Annex- A

Take the filtrate set aside in *Cl* 4.7.1 (remaining after CaO precipitation) and make up the volume in a 250 ml volumetric flask. Take 50 ml or suitable aliquot of the solution in a conical flask and add 10 ml of pH 10 buffer solution (*Cl* 4.1.13) till solution pH is 10 ± 0.1 followed by addition of 5 ml of Triethanolamine (1:1 by volume, Cl 4.1.2.8).
Add 3-4 drops of Eriochrome Black T indicator and titrate with 0.01M EDTA solution till colour changes to pure blue end point free from violet tinge.

Calculations —
Calculate the percentage of MgO as given below:

1 ml of 0.01 M EDTA = 0.4032 mg of MgO

$$\text{Magnesium oxide (MgO) percent} = \frac{0.04032 \times 5^* \times V}{W}$$

where,
V = Volume of EDTA used in this titration in ml and W = Weight of the sample in g.

*Note: Considering 50 ml of aliquot pipetted from 250 ml test solution.

भारतीय निर्देशक द्रव्य

BHARATIYA NIRDESHAK DRAVYA

(INDIAN REFERENCE MATERIAL)

Certificate

BND® 5052A

PORTLAND POZZOLANA CEMENT STANDARD (CHEMICAL PARAMETERS)

Certificate Number: BND® 5052A/312

This Bharatiya Nirdeshak Dravya, BND®5052A, an Indian Certified Reference Material (CRM), produced by National Council for Cement and Building Materials (NCB), India and it is intended to use as a primary standard for calibration of instruments and validation of method for the characterization of the measurand for the analysis of Portland Pozzolana Cement (PPC). One set of BND®5052A consists of 4 sealed vials, each containing approximately 5g of powdered PPC. The analysis of LOI, MgO, SO_3, IR and Cl have been determined as per IS 4032:1985. Estimation of alkalies have been done as per NCB standard procedure, MS-13-2010 (validated method).

Certified Value: The parameters have been analysed as w/w of the total material and reported in percent. The certified value is determined by National Council for Cement and Building Materials and further verified by CSIR-National Physical Laboratory, New Delhi, National Metrology Institute (NMI) of India. The associated measurement uncertainty was calculated at 95% confidence level with coverage factor k=2, considering major sources of uncertainty including measurement replication, instrument background, mass taken, possible heterogeneity and stability factors according to ISO GUM Guide [1] and ISO Guide 35 [2] as given in Table 1.

Table1: Certified values and associated measurement uncertainties of chemical parameters of PPC

CONSTITUENT	CERTIFIED VALUE (PERCENT BY WEIGHT)	EXPANDED UNCERTAINTY (Coverage Factor k=2)
LOI	1.25	±0.02
MgO	2.27	±0.05
SO_3	1.91	±0.02
IR	24.5	±0.38
Na_2O	0.49	±0.04
K_2O	0.77	±0.03
Cl	0.012	±0.002

Development of BND® 5052A has been carried out at NCB, as per ISO 17034:2016 [3] and testing is performed with compliance as per ISO/IEC 17025:2017 [4]. The certified values of the parameter given in the certificate are the best estimate of true value within the stated uncertainties. The certification of the BND® 5052A is also complying the requirements of ISO Guide 31 [5].

Nature of Material: Non-hazardous

Traceability: The BND®5052A is the metrological traceable to SI units through Indian national measurement standards at CSIR-National Physical Laboratory. All measurements have been carried out to establish traceability through an unbroken chain of comparisons, having stated uncertainty.

Expiration of Certification: The certification of BND®5052A is valid, within the measurement uncertainty specified, until **03 January 2025**, provided the BND is handled and stored in accordance with instructions given in this certificate. This certification is nullified if the BND® is damaged, contaminated or otherwise modified.

Maintenance of Certification: NCB will monitor the certified values of BND®5052A over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of certification, NCB will notify the purchaser.

Instructions for Storage and Use and Precautions for Handling:

1. BND® 5052A CRM should be used in controlled conditions, using calibrated equipment, by trained personnel.
2. The CRM is to be dried at 105±5°C for two hours before use.
3. After drying, the material should be protected from atmospheric moisture and used immediately. Leftover portion in a vial, if any, should not be used at a later date.
4. The material should be stored under non-humid conditions to avoid any ingress of moisture/CO_2.
5. Record of usage of CRM and the results must be maintained.

References:

1. JCGM 100.2008-Evaluation of measurement data- Guide to the expression of uncertainty in measurement.
2. ISO Guide 35-Reference Materials - General and statistical principles for certifications;.
3. ISO 17034:2016 - General Requirements for the competence of Reference Material Producers.
4. ISO/IEC 17025:2017- General Requirements for the competence of testing and calibration laboratories.
5. ISO Guide 31 - Reference Materials - Contents of certificate, labels and accompanying documentation.

Date of Certification: 04/01/2020

Document Version: BND/NPL/NCB/2020/2.0

Certificate issued by

Accredited as per ISO 17034:2016 vide Certificate No. RC-1016

Dr R P Pant
Head, BND Division
CSIR-National Physical Laboratory
Dr K S Krishnan Marg
New Delhi-110012

P N Ojha
Head of Centre-CQC
National Council for Cement and Building Materials
Ballabgarh-121004, Haryana

- In case of any query regarding this BND® please contact Dr. R. P. Pant, Head (BND Division), CSIR-NPL (NMI of India), New Delhi-110012.
- This certificate shall not be reproduced without written approval from CSIR-NPL, New Delhi.
- Responsibility for issue and release of this certificate lie with NCB.

