



A STUDY ON NOVEL SEPARATION OF FREE SILICA FOR CEMENT MANUFACTURING PLANT

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ABSTRACT

India ranks as the second-largest cement producer globally, trailing only China, with an annual output exceeding 298 million tonnes. Cement demand has seen consistent growth, with increases of 8% in 2022 and 12% in 2023. The key oxides required for cement manufacturing are Calcium Oxide (CaO), Silicon Dioxide (SiO₂), Aluminum Oxide (Al₂O₃), and Iron Oxide (Fe₂O₃). However, extracting metamorphic limestone from deeper layers of the earth's crust poses challenges due to higher concentrations of Silicon Dioxide, which has a high melting point of 1710°C. This bottleneck results in increased fossil fuel consumption during combustion and diminishes cement strength. To address this, a secondary classification technology is proposed to remove excess silica before combustion, aiming to enhance cement quality and reduce environmental impact. Additionally, implementing Gravimetric Analysis aids in optimizing raw material usage, minimizing waste, and controlling production costs. This paper aims to address excess silica, convert it into value-added products, and analyse the characteristics of the free silica component.

Keywords: Cement production, Silicon Dioxide, Fossil fuel consumption, Secondary classification technology, Environmental impact.

1. INTRODUCTION

CEMENT

Cement manufacturing involves a series of processes aimed at producing cement, a crucial ingredient in concrete, mortar, and other construction materials. The general view of cement manufacturing typically includes stages like quarrying raw materials (such as limestone, clay, shale, etc.), crushing and grinding these materials into a fine powder, mixing them in precise proportions to create a raw meal, and then heating this mixture in a kiln to around 1450°C to produce clinker. The clinker is then ground with gypsum to produce cement, which is finally packaged and distributed for use in construction projects. This process requires careful control of factors like temperature, composition, and grinding to ensure consistent quality and strength of the final product. Additionally, environmental considerations, such as emissions and waste management, are increasingly important in modern cement manufacturing.

1.1.1 COMPOSITION OF CEMENT

COMPONENT	FORMULA	CONCENTRATION
Lime	CaO	60-67%
Silica	SiO ₂	17-25%
Alumina	Al ₂ O ₃	3-8%
Iron oxide	Fe ₂ O ₃	0.5-6%
Magnesia	MgO	0.1-4%
Sulphur trioxide	SO ₃	2-3.5%
Alkalis	Na ₂ & K ₂ O	0.3-1.2%

1.2 CONCENTRATION OF SILICON DIOXIDE

Petrological studies of the limestone sample from which we collected indicated that the sample is dominantly composed of calcite with lesser amounts of quartz, clay and rarely some opaque minerals (mostly pyrite). These limestone rocks have fine- to medium-grained granular mosaics without any fossils. Calcite is generally fine-grained but patches of medium- to coarse-grained anhedral calcite are also common. The medium- to coarse-grained calcite crystals are generally interlocked and contain inclusions of silicates minerals.

Quartz occurs in the form of subhedral, medium-grained, and detrital material. The calcite of this limestone deposit seems to be authigenic in origin and has been precipitated in-situ. Micro-fractures filled with fine-grained calcite micro-veins which are considered to be diagenetic. Clay and iron pyrite in trace amounts are present as fine-grained disseminated material in many samples. The study that the siliceous limestone sample from the same area and reported the same mineralogical results for this limestone sample.

1.3 VARIOUS CONCENTRATION OF SILICON DIOXIDE IN LIMESTONE

SAMPLE NO.	LOI	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
1	34.60	17.60	0.88	1.55	13.51	0.46
2	34.94	18.44	0.61	0.32	44.23	0.15
3	35.92	14.76	1.59	0.45	45.24	0.64
4	40.07	7.70	0.53	0.40	49.29	1.30
5	30.79	27.18	0.96	0.38	38.90	0.42

2. METHODOLOGY

2.1 GRAVIMETRIC ANALYSIS METHOD (IS: 4032 - 1985)

2.1.1 FINDING OUT SILICON DIOXIDE

Transfer 0.5 g of the sample to an evaporating dish, moisten with 10 ml of distilled room temperature to prevent lumping, add 5 to 10 ml of hydrochloric acid, and digest with the aid of gentle heat and agitation until the sample is completely dissolved. Dissolution may be aided by light pressure with the flattened end of a glass rod. Evaporate the solution to dryness on a steam-bath. Without heating the residue any further treat it with 5 to 10 ml of hydrochloric acid and then with an equal amount of water, or pour at once upon the residue 10 to 20 ml of hydrochloric acid (1:1).

