



Raw Mix Design for Ordinary Portland Cement

Amala Fathima Rani¹, S. Lourdu Mary¹, M. Anu², P. Lakshmi Prabha², G. Kalpana²

¹Department of Chemistry, Holy Cross College of Arts and Science, Trichy.

²Department of Chemistry, Shrimati Indira Gandhi College, Trichy.

*E-mail: anu9487@gmail.com

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Abstract

Raw meal proportionating is the critical step in the manufacture of Cement. An Extensive Chemical analysis of the raw materials is required to achieve the desired Cement through the implementation of the raw mix designing techniques. Chemical analysis proves to be the critical step in the raw meal proportionating. So an adequate knowledge about the analytical techniques involved in the quantitative estimation of various constituents in a raw material becomes inevitable. This work may help a cement manufacturing chemist to keep himself abreast of the analytical techniques and their background in the quantitative estimation of various constituents in the raw materials used for Cement Raw meal proportion.

Keywords: Ethylene Diamine Tetra Acetic Acid, Erio Chrome Black-T, CaO, MgO

Introduction

Cement is the major industrial product next to steel and it is known and used by all people for building construction. Cement is a dirty greenish fine powder, which is a mixture of various silicate, dicalcium silicate, tricalcium aluminate and tetra calcium alumina ferrite^[1]. It was just 150 years ago, that CEMENT as we know it today was developed or invented. Joseph Aspdin of England first patented the manufacture of an improved type of cementitious material for building construction in 1824 and named it PORTLAND CEMENT because the hardened stone from his cement resembled Portland stone found in England^[2]. The government of India permits the use of coal with an ash content of 20%-25% for the manufacture of Cement. Most types of Portland cement Clinker when ground alone and then mixed with water will set immediately. The initial set should not occur in less than 30 minutes. To retard the setting gypsum is universally used. Thus gypsum also has to be considered as a raw material^[3]. Pioneer studies on the system $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ were made in the first quarter of this century at the geophysical laboratory of Carnegie Institutions in Washington^[4]. Eight different raw materials and required raw mix with specified percentages of Al_2O_3 , SiO_2 , Fe_2O_3 , CaO, MgO and alkalis were also studied^[5].

Materials and Methods

Coning and quartering method

Crushed Material shall be scooped into a cone shaped pile. It shall be flattened by pressing the top of the cone. Then it is cut into quarters. The sample is reduced to half by rejecting any two diagonally opposite quarters.

Gross sample

Quantity of Material consisting one or several increments or unit samples.

Gross samples → size determination → crushed to 10mm → mixing and reduction.

Experimental Techniques

Drying the Sample

About 10g of the sample is dried in an air oven at a temperature of 110° For one hour and then cooled in a desiccator for about 15-20 minutes. The cooled sample is used for the chemical analysis.

Decomposition of the Sample

The first step in the wet chemical analysis of a material involves decomposition of the sample and thereafter dissolution of the decomposed mass. After this basic step, the constituents are brought into solution and are determined following appropriate analytical methods.

Decomposition with HCl

Certain ceramic raw materials, such as carbonates (calcite, dolomite, magnesite) sulphates (gypsum) or hydrous oxides of aluminium (bauxite) and iron (haematite) are soluble in mineral acids. They can be decomposed and brought into the solution by treatment with hydrochloric acid. More often silica bearing minerals such as quartz, clay etc. are present in varying amounts as impurities. They are not decomposed by hydrochloric acid and remain as an insoluble residue. For complete chemical analysis, the insoluble residue is filtered out, fused with an alkaline flux and brought into the solution. When silica is determined from a separate sample, the residue may be decomposed by hydrofluorisation and constituents other than silica are brought into the solution^[6]

Hydrofluorisation

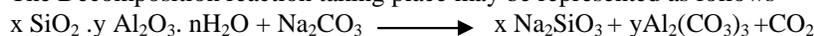
Many of the minerals containing large amount of aluminium such as the silicate group of minerals, calcined bauxite and corundum and also zirconia bearing materials are not completely decomposed after hydrofluorisation. In such cases, the other methods of decomposition involving fusion have to be employed.

