Investigation of Raw Material for the Manufacturing of White Cement in Darukhula Nizampur Khyber Pakhtunkhwa Pakistan

[1]NOOR-UL-AMIN*, [2]KHURSHID ALI AND [3]TAHIR SHAH
[1]*Department of chemistry, Abdul Wali Khan university, Mardan, Pakistan.*
[2]*Institute of Chemical Science, University of Peshawar, Pakistan.*
[3]*National Center of Excellence in Geology, University of Peshawar, Pakistan.*
noorulamin_xyz@yahoo.com*

(Received on 29th December 2010, accepted in revised form 24th February 2011)

Summary: In this paper we describe the discovery of new source of raw material for the manufacturing of white cement at Darukhuala area Nizampur, Khyber pakhtunkhwa, Pakistan. Limestone and clay of the area under investigation have been utilized in the raw mix designing and clinkerization of white cement. The physical and chemical parameters of resulting cement have been studied and compared with British and Pakistan standard specifications, including compressive strength, setting time, consistency, lechatelier expansion, Blaine and insoluble residue. Three samples of white cement were manufactured by mixing limestone samples in different proportion obtained from different locations of the study area. All the three cement samples were found with close agreement with British and Pakistan standard specification. It was found that the raw material available at the study area meets the standard specifications and the area is feasible for the cement plant installation. The raw material available at the study area is quite sufficient for the running of cement plant.

Introduction

It is a fact that cement is the major building material through out the world, playing a very important role in the construction industry of a country [1-4]. Therefore, the need and use of cement is increasing day by day. The installation of new cement plants is increasing with a rapid pace. The already explored reserves of the raw material for the cement are limited. Therefore, it is very much necessary to explore new reserves of raw material for different types of cement and sites for cement plants installation. Khyber pakhtunkhwa is bestowed with extensive deposits of suitable grade raw material for the manufacturing of cement. Out of twenty-seven cement plants in Pakistan, six are in the N.W.F.P., namely Cherat Cement Company Limited at Nowshera, Lucky Cement Limited at Lucky, Kohat Cement Company Limited at Kohat, Askary Cement Limited at Nizampur, Bestway Cement Company Limited and Mustehkam Cement plant in District Haripur. The annual production of cement in N.W.F.P. is about 4629000 tons [5]. All these cement plants produce high strength Portland cement and sulfate resisting cement. Until now there is no plant in our province which is producing white cement due to the lack of raw material. Therefore white cement is imported from other provinces of the country.

Limestone is a valuable raw material, which is widely used in the chemical, metallurgical and construction industries throughout the world. With huge deposits of limestone in Pakistan, it is immensely used as the major raw material in cement manufacturing. Limestone has two most important constituents such as calcite ($CaCO_3$) and dolomite ($CaMgCO_3$), but also has small amount of iron bearing carbonates. It can be classified into three major groups; organic, chemical and detrital or clastic. Many of the commonly occurring limestones contain organic and chemically precipitated material in varying proportions. Limestone is one of the raw materials used for cement manufacturing. In addition to other raw material such as chalk, clay, marl and shale, limestone may also be used in metallurgical and chemical industries.

The principal constituent of cement clinker is calcium oxide (CaO), which is obtained from naturally occurring calcium carbonate (calcite) which makes up approximately 75-80% of the raw materials mix used in cement clinker. This primary calcareous raw material may contain significant amounts of the other oxides as impurities. The secondary raw material is generally clay (Argil) or shale [6-10].

Introduction to Study Area

Location

The study area covers Darukhula and adjoining areas of Nizampur, District Nowshera, Khyber Pakhtunkhwa, Pakistan. The area is located on survey of Pakistan Topo sheet Nos 43 C/1, 43 C/2, 38 O/13 and 38 O/14 between the Latitudes 33°-45-0" to 33°-47-12 N" and Longitude 72°-0-0" to 72°-2-30 E".

*To whom all correspondence should be addressed.

Darukhula area is located at a distance of about 5 kilometers in the southwest of Nizampur village. Nizampur village is located at a distance of 32 kilometers in south west direction of Attock Bridge which in turn is located on the main GT road at a distance of about 110 km from Peshawar towards East.

