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DETERMINATION OF REACTIVE SILICA (SiO_2) OF FLY ASH

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ABSTRACT

The reactive silica of fly ash as that fraction of SiO_2 which is soluble after treatment with hydrochloric acid and with boiling potassium hydroxide solution. The quantity of reactive silica is determined by subtracting from the total silica content that fraction contained in the insoluble residue both on dry basis.

Keywords: Reactive Silica, Fly ash, Cement

INTRODUCTION

Fly ash is generated by burning of ground or pulverized or crushed coal or lignite fired boilers & extracted from flue gases by any suitable process such as cyclone separator or electrostatic precipitator. Fly ash is used as pozzolana in cement, mortar and concrete. Reactive silica is one of the parameter that determines the pozzolanic potential of a fly ash that is its tendency to react with available calcium hydroxide to form cementitious hydration products.

EXPERIMENITAL

Methods

The method for determination of reactive silica consists following steps

1. Determination of total silica
2. Determination of insoluble residue (IR)
3. Determination of silica in insoluble residue
4. Calculation of reactive silica

1. Determination of total silica (SiO_2)[1]

Determination of pure silica

Weighed an accurately about 1 g sample (m_1) of fly ash (previously finely ground and air dried at 105ºC for 2 hours) in a platinum crucible and mixed with about 10 g of sodium carbonate, kept the crucible with lid in a muffle furnace, heated slowly and finally ignited at 1050 ± 25ºC to complete the fusion, cooled the crucible then placed in 100 ml water in a 500 ml beaker, added slowly 30ml hydrochloric acid (sp. g. 1.16), warmed until the fused mass was completely disintegrated and removed from the crucible and lid, washed the crucible with hot water, crushed any lumps remaining in the solution by glass rod, then 5ml hydrochloric acid (sp.g. 1.16) was also added in excess.

Evaporated the solution, obtained from the fusion to completely dryness/baked, added 20 ml HCl (sp.g.1.16) shaken, then added 100ml hot water, heated on hot plate for boiling for 2 minutes with continuous stirring with glass rod. Filtered the solution through ashless filter paper No.40 (whatman) or pulp and washed the residue with 5 times of hot water (Reserved the filtrate for further analysis of soluble silica).

Transferred the residue with filter paper or pulp in a weighed platinum crucible (m_2), heated slowly until the papers were charred and finally ignited at 1050 ± 25ºC, cooled the crucible and weighed the mass of impure silica (m_3) (SiO_2 + IR).

Moistened the weighed residue with few drops of water, added few drops of sulphuric acid then added 10 ml hydrofluoric acid. Evaporated slowly to dryness on water bath then on hot plate in a fuming chamber. Kept the crucible with residue in a furnace with slowly heating upto 1050 ± 25ºC, cooled the crucible and weighed the mass of residue (m_4) till constant weight (If the residue weight more than 5 mg, repeat the treatment of hydrofluoric acid and sulphuric acid to ensure that all the silica is removed).

Expression of results in percentage

Subtracted the weight of this residue from the impure silica to obtain the amount of silica in the sample taken. The pure silica content was calculated in percentage from the formula:

$$Pure\ SiO_2 = \frac{m_3 - m_4}{m_1} \times 100$$

Where, m_1 = mass of sample taken in g
m_3 = mass of silica + impurities in g and
m_4 = mass of residue in g

Determination of soluble silica in the filtrate

To the filtrate about 3g ammonium chloride was added, warmed the solution to about 80ºC and then added dilute ammonia (1:3) with stirring until precipitation appears to be completed or solution just alkaline to methyl red. Boiled the solution for 2 minutes then allowed the solution to stand for 5 minutes. Filtered the solution through an ashless filter paper No.41 (whatman), washed the precipitate with 5 times with 2% hot faintly ammonical ammonium chloride solution.(just alkaline to methyl red).