Fusion with acid fluxes

The pyrosulphate attacks the oxides and converts them to sulphates with the expulsion of SO₃. The chemical changes taking place during the decomposition of the samples of pure alumina may be represented as follows

**Fusion with Alkaline fluxes**

The decomposition reaction taking place may be represented as follows

**Chemical Analysis of Limestone-1****Determination of Loss on Ignition**

Loss on ignition thus indicates the nature and amount of such constituents in a sample. The ignition temperature at 1000. After 30 minutes the crucible was taken out and cooled in a desiccator, to room temperature and weighed.

Determine of SiO₂ Gravimetric method

Weighed accurately 0.5 g of the sample and transferred it into a 250ml clean beaker. Added 20 ml of 1:1 hydrochloric acid and washed the sides of the beaker with little water and converted the beaker with a little water and converted the beaker with a watch glass. The beaker was kept on a hot plate. The beaker was cooled and added 20 ml of 1:1 hydrochloric acid and water and digested for a few minutes, on a hot plate. After digestion, the contents of the beaker was filtered through a Whatmann No 4 filter paper into a standard flask of capacity 250 ml. Cleaned the beaker with hot water and residue as well, till it was free from chloride. Transferred the crucible and incinerated in a low temperature. After charring of the paper was over transferred the crucible to a muffle furnace. It was taken out and cooled to room temperature and weighed. The silica was then moisturised and added about 15ml of hydrofluoric acid and evaporated the contents of the crucible on a hot plate. After complete evaporation, the crucible was kept at 1000° For one minute and cooled to room temperature and weighed. The percentage of SiO₂ present in the sample was calculated from the formula.

Determination of Fe₂O₃, Al₂O₃, CaO and MgO by complexometric method

Ethylene diamine tetra acetic acid [EDTA] is one of the most important member of a series of amino poly carboxylic acids, possessing the characteristic group. This is also called complexone-11 and abbreviated as H₄Y. EDTA is a tetra basic acid and the is being very poor, the disodium salt Na₂H₂Y.2H₂O termed as complexone-111 is used as analytical reagent. The disodium salt is obtainable in a high state of purity and chemical stability to be used as a primary standard.

Determination of Fe₂O₃

25 ml of the aliquot was taken in a 250 ml beaker. A pinch of Sulphosalicylic acid was added. The solution is neutralised with 1:1 ammonium hydroxide. Then the solution was brought to the pH paper. The solution was then titrated against 0.02M EDTA. The end point was the colour changes from wine red colour to colourless or yellow colour.

Determination of Al₂O₃

25 ml of the aliquot was taken in a 500 ml conical flask. Added a measure volume of 0.02M EDTA and neutralised the solution with 1:1 ammonium hydroxide in the presence of Methyl orange. Added 10ml of 5.3 buffer and kept it for boiling. Cooled the solution for 5 minutes. Added 5ml buffer and 10 drops of xylenol orange indicator. Titrated against 0.0m Zinc acetate, end point was the appearance of red colour. To that solution added 10 ml of 10% ammonium fluoride and boiled for another 10 minutes. Cooled to room temperature and added 10 ml of 5.3 buffer. Titrated against the standard zinc acetate till a red colour was obtained.

Determination of CaO and MgO

25ml of the aliquot was taken in a 250 ml beaker. 2ml of nitric acid was added and boiled for a few minutes. Added a pinch of ammonium chloride and then added ammonium hydroxide drop wise till a faint ammonia smell emerges out of the solution. Boiled once again for a few minutes and filtered through a whatmann 40 filter paper. Preserved the filtrate for CaO determination. The filtrate after being cooled to the room temperature was brought to the pH

between 12-13 and titrated against 0.02M EDTA in the presence of calcein fluorescence Indicator. End point was the change from green fluorescence to pink.

Determination of MgO

The same procedure was carried out, up to the collection of the filtrate was taken in a conical flask. 20 ml of buffer 10 was added and warmed for sometime. It was then titrated against 0.02 M EDTA with Erichrome Black-T as indicator. The end point was the colour change from wine red to blue.