The area is approachable by a metalled road which bifurcates from the G.T road near the old Attock Bridge and runs parallel to the Indus River and leads to Nizampur. The area has no rail link. The nearest railway station is Khairabad, located at a distance of about 32 kilometers.

Geology of the Area

The area of study is a part of the Kohat range, which is an extension of the Kalachitta range, west of the Indus River. The rocks of the Kalachitta range, ranging in age from Jurassic to recent, are exposed in the study area. This Range has well-established stratigraphy with eighteen lithostratigraphic units. These units are of marine and non-marine origin [11-13]. Among these eight stratigraphic units (i.e., Samana Suk Formation, Chichali Formation, Lumshiwal Formation, Lockhart Formation; Patala Formation, Kuldana Formation, Kohat Formation and Murree Formation) are exposed in the study area (Fig. 1). Lockhart formation, Murree formation and Lacustrine quarternary deposits are the main focus of this study as far as the cement manufacturing is concerned. Lockhart formation consists of limestone with marl and shale intercalations. The limestone is dark-gray on weathered surface and is massive. It is bituminous and gives off fetid smell on fresh surface. The marl and shale are also dark-gray on weathered surface and light gray to bluish-gray on fresh surface. It has uncomfortably upper contact with Patala Formation in the study area. The Lockhart formation, Murree formation and Lacustrine quarternary deposits of the study area have been evaluated during this study for the cement manufacturing.

In our previous works we have designed high strength Portland cement [14] and sulfate resisting cement [15] from the raw material of the study area which meet the British standard specifications and the area has been declared feasible for the installation of cement plants, manufacturing both these cements. The aim of our study is to give feasibility report of Darukhula area Nizampur and declare a new site for the installation of cement plant, for the manufacturing white cement. For this purpose the limestone and clay available at different locations of the study area has been utilized in the raw mix designing and preparation of white cement in our laboratory. The resulting cement samples were characterized for different parameters, and were compared with British and Pakistan standard specification

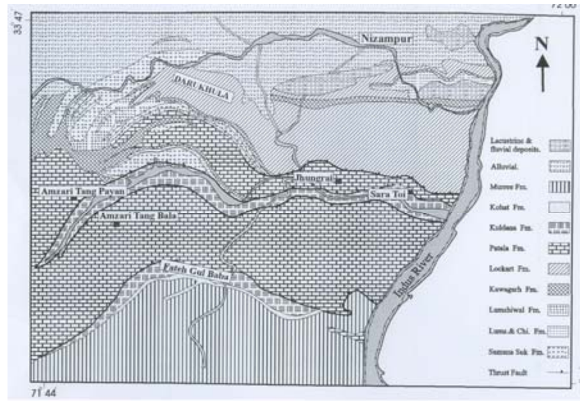

Fig. 1: Geological map of the western bank of the river Indus south of Nizampur showing Darukhula area.

Results and Discussions

Chemical Compositions of Limestone and Clay

In our previous work [16] we have performed the chemical analysis of the limestone and clay, and the results are reported in Table-1. On the basis of physical and chemical characteristics, the Limestone has been classified as High grade limestone (HLS), Darukhula limestone (DLS) and Siliceous limestone (SLS). Similary clay has been classified as Maroon clay (MC), yellowish green (YGC) and green clay (GC).

Table-1: Chemical composition of the studied Limestone at darukhula Nizampur.

Analyte	Wt % (average)Limestone			Wt % (average)Clay		
	High Grade Limestone (HLS)	Darukhula Limestone (DLS)	Siliceous Limestone (SLS)	Maroon Clay (MC)	Yellowish green clay (YGC)	Green clay (GC)
LOI	42.80	39.61	35.90	3.57	2.77	7.53
SiO_2	0.61	4.95	13.64	65.47	57.76	61.24
Al_2O_3	0.66	1.32	0.46	14.56	18.56	14.38
Fe_2O_3	0.23	0.32	0.21	6.82	7.59	6.81
CaO	53.00	49.03	45.19	6.77	8.36	7.49
MgO	0.58	0.83	1.02	1.79	3.87	1.63
Na_2O+K_2O	0.37	0.34	0.56	1.69	0.97	1.52

