Chemical Analysis of Some Commonly Used Brands of Ordinary Portland Cement in Sri Lanka

W S S Jayamanna
Scientist, Environmental Division, National Building Research Organization

N B M Ranathunga
Consultant and Former Deputy Director, Building Material Division, National Building Research Organization

Y. P. SSiriwardena
Chief Chemist, Geological Survey & Mines Bureau

ABSTRACT: Cement is a major industrial commodity that is manufactured commercially in over 120 countries. Mixed with aggregates and water, cement forms the ubiquitous concrete which is used in the construction of buildings, roads, bridges and other structures. 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. Despite rising costs cement has recorded a steady growth in its usage in the construction industry of Sri Lanka.Although there are several different types of cement, Ordinary Portland Cement (OPC) is the most widely used.

Portland cement is made by heating raw materials rich in oxides of Silicon, Calcium, Aluminium and Iron to temperatures of around 1,200-1,400ºC and the clinker formed is finally ground to fine particles to cement.
In the function of the cement in concreting, the fine cement particles are broken down into even smaller particles thus increasing the reactive surface by crystallizing out from the supersaturated solution formed. A series of immensely strong bonds form between the particles, making a network in which the aggregates are trapped.

All these aforementioned reactions continue to take place for some time and these reactions are highly dependent on the composition of the cement. Therefore it is vital to ensure the correct chemical compositions according to the Standards specified for Ordinary Portland Cement in the concreting process of the industry. Hence this study compares the quality of different Ordinary Portland Cement brands produced to be in conformity with SLS 107 and commonly available in Sri Lanka.

Therefore the amounts of main chemical constituents such as Silicon oxide (SiO2), Aluminum oxide (Al_2O_3), Iron Oxide (Fe2O3), Magnesium Oxide (MgO), Sulphur Trioxide (SO3), Calcium Oxide (CaO), Insoluble Residue (IR) , Loss On Ignition (LOI), Chloride (Cl) and Lime Saturation Factor (LSF) were determined in accordance with Sri Lanka Standard (SLS-107,2008) Specifications. All the results were presented to provide qualitative and quantitative variations between cement samples analysed with limits specified in the SLS. The possible reasons for variation in chemical composition and their consequences have been discussed.

Keywords: Ordinary Portland Cement, Chemical composition, Cement Quality

1 INTRODUCTION

The building of houses which is considered the main component in Sri Lanka's construction industry constitutes about 80% of the country's total construction. The balance 20% comprises infrastructure development such as roads, bridges, buildings and etc. Thus presently the construction industry in Sri Lanka is growing at a rate about 7% with the main thrust being housing construction. As a result of this, there is a high demand for the cement as it is one of the main raw materials in the construction industry. Although there are several different types of Portland Cement such as Portland Limestone Cement, Portland Blast Furnance Slag Cement, Portland Pozzolana Cement, Portland Masonary Cement and etc., Ordinary Portland Cement (OPC) has been the most widely used in the construction industry when there is no exposure to Sulphates in the soil or in ground water. Therefore different brands of Ordinary Portland Cement have been introduced to the Sri Lankan market.

There are three Sri Lanka standards specified for different varieties of cement produced and SLS 107 specifies the requirements and methods of test for Ordinary Portland Cement.

The cement to be used in construction must have certain qualities in order to play its part effectively in any of its applications. Concrete is an extremely versatile material which is made by mixing aggregates with Cement and water and allowing it to set. Concrete is being used in the production of anything from nuclear radiation shields to playground structures and from bridges to yachts. It is able to be used in such a wide variety of applications because it can be precast or poured in-situ into any shape, reinforced with steel or glass fibres and produced in a variety of colours and finishes. It can even set under water. Therefore quality assurance of Ordinary Portland Cement has become an important and critical factor.

There are several brands of Ordinary Portland Cement available in Sri Lankan market. The chemical composition of a cement and consequently its physical properties could vary as a result of variations in the raw materials, manufacturing conditions and etc.Therefore this study was aimed to conduct analysis of main chemical constituents of Ordinary Portland Cement. Main chemical constitutions such as Silicon oxide (SiO2), Aluminum Oxide (Al2O3), Iron oxide (Fe2O3), Calcium oxide (CaO), Magnesium oxide (MgO), Sulphur Trioxide (SO3), Insoluble Residue (IR) and Loss On Ignition (LOI) Chloride (Cl) and Lime Saturation Factor (LSF) were determined.