For Further Information, Please Contact: National Council for Cement and Building Materials, 34 Km. Stone, Delhi-Mathura Road (NH-2), Ballabgarh, Haryana – 121004, India; phone +91-129-4192239/303, +91-129-2242051, +91-129-4192222; Fax +91-129-2242100, +91-129-2246175 Email: ncb.cqc@gmail.com, cqcb@ncbindia.com, nccbm@ncbindia.com, website: www.ncbindia.com

भारतीय निर्देशक द्रव्य

INDIAN REFERENCE MATERIAL

(BHARATIYA NIRDESHAK DRAVYA, BND)

BND Certificate

BND® 5053

PORTLAND SLAG CEMENT STANDARD

(CHEMICAL PARAMETERS)

Certificate Number: BND® 5053/1.0/19

This Bharatiya Nirdeshak Dravya, BND® 5053, is an Indian Certified Reference Material of Portland Slag Cement Standard produced by National Council for Cement and Building Materials (NCB), India. It is intended to be used as a primary standard for calibration of instruments and validation of method for characterization of the measurand for analysis of Portland Slag Cement. One set of BND® 5053 consists of 4 sealed vials, each containing approximately 5g of powdered Portland Slag Cement. The estimation of Loss on Ignition (LOI), SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO, SO_3, Insoluble Residue (IR), Cl and Sulphide Sulphur (S) has been carried out as per IS 4032: 1985. The estimation of Mn_2O_3, TiO_2, P_2O_5 has been carried out as per IS 12423:1988. The analysis of Alkalis has been carried out as per NCB standard procedure, MS-13-2010 [1]. The parameters have been analysed as w/w of the total material and reported in percent. The certified value is assigned by National Council for Cement and Building Materials and further ascertained by CSIR-National Physical Laboratory, New Delhi, National Measurement Institute (NMI) of India. The certified value of Portland Slag Cement along with the associated uncertainty was calculated at 95% confidence level with coverage factor k=2, considering major sources of uncertainty including measurement replication, instrument background, mass taken, possible heterogeneity and stability factors according to ISO GUM Guide 100:2008 [2] and ISO Guide 35:2017 [3] as given in Table 1.

Table1: Certified value

CONSTITUENT (PERCENT BY WEIGHT)	CERTIFIED VALUE	EXPANDED UNCERTAINTY k=2
LOI	3.13	±0.12
SiO_2	25.12	±0.14
Fe_2O_3	2.48	±0.09
Al_2O_3	9.42	±0.12
CaO	51.40	±0.14
MgO	2.73	±0.21
SO_3	3.12	±0.07
IR	0.19	±0.09
Cl	0.013	±0.007
S	0.13	±0.03
Na_2O	0.38	±0.02
K_2O	0.49	±0.05
TiO_2	0.75	±0.05
Mn_2O_3	0.20	±0.04
P_2O_5	0.05	±0.01

Traceability: The BND® 5053 is the metrological traceable to SI units through national measurement standards at CSIR-National Physical Laboratory (National Measurement Institute of India). All measurements have been carried out to establish traceability through an unbroken chain of measurements having stated uncertainty.

Nature of Material: Non-hazardous

Homogeneity: Ten vials of BND® 5053 were selected and homogeneity assessment was carried out within and between these bottles as per ISO Guide 35:2017 [3].

Instructions for Storage, Usage and Precautions for Handling:

1. BND® 5053 should be used in controlled conditions, using calibrated equipment, by trained personnel.
2. The BND® is to be dried at 105±5°C for two hours before use. The minimum quantity of the sample is recommended for the analysis as given in the standard as per the standard method.
3. After drying, the material should be protected from atmospheric moisture and used immediately. Leftover portion in a vial, if any, should not be used at a later date.
4. The material should be stored under non-humid conditions to avoid any ingress of moisture/CO_2.

Expiration of Certification: The certification of BND® 5053 is valid, within the measurement uncertainty specified, until **31st December 2026**, provided the BND is handled and stored in accordance with instructions given in this certificate. This certification is nullified if the BND is damaged, contaminated or otherwise modified.

Maintenance of Certification: NCB will monitor the certified values of BND® 5053 over the period of its certification. If substantial technical variation is observed that deviate the certified value before the expiration of validity, NCB will notify the customer.

Disclaimer: Development of BND® 5053 has been carried out at NCB, accredited as per ISO 17034:2016 [4] and testing is performed with compliance as per ISO/IEC 17025:2017 [5]. The certification of the BND® 5053 is also complying to the requirements of ISO Guide 31: 2015 [6]. However, it assumes no liability with respect to or for damages resulting from the misuse of any information, material, apparatus, method or process disclosed in this certificate or any warranties with respect to the material safety. The certified values of the parameters given in this certificate are the best estimates of true values within the stated uncertainties.

References:

1. MS-13-2010- NCB monograph for analysis of Alkalis.
2. JCGM 100.2008- Evaluation of measurement data- Guide to the expression of uncertainty in measurement
3. ISO Guide 35:2017- Reference Materials - General and statistical principles for certifications.
4. ISO 17034:2016- General Requirements for the competence of Reference Material Producers.
5. ISO/IEC 17025:2017- General Requirements for the competence of testing and calibration laboratories.
6. ISO Guide 31-2015- Reference Materials - Contents of certificate, labels and accompanying documentation.

Date of Certification: 01/01/2022

Document Version: BND/CSIR-NPL/NCB/2022/1.0

Accredited as per ISO 17034:2016 vide Certificate No. RC-1016

Certificate issued by:

Nahar Singh

Dr Nahar Singh
Head, BND Division
CSIR-National Physical Laboratory
Dr K S Krishnan Marg
New Delhi-110012

Amit Trivedi
Head of Centre-CQC
National Council for Cement and Building Materials
Ballabgarh-121004, Haryana

- In case of any query regarding this BND® 5053 please contact Dr Nahar Singh, Head (BND Division), CSIR-NPL (NMI of India), New Delhi-110012.
- This certificate shall not be reproduced without written approval from CSIR-NPL, New Delhi.
- Responsibility for issue and release of this certificate lie with NCB.

For Further Information, Please Contact: National Council for Cement and Building Materials, 34 Km. Stone, Delhi-Mathura Road (NH-2), Ballabgarh, Haryana – 121004, India; Phone +91-129-4192239/303, +91-129-2242051, +91-129-4192222; Email: ncb.cqc@gmail.com, cqcb@ncbindia.com, nccbm@ncbindia.com; website: www.ncbindia.com

INVOICE-324

NATIONAL COUNCIL FOR CEMENT AND BUILDING MATERIALS

Centre for Quality Management, Standards and Calibration Services

CERTIFICATE OF ANALYSIS

ORDINARY PORTLAND CEMENT STANDARD
CRM-1012M

Date: 12TH February 2018
Certificate No.: OPC/1012M/108

The Certified Reference Material **CRM-1012M** has been developed by National Council for Cement and Building Materials (NCB), India, for evaluating proficiency of analysts, evaluating/comparing various test methods and calibration of equipment for analyzing minor constituents, for analysis of Ordinary Portland Cement and material of similar matrix. This **CRM-1012M** is packed in 4 sealed vials, each containing approximately 5g of powdered Ordinary Portland Cement.

