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

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RESEARCH ARTICLE

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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).

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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].

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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.
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