2 BASIC CHEMISTRY OF PORTLAND CEMENT

Limestone and a 'cement rock' such as clay or shale are quarried and brought to the cement works. These rocks contain Lime (CaCO3), Silica (SiO2), Alumina (Al2O3), and Ferrous Oxide (Fe2O3).

Portland cement is made by heating aforementioned raw materials rich in oxides of Silicon, Calcium, Aluminium and Iron to temperature of around 1,200-1,400ºC.The chemical reactions that occur within the partially molten mass result from the formation of four main cement materials. Table 01 shows the major mineral constituents of Portland cement clinker. In addition to the main chemicals constituents listed in Table-01, there exist minor compounds such as TiO2, MnO2, K2O and Na2O.

Table 01Major mineral constituents of Ordinary Portland Cement

Name of compound	Oxide composition	Abbreviation
Tricalcium Silicate	3 Cao.SiO_2	C3S
Dicalcium Silicate	2CaO.SiO_2	C2S
Tricalcium Aluminate	3CaO.Al_2O_3	C3A
Tetracalcium Aluminoferrite	4CaO.Al_2O_3.Fe_2O_3	C_4AF

Of these compounds, C3S and C3A are mainly responsible for the strength of the cement. High percentages of C3S (low C2S) results in high early strength but also heat generation as the concrete sets. The reverse combination of low C3S and high C2S develops strengths more slowly and generates less heat.C3A causes undesirable heat and rapid reacting properties which can be prevented by adding Gypsum (CaSO4) to the final product.C3A can be converted to the more desirable C4AF by the addition of Fe2O3 before heating, but this also inhibits the formation of C3S.C4AF makes the cement more resistant to seawater and results in a somewhat slower reaction which evolves less heat. For this reason considerable efforts should be made during the manufacturing process to ensure the correct chemical compounds in the correct ratios are present in the raw materials before introduction of the material to the kiln.

The cement manufacturing process involves four distinct stages.

1. Quarrying
2. Raw material preparation
3. Clinkering
4. Cement milling

1. Quarrying

The raw material for cement manufacture is a rock mixture which is about 80% limestone which is rich in CaCO3 and 20% clay which contains Silica, Alumina and Iron oxide. These are quarried and stored separately. The lime and silica provide the main strength of the cement while the Iron reduces the reaction temperature and gives the cement its characteristic grey color.

2. Raw material preparation

The quarried clay and limestone are crushed separately until nothing bigger than a tennis ball remains.

3. Clinkering

This is the step which is characteristic of Portland cement. The finely ground material is dried, heated and then cooled down again. While it is being heated various chemical reactions take place to form the major mineral constituents of Portland cement. The reactions processes occurring within the kiln are not easily understood due to the wide variations in raw –mix chemistry, raw-mix physical properties and kiln operating conditions, and the physical difficulties of extracting hot materials from the process for investigation before they cool.

But the chemistry of clinker formation could be explained in accordance with the formation of main clinker minerals into a number of simple zones in the Kiln according to the composition of the raw materials and firing conditions in the Kiln. The major constituents that are formed in the kiln are,

(a) Alite-C3S (3CaO.SiO2)
(b) Belite-C2S (2Cao.SiO2)
(c) Aluminate-C3A (3CaO.Al2O3)
(d) Ferrite-C4AF-(4CaO.Al2O3.Fe2O3)

Zone-01:0-35minutes, 800ºC-1100ºC

Formation of 3CaO.Al2O3 above 900ºC and melting of compounds of Al2O3 and Fe2O3.

$$CaCO_3 \rightarrow CaO + CO_2$$

Zone-02:35-40minutes,1,100ºC-1,300ºC

Exothermic reactions and the formation of secondary silicate as follows.

$$2\mathrm{CaO} + \mathrm{SiO_2} \longrightarrow 2\mathrm{CaO.SiO_2}$$

Zone-03:40-50minutes, 1,300ºC-1,450ºC

Sintering and reaction within the melt to form ternary silicate and tetracalcium aluminate-ferrates.

$$2\mathrm{CaO.SiO_2} + \mathrm{CaO} \rightarrow 3\mathrm{CaO.SiO_2}\,(\text{Binary System})$$

$$3\mathrm{CaO.Al_2O_3} + \mathrm{CaO} + \mathrm{Fe_2O_3} \rightarrow 4\mathrm{CaO.Al_2O_3.Fe_2O_3}\,(\text{Ternary system})$$

Zone-04:0-50-60mi., 1,300ºC-1000ºC

Cooling and crystallization of the various mineral phase formed in the Kiln.

