Investigation of raw materials for cement industry of Upper Hunza, Gilgit-Baltistan, Pakistan.

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Abstract: Limestone is the main constituent as raw material used in manufacturing of cement. In this study the limestone deposits of Khyber Karimabad, Passu and Morkhun-Gircha Upper Hunza Valley, Gilgitbaltistan were evaluated for its suitability to be used raw material for cement industry through chemically and mineralogical techniques. The representative limestone’s samples from different geological beds of the proposed area were collected. These samples were investigated petrographic study, X-ray diffraction (XRD), Scanning electron microscopy coupled with X-ray diffraction (SEM-EDX), X-ray fluorescence (XRF) and reserve estimation of the proposed deposit was carried out using Geological Information System (GIS). Geological review shows that there is a good potential for industrial-grade limestone, the composition of this limestone can be generally expressed in terms of CaO, MgO, Al₂O₃, and SiO₂, that may be used in place of similar commodities of good quality cement raw materials. After analysis of results, it is concluded that limestone and other raw materials of Khyber Karimabad (KKLS) are is of good quality and can fulfills the international standards of cement and while limestone and other raw materials of Passu and Morkhun-Gircha is not suitable to be used as raw material for cement industry.

Keywords: Limestone, dolomite, mineralogical, elemental, Hunza Valley.

1. Introduction

In cement manufacturing about thirty different raw materials are used but limestone and clay are the primary raw materials [4]. In addition to this, secondary raw materials include clay, shale,
laterite, gypsum etc. Cement plant can be established at any region where limestone and clays are sufficient for forty years [5]. To evaluate the suitability of raw materials for cement plant it is very important to observe their chemical and mineralogical properties [6]. In this research study raw material were investigated chemically and mineralogical for cement manufacturing in Gilgit-Baltistan, Pakistan.

![Location map of the study area](image)

**Figure 1.** Location map of the study area

2. Geology of study area

Upper Hunza Valley (UHV) is located along the northern most extremity of western Gilgit-Baltistan. Hunza connected with Gilgit through Karakoram Highway (KKH) [3, 7]. It is border with China in north, with Ghizer in south and southwest and with Gilgit in south and southeast [7]. It is about 150 km from Gilgit, a capital city of Gilgit-Baltistan and constitutes southern margin of Eurasian plate [8]. These rock formations range from Permian (Gircha fm) to early Tertiary (Shahnoz Cong). Khyber Karimabad limestone deposits fall in Gojal formation [9]. This formation is mainly composed of extensive carbonate deposit. The age of this deposit is Triassic but later on scientists proved that the
age of this unit starts from Permian [10]. The detail information of area are describe in geological map of the area are shown in figure 2.

![Geological map of Upper Hunza Valley (R.A Khan Tahirkheli)](image)

**Figure 2.** Geological map of Upper Hunza Valley (R.A Khan Tahirkheli)

### 3. Materials and methods

#### 3.1. Field and lab works

Six representative Samples were collected in bags with noting coordinates from Upper Hunza Valley, Gilgit-Baltistan by channel sampling methods. The collected samples were prepared using crusher and grinder JXC of model LYN to produced mesh size of 120 micrometer. The ground sample was prepared for investigation purpose using conning and quartering by John Riffle box.

#### 3.2. Cement ratios

Cement manufacturing need preparation of suitable raw mix balancing of many oxides are very important. These oxides are CaO, SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$. These oxides are very important for proper burning and for the required qualities of final product. To achieve the balance of these oxides many indices are required. These indices are silica ratio (SR), lime saturation factor (LSF) and alumina ratio (AM) [11].

These ratios are given by

\[
SR = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \quad (1)
\]

\[
LSF = \frac{CaO}{2.8SiO_2 + 1.18Al_2O3 + 0.65Fe_2O_5} \quad (2)
\]
The standard range of SR (2.0-3.0) and AM (1.0-4.0) [12]. The calculated cement ratios during the research are, silica ratio is 2.375, and alumina mean is 2.45. These ratios are very close to standard ratios where these raw materials can be used for cement preparation.

3.3. Material characterizations

X-ray diffraction (XRD) analysis was used to find the mineralogical composition of raw materials. The chemical, mineralogical and thin sectioning have been carried out in Geological survey Pakistan laboratory (GSP) Islamabad. Minerals were identified by X-ray diffraction machine (XRD) X’PERT-PRO MPD with Cu Kα (λ = 0.15406 nm) irradiation. Chemical analysis was carried out by X-ray fluorescence machine (XRF) model Philips (type PW, 1404). Polarizing light microscope of model LEICA DM 750P was used to find minerals and their arrangement of particles based on optical properties of minerals in thin section analysis. Energy dispersive x-rays (EDX) model (Oxford INCA x-act) were used for elemental analysis of raw materials.

3.4. Evaluation of suitability of raw materials

In order to evaluate the suitability of raw materials for cement manufacturing their chemical and mineralogical results were compared with international standard especially with British standards (BS) because in Pakistan cement is on the basis of British standard [13].