Chemistry of Limestone

Chemical analysis of the limestone is given in Table-1. High grade limestone (HLS) varies from white to greenish white. It is clear from Table-1, that high grade limestone, as the name indicates, has high amount of calcium oxide. The maximum percentage of CaO present in 100% pure calcium carbonate ($CaCO_3$) is 56 %. The purity of limestone is directly related with loss on ignition (LOI). Table-1 show that the loss on ignition of high grade limestone (HLS) is 42.80%. The highest possible loss on ignition of limestone is 44 % which can be observed in 100 % pure calcium carbonate as given below,

$$\underset{100}{CaCO_3} \rightarrow \underset{56}{CaO} + \underset{44}{CO_2}$$

So from the percentage of CaO and LOI of the studied high grade limestone, it is concluded that this limestone contains roughly 94 % calcium carbonate.

SiO_2 is present in this limestone as impurities in various forms, for example as in cement stone and cherty limestone. It generally has low concentration of SiO_2 which reaches only up to 0.81%. Alumina (Al_2O_3) is the second largest impurity in the limestone. Both the alumina and silica concentration in limestone usually originate from the shales [14]. The alumina content of the studied samples is generally less than 0.66% (Table-1). Iron occurs as impurity in the limestone in the form of oxides and sulfides, which if present in higher amount, then cause deterioration in building construction. In limestone, iron can be homogeneously disseminated during chemical displacement of the calcium bearing iron carbonate or can heterogeneously distribute through iron bearing strata. The Fe_2O_3 content of the studied limestone is less than 0.3 (Table-1). Magnesium oxide (MgO) which is less than 0.6% in the studied limestone is a function of both the magnesium content of skeletal debris and also the other dolomitization processes due to post depositional events. The increase in MgO, in limestone therefore, increases the dolomitic component of limestone, which can not be used for the manufacture of cement because of its high magnesium. Alkalies i.e sodium oxide (Na_2O) and potassium oxide (K_2O) are considered as traces with respect to the pure limestone chemistry. Na_2O and K_2O in the studied limestone are in the range of normal limestone [14]. From the Table-1, it is evident that high grade limestone is very suitable for high strength Portland cement manufacturing, but the requirement of iron can not be fulfilled by adding clay only with it. The only solution to this problem is that some amount of iron rich material like laterite has been used with this limestone. The low alkalies (Na_2O and K_2O) in the high grade limestone are good for cement manufacturing.

Darukhula limestone (DLS), mainly occurring in Darukhula area, is very hard and compact and is generally white in color. The silica and alumina contents of this limestone are high as compared to that of high grade limestone, which suggests the detrital input in these limestone samples. Darukhula limestone contains comparatively greater amount of silica and alumina and smaller amount of calcium which make it more important for high strength Portland cement. The silica and alumina contents of Darukhula limestone can be compensated by clay but the iron content is required to be added. The alkalies in this limestone are in smaller quantities which make it suitable for cement. For the manufacturing of high strength Portland cement some laterite may be used to compensate for the percentage of iron.

Siliceous limestone (SLS) is occurring as minor bodies in Darukhula and its surrounding areas. It is very hard, compact and white in color on fresh surface. This limestone contains relatively high SiO_2 and low CaO and LOI as compared to the other varieties of limestone of Lockhart formation. The high silica content of the siliceous limestone in comparison to high grade and Darukhula limestone (Table-1), suggests that this limestone will require very little clay for cement manufacturing. However the alumina and iron contents of this limestone are smaller than Darukhula limestone and high grade limestone. The lime content of this limestone is considerably low as compared to Darukhula limestone and high grade limestone. However it is in the range of argillaceous limestone [16] and meets the requirement for cement manufacturing. Siliceous limestone on the other hand, is different from both high grade limestone and Darukhula limestone due to a greater percentage of silica. It is not suitable for the manufacturing of high grade Portland cement

Chemistry of Clay

Maroon clay is generally soft and maroon in color, and is widely exposed in the study area and. The average composition of the studied clay is shown in Table-1. The silica rich nature of maroon clay makes it suitable for the manufacturing of all types of high strength Portland. Alkalies are in permissible a range which makes it more suitable for high strength portland cement. Thus this clay can be used with all types of limestone and can also be mixed with other types of clays. Yellowish green clay (YGC) is present in a vast area within Nizampur. Yellowish-green clay having high concentration of silica can be used in very small quantity in cement manufacturing. However its high alkalies contents make it less important and it can be easily used with high grade limestone or in combination with other clays for the manufacturing of high strength Portland.