Traceability, Certified Value and Uncertainty: The **CRM-1012M** is metrologically traceable to SI units of measurement. Each constituent has been analysed as g/g of the total material and reported in percent. The certified value and expanded uncertainty of each constituent, estimated with known sources of bias, is given below:

CONSTITUENT	CERTIFIED VALUE (PERCENT BY WEIGHT)	EXPANDED UNCERTAINTY (Coverage Factor k=2)
LOI	2.51	±0.07
SiO_2	20.81	±0.24
Fe_2O_3	4.30	±0.06
Al_2O_3	4.59	±0.08
CaO	59.94	±0.23
MgO	4.34	±0.20
SO_3	1.87	±0.03
IR	2.23	±0.06
Na_2O	0.44	±0.03
K_2O	0.57	±0.03
Mn_2O_3	0.10	±0.014
TiO_2	0.25	±0.01
Cl	0.032	±0.004

The expanded uncertainty of the certified value for a constituent is estimated according to the Guide to the expression of Uncertainty in Measurement (GUM) at 95.45% confidence level. The uncertainty includes the measurement variability among the participating laboratories and material inhomogeneity, latter controlled through statistical means. The value listed for LOI, SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO, SO_3, IR, Na_2O, K_2O and Cl is the best estimate of the true value based on the inter-laboratory comparison (ILC) results of 17 laboratories, and for minor constituents, it is based on the results of analytical programme carried out in three NCB laboratories. The analysis of major constituents, alkalis and Cl has been carried out as per IS 4032:1985. Estimation of Mn_2O_3 and TiO_2 has been done as per IS 12423:1988.

Instructions for Use:

1. CRM should be used in controlled conditions, using calibrated equipment, by trained personnel.
2. The CRM is to be dried at 105±5°C for two hours before use.
3. After drying, the material should be protected from atmospheric moisture and used immediately. Leftover portion in a vial, if any, should not be used at a later date.
4. The material should be stored under non-humid conditions to avoid any ingress of moisture/CO_2.
5. Record of usage of CRM and the results must be maintained.

Nature of Material: Non-hazardous

Expiry Date of CRM: This **CRM-1012M** with all its values and uncertainty is developed in **February 2018** and valid upto **31st January 2023** in sealed condition. The CRM will be **monitored** over the period of its certification.

Certification: NCB has provided only one set of material against the Certificate No. mentioned at the top.

Date of release: 04.09.18

Dr. S K Breja
Joint Director & Head
Centre for Quality Management,
Standards and Calibration Services

For Further information, please contact: National Council for Cement and Building Materials,
34KM Stone, Delhi Mathura Road (NH-2), Ballabgarh-121004, phone: 0129-2242051, 4192222, 4192239 (D)
Fax: 0129-2242100, E-mail: cqcb@ncbindia.com; ncb.cqc@gmail.com, website: www.ncbindia.com

American Journal of Applied Chemistry
2016; 4(1): 14-17
Published online February 16, 2016 (http://www.sciencepublishinggroup.com/j/ajac)
doi: 10.11648/j.ajac.20160401.13
ISSN: 2330-8753 (Print); ISSN: 2330-8745 (Online)

Determination of Major Oxides Percentages in Portland Cement of Some Sudanese Cement Manufactories

Asrar Adil El-gray, Faroug Bakheit Mohamed Ahmed

Department of Chemistry, Faculty of Science and Technology, Shendi University, Shendi, Sudan

Email address:
farourgmhmd@gmail.com (F. Bakheit Mohamed Ahmed)

To cite this article:
Asrar Adil El-gray, Faroug Bakheit, Mohamed Ahmed. Determination of Major Oxides Percentages in Portland Cement of Some Sudanese Cement Manufactories. *American Journal of Applied Chemistry.* Vol. 4, No. 1, 2016, pp. 14-17. doi: 10.11648/j.ajac.20160401.13

Abstract: In this quality control study, four samples of Portland cement from four Sudanese factories (Atbra, Barbar, Sakhar and Elshamal) were subjected aiming to assess the percentage of mainly oxides in the Portland cement. The study revealed that the percentages of minerals oxides; Calcium oxide, Silicon dioxide, Aluminum oxide, Ferric oxide and Magnesium oxide of the four factories were in the specified limit of quality control according to the American Society for Testing and Materials - Cement (ASTM C150).

Keywords: Portland Cement, Limestone, EDTA, Clinker

1. Introduction

Cement is a major industrial commodity that is manufactured commercially in over 120 countries. [1] Mixed with aggregates and water cement forms the ubiquitous concrete is used in the construction of buildings, road, bridges and other structure. In countries even where wood is in good supply concrete also features heavily in the construction of residential buildings. In fact twice as much concrete is used in construction around the world than the total of all other building materials. [2] There is huge requirement of cement in construction work all over the world. The quality of cement as per standard specification is very important for the cement manufacturing industries as well as for the civil construction industries for making solid and long life structure. The main constituent of the cement and clinker is calcium oxide (CaO) which is the major factor for cement quality. [3]

Cement is a defined chemical entity formed from predetermined ratios of reactants at a fairly precise temperature. Ordinary Portland cement results from the calcination of limestone and silica in the following reaction; [3]

$$5CaCO_3 + 2SiO_2 \longrightarrow (3CaO, SiO_2)\,(2CaO, SiO_2) + CO_2$$

Limestone Cement carbon dioxide

In addition to gypsum ($CaSO_4.2H_2O$), the cement composed of some minerals oxides; Lima (CaO), Silica (SiO_2), Alumina (Al_2O_3), Magnesium oxide (MgO) and ferric oxide (Fe_2O_3). Because of the complex chemical nature of these oxides in the cement industry, they have shorthand (C, S, A, M and F respectively) are used to denote the chemical compound. [4, 5]

Cements consist of different materials and are statistically homogeneous in composition resulting from quality assured production and material handling processes. Portland cement clinker is made by sintering a precisely specified mixture of raw materials (raw meal, paste or slurry) containing elements, usually expressed as oxides, CaO, SiO_2, Al_2O_3, Fe_2O_3 and small quantities of other materials. The raw meal, paste or slurry is finely divided, intimately mixed and therefore homogeneous. [6]