4. Results and discussions

4.1. Chemical analysis

The chemical analyses were carried by X-ray fluorescence (XRF) to investigate percentages of main oxides. They were then compared with international values to evaluate their suitability as raw materials.

4.1.1. Chemical composition of Passu deposit

Table 1 showed that the composition of MgO is 35.135%. The maximum concentration of MgO for cement should be less than 5% according to International cement standards. Because of MgO concentration, the Passu limestone is discarded and concluded that this deposit is not suitable for cement manufacturing.

4.1.2. Chemical composition of Morkhun-Gircha deposit

The chemical composition of this deposit shows that MgO is 35.337% that is unsuitable for cement manufacturing. Hence, the deposit of this region is dolomitic in nature. For manufacturing of cement, the percentage of MgO in limestone must be less than 5%. If it is greater than 5% then the limestone will be unsuitable for cement manufacturing.

| Chemical compounds | Passu Deposit Percentage | Chemical compounds | Morkhun-Gircha Deposit Percentage |
|--------------------|--------------------------|-------------------|----------------------------------|
| CaO                | 63.8817                  | CaO               | 59.9691                          |
| MgO                | 35.1375                  | MgO               | 35.3375                          |
| SiO₂               | 0.3017                   | SiO₂              | 0.6217                           |
| Fe₂O₃              | 0.2272                   | Fe₂O₃             | 1.4076                           |
| Al₂O₃              | 0.1625                   | Al₂O₃             | 0.1898                           |
| CuO                | 0.1398                   | CuO               | 1.6617                           |
| SO₃                | 0.0936                   | SO₃               | 0.7547                           |
| SrO                | 0.0377                   | SrO               | 0.0182                           |
| P₂O₅               | 0.0183                   | P₂O₅              | 0.0311                           |
### 4.1.3. Composition of Khyber Karimabad limestone deposit.

Table 2 shows that the percentage of MgO is within the standard limit and meets the international standards. Moreover, the percentage of CaO also fulfills the international standards. Therefore, it has concluded that the lime Khyber Karimabad limestone (KKLS) can be used for manufacturing of indigenous cement.

**Table 2. Composition of Khyber Karimabad limestone deposits**

| Name | KKLS1 | KKLS2 | KKLS3 | KKLS4 | KKLS5 | KKLS6 | Ave. value | Std. values |
|------|-------|-------|-------|-------|-------|-------|------------|-------------|
| SiO₂ | 3.14  | 2.12  | 2.61  | 4.98  | 3.18  | 2.24  | 3.04       | 3.64        |
| TiO₂ | 0.1   | 0.01  | 0.09  | 1.36  | 0.00  | 0.01  | 0.26       | 1.3         |
| Al₂O₃| 0.02  | 2.15  | 1.27  | 1.93  | 0.04  | 0.05  | 0.91       | 1.55        |
| Fe₂O₃| 0.40  | 0.27  | 0.34  | 0.60  | 0.25  | 0.37  | 0.37       | 1.90        |
| MnO  | 0.16  | 0.22  | 0.20  | 0.17  | 0.01  | 0.02  | 0.13       | 0.5         |
| MgO  | 2.01  | 1.44  | 0.09  | 1.60  | 0.31  | 16.44 | 3.64       | 3.0-3.5     |
| CaO  | 50.92 | 47.35 | 55.60 | 47.20 | 55.59 | 36.35 | 48.83      | 44-45       |
| Na₂O | 0.30  | 0.11  | 0.21  | 0.40  | 0.13  | 0.16  | 0.218      | 0.15        |
| K₂O  | 0.03  | 1.33  | 0.06  | 0.02  | 0.01  | 0.01  | 0.39       | 0.15        |
| P₂O₅ | 0.01  | 0.50  | 0.03  | 0.22  | 0.00  | 0.01  | 0.12       | 0.16        |
| LOI  | 45.48 | 43.34 | 42.01 | 44.19 | 43.48 | 46.34 | 44.14      | 42.22-44    |

### 4.1.4. Composition of Khyber Karimabad clay deposit

Table 3 shows that the silica content of in Khyber Karimabad clay (KKCL) was higher than standard values hence this clay is unsuitable for cement manufacturing. Due to this reason, the alternative of clay was very important to investigate at the research area. The alternative to the clay is slate. After chemical analysis of clay, chemical analysis of slate was carried out to check its suitability to be used for cement production.

