

## Exploitation Of Some Raw Minerals For Increasing Productivity Of Ordinary Portland Cement.

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### ABSTRACT

This study aims to utilize a local natural mineral material from different places in western area of Saudi Arabia namely, (Osfan, Alkamel, Wadi starah, Khulais, Jeddah and Alghowla) as a partial replacement of ordinary portland cement (OPC) in order to increase the productivity of ordinary portland cement (OPC), minimizing the problems associated with its industry involving energy consumption and air pollution. In addition to the reference sample (C:100% wt. OPC), other six mixes were prepared from 75% wt. of OPC and 25 wt. %) of each raw mineral, they are denoted as (C1, C2, C3, C4, C5 and C6). Different cementing, sintering, chemical and mechanical properties of the prepared mixes were tested according to the international standard specifications. It was concluded that OPC blended with 25 wt.% of local natural minerals from Jeddah (C5), Wadi starah (C3) and Alkamel C2 show outstanding cementing and mechanical properties compared with the reference sample. They recorded relatively longer setting time ranges from (55-160, 52-145, 52-144) minutes compared with the reference sample (C) which recorded only (48-120) minutes, relatively higher percent of combined water at different ages of hydration (23.75-28.23, 20.84-24.59, 16.34-19.31%), respectively whereas the reference sample (C) recorded (15.59-18,00 %), higher heat of hydration (81-97, 77-94, 75-90 cal/g), respectively compared with reference sample which recorded (70- 85 cal/g ), higher bulk density (1.61-1.96, 1.66-1.84, 1.65-1.84 g/cm<sup>3</sup>), respectively compared with the reference sample that recorded (1.61-1.84 g/cm<sup>3</sup>), lower apparent porosity (15.02-10.41, 16.25-12.75, 17.40-13.96%), respectively whereas the reference sample noted (24.11-14.39%) and relatively higher values of compressive strength (90-125, 80-120, 75-113 kg/cm<sup>2</sup>), respectively compared with the reference sample which recorded (60-110 kg/cm<sup>2</sup>). The remaining samples C1, C4 and C6 showed less cementing and mechanical properties compared with the reference sample (C). The improved properties of C5, C3 and C2 are due to their relatively higher content of portlandite mineral (Ca(OH<sub>2</sub>)) one of the main hydration of cement, as well as their relatively better microstructure.

**Keywords:** local minerals, cement, compressive strength, XRD, SEM.

### INTRODUCTION

Cement industry is one of the strategic industries in the world. The industrial revolution began to use of cement since 1911 as a hydraulic link and as basic component of various types of concrete and mortar. Many historical developments in cement industry and innovations succeeded in converting this cement material into a high technical product. The technology has different applications and faces many of the challenges posed by the high cost of energy

(thermal or electric) and the environmental impact of pollution (i.e. The thermal and dust emissions) during the various processes in the cement industry.

Through experiments and research, many additions were used to develop and improve cement properties, including different quantities of metals, which are added during the final phase of the cement industry. With these additives, various types of cement can be obtained with a variety of properties, such as natural limestone, volcanic and pozzolanic, and additives of industrial origin such as by-products of the steel industry (blast furnace slag, silica fume) and fly ash originate from thermal power plants.

In recent years the world in general and the Kingdom of Saudi Arabia particularly have shown tremendous urban development which necessitates the consumption of huge quantities of building materials, particularly portland cement, this led scientists and researchers in this field to intensify their research in order to improve and develop the efficiency of portland cement. However, the increase in production collides with many environmental and economic problems associated with the cement industry. As the raw materials of the cement industry are the clays (aluminum silicate) and limestone (calcium carbonate), it is produced during the heating of these materials during the industry, the accumulation of large amounts of gases, especially carbon dioxide. Almost half of the raw material was found to be lost in the form of gases, leading to severe pollution of the environment and the consumption of huge amounts of energy during the production process. This has led researchers and producers to seek natural sources to increase production without the need for additional industrial processes. Many scientists used some industrial wastes as mentioned below as additives to cement, such as iron industry wastes, remnants of the silicon alloy industry, some ceramic wastes, metallurgical and petroleum wastes, and coke ash, rice straw ash and barley straw ash. Exploitation of natural ores to achieve this goal. The materials used must have a pozzolan nature (i.e., the total ratio of silica oxides, alumina and iron exceeds 70% of the sample components). These components are therefore correlated with portland cement components.

N. M. Khalil et al [1] studied the effect of rice husk, barely husk and coal fly ashes on the cementing properties of portland cement. They could improve the characteristics of portland cement through addition of 15-20 wt. % of either additive. Many research works [1-25], studied the effect of pozzolanic materials either as agriculture wastes (rice husk and barely husk ashes), industrial wastes (silica fume wasted during ferrosilicon industry, blast furnace slag or incinerator ashes) as well as raw minerals (clay, kaolin, quartz) on the workability of the ordinary Portland cement. These additives assist the permeability, workability and durability of the hardened cement pastes.

H. Lindgreen et al [26] studied the effect of addition of ultrafine layer silicates on the microstructure of portland cement pastes and mortars. They concluded that the cement pastes containing palygorskite and bentonite show a relatively better open structure compared with the pure or kaolin added cements. The addition of silica fume results in a significant number of closed pores. The cementing characteristics depend on the degree and duration of the drying process.

L. S. Wong et al [27] used kaolin, silica and calcium chloride as additives to portland cement. They recorded that the addition of kaolin results could refine the pores of stabilized peat. R. Snellings et al [28] studied the supplementary cementitious materials. They stated that the current widespread use of calcium silicate or aluminate hydrate binder systems in the construction industry finds its roots in the Antique world where mixtures of calcined lime and finely ground reactive aluminosilicate materials were pioneered and developed as competent

## inorganic binders

W. Mechti et al [29] employed finely ground sand and calcined clay as additives to portland cement. They could achieve a relatively better mechanical property through addition of 15 wt. % of the additives.