Ability to calculate compositions of cements in terms of the amounts of the main compounds present provided a valuable new tool for explaining, or predicting, differences in engineering performance among Portland cements. The ability to calculate the amounts of the major compounds in a clinker or cement had important implications. [7]

One of the analytical techniques to determine calcium oxide is complexometric titration with EDTA. The method uses a very large molecule called EDTA which forms a complex with calcium and magnesium ions. [3] A blue dye called Eriochrome Black T (EBT) is used as the indicator. This blue dye also forms a complex with the calcium and magnesium ions, changing colour from blue to pink in the process. The dye–metal ion complex is less stable than the EDTA–metal ion complex. For the titration, the sample

solution containing the calcium and magnesium ion reacts with an excess of EDTA. The indicator is added and colour changes to blue as all the Ca^{2+} and Mg^{2+} ions present are complexed with the EDTA. The main reaction is:

$$Ca^{2+} + EDTA^{4-} \longrightarrow [Ca\text{-}EDTA]^{2-}$$

2. Materials and Methods

2.1. Sample

30g of Portland cement from each cement factory of study factories were obtained and subjected to studied and analyzed.

2.2. Chemicals and Reagents

- Concentrated hydrochloric acid.
- Ammonium nitrate, Ammonium chloride, Ammonium oxalate and Ammonia solution.
- Methyl red indicator.
- Buffer solution (pH =4) and Buffer solution (pH=10).
- Salicylic acid.
- Ammonia solution.
- EDTA.

2.3. Equipments and Apparatus

- Sensitive balance.
- Furnace.
- Beakers.
- Measuring cylinder.
- Volumetric flask.
- Ash less filter papers.
- Crucible.
- Burette.
- Funnel**.**

2.4. Determination Procedures of Oxides

2.4.1. Determination Procedure of Silicon Dioxide (Silica)

1g of cement for each sample was weighted in 100 ml beaker, 10 cm^3 of concentrated hydrochloric acid was added to it and then was heated on electric hotplate to dryness (in hood). Another 6 cm^3 of the acid and 30 cm^3 of distilled water were added respectively, the mixture was heated at boiling point.

The hot solution was filtered through ash less filter paper, the precipitate was washed with 30 cm^3 of hot distilled water (the filtrate was kept to estimate the iron and aluminum). The precipitate and filter paper was conveyed to clean and weighted crucible. The crucible and its contents were burned to 800°C for 50 minutes and the crucible was leaved to cool in the dryer and then was weighted it.

Calculation:

$$\text{Percentage of silicon oxide} = \frac{Weight of si_2o}{Weight of sample} \times \%100$$

2.4.2. Determination of the Combined Oxides (Al_2O_3 & Fe_2O_3)

The filtrate remaining after precipitation of silica was diluted to about 200ml in a beaker; 2g of ammonium chloride was added and drops of methyl red indicator, was heated to boiling. Ammonia solution was added gradually until the color turns to yellow. The beaker was leaved for 10 minutes. The solution was filtered through ash less filter paper, the precipitate and filter paper was washed with ammonium nitrate solution 2% (*the filtrate was kept to estimate the calcium ions*). The precipitate and filter paper was conveyed to clean and weighted crucible. The crucible and its contents were burned at 800°C for 50 minutes, the Crucible was leaved to cool in the dryer and then was weighted to determine of combined oxides.

Ferric oxide percentage:

1g of cement was weighted in a 100 ml beaker, 5 cm^3 of concentrated hydrochloric acid was added to it, was steered well until disappearing of the green color then 10ml of distilled water, the solution was transferred quantitatively to 100 ml volumetric flask, then was purred in a beaker and leaved to settle down. 20ml from the clear solution was pipette in volumetric flask; 5ml buffer solution and 1ml of salicylic acid was added. The mixture was titration against standard EDTA solution (0.01M) until the end point. The titration was repeated until two consecutive reading that equal. From titration, number of moles and weight in g were calculated and then the percentage was calculated.

Aluminum oxide percentage:

Aluminum oxide percentage = combined oxides percentage –ferric oxide percentage.

2.4.3. Determination of the Calcium Oxide Percentage

The filtrate remaining after precipitation of Iron III and Aluminum III was acidified, and heated to boiling. By measuring cylinder 40ml of hot ammonium oxalate 4% was added and ammonia solution was added gradually until the color turns to yellow. The beaker was leaved for 10 minutes. Then the solution was filtered through ash less filter paper; the precipitate and filter paper was washed with ammonium oxalate solution 0.1%. The precipitate and filter paper was conveyed to clean and weighted crucible, the crucible and its contents was burned at a temperature of 550°C for 50 minutes. Then The Crucible was leaved to cool in a dryer and then was weighted.

Calculation:

$$\text{Percentage of calcium Oxide} = \frac{Weight of si_2o}{Weight of sample} \times \%100$$

2.4.4. Determination of Magnesium Oxide

50 ml was pipette from the filtrate remaining after precipitation of CaO to conical flask and drops of indicator was added and 10 ml of buffer solution was added then 10 ml of ammonia solution was added after that the mixture was titrated against standard EDTA solution (0.01M) until the endpoint. The titration was reading three times or until two

consecutive reading that equal or agree within 0.1 cm difference. From titration, number of moles and weight in g were calculated and then the percentage was calculated.

3. Results

Four samples of portal cement were collected from four Sudanese factories and then were subjected to analysis processes and the oxides percents were determined. The Silicon dioxide, and Calcium, Aluminum, Magnesium and Ferric oxide percentage and the limits of quality control standard were illustrated in table 1.

Table 1. *The percentages of four oxides detected in study samples.*

Factory	SiO_2	CaO	Al_2O_3	MgO	Fe_3O_2
Atbara	20.54%	62.73%	4.44%	2.94%	3.68%
Barbar	21.15%	63.78%	5.00%	2.16%	3.24%
Elshamal	21.65%	65.02%	5.11%	1.87%	3.01%
Sakhr	20.11%	60.44%	4.93	2.8%	3.85%
ASTM C150	19 – 23%	61 – 67%	2.5 – 6.0	0 – 5.0%	0 – 6.0%
P value	0.442	0.263	0.077	0.092	0.659

P =probability value

The variation of different brands of five oxides which were determined in four samples from Sudanese factories were represented in figures 1, 2, 3, 4 and 5.