Transferred the precipitate and filter paper to the same beaker in which the first precipitation was effected. Dissolved the precipitate in hot HCl (1:3), diluted the solution about 100 ml and re-precipitated the hydroxides by the addition of dilute ammonia solution (1:3). Filtered the solution by filter paper No.41 and washed the precipitate 2 times with 2% hot faintly ammonical ammonium chloride solution. Placed the precipitate with filter paper in a weighed platinum crucible (m_5), heated slowly until the papers were charred and finally ignited to constant weight at 1050 ± 25ºC, cooled and taken the mass of crucible (m_6) contained mixed oxides and soluble silica.

Treated the residue with few drops of water, about 5 ml hydrofluoric acid and few drops of sulphuric acid. Evaporated cautiously to dryness on water bath and hot plate, finally ignited at 1050 ± 25ºC with slow rising of temperature. Cooled the crucible and weighed (m_7).

Expression of results in percentage

$$Soluble\ silica = \frac{m_6 - m_7}{m_1} \times 100$$

Where, m_1 = mass of sample taken in g
m_6 = mass of mixed oxide and soluble silica in g and
m_7 = mass of mixed oxides in g

Total Silica in fly ash

Expression of results in percentage

The total silica content is equal to the sum of the pure silica and the soluble silica content, as-

$$\text{Total } SiO_2 = \text{Pure } SiO_2 + \text{Soluble } SiO_2$$

2. Determination of insoluble reside (IR)[2, 3]

Weighed an accurately about 1g sample of fly ash (m_8) (previously finely ground and air dried at 105ºC for 2hours) and taken in 250 ml beaker, added 50 ml water, 40 ml hydrochloric acid (sp.g.1.16) with continuous stirring, warmed the solution and then heated slowly on the hot plate for dryness/baking. Repeated the operation twice more with 40ml hydrochloric acid (1:1).Treated the residue from the last evaporation with 100ml of dilute hydrochloric acid (1:3),heated the solution to just boiling & filtered through ashless filter paper or pulp, washed the beaker and residue with 5times with hot water.

Transferred the filter paper or pulp and its content to a 250 ml conical flask fitted with a bulb condenser and then added 100 ml KOH solution (25%). Mixed it and kept the solution to stand 16 hours at room temperature and then boiled the solution under reflux for 4 hours. Filtered the solution through pulp and washed with hot water then 100 ml of HCl (1:9) and finally with hot water until free from chloride ions. Transferred the residue with pulp in weighed platinum crucible (m_9) and slowly ignited at 975℃ upto the constant weight. Cooled the crucible and weighed (m_{10}).

Expression of results in percentage

$$Insoluble\ residue = \frac{m_{10} - m_9}{m_8} \times 100$$

Where, m_8 = mass of sample taken in g
m_9 = mass of empty crucible in g and
m_{10} = mass of empty platinum crucible + IR in g

3. Determination of silica in insoluble residue[1]

Determination of pure silica

Weighed an accurately about 0.5g finely powdered mass of insoluble residue (m_{11}) and mixed with about 5g sodium carbonate in platinum crucible, kept the crucible with lid in a muffle furnace, heated slowly and finally ignited at 1050 ± 25°C to complete the fusion, cooled the crucible then placed in 100 ml hot water in a 500 ml beaker, added slowly 30ml hydrochloric acid (sp.g.1.16), warmed until the fused mass was completely disintegrated and removed from the crucible and lid, washed the crucible with hot water, crushed any lumps remaining in the solution by glass rod, then 5ml hydrochloric acid (sp. g.1.16) was also added in excess.

Evaporated the solution, obtained from the fusion to completely dryness/ baked, added 20 ml HCl (sp. g. 1.16) shaken, then added 100ml hot water, heated on hot plate for boiling for 2 minutes with continuous stirring with glass rod. Filtered the solution through ashless filter paper No.40 (whatman) or pulp and washed the residue with 5 times of hot water (Reserved the filtrate for further analysis of soluble silica).

Transferred the residue with filter paper or pulp in a weighed platinum crucible (m_{12}), heated slowly until the paper were charred and finally ignited at 1050 ± 25°C, cooled the crucible and weighed the mass of impure silica (m_{13}) (SiO_2 + IR).

