq. (2)]:

$$SiO_2 + nL \rightarrow (SiL_n)^{4-nq} + (4-nq)H^+ + (nq/2)H_2O. \tag{2}$$

Thus, glycerol becomes an acidic medium and this acidity is titrated using $Ba(OH)_2$. When the titrant is added

Table 1
Percentage of FAS values obtained by the KOH method and the glycerol method

Sample	FAS_{KOH}	FAS_{gly}
Fine powdered quartz	4.16	4.02
RHA-1	8.25	8.04
RHA-2	8.48	8.86
RHA-3	9.36	9.44
RHA-4	10.11	12.33
RHA-5	11.45	9.98
RHA-6	13.99	12.46
RHA-7	26.73	26.61
RHA-8	29.72	28.40
RHA-9	60.57	58.93
RHA-10	83.88	82.86

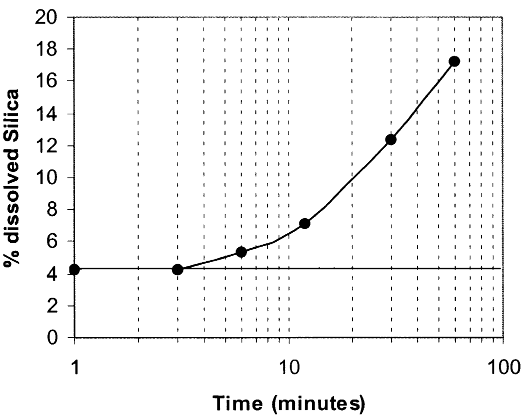

Fig. 1. Dissolution of fine powered quartz in boiling KOH solution: dependence with treatment time.

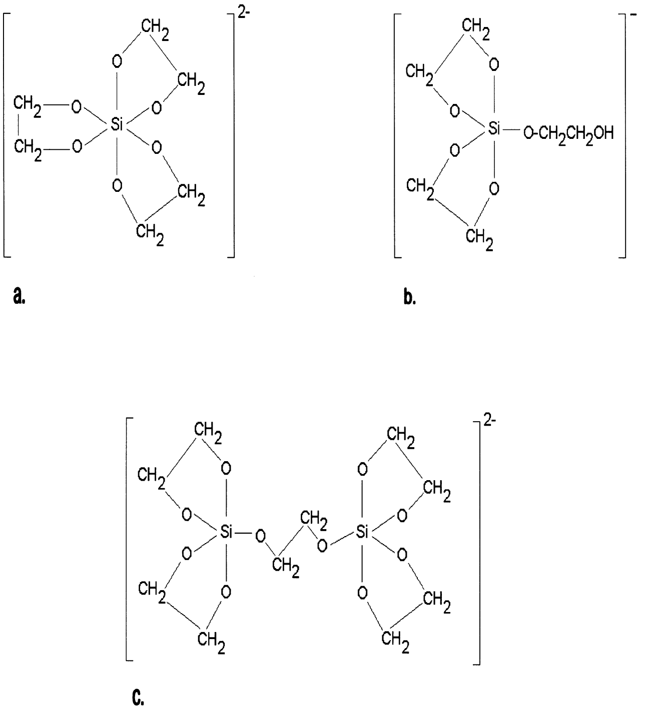

Fig. 2. Different coordination modes for alkoxy ligands in alkoxysilicate anions: (a) bidentate; (b) monodentate; (c) bridging.

to glycerosilicate solution, a white precipitate is obtained. Attempts to isolate pure barium glycerosilicate salt from the reaction solution were unsuccessful. Probably, a polyglycerosilicate/barium salt was obtained in this reaction, different coordination modes for glycerate ligands (L^{q-}) could be found in this compound and Si–O–Si bridges were probably formed in the yielded barium compound. The complexity in the stoichiometry for the barium salt was attributed to several coordination modes for glycerol. The analogous barium salt with ethylene glycol [9] presents a very simple stoichiometry, $Ba[Si(OCH_2CH_2O)_3]$, due to the ethyleneglycolate $(OCH_2CH_2O)^{2-}$ anion working as a bidentate ligand in a chelating mode (see Fig. 2a). For ethyleneglycolate ligands in silicon complexes, different coordination modes have been reported [10] — as monodentate monoanion ligands (Fig. 2b) and as bridging ligands to two silicon centers (Fig. 2c). Thus, the complexity in the coordination modes for polyalkoxy anions in silicon complexes explains the difficulty in characterizing the nature of the barium salt using glycerate ligands.

Despite the incomplete characterization of the barium glycerosilicate salt, the amount of titrant (barium hydroxide) used for RHA samples can be compared to those used for an amorphous standard silica sample. The percentage of FAS by the glycerol method (FAS_{gly}) is calculated according to Eq. (1). The values obtained are summarized in Table 1.

