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Development of rapid method for the estimation of reactive silica in fly ash

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Abstract

Reactive silica (SiO_2) is an important component of fly ash controlling its use in cement and building materials. Literature search shows that the methods available for the estimation of reactive silica are very time consuming and tedious. It requires a minimum of four days by the conventional gravimetric method described in the standards. In the current paper a rapid volumetric method has been developed where it is possible to estimate reactive silica in fly ash in 4 h. Besides this a gravimetric method has been developed which takes two and half days.

Keywords: Reactive silica; Pozzolana; Fly ash; Portland pozzolana cement; Standards

1. Introduction

The factors generally considered for finding the suitability of a fly ash for making Portland pozzolanic cement (PPC) are chemical composition, fineness and crystalline structure. However the most important constituent of a fly ash for determining its suitability for making cement is the reactive silica, which controls the reactivity. A fly ash containing reactive silica less than 20% is generally not considered suitable for making PPC [1].

In a method reported by Sivapullaiha et al. [2] the reactive silica content was obtained by digesting fly ash samples with hydrochloric acid. The reactive silica so obtained is incomplete because, for obtaining complete reactive silica from fly ash, further digestion with potassium hydroxide is essential after acid treatment [1,3]. So, the method gives an under estimated reactive silica and hence the method is not suitable for the assessment of reactive silica for making PPC.

Reactive silica estimation has not been covered in American and British standards [4,5].

As per Indian and Sri Lankan standards [1,3], reactive silicon dioxide (SiO_2) is that fraction of the silicon dioxide, which is soluble after treatment with hydrochloric acid (HCl) and with boiling potassium hydroxide (KOH) solution. The quantity of reactive silicon dioxide is determined by subtracting from the total silicon dioxide content that fraction contained in the residue insoluble in hydrochloric acid and potassium hydroxide [1,3].

$$\text{Reactive } SiO_2 = \text{Total } SiO_2 - SiO_2 \text{ present in insoluble residue}$$

This is an indirect approach of estimating reactive silica and is the only method available in the standards, which takes more than four days.

In the current paper two methods have been developed for the estimation of reactive silica, the first method is the rapid volumetric method and the other one is a gravimetric method. The volumetric method takes only 4 h; the gravimetric method takes two and half days, vis a vis the method described in the standards which takes more than four days [1,3].

2. Experimental

Ten samples of fly ash were obtained from different sources and reactive silica was estimated using the conventional method (Indirect method) [1,3] and the developed volumetric and the gravimetric methods.

2.1. Conventional indirect method of estimation

Reactive silica content was estimated in all the ten samples as per the conventional method [1,3].

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2.2. Volumetric method developed

Reactive silica was extracted from the fly ash sample by acid treatment followed by alkali digestion in a digestion bomb under pressure. The SiO_2 content so obtained was precipitated as potassium hexafluorosilicate (K_2SiF_6). The precipitate was filtered, washed and hydrolyzed with warm water.

$$K_2SiF_6 + 3H_2O \rightarrow 2KF + H_2SiO_3 + 4HF$$

The hydrofluoric acid so obtained was titrated with sodium hydroxide and the silica content calculated.

2.2.1. Preparation of reagents

All the reagents/chemicals used were of AR/GR grade.

I. Wash solution for washing the precipitate: 75 g KCl was dissolved in 500 ml water and 500 ml ethanol was added. After mixing, the excess KCl was allowed to settle and the solution was decanted. To this solution 5 ml of 0.2% methyl red was added and the solution was neutralized to a yellow orange color.
II. Indicator: 0.5% bromothymol blue + 0.5% phenol red in pure ethanol.

2.2.2. Digestion of sample

0.2 g sample dried at 110 °C was weighed in a 250 ml beaker and 15 ml concentrated HCl and an equal amount of distilled water was added. The contents were evaporated to dryness. The process was repeated once more. Finally 15 ml HCl and 30 ml water was added, boiled and filtered using a medium filter paper (Whatman 40) in a plastic beaker. Washing was done with hot distilled water and the filtrate was preserved.

The insoluble part in the filter paper along with the filter paper was transferred to a teflon container of the Digestion Bomb. 20 ml of 25% KOH was added followed by 20 ml of distilled water. The contents were digested on a hot plate at 500 °C for 15 min. The extracted mass was cooled and filtered through Whatman 40 filter paper into the filtrate already preserved. 10 ml of concentrated HCl and 10 ml of nitric acid were added to the filtrate. To this 5 ml of 20% calcium chloride and 1 g sodium fluoride were added. After dissolution, potassium chloride was added to saturate the solution and then 1–2 g in excess. The precipitate was allowed to settle and then filtered through Whatman 40. The precipitate was washed with the wash solution till free of acid i.e. until the color of the wash solution did not change.