Green color clay is found in Darukhula and adjoining area of Nizampur. Green color clay is somewhat similar to that of maroon clay with a very little variation in chemical composition. It has calcium oxide in comparatively greater quantity. This clay can be used in combination of all types of clay of the study area for the manufacture of cement

Raw Mix Designing

Raw material from the study area was used for the raw mix designing of white cement. Different raw mixes were prepared in different proportion, three of which were used for further processing and are given in Table-2. It is clear from the table that in the raw mix designing of white cement, all the three types of limestone i.e. high grade limestone, siliceous limestone and Darukhula limestone and only one type of clay i.e. green color clay sampled from the study area were used. In the first blend high grade limestone and siliceous limestone were mixed with high alumina clay. In the second blend only Darukhula limestone was mixed with high alumina clay and silica sand. In this blend no clay of the study area was used. In the third blend for white cement, high grade limestone and green color clay were mixed. In order to bring the MA as per with the standard specification of cement, high alumina clay of chemical composition, given in Table-3, were also mixed in different proportions in these raw mix. The percent composition of the resulting three raw mixes for white cements is shown in Table-4.

Table-2: Blending ratio of Raw Mix for white Cement.

Raw Mix Title	Material Taken	Percentage
Raw mix –1	High grade lime stone	65
	Siliceous Lime stone	18
	High Alumina Clay	9
	Silica Sand	8
	Total	100
Raw mix –2	Darukhula Limestone	85
	High Alumina Clay	10
	Silica Sand	5
	Total	100
Raw mix -3	High grade lime stone	51
	Green colour clay	31
	High Alumina Clay	10
	Silica sand	8
	Total	100

Table-3: Chemical Composition of High Alumina Clay.

Analyte	Percent Composition
SiO_2	50.66
Al_2O_3	47.00
Fe_2O_3	1.56
CaO	1.24
MgO	0.11
Na_2O	0.03
K_2O	0.15
SO_3	0.20

Table-4: Chemical Composition of Raw Mix for White Cement.

Analyte	Percent composition		
	WRM-1	WRM-2	WRM-3
SiO_2	14.85	13.84	14.57
Al_2O_3	4.85	5.89	5.55
Fe_2O_3	0.38	0.46	0.43
CaO	42.65	41.91	42.40
MgO	0.34	0.72	0.58
Na_2O	0.11	0.71	0.14
K_2O	0.42	0.20	0.21
SO_3	0.13	0.05	0.07
LOI	33.00	33.35	33.85
Total	97.98	97.63	97.6
Moduli			
MA	12.76	12.78	13.06
MS	2.84	2.18	2.44
LSF	0.90	0.91	0.89

The raw mixes of different composition were subjected to clinkerization. The clinker thus obtained was analyzed according to British Standard Specifications (BS). The chemical composition the clinker along with the moduli and clinker potential are presented in Table-5. The percentages of major and minor element oxides of all the three cements are almost the same which shows that all types of limestone and clay of the study area are suitable for manufacturing of white cement, when used in different proportion.

Table-5: Chemical Composition of Clinker for White Cement.

Analyte	Percent composition		
	WCR-1	WCR-2	WCR-3
SiO_2	22.30	22.15	22.89
Al_2O_3	8.30	8.09	7.54
Fe_2O_3	0.60	0.62	0.41
CaO	66.60	64.81	65.78
MgO	0.66	0.96	0.56
Na_2O	0.34	0.34	0.18
K_2O	0.60	0.61	0.24
SO_3	0.28	0.28	0.11
LOI	1.50	0.98	0.96
Free lime (CaO)	5.23	4.11	3.65
Liquid Phase	28.14	27.86	24.63
MODULI			
MA	13.83	13.05	18.39
MS	2.51	2.54	2.88
LSF	0.90	0.90	0.90
Clinker Potential			
C_3S	44.23	39.47	42.27
C_2S	30.58	33.75	33.75
C_3A	20.98	20.39	19.29
C_4AF	1.82	1.88	1.25