**Table 3. Composition of Khyber Karimabad clay deposit**

| Mineral | KKCL | Normal Clay |
|---------|------|-------------|
| SiO₂    | 60.55| 50.33       |
| Al₂O₃   | 17.3 | 19.17       |
| Fe₂O₃   | 7.1  | 6.50        |
| MgO     | 5.34 | 3.77        |
| CaO     | 3.55 | 1.43        |
| Na₂O    | 0.00 | 0.81        |
| K₂O     | 6.66 | 2.32        |

### 4.1.5. Alternate to clay:

Since the chemical analysis of clay showed that it could not be used for cement manufacturing due high silica content, therefore alternatives to clay called slates were investigated from the field region. There is huge quantity of slates at the region of Khyber Karimabad region. This slate can be used in place of clay to acquire the required standard. For this reason, the chemical composition of slate was compared with standard values and to check their suitability to be used as cement raw material. Table 4, shows the chemical composition of slates. From the chemical composition, it was confirmed that the slate can be used as raw material for cement because it fulfills the international standards. This
shows that the slate can be used for cement manufacturing in place of clay. Hence, there is no any problem of raw materials at the research area for cement manufacturing. Hence, the raw materials can be used for manufacturing of indigenous cement to fulfill the local requirements.

Table 4. Composition of Passu slate deposit

| Mineral | PS 1   | PS 2   | Normal shale |
|---------|--------|--------|--------------|
| SiO₂    | 66.71  | 68.18  | 58.10        |
| Al₂O₃   | 14.57  | 12.93  | 15.40        |
| Fe₂O₃   | 6.54   | 5.60   | 4.02         |
| MgO     | 3.09   | 2.69   | 4.44         |
| CaO     | 1.60   | 2.20   | 3.11         |
| Na₂O    | 1.91   | 2.00   | 4.54         |
| TiO₂    | 0.69   | 0.66   | *            |
| MnO     | 0.20   | 0.16   | *            |
| P₂O₅    | 0.23   | 0.22   | *            |
| K₂O     | 2.68   | 2.1    | 2.12         |
| LOI     | 2.78   | 3.19   | *            |

Note: * show traces of TiO₂, MnO, P₂O₅, and loss of ignition less than 0.1%.

4.2 Mineralogical composition of raw materials

4.2.1 Mineralogical composition of limestone

X-ray Diffraction (XRD), model (X’PERT-PRO MPD) with Cu Kα (λ = 0.15406 nm) irradiation, was used for mineral identifications. The identified minerals are present in the following graphs by XRD software X’pert high score. The achieved pattern identified the phases of calcite, dolomite, ankerite and wollastonite, which show intense peaks at 30°, 33.4°, 47.2° and 49°. The XRD pattern of KKSL-5 and KKSL-6 are very sharp which indicates the crystalline nature of raw materials. Figure 1(a)-(b) is the XRD result of KKSL-5, which shows that Khyber Karimabad contains major minerals like calcite, ankerite, dolomite, wollastonite and many other minerals in minor amount. In all samples, calcite is present as major mineral. It is very important to note that the limestone must not contain greater amount of quartz. Otherwise, this will cause the grinding and crushing of limes difficult.

The XRD result of KKSL-5 shows that Khyber Karimabad contains major minerals like Dolomite, Moscovite, Biotite and many other minerals in minor amount. In this sample Dolomite is present in greater percentage and will cause problem but this can be solved by blending with other samples of limestone.

4.2.2 Mineralogical composition of slate:

Figure 1 shows the different peak of different mineral in different samples of Khyber Karimabad limestone (KKSL-5, KKSL-6) and Passu slate (PS-1, PS-2). Figure 1(c)-(d) shows that calcite is the major mineral present in Passu slates with biotite, muscovite and other minerals as minor minerals. The XRD results show that the slates can be used for cement manufacturing as raw materials alternative to Khyber Karimabad clay. This result also shows that the mineralogy of slates fulfills the international standards of slate and shale that are used in cement manufacturing.
4.3 Petrography

The petrographic study of limestone samples from Khyber Karimabad area was carried out. The limestone is a medium to fine and clastic texture. In thin section analysis different types of minerals present in rocks can be found out on the basis of their optical properties under polarizing microscope. In this study four samples were analyzed to find the minerals present in limestone. This figure 4(a) shows that KKSL-1 contains quartz and volcanic clasts, figure 4(b)-(c) contains calcite crystal while figure 4(d) contain micritic limestone. However, quartz is present in small quantity therefore it will not create grinding problem during cement manufacturing.
Figure 4. Texture mineralogy of (a) shows different volcanic clast, (b) shows calcite crystal, (c) shows show grain of calcite and calcite crystal and (d) shows micritic limestone.

5. Conclusions
The detailed field and laboratory investigations of limestone and other raw materials were carried out of Khyber Karimabad (KKLS), Passu and Morkhun-Gircha deposits. After analysis of results it concluded that Khyber Karimabad (KKLS) deposit is of good quality which can fulfill the international standards of cement. Therefore, it can be used for manufacturing of cement. Moreover, the reserve of this region is very large where a cement plant can easily be established for production of indigenous cement. However, deposits of Passu, Morkhun-Gircha are not feasible for cement manufacturing because these deposits contain low percentage of CaO and high percentage of MgO. This showed that the limestone of these regions is dolomitic in nature.

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