2.2.3. Titration of reactive silica

About 500 ml of hot distilled water (temperature not less than 70 °C) was taken in a 1 l conical flask, five drops of the indicator were added and the water neutralized with N/15 NaOH to blue color. The filter paper containing the precipitate was transferred to the conical flask and the solution was vigorously mixed. The color of the solution changed to yellow due to liberation of hydrofluoric acid. The solution was titrated with N/15 NaOH till the same blue color tint was obtained.

Calculation:

$$\%\ \text{Reactive}\ SiO_2 = \frac{\text{ml of NaOH} \times 0.001 \times 100}{\text{Weight of sample}}$$

2.3. Gravimetric method developed

2.3.1. Digestion of the sample for the extraction of reactive silica

1 ± 0.05 g of fly ash sample was taken in a 250 ml beaker, 25 ml distilled water and 40 ml concentrated HCl was added. The contents were evaporated to dryness on a hot plate. This operation was repeated after adding 20 ml concentrated HCl. 50 ml of 1:3 HCl was added, heated just to boil and the contents filtered through a medium filter paper (Whatman 40). Washing was done with hot distilled water till free from chloride. The filtrate was preserved. The filter paper along with its contents was transferred to a 250 ml conical flask fitted with a bulb condenser. 100 ml of 25% KOH was added and left to stand for 16 h at room temperature. After this the solution was boiled under reflux for 4 h. The contents were then filtered through a medium filter paper in a 500 ml beaker. Washing was done 6–7 times with hot distilled water. The solution was acidified and mixed in the filtrate preserved already. SiO_2 was estimated in the solution [6], which represents the reactive silica.

Table 1
Chemical composition of the fly ashes

Constituents %	Sample no									
	1	2	3	4	5	6	7	8	9	10
LOI	3.01	4.02	2.51	2.23	2.26	0.89	0.63	3.30	1.20	1.00
SiO_2	50.00	52.80	59.31	54.99	62.08	61.64	65.00	62.51	66.68	58.83
Fe_2O_3	15.02	10.09	8.21	4.58	3.65	5.48	3.24	5.93	5.12	4.34
Al_2O_3	20.41	23.62	25.00	31.53	25.46	23.39	25.71	23.07	23.39	32.21
CaO	8.02	6.51	2.20	1.45	3.16	5.21	1.03	1.04	0.60	0.54
MgO	2.21	1.52	1.60	0.42	0.46	0.43	0.59	0.60	0.27	0.32
TiO_2	0.26	0.40	0.24	2.08	1.52	0.40	1.47	1.76	0.16	0.36
Na_2O	0.40	0.36	0.24	0.21	0.11	0.14	0.11	0.11	0.21	0.15
K_2O	0.29	0.32	0.51	1.10	0.69	1.02	0.41	0.40	0.80	0.88
SO_3	0.15	0.10	0.16	0.28	0.28	0.32	0.40	0.40	0.11	0.36

Table 2
Reactive silica (%SiO2)

Sample no	Developed gravimetric method	Developed volumetric method	Existing (Indirect) method
1	38.09	37.90	38.10
2	35.32	35.10	35.20
3	31.48	31.68	31.59
4	33.05	33.21	33.27
5	32.84	32.98	33.01.
6	33.79	33.56	33.82
7	31.20	31.01	31.31
8	34.47	34.30	34.52
9	33.83	34.01	34.15
10	30.48	30.29	30.51
Time required	Two and half days	4 h	More than four days

Reactive silica was found by the gravimetric method in all the ten samples.

3. Results and discussion

The chemical composition of the ten fly ashes used is given in Table 1.

Results of reactive silica as obtained by the two developed methods and the conventional indirect method are presented in Table 2.The results obtained by the two developed methods are within the permissible limits of variation. A good agreement was found in the existing Indirect Method results and the results obtained by the developed methods.

4. Conclusions

The methods devised are accurate and time saving. The volumetric method is very fast and takes only 4 h. The gravimetric method takes two and half days but is considered as the referee method and requires less time than the conventional method reported in the standards (more than four days). The methods shall be highly useful for the cement manufacturers, thermal power stations, testing laboratories and the chemists.

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