Then cover the dish and digest for 10 minutes on the water-bath or hot-plate. Dilute the solution with an equal volume of hot water, immediately filter through an ash less filter paper (Whatman No. 40 or its equivalent), and wash the separated silica (SiO₂) thoroughly with hot water and reserve the residue.

Sample before fusing



Hot oven**Sample after fusing**

Again evaporate the filtrate to dryness, baking the residue in an oven for one hour at 105 to 110°C. Then treat the residue with 10 to 15 ml of hydrochloric acid (1: 1) and heat the solution on water-bath or hot-plate. Dilute the solution with an equal volume of hot water catch and wash the small amount of silica it contains on another filter paper. Reserve the filtrate and washings for the determination of combined alumina and ferric oxide. Transfer the papers containing the residues to a weighed platinum crucible. Dry and ignite the papers, first at a low heat until the carbon of the filter paper is completely consumed without inflaming and finally at 1100 to 1200°C until the weight remains constant. Treat the ignited residue thus obtained, which will contain small amounts of impurities, with 1 to 2 ml of distilled water, about 10 ml of hydrofluoric acid and 2 drops of sulphuric acid and evaporate cautiously to dryness. Finally heat the small residue at 1050 to 1100°C for a minute or two; cool and weight. The difference between this weight and the weight of ignited sample represents the amounts of silica: Silica percent = $200 (W1 - W2)$. Where, W1 = weight of silica + (insoluble impurities - residue), W2 = weight of impurities.

2.1.2 FINDING OUT FERRIC OXIDE (POTASSIUM PERMANGANATE METHOD)

To one gram of the sample, add 40 ml of cold water and, while the mixture is being stirred vigorously, add 15 ml of hydrochloric acid. If necessary, heat the solution and grind the cement with the flattened end of a glass rod until it is evident that the cement is digested fully. Heat the solution to boiling and treat it with stannous chloride solution added drop by drop while stirring, until the solution is decolorized. Add a few drops of stannous chloride solution in excess and cool the solution to room temperature.

Rinse the inside of the vessel with water, and add 15 ml of a saturated solution of mercuric chloride in one lot. Stir, add 25 ml of manganese sulphate solution and titrate with standard solution of potassium permanganate until the permanent pink colour is obtained. Calculate iron as ferric oxide.

Calculation — Calculate the percentage of Fe₂O₃ as below: $1 \text{ ml of } 0.01 \text{ M EDTA } 0.7985 \text{ mg of Fe}_2\text{O}_3$ Iron oxide (Fe₂O₃) percent = $(0.7985 \times V) / (W)$. Where, V = Volume of EDTA used in ml, W = Weight of the sample in g.

2.1.3 FINDING OUT ALUMINIUM OXIDE

Subtract the calculated weight of ferric oxide and small amount of silica from the total weight of oxides found under silica process. The remainder is the weight of alumina and small amounts of other oxides which are to be reported as alumina.

Calculation — Calculate the percentage of Al₂O₃ as below: $V = V_1 - V_2 - (V_3 \times E)$. Where, V = Volume of EDTA for alumina in ml, V₁ = Total volume of EDTA used in the titration in ml, V₂ = Volume of EDTA used for iron in ml, V₃ = Total volume of bismuth nitrate solution used in the titration in ml. E = Equivalence of 1 ml of bismuth nitrate solution 1 ml of 0.01 M EDTA 0.5098 mg of Al₂O₃, Aluminium oxide (Al₂O₃) percent = $(0.5098 \times V) / (W)$. Where, W = Weight of the sample in g. $E = V_4 / 100$ V₄ = Volume of EDTA solution in ml.

2.1.4 FINDING OUT CALCIUM OXIDE

Acidify the combined filtrates set aside under ferric oxide and alumina with hydrochloric acid and evaporate them to a volume of about 100 ml. Add 40 ml of saturated bromine water to the hot solution and immediately add ammonium hydroxide until the solution is distinctly alkaline. Boil the solution for 5 minutes or more, making certain that the solution is at all times distinctly alkaline. Allow the precipitate to settle; filter and wash with hot water. Wash the beaker and filter once with nitric acid that has been previously boiled to expel nitrous acid, and finally with hot water. Discard any precipitate (of manganese dioxide) that may be left on the funnel. Acidify the filtrate with hydrochloric acid and boil until all the bromine is expelled. Add 5 ml of hydrochloric acid, dilute to 200 ml, add a few drops of methyl red indicator and 30 ml of warm ammonium oxalate solution.