The cement obtained were tested for all possible physical parameters as per requirement of British Standard Specifications (BS) like blaine, compressive strength, setting time, consistency, and expansion and chemical parameters like insoluble residue, loss on ignition, and percent composition etc and presented in Table-6. This also shows the British and Pakistan Standard Specifications for white cement. The minimum limit of compressive strength for three and seven days is 1740 and 2755 PSI respectively, while the compressive strength of twenty eight days has no standard according to British and Pakistan Standard Specifications. Similarly the minimum initial setting time for White cement is 45 minutes and the maximum final setting time is 10 hours, while the minimum range of consistency is 28 %. The upper limit of lechatlier expansion is 10 mm while the minimum limit of blaine is 2250 Sq. cm/gram according to British and Pakistan Standard Specifications. The upper limit of loss on ignition and insoluble residue is 4.7 % and 1.5 % respectively.

Table-6: Physical and Chemical Properties of White Cement.

Parameters		Results			
		WCM-1	WCM-2	WCM-3	Standard (BS %)
Physical Testing					
Compressive Strength (PSI)	**3 Days**	4150	3945	4100	1740 PSI (Min)
	7 Days	4825	4580	4850	2755 PSI (Min)
	28 Days	5640	5860	5890	No standard
Setting Time (minute)	**Initial**	150	124	145	45 min (Min)
	Final	240	280	265	10 Hours (Max)
Consistency (%)		28	29	28	28% (Min)
Expansion (Lechatlier) mm		1.69	1.92	1.68	10mm (Max)
Blaine (sq cm/gram)		4350	4200	4500	2250 Sq cm/g (Min)
Chemical Testing					
Loss on Ignition (%)		0.77	0.78	0.88	4.7 (Max)
Insoluble Residue (%)		0.9	0.27	0.47	1.59 (Max)

Experimentation

The chemicals used were moisture free and of analytical grade, Merck or BDH. The glass wares used were mostly Pyrex. All of them were used after thorough cleaning with distilled water and drying in the oven. The detail of glassware is given along its name.

Raw mix designing was made very carefully by combining different limestone and clay samples in different proportion keeping in view the chemical composition of the resulting raw mix. The raw mixes were named as WRM-1, WRM-2 and WRM-3.

Analysis of the Samples

Chemical Analysis of Raw Mixes

Analysis of raw mix was carried out through atomic absorption spectrometer (3300 Perkin Elmer) and UV/VISIBLE Spectrophotometer (SP8-PYE UNICAME). For this purpose two types of solutions (A & B) of stock solutions were prepared. Stock solution 'A' was prepared by fusing appropriate amount of powdered sample with NaOH in the nickel crucible and final dissolution in 1000 ml distilled water. This solution was used for the determination of SiO_2 by the method of ammonium molybdate and Al_2O_3 by the method of 8-Hydroxyquinoline by using the Pye-Unicam UV/visible spectrophotometer [17]. Stock solution 'B' was prepared by decomposing the appropriate powdered sample in Hydrofluoric-perchloric acids mixture and final dissolution to 250 ml with distilled water. This solution was used for the quantitative determination of Fe_2O_3,CaO, MgO, K_2O and Na_2O at a wavelength 248.3 nm, 422 nm, 285.2 nm, 766 nm and 589 nm respectively, using certified standards of by using Perkin Elmer atomic absorption spectrophotometer.

After chemical analysis, the raw mixes were subjected to clinkerization. For this purpose raw mixes were made wet with water and small pellets ranging 5-10 mm in size were made. The pellets were dried in oven at 105 C° up to constant weight and then in furnace at 1250 C° for one hour. The clinkers were named as WCR-1, WCR-2 and WCR-3. The clinker samples after complete analysis were converted in to cement by grinding in to fine powder with 5% gypsum. The three Cement samples were named as WCM-1, WCM-2 and WCM-3. The cement samples were tested for all possible physical parameters as per requirement of British and Pakistan Standard Specifications [18] like blaine, compressive strength, setting time, consistency, and expansion and chemical parameters like insoluble residue, loss on ignition, and percent composition.