4. Cement milling

To produce the final product the clinker is mixed with gypsum (CaSO4.2H2O) which is added as s set retarder and ground for approximately 30 minutes in large tube mills. The cement flows from the inlet to the outlet of the mill being first ground with 60mm and then 30mm diameter steel balls. The first grinding breaks up the material and the second grinds it to a fine powder.

5EXPERIMENTAL PROCEDURE

The experimental methods and test procedure adopted in this study are described as follows.

(1) The main chemical constituents of Ordinary Portland Cement to be analysed were selected according to the Sri Lanka Standard, SLS-107-2008.

Chemical constituents:

1. Calcium Oxide (CaO)
2. Silicon Oxide (SiO2)
3. Aluminium Oxide (Al2O3)
4. Iron Oxide (Fe2O3)
5. Magensium Oxide (MgO)
6. Sulphur Trioxide (SO3)
7. Chloride (Cl)
8. Lime Saturation Factor (LSF)
9. Insoluble Residue (IR)
10. Loss On Ignition (LOI)

(2) The market survey was carried out within some areas of Colombo district to study the available brands of Ordinary Portland Cement in Sri Lanka.

(3) During the market survey, the following information was gathered to implement the experimental procedure in the identification of the quality of the different available OPC brands.

(a) Different brands of OPC

(b) Country of manufacture
(c) Exporter and Distributer
(d) Date of manufacture and/or packing
(e) Date of expiry after packaging

(4) According to the information gathered from the market survey six different OPC brands found in the Sri Lankan market and widely used in the construction industry were selected for the study (See Table 02).

Table 02 Common OPC brands in Sri Lanka market

No.	**Name of Brands**	**Country of Origin**	**Importer or Distributer**
1	Lafarge Marine Cement	Pakistan	Mahaweli Cement (Pvt) Ltd
2	Tokyo Super - Indonesia	Indonesia	Tokyo Cement Colombo Terminal (Pvt) Ltd
3	Ultratech Ceylinco	India	Ultratech Ceylinco (Pvt) Ltd
4	Sri Lanka Cement Coperation-107	Pakistan	Sri Lanka Cement Cooperation
5	Singhe-107	-	Singhe Cement (Pvt) Ltd
6	Mascons-SLS-107	Pakistan	Mascons Ltd

(5) Samples having different dates of production were particularly selected (from the survey data) because it would have an effect on the quality and performance of the cement. Samples selected were those produced during the periods of July 2010 to September 2010.

(6) Sample were collected into polythene bags and tightly sealed at the collection point.

(8) Each sample was homogeneously mixed before analyzing it.

(9) Three replicates of cement samples of same production date were analyzed to minimize the experimental error of the test.

(8) Testing and analysis was carried out according to the test methods given in the SLS-107, 2008, Specification for Ordinary Portland Cement, Part 2,Test Methods.

(9) The Lime Saturation Factor and Tricalcium aluminate was calculated using following equations given in the SLS 107: Part-01.

Lime Saturation Factor (LSF),

$$\frac{(\mathrm{CaO}) - 0.7(\mathrm{SO_3})}{2.8(\mathrm{SiO_2}) + 1.2(\mathrm{Al_2O_3}) + 0.65(\mathrm{Fe_2O_3})}$$

Where,
CaO=Calcium Oxide
SO3=Sulphur Trioxide
SiO2=Silicon Oxide
Al2O3=Aluminium Oxide
Fe2O3=Iron Oxide

Tricalcium Aluminate (C3A),

$$2.65(\mathrm{Al_2O_3}) - 1.69(\mathrm{Fe_2O_3}) \quad - (\text{Bogue calculation})$$

6 RESULTS AND DISCUSSION

The average test results on chemical constituents of each brand were calculated and expressed in relation to production dates are given in the Table-02 along with the limits specified in SLS. For better comparison of these variations with the limits specified in SLS-107 could be presented graphically. (Table 3)

A Sri Lanka standard does not specify the amounts of CaO, SiO2, Al2O3 and Fe2O3 separately in Portland cement. But it specifies as a Lime Saturation Factor and the variation of LSF in different brands with the SLS limits could be illustrated in Fig 01.