Determination of Na₂O by flame photometry

About 0.02542g of dry sodium chloride was dissolved and diluted to 500ml in a calibrated flask. 1, 2, 3, 4 and 5 ppm solutions were prepared by proper dilution

Preparation of the sample solution

About 0.1g of dried sample was weighed in a platinum crucible. The sample was moistened with water and 1ml of perchlorate and 5ml of hydrofluoric acid were added to it. The crucible was placed on a heated sand bath until the strong fumes of perchloric acid disappeared. The crucible was cooled and 5ml of hydrofluoric acid was added and evaporated as before. To the dry mass in the basin added 5 drops of HCl (1:1) and water. The crucible was placed on a steam bath. The contents were quantitatively transferred to a 250ml calibrated flask after 10 minutes.

Determination of Na₂O

A few ml of the sample solution was placed in the cup of a flame photometer. The emission at 589 nm was measured. The same was repeated for all the standard solutions. A calibration graph was drawn. The sodium content of the sample was calculated by referring to the graph.

Determination of K₂O

Preparation of standard solution of potassium (200 ppm)

About 0.1907g of dry potassium chloride was dissolved in water and diluted to 500ml in a calibrated flask. 1-15 ppm standard solutions were prepared by proper dilutions. A few ml of the sample solution was placed in the small cup of the flame photometer and the emission at 767nm was determined. The same was repeated for all standard solutions. A calibration graph was drawn. The potassium content of the sample was calculated by referring to the calibration graph.

Determination of TiO₂

Spectrophotometric method

Titanium when present in minor or trace amounts in silicates and other ceramic materials are best determined by spectrophotometric methods. For spectrophotometric determination of a metal ion, it is first allowed to react with an appropriate chromogenic reagent to form a coloured complex and then the concentration of the metal ion is determined by measuring the intensity of the colour. For determination of titanium, the widely accepted reagents are hydrogen peroxide, which form a yellow titanate complex and chromotropic acid.

Preparation of standard titania solution

About 0.5g of calcined titania was dissolved in concentrated hydrofluoric acid in a platinum dish. Then 25ml of concentrated sulphuric acid was added and heated to strong fumes to remove fluoride. It was cooled and diluted with water and made up to 500ml in volumetric flask. Transferred two 25ml of aliquot to two 100ml volumetric flasks A and B. 10ml of dilute phosphoric acid was added to each flask. 10ml of hydrogen peroxide was added to flask A and both the flasks were made up to the volume. The absorbance of solution A against B was measured at 410nm.

Calibration curve

About 0, 1, 2, 3, 4 and 6ml of standard titania solutions were taken and the absorbance was measured against the solution B. A graph was drawn by taking absorbance along the y axis and concentration along the x axis similarly chemical analysis of limestone-II and bauxite were carried out and the results are tabulated in table

Chemical analysis of Limestone I, Limestone II and Bauxite

Name of the constituents	Limestone I (%)	Limestone II (%)	Bauxite (%)
L.O.I	41.39	34.4	29.45
SiO ₂	3.42	17.1	4.65
Al ₂ O ₃	1.05	4.0	52.8
Fe ₂ O ₃	1.79	2.0	6.90
CaO	51.3	40.5	1.05
MgO	0.3	1.0	0.45
Na ₂ O	0.37	0.75	---
K ₂ O	0.12	0.4	---
TiO ₂	---	---	4.64

Raw mix design

Raw mix proportioning is one of the main responsibilities of a chemist in producing the best quality cement. Quality cement can be produced by selecting appropriate available source of raw materials and proportioning the same to feed as raw meal, burning them at correct thermal condition, grinding the same resultant clinker with required gypsum to specific fineness. So importance of cement quality is purely based on the responsibility of chemist in doing the best raw mix proportion. To perform raw mix design a chemist requires complete knowledge about the chemical analysis of cement raw materials through which one can achieve the good quality cement.