Chemical Analysis of Clinker and Cement

Clinker and cement were analyzed using X-Ray fluorescence spectrophotometer for which glass bead was formed from the test material. One gram powdered material was mixed with six gram of dilithium tetraborate (spectromelt, Merck) in a platinum crucible to which 0.001g of lithium bromide (Merck) was also added. The ingredients were thoroughly mixed. The crucible was heated in a muffle furnace at 1150 C° for 15 min. Then the content of the crucible was transferred to a platinum mould inside the furnace and shaked to acquire the shape of the mould. The mould was cooled and the glass bead was obtained. After calibrating the XRF with certified standards, the sample bead was subjected for analysis in the machine and the result was obtained.

Sulphuric anhydride was determined gravimetrically by fusing the samples with fusion mixture (Na_2CO_3+K_2CO_3). The SO_3 in the form of Barium sulphate ($BaSO_4$) was obtained and ignited in the muffle furnace. Loss on ignition of all the collected samples was determined using muffle furnace by heating the samples at 400 C° for 30 min and then at 1000 C° for 2 hours up to constant weight in a muffle furnace.

All these analysis were performed by using the facilities at the National Center of Excellence in Geology, University of Peshawar Pakistan.

Conclusion

Three types of white cement were prepared from the raw material obtained from study area. All the three cement samples were found in accordance to the British and Pakistan standard specification. The area is fit for cement plant installation. All the available material is easily approachable and can be used in proper ratio to give cement of standard quality [19, 20].

References

1. A. Bentur, *ASCE Journal of Materials in Civil Engineering*, **14**, 1 (2002).
2. S. K. Antiohos, A. Papageorgiou, V. G. Papadakis abd S. Tsimas, Influence of Quicklime Addition on the Mechanical Properties and Hydration Degree of Blended Cements containing Different Fly Ashes Construction and Building Material, accepted, (2007).
3. Noor-ul-Amin, *Journal of the Chemical Society of Pakistan*, **32**, 481 (2010).
4. Y. J. Kim, J. H. Choi, J. H. Kim, C. S. Lee and T. I. Qureshi, *Journal of the Chemical Society of Pakistan*, **32**, 7 (2010).
5. A. Hussain. Cement raw materials in the North West frontier province Pakistan, Geological Survey of Pakistan, SEGMITE-UNESCO (IGCP) Int. Symp. Proc, 35-39, (1995).
6. Anon. Raw material in Cherat cement, project area, District Peshawar, Pakistan. Cherat Cement Company Brochure, 3-4, (1995).
7. E. Fundal, *World Cement*, **27**, 63 (1996).
8. Hewlett, P.C. Lea's chemistry of cement and concrete. Arnold London. 40-50, (1998).
9. G. C. Bye, Portland cement composition, production and properties. Thomas Telford limited London. 145-190, (1999).
10. F. M. Miller, Conway, T. Use of ground granulated blast furnace slag for reduction of expansion due to delayed ettringite formation. Cement Concrete and Aggregate. 25, (2003).
11. A. Hussain, R.S. Yeats. Stratigraphy and structural events around the southern margin of Peshawar basin, Pakistan. Geol. Bull. Univ. Pesh. **22**, 45-54. (1989).
12. P.W, Birkeland. Soils and Geomorphology. Oxford University Press, New York, 200-250, (1999).
13. M. D, Hylland, M. Riaz and S. Ahmad. Stratigraphy and structure of the southern Gandghar range Pakistan. Geol. Bull. Univ. Peshawar 1-14, (1988).
14. N. Amin, M. T. shah and K. Ali, *Chinese Journal of Geochemistry*, **28**, 3, (2009)
15. N. Amin, M. T. shah and K. Ali, *Magazine of Concrete Research*, **61**, 10 (2009).
16. K. Ali, N. Amin and M. T. shah, *Chinese Journal of Geochemistry*, **27**, 3, 2008).
17. P. G. Jeffery and D. Hutchison, Chemical methods of rock analysis. Pergamon Press, New York. 122-130 (1986).
18. European Standard EN 196-3 Methods of testing cement-Part 3: Determination of setting time and soundness, (2005).
19. Noor-ul-Amin and K. Ali, *Journal of the Chemical Society of Pakistan,* **33**, 147 (2011).
20. Noor-Ul-Amin and S. Sultana, *Journal of the Chemical Society of Pakistan,* **33**, 171 (2011).