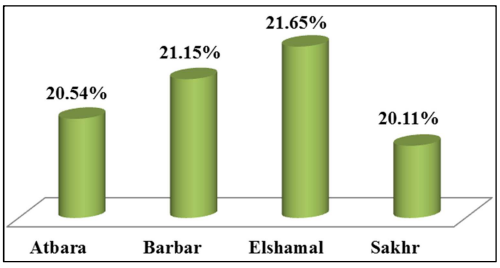

Figure 1. *The percentages of silicon dioxide in four samples.*

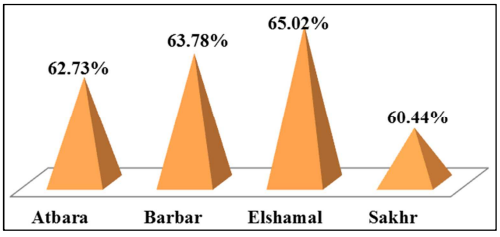

Figure 2. *The percentages of calcium oxide of five factories.*

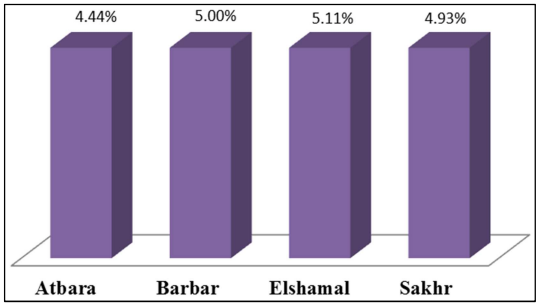

Figure 3. *The percentage of aluminum oxide of study samples.*

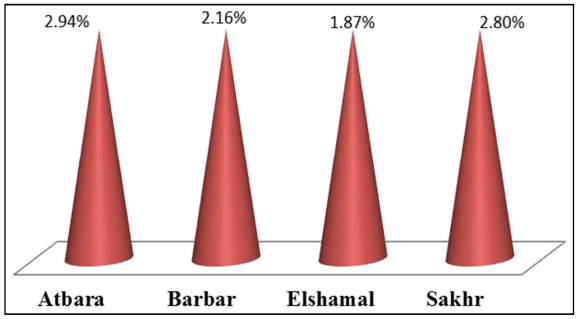

Figure 4. *The magnesium oxide percentage of five factories.*

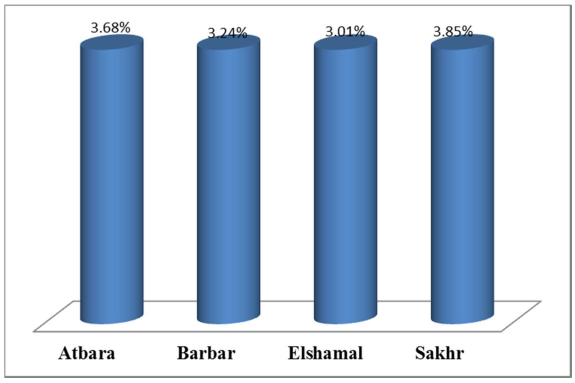

Figure 5. *The percentage of ferric oxide of four factories.*

4. Discussion

The proper lime content is limited due to the lower early strength produced when lime content of ordinary Portland cement is too low and unsoundness when it is too high. [8] our study revealed that the calcium oxide percentage in Sakhar factory was slightly low comparison with other factories, however all percentages of calcium oxide in four samples were in the normal range according to the American standard of Portland cement ($p = 0.263$). High lime content is associated with early strength whereas slightly lower content of lime favors ultimate strength which develops gradually over a long period time.

By using the American standard limit of silicon dioxide in Portland cement as cut off point, the present study showed that all the factories samples with in specified limit and there is no variation in the different brands.

The study was represented the aluminum oxide of Atbra, Barbar, Elshamal and Sakharas 4,44%, 5.00%, 5.11 and 4.93%respectively and all these values were in the standard limit of ASTM C150.

Due to high magnesia in cement may be detrimental to the firmness of the portal cement, so that amount of magnesia must not exceed 2% especially at late ages. [9] The study showed that the magnesium oxide of four samples within the specified limit (0 – 5.0%) of the ASTM C150 and there was no significant difference between percentages of all samples ($p = 0.0658$).

Ferric oxide amount was found in specified limit of ferric oxide acceding to the united state standard for Portland cement. Variations in chemical constituents affect the cement

properties like, hardening, setting time, corrosion resistance color, etc. [10] Possible and potential source of error in testing might be grade of chemicals, and preparation of reagents and accuracy of method performance which depends on the investigator proficiency.

5. Conclusion

The study compares the quality of different oxides of Sudanese Portland cement factories. The percentage of Silicon dioxide, Calciumoxide, Aluminum oxide, Ferric oxide and Magnesium oxide were calculated in according with united state standard. All the values were found in the specified limit of the standard.

References

[1] IUCC. (1993). Why cement making produces CO2.Information Unit on climate change. www.cs.ntu.edu/homepages.

[2] Sustainable settlement in South Africa (2002). Climate changes. www.sustainable settlement.co.2alissues/climate.html

[3] Rajwar B. S, and Pandey I.K. (2014). Determination of Calcium and Magnesium in clinker, Cement & Fly Ash based Cement by EDTA without using making reagents International Journal of Advanced Research in Engineering and Applied Sciences. Vol. 3 (4); April 2014: 8-9.

[4] Daivdovits J. (1994). Global warming impact on the cement and aggregates industry. World resource review, 6(2); 263-78. www.geopolymers.org/libarary

[5] Sidney Mindess & J. Francis Young (1981): Concrete, Prentice-Hall, Inc., Englewood Cliffs, NJ, pp. 671.

[6] Cement - Part 1: Composition, specifications and conformity criteria for common cements, British standard. The European Standard EN 197-1:2000, with the incorporation of amendment A1:2004, has the status of a British Standard.

[7] Standard Specification for Portland Cement, ASTM C-150, Annual Book of ASTM Standards, Vol. 04.01, Cement, Lime and Gypsum, American Society for Testing and Materials, West Conshohocken, PA (1999).

[8] Pandey G, N and Shukla S.D. Atext book of chemical technology. New Delhi: Vikas publishing; Vol 1; 1980.