Chemical Analysis of Limestone I, Limestone II, Bauxite

Components	Limestone I	Limestone II	Bauxite
L.O.I	41.396	34.40	29.45
SiO ₂	3.42	17.10	4.89
Al ₂ O ₃	1.05	4.00	52.80
Fe ₂ O ₃	1.79	2.00	6.90
CaO	51.30	40.50	1.05
MgO	0.30	1.00	0.45
Na ₂ O	0.37	0.75	-
K ₂ O	0.12	0.40	-
TiO ₂	--	--	4.4

In order to find the raw mix design and ultimate C₃S, C₂S, C₃A and C₄AF values using 3 component system. Calculation of Raw mix with Lime saturation factor and silica ratio

Lime saturation factor (KSK) = 0.90

Silica modulus (Sm) = 2.9

Chemical Analysis of Limestone I, Limestone II, Bauxite

Constituents	Cement Clinker Composition
L.O.I	--
SiO ₂	22.57
Al ₂ O ₃	5.91
Fe ₂ O ₃	3.11
CaO	65.63
MgO	1.34
Na ₂ O	1.06
K ₂ O	0.53
TiO ₂	0.05
LSF	0.91
Sm	2.51
Am	1.90
C ₃ S	51.42
C ₂ S	26.00
C ₃ A	10.41
C ₄ AF	9.46

Influence of the chemical composition

In addition to the titration value the production personal considers mostly the ratios of the compounds as important for quality control because these ratios have proved of practical assistance in estimating the suitability of a particular raw mix composition.

Influence of the Silica Ratio

The Silica ratio indicate, if the raw meal has a high or low silica content

Silica content	Silica Ratio
High	2.5-3.5
Mean	2.0-2.5
Low	1.7-2.0

Higher Silica Ratio

When the iron oxide and aluminium oxide content of the raw meal are lower:

- Smaller amount of C_3O
- Increased amount of C_2S
- Lower early strength, but progression with age and higher ultimate strength.
- Setting time easier to control

Lower Silica Ratio

When the iron oxide and aluminium content of the raw meal are higher

- Reduction of Clinkering temperature
- Clinkering is easier
- Tends to cause ring formation, in the kiln specially when lime saturation is low
- higher amount of C_3S
- Higher early strength, but little progression with increasing age.

Influence of the Aluminium Ratio

The Alumina ratio indicates if the raw meal has high or low aluminium content.

Aluminium Content	Aluminium Ratio
High	2.5-3.0
Mean	1.5-2.0
Low	1.0-1.5

Higher Alumina Ratio

When aluminium content increase with or no change or with reduction in iron oxide content

- Hastens setting of cement, a point is reached at which it becomes possible to control
- Higher C_3S content
- Higher heat evolution during setting
- Lower Resistance to sea water and chemical attack

Lower Alumina Ratio

When iron oxide content increase

- clinkering temperature is reduced
- Higher liquid phase
- clinkering reactions are therefore accumulated
- improved resistance to sea water
- Lower heat evolution by hydration

Influence of Lime Saturation

The lime saturation is the relationship between the real and the highest theoretically possible lime content[CaO].Lime that may be combined with the hydraulic factors are $SiO_2, Al_2O_3,$ and Fe_2O_3 .The lime saturation is based on the maximum amount of lime which can be combined under optimum manufacturing conditions.

- without free lime in the clinker
- when raw materials are sufficiently fine and mixed
- when burning is adequate to allow complete combination in the kiln^[3]

Lime Content	Lime Saturation
High	102
Mean	97
Low	90

Higher Lime Saturation

- High C_3S content
- Higher early strength but little progression with increasing age