In general, good agreement is obtained between the results derived using the KOH treatment, FAS_{KOH}, and those obtained by the glycerol method, FAS_{gly}. The plotting of FAS_{gly} values vs. FAS_{KOH} values in Fig. 3 showed excellent concordance between the two methods. The glycerol method offers a rapid procedure for samples containing a wide range of amorphous silica content.

Two aspects should be taken account of in relation to the titrimetric procedure. Firstly, the optimal amount of RHA to be analyzed depends on its amorphous content. Thus, for high crystallinity RHA, aliquots of RHA must be in the 200–300 mg range; whereas for high amorphousness RHA, samples must be in the 40–100 mg range. For an unknown material, a sample amount of 80–90 mg is taken; if the $\%FAS_{gly}$ is $\geq 50\%$, the result is recorded, but if the $\%FAS_{gly}$ is lower than 50%, the titration is repeated with a sample amount of 200–300 mg.

When the RHA sample has a high vitreous content and the amount of the sample for titration is above 200 mg, the total volume of titrating agent to determine the endpoint exceeds 20 ml. Thus, there is a large amount of water present and, consequently, the chemical stability of the glycerosilicate complexes is negatively affected. In these conditions, SiO_2 is precipitated and a premature endpoint is obtained. On the other hand, when the RHA sample has a low vitreous content and the amount of sample used for titration is lower than 100 mg, the total volume of titrating solution is too small and, consequently, the error in calculating the vitreous fraction in RHA is high.

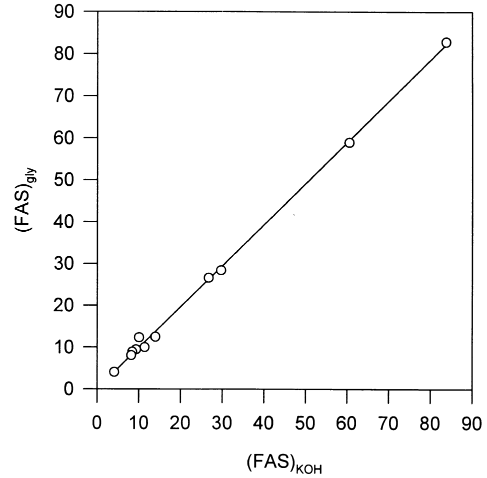

Fig. 3. Free amorphous silica (FAS) content in samples: comparisons between FAS data obtained by the KOH method and the glycerol method.

Secondly, for determining the color change of the solution with the indicator, two drops of the solution must be taken from the floating liquid, avoiding any white barium glycerosilicate precipitate; if not, a premature endpoint could be obtained. Then, stirring should be stopped and the suspension should be allowed to settle before removing the solution for testing with indicator.

4. Conclusions

It can be concluded that the proposed titrimetric method is suitable for determining the percentage of amorphous silica in RHA. This method has been used for the first time to assess the pozzolanic activity of a pozzolanic material. The advantage of this titrimetric method is the reduced time required in the determination. The results are in good concordance with those provided by a standard method.

Acknowledgments

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References

[1] P.K. Mehta, Rice husk ash — a unique supplementary cementing material, in: V.M. Malhotra (Ed.), Adv. Concr. Technol., Proc. CANMET, 1994, pp. 419–444 (MSL Report, 94-1(R)).
[2] M.H. Zhang, V.M. Malhotra, High-performance concrete incorporating rice husk ash as a supplementary cementing material, ACI Mater. J. 93 (6) (1996) 629–636.
[3] P. Barkakati, D. Bordoloi, P.C. Borthakur, Paddy husk as raw material and fuel for making Portland cement, Cem. Concr. Res. 24 (4) (1994) 613–620.
[4] D.J. Cook, Rice husk ash, in: R.N. Swamy (Ed.), Concrete Technol-

ogy and Design, Cement Replacement Materials, vol. 3, Surrey University Press, London, 1986, pp. 171–196.

[5] P.K. Mehta, Belgian Patent No. 802909, July 1973.

[6] A.P. Kreshkov, A.N. Chivikova, A.A. Zagorovskava, A rapid method for determining free amorphous silica in clay, J. Anal. Chem. URSS 20 (1965) 1295–1296.

[7] UNE 80225:1993 Ex, Métodos de ensayo de cementos. Análisis Químico. Determinación del dióxido de silicio (SiO_2) reactivo en los cementos, en las puzolanas y en las cenizas volantes.

[8] UNE-EN 196-2:1996, Métodos de ensayo de cementos: Parte 2. Análisis Químico de cementos.

[9] M.L. Hoppe, R.M. Laine, J. Kampf, M.S. Gordon, L.W. Burggraf, $Ba[Si(OCH_2CH_2O)_3]$, a hexa-alkoxysilicate synthesized from SiO_2, Angew. Chem., Int. Ed. Engl. 32 (2) (1993) 287–289.

[10] R.M. Laine, K.Y. Blohowiak, T.R. Robinson, M.L. Hoppe, P. Nardi, J. Kampf, J. Uhm, Synthesis of pentacoordinate silicon complexes from SiO_2, Nature 353 (1991) 642–644.