[9] Austin G. T. (1985). Shreve's chemical process industries, 5th Singapore: McGraw Hill Book Company.

[10] Neville A. M. (1996). Concrete technology, 4th ed. Singapore, Long man Singapore published Ltd.

European Journal of Chemistry

View Journal Online
View Article Online

Chemical analysis of some Pakistani Portland cement/clinker and their compliance with ASTM standards

Sufian Rasheed [1], Niamat Ullah [1] and Amir Ullah [2,*]

[1] *Department of Chemistry, Faculty of Chemistry, Government Post Graduate College (KUST), Kohat, 26000, Pakistan*
sufianrasheed75@gmail.com (S.R.), uniamat852@gmail.com (N.U.)
[2] *Department of Chemistry, Faculty of Chemistry, Hazara University, Mansehra, Khyber Pakhtunkhwa, 21120, Pakistan*
amirktk722@gmail.com (A.U.)

* *Corresponding author at: Department of Chemistry, Faculty of Chemistry, Hazara University, Mansehra, Khyber Pakhtunkhwa, 21120, Pakistan.*
e-mail: amirullah@hu.edu.pk (A. Ullah).

RESEARCH ARTICLE

10.5155/eurjchem.11.3.194-197.1980

Received: 10 March 2020
Received in revised form: 13 June 2020
Accepted: 19 June 2020
Published online: 30 September 2020
Printed: 30 September 2020

KEYWORDS

EDTA
Clinker
Limestone
Mineral oxides
Portland cement
Chemical analysis

ABSTRACT

This is a quality control study and analysis of Portland cement taken from four Pakistani cement plants (Deewan, Kohat, Lucky and Maple Leaf). These four samples were analysed and the determination of major oxides present was carried out. Loss on ignition and the percentage of insoluble residue was also determined. Our research shows percentage of major oxides present in these four samples i.e. calcium oxide, silicon dioxide, aluminium oxide, iron oxide, sulphur trioxide and magnesium oxide. According to the American Society for Testing and Materials Cement (ASTM C150), the percentage of these oxides, loss on ignition and insoluble residue of these four plants are within the specified quality control range. The present study compared the quality of different oxides at the Portland cement brands in Pakistan. The percentages of SiO_2, SO_3, CaO, Al_2O_3, MgO and Fe_2O_3 were calculated according to American Society for Testing and Materials (ASTM C150) uniform standards. The percentages of all of the brands were within the limits specified by the standard (ASTM C150).

Cite this: *Eur. J. Chem.* **2020**, *11(3)*, 194-197 **Journal website**: www.eurjchem.com

1. Introduction

Joseph Aspdin, a British mason, was the first one who invented cement in 1824. He manufactured cement in his kitchen by mixing limestone with clay powder and then by grinding that mixture which hardens upon mixing with water. Cement is the most important industrial product which is count as one of the necessary materials used for construction purposes; commercial production is done in more than 120 countries. Cement is mainly used as binding agent in concrete, which is second most used material after water, used for all type of construction purposes i.e. houses, hospital, schools and dams etc. [1]. 2.7 Billion tonnes of cement are manufactured by the 120 countries around the world annually which used in amount double to all of the other construction materials [2]. Even those countries which have enough supply of wood is available also use cement in heavy amount for construction. In short cement is essential need for the construction purposes all over the world.

Since Pakistan is developing country, its construction industry is highly depended upon Portland cement for almost every type of construction like schools, offices, dams and houses. Pakistan has 22 cement manufacturing companies and there is an increase from 2910 thousands of tonnes to 3110 thousands of tonnes since June 2019 to July 2019. The average cement production of Pakistan is 2394.33 thousands of tonnes from 2003 to 2019 [3].

The major raw material used for the synthesis of Portland cement is calcium, aluminium, iron, magnesium and silicon. These raw materials are mixed in specific proportions for production of high-quality cement. The raw materials are separately crushed into smaller pieces (2-5 cm) and then grinded to convert them into fine powder. The fine powdered raw materials are mixed in required proportion which is sent to rotary kiln. In order to get a maintained proportion product, the powdered raw materials are mixed in a defined ration in rotary kiln. Rotary kiln is made up of steel in which the burning process of raw material take place as well as mixing of raw material and its conversion into clinker also takes place in rotary kiln at elevated temperature i.e. 1500-1700 °C [4].

Among all the other constituent's calcium oxide (CaO) is the main constituent of cement and clinker which is responsible for the quality of cement. Some of other important constituents of cement are; lime (CaO), silica (SiO_2), alumina (Al_2O_3), ferric oxide (Fe_2O_3), magnesia (MgO), sulphur trioxide (SO_3), soda and potash ($Na_2O + K_2O$) [5].

http://dx.doi.org/10.5155/eurjchem.11.3.194-197.1980

Table 1. Chemical data of constituents required for the manufacturing of Portland cement.

Constituent	Minimum (%)	Average (%)	Maximum (%)
CaO	58.10	64.18	68.00
SiO_2	18.40	21.02	24.50
Al_2O_3	3.10	5.04	7.56
Fe_2O_3	0.16	2.85	5.78
K_2O	0.04	0.70	1.66
MgO	0.02	1.67	7.10
Na_2O	0.00	0.24	0.78
SO_3	0.00	2.58	5.35
Equivalent alkalies	0.03	0.68	1.24
Free lime	0.03	1.24	3.68

Each of the mentioned oxides have their own role and function during the hydration of cement that's why each of the constituent must be in a defined specific proportion during the process of manufacturing of Portland cement. Table 1 shows the oxides composition quantity required for the manufacturing of Portland cement proposed by F. M. Lea [6].

Cement analysis in term of major constituents is an important aspect of cement manufacturing and used as valuable tool for research in cement engineering. Several techniques are used for the analysis of cement in terms of major constituents' present. Some of them are more frequently used because the proper ratio of raw materials present in cement decides the quality and strength of cement and they have important applications [7].

Ethylenediaminetetraacetic acid (EDTA) method which is basically complexometric titration method and that is one of most commonly used analytical technique used for the determination of calcium oxide in cement/clinker. Ethylene diaminetetraacetic acid, a very large molecule, forms complex with calcium and magnesium ions, is used in this method [8]. The indicator used for such complexometric titration is a blue coloured dye known as Eriochrome Black T (EBT). Eriochrome Black T, by forming complex with calcium and magnesium ions, turns colour from blue to pink during the titration process. The complex formed by EDTA with metal ion is more stable as compared to complex formed by dye with metal ion.