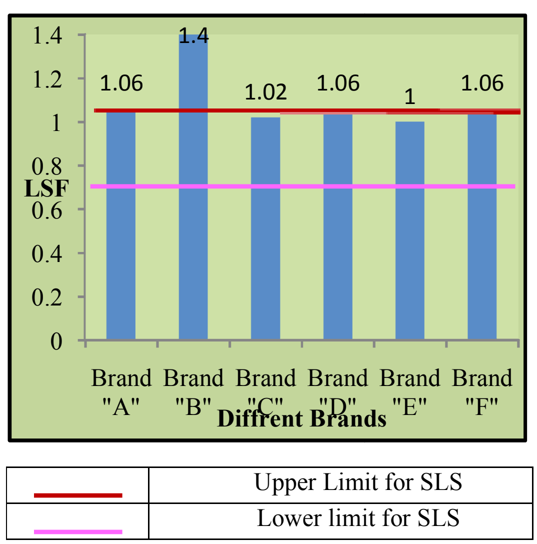

Fig 01: Variation of LSF compared with specified limits

Upper Limit for SLS

Lower limit for SLS

The definition of the Lime Saturation Factor is theoretically based and when it is applied to clinker it is expressed as a ratio of percentage of lime to percentage of Silica, Alumina and Iron Oxide .But when it applies to cement, the sulphur trioxide content should be subtracted from the Calcium Oxide content in calculating LSF.SLS specifies that this should be within the range of 0.66 to 1.02. The impure forms of C3S and C2S are known as Alite and Belite respectively.LSF largely governs the ratio of this C3S (alite) to C2S (belite) and also shows whether the clinker is likely to contain an unacceptable proportion of free lime. Alite and belite are the most important constituents of the Portland cement clinkers which are responsible for the strength of hydrated cement paste. Alite reacts relatively quickly with water and contributes to early strength development below 28 days. Belite reacts slowly with water thus contributing little to the strength during the first 28 days but subsequently to the further increase in strength that occurs at later ages. And also it is essential that the cement paste, once it has set, does not undergo a large change in volume. One restriction is that there must be no appreciable expansion, which under conditions of restraint could result in disruption of the harden cement paste. Such expansion may occur as a result of excess free lime in cement. This type of expansion of cement is classified as unsound. These factors indicate the importance of ensuring that LSF is within the specified limits.

According to the results obtained from the analysis, four brands out of six brands are above the upper limit specified for LSF in SLS 107.It indicates an excess of CaO in cement. Improper proportioning of raw materials, inadequate grinding and homogenization of the raw mix and insufficient temperature or hold time in the kiln burning zone are among the principle factors that account for the free or crystalline calcium oxide in Portland cement clinker.

According to the SLS standard the amount of Magnesia should not be more than 5%. It was found that the content of Magnesia in all samples tested were lower than that of the maximum specified limit indicating 100% conformance.The variation of Magnesium Oxide could be shown in Figure 02.

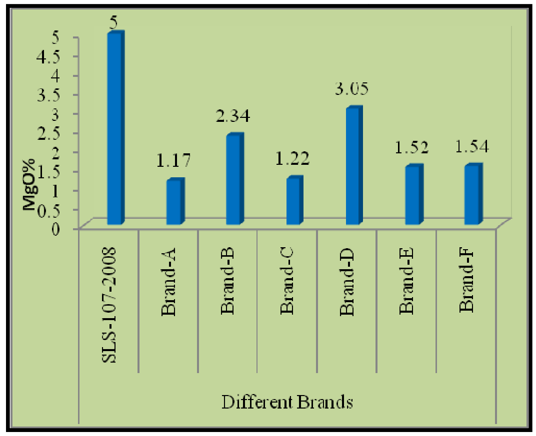

Fig 02 Variation of MgO content compared with specified limits

Higher magnesia contents may be detrimental to the soundness of cement especially at late ages.Magnesia reacts with water to form Mg (OH) 2 and this is slowest reaction among all other hardening reactions. Since Mg(OH)2 occupies a larger volume than the MgO and is formed on the same spot where the MgO molecule is located. It can spilt apart the binding of the hardened cement paste, resulting in expansion cracks.

Calcium sulphate is a third compound liable to cause expansion through the formation of Calcium sulphoaluminate from excess Gypsum. The main purpose of adding gypsum is to retard the quick – setting tendency of ground Portland clinker, attributable to the highly reactive C3S phase. But excess can cause for the expansion of hardened cement paste and low proportion of SO3 in cement would result in flash of cement thereby affecting strength and other properties of mortar or concrete in which it is used.SLS standard specifies the Sulphur trioxide content should be less than 2.5%.But a maximum limit of 3.0% is permitted if the cement contains more than 5.0% of C3A. It was found that Sulphur trioxide content of all cement brands tested were within the above limits as shown in Figure 03.