Heat the solution to 70 to 80°C and add the ammonium hydroxide (1: 1) dropwise, while stirring, until the colour changes from red to yellow. Allow the calcium oxalate precipitate to stand without further heating for one hour, with occasional stirring during the first 30 minutes; filter through Whatman filter paper No. 42 or equivalent, and wash moderately with cold 0.1 percent ammonium oxalate solution. Set aside the filtrate and washings for estimating magnesia.

Calculation -Calculate the percentage of CaO as below: 1 ml of 0.01 M EDTA 0.5608 mg of CaO. Calcium Oxide (CaO) percent = $(0.05608 \times 25 \times V) / (W)$. Where, V = Volume of EDTA used in ml, W = Weight of the sample in g.

2.2 ANALYSED RESULT OF PRIMARY SEPARATION PRODUCT

Sample 1

MICRO N SIZE	RESIDUE RETAINED %	SiO2	Al2O3	Fe2O3	CaO	MgO
(-)212 (+)150	6.46	30.16	4.59	4.18	30.02	2.53
(-)150 (+)90	13.14	21.12	4.12	4.25	35.95	2.22
(-)45	59.47	7.39	2.83	3.26	48.50	1.94

Sample 2

MICRO N SIZE	RESIDUE RETAINED %	SiO2	Al2O3	Fe2O3	CaO	MgO
(-)212 (+)150	7.11	30.66	4.57	4.46	29.93	2.50
(-)150 (+)90	12.39	20.80	4.16	4.40	36.06	2.22
(-)45	60.08	7.13	2.94	3.37	48.44	1.43

Sample 3

MICRO N SIZE	RESIDUE RETAINED %	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
(-)212 (+)150	2.84	47.14	5.30	4.30	20.60	3.11
(-)150 (+)90	10.65	30.95	4.81	4.25	29.35	2.55
(-)45	66.84	8.09	2.85	3.22	47.87	1.48

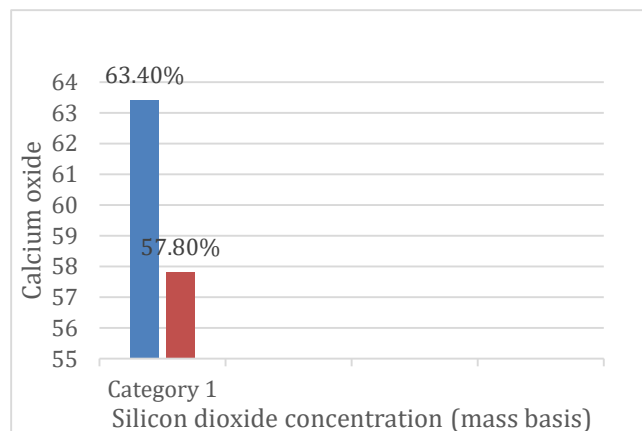
3. FORMULA USE FOR ENERGY SAVINGS

The heat required to form clinker from dry raw mix is obtained by ZKG formula (German formula):
 $Q_t = 4.11 (\text{Al}_2\text{O}_3) + 6.47 (\text{MgO}) + 7.64 (\text{CaO}) - 5.11 (\text{SiO}_2) - 0.60 (\text{Fe}_2\text{O}_3)$
 If no clinker analysis: assume $Q_t = 420$ kcal/kg cl.

4. AIM OF SECONDARY SEPARATION SYSTEM

Secondary separation system can be adopted in order to increase the fines of raw meal after the primary separation product which can reduce the concentration of silicon dioxide composition in mass basis. As the silicon dioxide oxide concentration reduces, the secondary separation product will reduce the demand of calcium oxide in mass basis. In final the overall requirements of heat energy will reduce (reduces the fossil fuel consumption).

Graph: Decrease in SiO₂ and increase in CaO concentration.

**5. CLINKER ANALYSIS OF SECONDARY SEPARATION PRODUCT**

Secondary separation product have been put into the clinkering process and we got the following result,

COMPONENTS	PERCENTAGE (mass basis)
SiO ₂	21.92
Al ₂ O ₃	5.50
Fe ₂ O ₃	4.94
CaO	63.40
MgO	1.70

6. CALCULATION ADOPTED

Therefore we considered SiO₂ is 90% purity, another 10% is free silica (quartz). Therefore corrected silica from clinker analysis table is SiO₂ = (21.92) * (0.90) = 19.73%. The table above shows that rawmeal which has converted into clinker.