Lower Lime Saturation

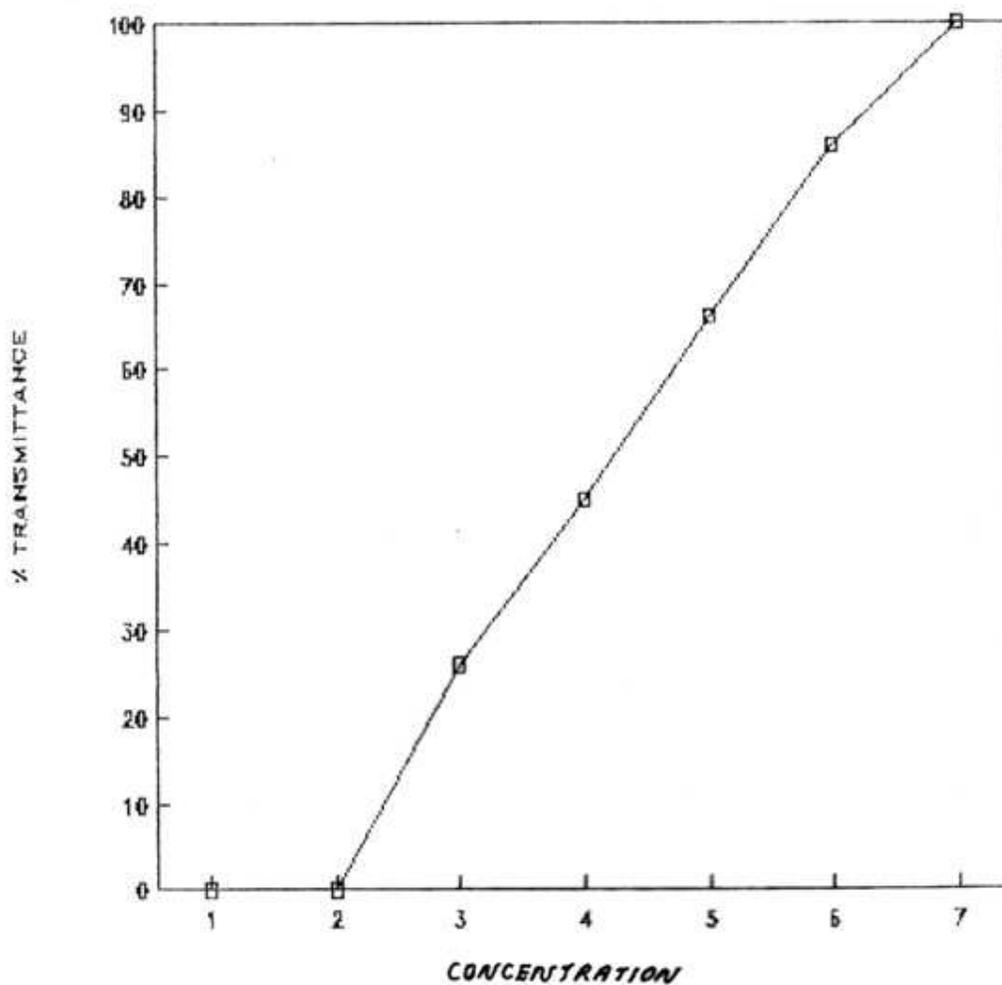
- Lower C_3S content
- Higher C_2S content