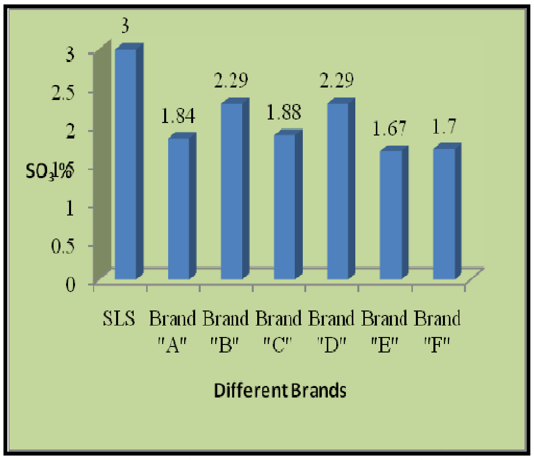

Fig 03Variation of SO_3 content compared with specified limits

SLS standard specifies the Chloride content should not exceed 0.1%.Chloride present in concrete are harmful to the reinforcement, steel embedment and prestressed steel wires. Due to presence Chlorides in steel starts rusting. This results in formation of Iron Oxide. Due to formation oxide, steel increases in volume, at times, even up to eight times its original volume. This creates tension in concrete which ultimately results in disintegration of concrete and reduction in its load carrying capacity. According to the results obtained Chloride content in all the brands were within limit. This is shown in Figure 04.

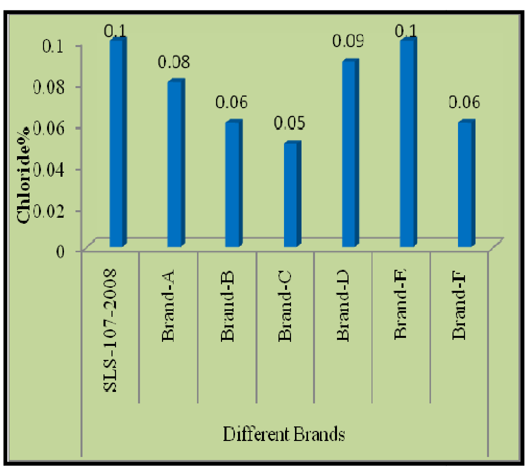

Fig 04Variation of Chloride content compared with specified limits

Insoluble Residue is a non-cementinous material which eventually exists in Portland cement. This residual material affect the properties of cement especially its compressive strength. To control the non cement material in Portland Cement SLS standard allows the insoluble residue content to a maximum limit of 1.5% .Figure 05 shows that all the cement samples except Brand “E” and Brand “F” were within this limit.

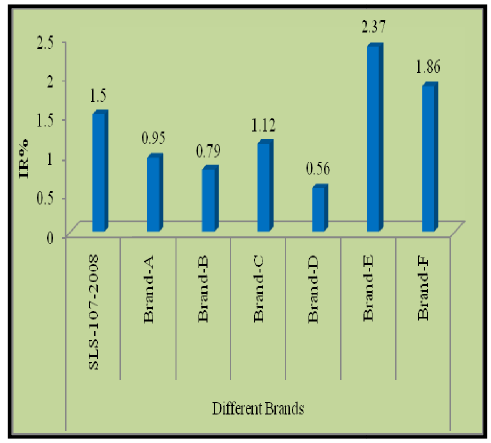

Fig 05: Variation of Insoluble Residue compared with specified limits

A high Loss On Ignition (LOI) indicates pre-hydration and carbonation which may be caused by improper and prolonged storage or adulteration of OPC during transport or transfer. This effect may also be caused when certain minor additives are introduced (at clinker grinding stage) in excess of the specified limit All the cement samples except Brand “E” were found to be within the limits given in SLS 107 namely maximum of 4%. SLS 107 permits the use of minor additive to a maximum limit of 5%. The amount of ignition loss is generally an indication of the freshness of cement.This is shown in Figure 06.