Actual LSF by formula: Actual LSF = (CaO) / 2.8 (SiO₂) + 1.18 (Al₂O₃) + 0.65 (Fe₂O₃)

Actual LSF = (62.40) / (2.8)*(21.92) + (1.18)*(5.50) + (0.65)*(4.94) = 89.20%

Calculation for Corrected LSF: Corrected LSF = (63.40) / (2.8)*(19.73) + (1.18)*(5.50) + (0.65)*(4.94) = 97.62%

Required LSF is 89.20%, for 89.20% of LSF, the required CaO is,

$89.20 = (\text{CaO}) / (2.8 * 19.73) + (1.18 * 5.50) + (0.65 * 4.94)$

CaO = 57.80%

Hence, from the above calculations by providing the secondary separator, the required calcium oxide concentration can be reduced to 57.80% from 63.40%, which represents that the reduction in silica will be the low heat energy consuming oxide during combustion process.

7. ENERGY SAVINGS

7.1 ENERGY SAVINGS ACHIEVED BY ZKG

FORMULA (GERMAN FORMULA)

Before installing secondary separator, taking the values from clinker analysis table,

$Q_{th} = (4.116 * 5.50) + (6.48 * 1.70) + (7.646 * 63.40) - (5.116 * 21.92) - (0.59 * 4.94)$ $Q_{th} = 403.35$ Kcal / Kg Clinker.

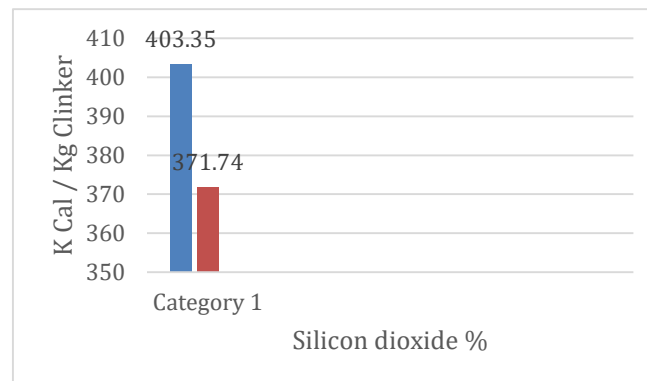
After installing the secondary separator, taking the values from clinker analysis table,

$Q_{th} = (4.116 * 5.50) + (6.48 * 1.70) + (7.646 * 57.80) - (5.116 * 19.73) - (0.59 * 4.94)$ $Q_{th} = 371.74$ Kcal / Kg Clinker.

Reduction in heat (Q_{th}) = 403.35 – 371.74 Kcal / Kg clinker. $Q_{th} = 31.61$ Kcal / Kg Clinker.

Therefore, we reduce the energy nearly 31.61 Kcal / Kg heat after installing the secondary classification technology. Converting the Specific heat energy in terms of fossil fuel savings.

Graph: Energy savings



8. RESULT

From the study experiment of secondary separation system we get the following result as energy savings. We can reduce the overall heat energy requirement for cement manufacturing process by using secondary separation system.

Before installing secondary separator: 403.35 Kcal / kg clinker. After installing secondary separator: 371.74 Kcal / Kg Clinker. Energy savings is up to 31.61 Kcal / Kg Clinker. Fossil fuel cost (Bituminous coal): 11000 – 12000 Rs / Ton.

Bituminous coal calorific value: 6000 Kcal / Kg coal. Considering 31.71 Kcal / Kg Clinker these will be 21 tonnes of coal can be saved and around 2, 30,000 Rs can be saved in terms of cost.

9. CONCLUSION

In conclusion, reducing silica content from limestone raw meal is crucial for optimizing industrial processes like cement production. By minimizing silica levels, industries can enhance the formation of essential cement components, improve clinker quality, reduce refractory wear, lower energy consumption, and mitigate emissions. This optimization not only ensures consistent product quality but also enhances operational efficiency, reduces costs, and promotes environmental sustainability. Overall, reducing silica content in limestone raw meal is a vital step towards achieving efficient and sustainable industrial processes.

By installing the secondary classifier, we can reduce the fossil fuel consumption and secondly, the separated SiO₂ can be considered as value added product by mixing with M-sand and P-sand for construction purposes.

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