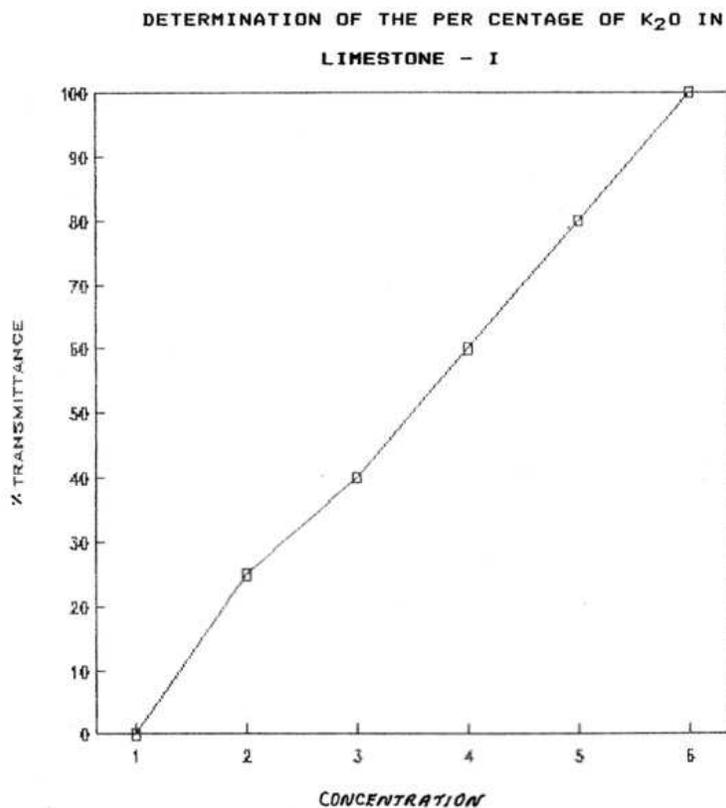
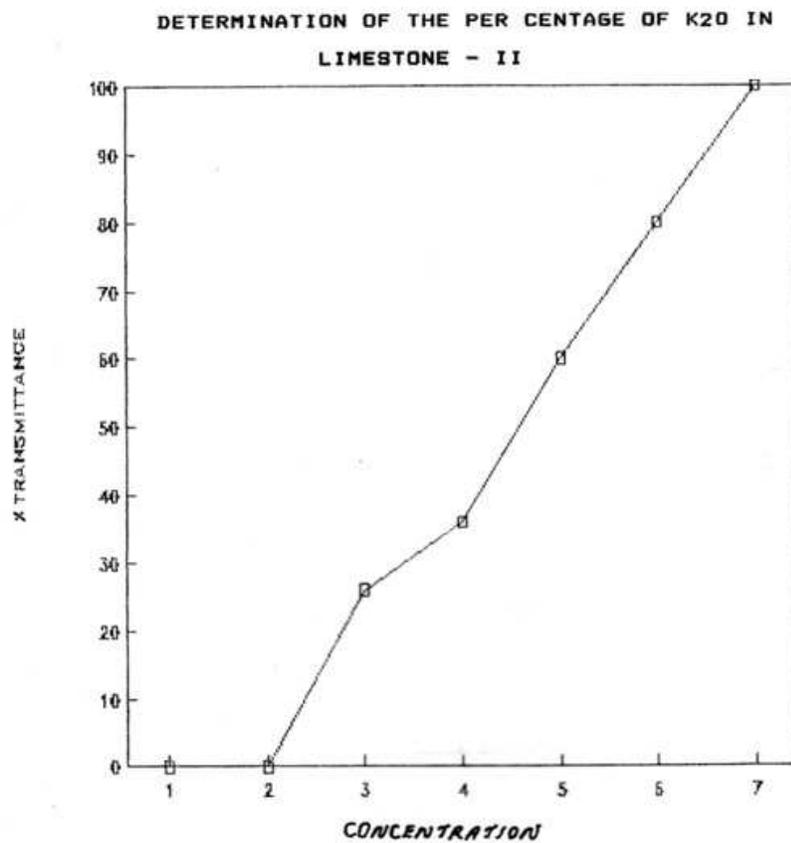
Results and Discussion

The results obtained from the raw-mix design are as follows: They are found to fall within the range of Indian standard specification. So the raw materials chosen are fit for the production of aa good quality Portland cement. 18.24% of Limestone I, 81.12% of Limestone II and 0.64% of bauxite can be taken to produce ordinary Portland cement.

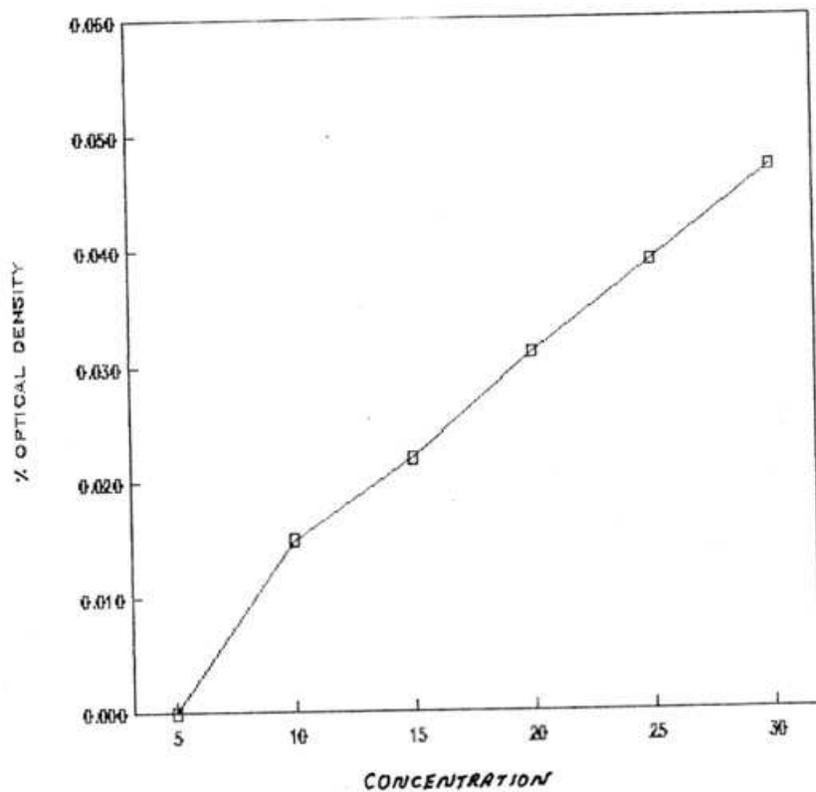
Target As Per IS:8112	Result of the Raw Mix Design
Lime saturation factor=0.66-1.02	Lime saturation factor=0.86
Aluminium/Iron Oxide ratio=0.66(min)	Aluminium/Iron Oxide ratio=1.90(min)
MgO=0.6	MgO=0.88