2. Experimental

2.1. Sample

Portland cement (25 g) were taken from the commercially available brands in the city of Pakistan, Kohat, Khyber Pakhtunkhwa on September 2019. The collected cement samples were from the Deewan Cement Co. Inc., Kohat Cement Co. Inc., Lucky Cement Co. Inc. and Maple Leaf Cement Co. Inc. The obtained Portland cement was subjected to study and analysed in the Laboratory of Department of Chemistry, Government Post Graduate College Kohat, Pakistan.

2.2. Reagents used

All of the chemicals and reagents (EDTA, zinc oxide, concentrated ammonia, concentrated HCl, buffer solution (pH = 1.5) and buffer solution (pH = 10), salicylic acid, ammonium acetate, methyl red indicator, Eriochrome black T) were purchased from Sigma Aldrich by Department of Chemistry, Government Post Graduate College Kohat, Pakistan.

2.3. Determination of silica

The methods used for the determination and analysis of various components of cements followed the previous work published [9]. One gram of cement sample was weighted from each brand and taken separately into a 100 mL beaker and then 10 mL of hydrochloric acid (concentrated) was added. The solution was heated to dryness on a hot plate. Hydrochloric acid (concentrated) (10 mL) and water (30 mL) were added and the mixture was heated to boiling. The hot solution was filtered through a Whatman filter paper No. 40, and the precipitate was washed with 30 mL of hot distilled water (the filtrate was retained to estimate iron and aluminium). The residue was placed in a weighed crucible along with filter paper and ignited at 1000 °C for one hour. The crucible was cooled and weighed, and the percentage of SiO_2 is calculated according to Ref. [9].

2.4. Determination of combined oxides

After silica precipitation, the remaining filtrate was diluted to about 200 mL in a beaker and then 2 grams of NH_4Cl was added after the drop wise addition of the methyl red indicator, the solution was heated to boiling after which NH_3 solution was added till the colour changes to yellow. The beaker was cooled for 10 minutes and then filtered through Whatman filter paper No. 40. The residue was washed with a 2% ammonium nitrate solution (the filtrate was retained for the determination of calcium ions). The residue was transferred together with filter paper to a weighed crucible and ignited at 1000 °C for 50 minutes. The crucible is cooled in a desiccator and then weighed to determine the combined oxides [9].

2.4.1. Determination of ferric oxide

From each brand 1 gram of cement sample was taken into 100 mL beaker and 5 mL hydrochloric acid (concentrated) was added with continuous stirring until the greenish colour of solution disappeared. After this, 10 mL of distilled water was added in that solution and it was transferred into another clean and dry beaker. The mixture was divided into two layers when leaved for 15-20 minutes. Precipitates settle down at the bottom and clear solution was on the top side and from the clear solution 20 mL was transferred into volumetric flask with the help of pipette in which 5 mL of pH = 1.5 was added and 1 mL of 4% solution of salicylic acid was added the solution turn purple and the mixture was titrated against 0.01 M standardized EDTA solution. The titration was repeated three times and the percentage of Fe_2O_3 was calculated according to Ref. [9].

2.4.2. Determination of aluminium oxide

The percentage of aluminium oxide was calculated by subtracting the percentage of ferric oxide from the percentage of combined oxides [9].

2.5. Determination of the calcium oxide

After the precipitation of Fe^{3+} and Al^{3+} the remaining filtrate was acidified and heated. 40 mL of hot 4% ammonium oxalate solution was added and the ammonia solution was gradually added until the colour turned yellow. The beaker was left for 15 minutes to cool and then filtered through a Whatman no. 40 filter paper.

Table 2. The percentages of oxides, insoluble residue and loss on ignition determined in the studied samples.

Cement brand	SiO_2 (%)	SO_3 (%)	CaO (%)	Al_2O_3 (%)	MgO (%)	Fe_2O_3 (%)	IR (%)	LOI (%)
Deewan	19.5	2.75	65.23	4.35	2.61	2.06	0.896	2.00
Kohat	22.0	3.00	62.00	3.28	2.41	3.10	0.780	1.97
Maple Leaf	20.0	2.40	62.40	2.93	1.45	1.82	1.060	2.00
Lucky	19.0	2.55	64.37	4.35	2.71	2.06	0.850	2.00
ASTM C150	19-23	0.00-5.35	61-67	2.5-6.0	0-5	0-6	0.3-5.0	1-5

The filter paper was washed with 0.1% ammonium oxalate solution, and the precipitate was transferred along with filter paper to a clean and weighed crucible and burned at 550 °C for 50 minutes. The crucible is cooled in a desiccator and then weighed. The percentage of CaO is calculated according to Ref. [9].

2.6. Determination of magnesium oxide

The filtrate remaining after CaO precipitation was sufficiently diluted, and then 50 mL of this solution was added to a titration flask by adding 15 mL of a buffer solution (pH = 10) to maintain its pH. Erichrom Black T indicator (3-4 drops) were added, then the mixture was titrate against 0.02 M standardized EDTA solution from purple to blue endpoint, the titration was repeat three times, and calculated the moles and weight (grams) from the titration, then the percentage of MgO was calculated [9].

2.7. Determination of sulphur trioxide

From each brand 1 gram of cement sample was weighed on an analytical balance and transferred to a 250 mL dry beaker, 50 mL of distilled water was added, and 10 mL of HCl was added while shaking. The mixture was boiled and filtered through a Whatman no. 41 filter paper. The residue was washed three times with hot distilled water. The filtrate was boiled, then 15 mL of 5% barium chloride was added, the solution was boiled, and the beaker was placed on a hot plate at 80-90 °C for 3-4 hours. The reaction mixture was filtered and washed with hot distilled water until it was free of chloride. The precipitate was transferred to a clean, dry and weighed crucible and ignited in furnace at 1000 °C for 50 minutes, then allowed to cool, and then the percentage of SO_3 was weighed. The percentage of SO_3 is calculated according to Ref. [9].