Moistened the weighed residue with few drops of water, added few drops of sulphuric acid then added 10 ml hydrofluoric acid. Evaporated slowly to dryness on water bath then on hot plate in a fuming chamber. Kept the crucible with residue in a furnace with slowly heating upto 1050 ± 25°C, cooled the crucible and weighed the mass of residue (m_{14}) till constant weight (If the residue weight more than 5 mg, repeat the treatment of hydrofluoric acid and sulphuric acid to ensure that all the silica is removed).

Expression of results in percentage

Subtracted the weight of this residue from the impure silica to obtain the amount of silica in the sample taken. The pure silica content was calculated in percentage from the formula:

$$Pure\ SiO_2 = \frac{m_{13} - m_{14}}{m_{11}} \times 100$$

Where, m_{11} = mass of insoluble residue taken in g
m_{13} = mass of silica + impurities in g and
m_{14} = mass of residue in g

Determination of soluble silica in the filtrate

To the filtrate about 3g ammonium chloride was added, warmed the solution to about 80°C and then added dilute ammonia (1:3) with stirring until precipitation appears to be completed or solution just alkaline to methyl red. Boiled the solution for 2 minutes then allowed the solution to stand for 5 minutes. Filtered the solution through an ashless filter paper No.41 (whatman), washed the precipitate with 5 times with hot faintly ammonical ammonium chloride solution (just alkaline to methyl red).

Transferred the precipitate and filter paper to the same beaker in which the first precipitation was effected. Dissolved the precipitate in hot HCl (1:3), diluted the solution about 100 ml and re-precipitated the hydroxides by the addition of dilute ammonia solution (1:3). Filtered the solution by filter paper No.41 (whatman) and washed the precipitate 2 times with 2% hot faintly ammonical ammonium chloride solution. Placed the precipitate with filter paper in a weighed platinum crucible (m_{15}), heated slowly until the papers were charred and finally ignited to constant weight at 1050 ± 25°C, cooled and taken the mass of crucible (m_{16}) contained mixed oxides and soluble silica. Treated the residue with few drops of water, about 5 ml hydrofluoric acid and few drops of sulphuric acid. Evaporated cautiously to dryness on water bath and hot plate, finally ignited at 1050 ± 25°C with slow rising of temperature. Cooled the crucible and weighed (m_{17}).

Expression of results in percentage

$$Soluble\ silica = \frac{m_{16} - m_{17}}{m_{11}} \times 100$$

Where, m_{11} = mass of insoluble residue taken in g
m_{16} = mass of mixed oxide and soluble silica in g and
m_{17} = mass of mixed oxides in g

Total Silica in insoluble residue

Expression of results in percentage

The total silica content in insoluble residue is equal to the sum of the pure silica and the soluble silica content, as-

$$\text{Total } SiO_2 \text{ in IR} = \text{Pure } SiO_2 + \text{Soluble } SiO_2$$

4. Calculation of reactive silica

The reactive silica was calculated in percentage as follows-

$$\text{Reactive } SiO_2 = \text{Total } SiO_2 - [SiO_2 \text{ contained in insoluble residue x (IR/100)}]$$

Where, Total SiO_2 = In accordance with 1
SiO_2 contained in IR = In accordance with 3 and
IR = In accordance with 2

RESULTS AND DISCUSSION

Reactive silica is one of the testing parameter as per requirements of IS 3812 (Part-1) 2013 for fly ash. The method of reactive silica given in IS 3812 (Part-1) 2013 Annexure-B is incomplete. The above (proposed) method is based on the classical analysis[1,2] and may be adopted in a chemical laboratory. However, other methods are also available based on the analysis by XRF[3]. The reactive silica was checked in some samples of fly ash and found satisfactory repeatability with expanded uncertainty 0.42% at 28.87% of reactive silica using the coverage factor k= 2 at a level of confidence 95.45%. This method is in-house development of NTH (NWR) Jaipur and we hope this method may be useful for cement industries & thermal power plants also.

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REFERENCES

1. Method of Test for Pozzalonic Materials, Indian Specification, IS-1727-1967 (Reaffirmed 2004).
2. Pulverized Fuel Ash, Indian Specification, IS-3812 (part1) 2013.
3. European Coal Combustion Products Association (ECOBA) May-2008.

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