DETERMINATION OF THE PER CENTAGE OF Na₂O IN LIMESTONE - II

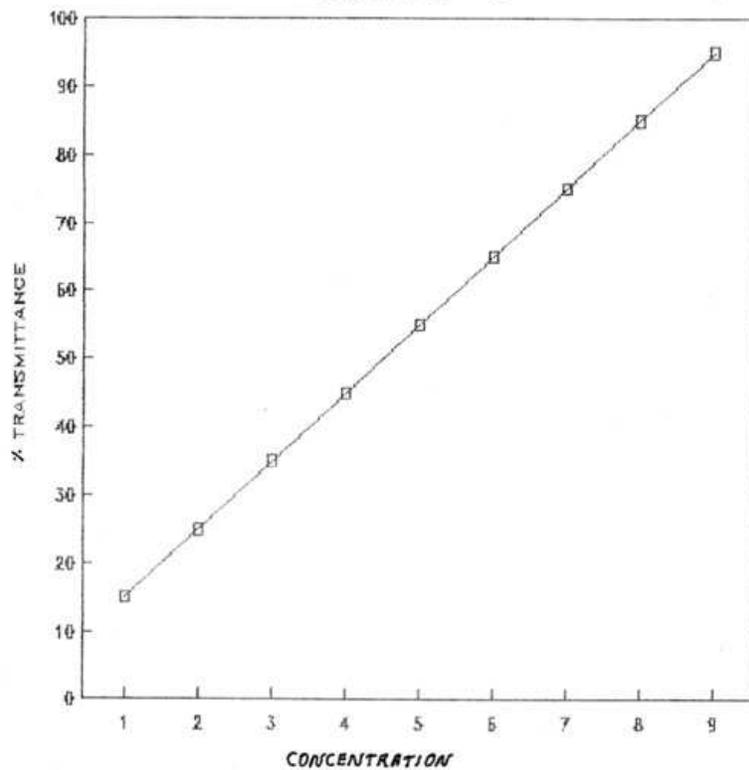




**DETERMINATION OF THE PER CENTAGE OF TiO₂ IN
BAUXITE**



**DETERMINATION OF THE PER CENTAGE OF Na₂O IN
LIMESTONE - I**



Conclusion

Raw mix design for ordinary Portland cement [43 Grade] shows that the chemical analysis of raw materials plays major role in proposing the raw mix design. The raw mix design was made for three component system using lime saturation factor and silica modulus by using kind's formula. The targeted values of lime saturation factor and silica modulus were 0.91 and 2.70 respectively. After carrying out the raw mix design using the raw materials it has been found that 18.24% limestone I, 81.12% limestone II and 00.64% bauxite were required to achieve the lime saturation factor of 0.91 and silica modulus as 2.51. The results obtained fall within the range given by Indian standard specification, which shows that the raw materials, when taken in exact amounts proposed by the raw-mix design can be used for making the best quality Portland cement [IS:OPC,8112]. Thus raw mix design is the heart of best manufacture of cement.

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