2.8. Determination of insoluble residue (IR)

One gram of cement sample from each brand was weighed and transferred to a dry 250 mL beaker, H_2O was added and steered to disperse the sample and 5 mL of HCl (concentrated) was added to dissolve it. The solution was heated slightly and manipulated with a glass rod to break any agglomerates and dissolve properly. 50 mL of warm distilled water was added and heated on a hot plate for 10 minutes, and the solution was filtered through Whatman no. 41 filter paper, washed 6-8 times with hot water.

The filter paper was placed in the same beaker from which the solution was filtered and 2-3 g of Na_2CO_3 were added steered well to loosen the filter paper, the beaker was covered with a watch glass and heat in a sand bath for 15 minutes. 2-3 drops of methyl red indicator were added, and 1:1 HCl was added drop wise to neutralize until the solution turned red. The mixture was filtered through Whatman no. 41 filter paper, and rinsed with warm water 10 times until the solution is free from chlorides and it is further tested by washing with $AgNO_3$ solution. Filter paper and insoluble materials were transferred to a weighed crucible and ignited at 1000 °C for one hour. The percentage of insoluble residue was calculated according to Ref. [9].

2.9. Determination of loss on ignition

Three grams sample was weighed from each brand and shifted to watch class and dried in the oven at 105 °C for 1 hour. The sample was cooled in the desiccator. 1 g of the sample was weighed and transferred to a weighted china dish and kept in a furnace at 1000 °C for 45 minutes. China's dish was cooled in a desiccator and the loss on ignition was calculated according to Ref. [9].

3. Results

Four samples from different Pakistani cement brands were collected and analysed. The determination of major oxides, insoluble residue and loss on ignition of these cement were carried out. The percentage of SiO_2, CaO, Al_2O_3, MgO, Fe_2O_3, IR and LOI and limits of compositional constituents of Portland cement according to American Society for Testing and Materials (ASTM) are shown in Table 2.

4. Discussion

The appropriate lime content is important and plays and important role in the strength of cement and if the lime content in the Portland cement is too low or too high then it causes lack of solidity and low strength of the cement and cement will be baseless [10]. Our research shows that calcium oxide content in Kohat cement was a bit low compared to others brands. However, the percentages of all of the four cements brands were in the normal range of standard Portland cement suggested by ASTM. High lime content is related to early strength, but slightly lower Lime contributes to the ultimate strength of gradual development for a long time [11]. Our study further showed that the percentage of silicon dioxide in Lucky cement is slightly lower as compared to the other three brands but all of four were in the ASTM range for Portland cement. Our study showed aluminium oxides percentage for Deewan cement was 4.35%, Kohat cement was 3.28%, Maple Leaf cement was 2.93 and Lucky cement was 4.35% in which there was variation but overall, all of the brand was up to the standard of ASTM C150. Due to the high content of magnesium oxide in the cement, it may be the hardness of the portal cement, the amount of magnesium oxide should not more than 2% particularly at late years [12]. Study of the four samples of magnesium oxide is indicated accordingly to the ASTM C150 specific range (0-5.0%) and there was no significant variance among the percentages of all samples. The content of ferric oxide was found to be in the specified limit of ferric oxide so the Fe_2O_3 percentages of all samples meet US Portland standards cement (ASTM C150). Changes in chemical composition can affect the properties of cement, such as hardening, setting time, corrosion, resistance, colour, etc. [13]. Prospective and potential source of error in the tests can be of chemical quality, and the preparation of reagents and accuracy of the performance of the method that depends on the competence of the investigator.

5. Conclusion

This study compared the quality of different oxides at the Portland cement brands in Pakistan. The percentages of SiO_2,

SO_3, CaO, Al_2O_3, MgO and Fe_2O_3 were calculated according to American Society for Testing and Materials (ASTM C150) uniform standards. The percentages of all of the brands were within the limits specified by the standard (ASTM C150). Further, the components of Portland cement can be determined according to ASTM C114 which is modern techniques like XRF etc. which can give more details. Although all of the cements brands analysed during our research were within the limits suggested by ASTM C150 but the percent of calcium oxide in Deewan cement is higher and closer to ASTM C150 standard which give a little advantage to Deewan cement over other brands in case of strength according to our opinion but the present work also suggest that all of the selected cement brands of Pakistan manufacture quality cement which are up to the mark of American Society for Testing and Materials.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

ORCID

Sufian Rasheed
http://orcid.org/0000-0003-4975-720X
Niamat Ullah
http://orcid.org/0000-0001-8188-2778
Amir Ullah
http://orcid.org/0000-0003-1514-1562

References

[1]. Hansson, C. M. *Metall. Mater. Trans. B* **1995**, *26(3)*, 417-437.
[2]. U. S. Geological Survey, Mineral commodity summaries 2008: U. S. Geological Survey, 2008, pp. 44-45.
[3]. State Bank of Pakistan (2019). Retrieved Feb 05, 2020, http://tradingeconomics.com/pakistan/cement-production
[4]. Winter, N. B. Microanalysis Consultants. Understanding cement: An introduction to cement production, cement hydration and deleterious processes in concrete, WHD Microanalysis Consultants Ltd., Woodbridge, U. K., 2012.
[5]. Davidovits, J. *World Resour. Rev.* **1994**, 6(2), 263-278.
[6]. Lea, F. M. The Chemistry of Cement and Concrete, 3rd edition, Arnold Publishers, London, UK, 1970.
[7]. Standard Specification for Portland Cement, ASTM C-150, Annual Book of ASTM Standards, Vol. 04. 01, Cement, Lime and Gypsum, American Society for Testing and Materials, West Conshohocken, PA (1999).
[8]. Rajwar, B. S.; Pandey, I. K. *Inter. J. Adv. Res. Eng. Appl. Sci.* **2014**, *3(4)*, 7-16.
[9]. El-Gray, A. A.; Ahmed, F. B. M. *Am. J. Appl. Chem.* **2016**, *4(1)*, 14-17.
[10]. Pandey, G. N.; Shukla, S. D. A text book of chemical technology, New Delhi: Vikas Publishing; Vol 1; 1980.
[11]. Bediako, M.; Amankwah, E. O. *Advances in Materials Science and Engineering* **2015**, *2015*, 349401.
[12]. Austin, G. T. Shreve's Chemical Process Industries, 5th Edition, McGraw Hill Book Company, Singapore, 1985.
[13]. Neville, A. M. Concrete Technology, 4th Edition: Longman Singapore Publishers Ltd., 1996.