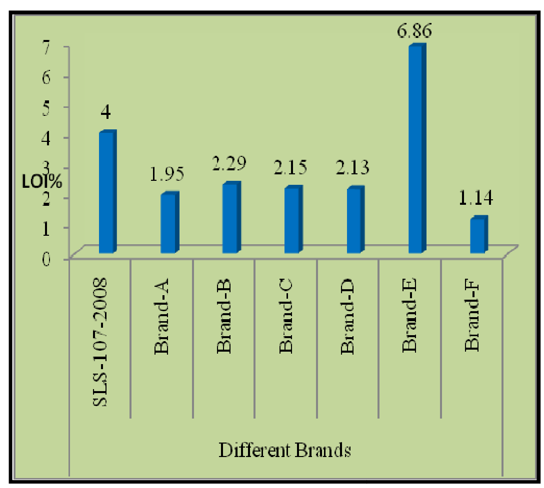

Fig 06Variation of LOI with specified limits

7 CONCLUSION

According to the above explanation on the variation of chemical constituents in different OPC brands it is clearly shown that the different chemical constituents are directly related to the physical and chemical properties such as setting time, soundness, compressive strength and hardening/hydration, corrosion resistance, color etc.of OPC cement. The reason for the variation of the chemical continents could be improper proportioning of raw materials, inadequate grinding and homogenization of the raw mix and insufficient temperature or hold time in the kiln burning zone. The quality of cement is vital for the production of good concrete and other cement based products. The manufacture of cement requires stringent control to ensure the desired quality to conform to the requirement of the relevant national standards Test results indicate that several brands of OPC do not conform to SLS requirements in respect of Lime Saturation Factor, Loss On Ignition and Insoluble Residue. It is obligatory for the cement producer to ensure conformity to all the requirements of SLS 107 before issuing each batch of cement to the market as a certified procedure .It is also desirable for the purchaser or for the independent laboratory to make periodic acceptance tests or to examine the properties of a cement to be used for some special purpose.

REFERENCES

1. Arthur L Vogel (3rd Edition),"A text book of Quantitative Inorganic Analysis", 663-666.

2. Annual Book of ASTM Standard, Section 4, Construction Cement, Lime, Gypsum, Volume 04.01, C114.

3. BSEN 197:2000, British Standard for cement-Part 1: Composition, specification and conformity criteria for common cement.

4. BSEN 196:2005, British Standard Methodology for chemical analysis of cement.

5. Concrete Technology by A M Neville J Brooks, third impression,2008,published by Dorling Kindesley (India) Pvt Ltd.

6. Concrete, Microstructure, Properties and Materials by P Kumar Mehta and Paulo J M Moteiro, 3rd revision, 2006.

7. Sri Lanka standard 107:2008, Specification for Ordinary Portland Cement -Part-01: Requirements, 4th Revision.

8. Sri Lanka Standard 107:2008, Specification for Ordinary Portland cement - Part-02: Tests Methods, 4th Revision.

Table 03Amount of chemical constituents of different brands compared with the limits specified in SLS for OPC

			OPC Brands						
			Productions dates						
			26/07 15/08 9-Mar 9-Jun 9-Aug 15/09	28/07 27/08 9-Apr 9-Oct 14/09 16/09	27/07 31/08 9-Apr 9-Aug 9-Dec 16/09	22/07	9-Oct	16/09	
No	**Constituents**	**Limits specified in SLS-107-2008**	**Brand-A**	**Brand-B**	**Brand-C**	**Brand-D**	**Brand-E**	**Brand-F**	**Compliance with specification**
1	CaO	*	67.09	66.2	67.31	64.31	62.84	66.79	Not applicable
2	SiO_2	*	19.72	17.32	20.94	18.98	20.18	20.32	Not applicable
3	Al_2O_3	*	4.11	3.65	3.54	3.57	3.11	2.41	Not applicable
4	Fe_2O_3	*	3.09	2.77	3.06	2.46	2.09	3.15	Not applicable
5	MgO	5.0_{max}	1.17	2.34	1.22	3.05	1.52	1.54	All brands
6	SO_3	†	1.84	2.29	1.88	2.29	1.67	1.7	All brands
7	Cl	0.10_{max}	0.08	0.06	0.05	0.09	0.1	0.06	All brands
8	LSF	0.66-1.02	1.06	1.4	1.02	1.06	1	1.06	Except three brands
9	IR	1.5_{max}	0.95	0.79	1.12	0.56	2.37	1.86	Except one brand
10	LOI	4.0_{max} §	1.95	2.29	2.15	2.13	6.86	1.14	Except one brand

* Relevant limits are not directly specified but used for the calculation of LSF
† A higher limits of 3.0% (maximum) is permissible if the cement contains C3A in excess of 5.0%.
§ A higher limit of 5.0% (maximum) is permissible if when calcareous minor additional constituents are used.