R. Kaminskas et al [30] studied the effect of fly ash and silica clay composite on hydration behavior of OPC. They recorded an improvement in cement hydration as a result of increasing the amount of the formed hydrated product (calcium silicate hydrate) namely stratlingite ( $C_2ASH_8$ ) and hydrogarnet ( $C_3AS_xH_{6-2x}$ ).

D. Bondar et al [31] reported about different natural pozzolans. They added different natural raw materials e.g. lime, kaolinite and other pozzolanic additives to OPC. They investigated the hydrated mixes with XRD and SEM to determine the gel phase. They could substitute CaO,  $Al_2O_3$  and  $SiO_2$  content in natural pozzolan by adding some mineral additives for improving the cementing properties.

P. Sandra et al [32] reported about fly Ash a wasted during coal combustion as a type of artificial pozzolan, which improves the durability and microstructure of the hydrated cement. They studied the mineralogical composition of the hydrated cement pastes and correlating them with their physicommechanical properties.

A. Rashad [33] used Disposal of fly ash (FA) resulting from the combustion of coal-fired electric power stations as a partial replacement of cement in traditional paste/mortar/concrete mixtures based on portland cement (PC). He could improve the different mechanical and physical properties of portland cement pastes through fly ash additions.

A. Usón et al [ 34] studies five solid wastes, namely, municipal solid waste (MSW), meat and bone animal meal (MBM), sewage sludge (SS), biomass, and end-of-life tyres (ELT), in the cement industry.

Wewei Han et al [35] studied the borosilicate glass waste as a cement additive in their investigation to improve the properties of cement and concrete.

Ravil Z. Rakhimov et al [36] studied, the effect of marl on the properties of hardened portland cement they have added (5-20%) which shown better result.

Rui Yu and Zhonghe Shui [37] have studied the possibility of recycled cement additive on the hydration and microstructure development of cement-based materials.

K. Lin et al [38] studied, the possibility of using limestone wastes, iron oxide sludge and catalysts wastes in different percentages as raw materials to produce environmentally friendly cement and shown a good cementing, sintering and mechanical results.

This work aims to utilize some local natural mineral materials, wide spread in the western area of KSA, as additives for ordinary portland cement and to study their effect on different cementing, sintering, chemical and mechanical properties of its hardened pastes.

## MATERIALS AND EXPERIMENTAL

### Materials

The starting materials used in this study are:

- Ordinary Portland Cement from Alsafwa Cement Company, west KSA.
- Local mineral materials collected from six locations in western area of Saudi Arabia namely; (Osfan, Alkamel, Wadi starah, Khulais, Jeddah and Alghowla).
- Some chemicals namely; methyl alcohol and diethyl ether were used for stopping the hydration of the cement pastes at different curing times of cement hydration 3, 7, 28 and 90 days

### Experimental

#### *Processing of local mineral materials*

The six samples of natural minerals were grounded, sieved to a particle size smaller than 1 mm. The chemical and mineral composition of collected samples were carried using Philips X-ray fluorescence (XRF) machine) and X-ray diffractometer (XRD), D8 ADVANCE, Bruker, Germany, (diffractometer with Ni filtered Cu Ka radiation operating at 30 mA and 40 kV).

#### *Preparation of cement pastes*

Different cement mixes were prepared from OPC with a fixed content (25 wt.%) of local minerals as given in Table (1) using the optimum amount of mixing water.

**Table 1. Composition of (OPC) and raw minerals**

| Sample | Ordinary portland cement (%) | Additive (% wt.)          |
|--------|------------------------------|---------------------------|
| C      | 100                          | Control without additives |
| C1     | 75                           | 25 % Osfan area           |
| C2     | 75                           | 25 % Alkamel area         |
| C3     | 75                           | 25 % Wadi Starah area     |
| C4     | 75                           | 25 % Khulais area         |
| C5     | 75                           | 25 % Jeddah area          |
| C6     | 75                           | 25 % Algowla area         |

The prepared batches were dry-mixed separately for 2 minutes, then further mixed in an electric mixer for 15 minutes to assure homogenous mixing. Cubic samples of each batch were prepared using the optimum amount of mixing water (water of consistency), then pouring in a stainless steel cubic mold (1cm x 1cm x 1cm), molds were kept in a 100 % relative humidity atmosphere. After 24 hrs., the cubes were demolded, and the produced cement cubes were kept under water until time of investigation (3, 7, 28 and 90 days). At each age of hydration, the sintering (bulk density and apparent porosity), mechanical strength and heat of hydration were tested. The hydration process was stopped at each age of hydration using methanol-ether mixture. The chemically combined water was determined after firing at 900°C according to the following equation:

$$\% \text{ of chemically combined water} = \frac{\text{Wt. before ignition} - \text{Wt. after ignition} \times 100}{\text{Wt. after ignition}}$$

#### *Characterization of the prepared cements*

- Surface area was determined using Blain air permeability apparatus.
- Water of consistency and setting time were determined using Vicat apparatus [39,40].
- Bulk density (B.D) and apparent porosity (A.P) were measured using kerosene displacement method [41].
- Heat of hydration was determined according to the International Standard using [42].

- Mechanical properties cold crushing strength (C.C.S) was determined using a compressive strength testing machine (ELE International compression tester 1881 A0030) [43].
- The phase composition of the hydrated cements were followed using XRD-technique.
- The microstructure of some selected samples were depicted using Scanning electron microscope (SEM-JEOL JAX-840A electron microanalyzer -Japan).

## RESULTS AND DISCUSSION

### Surface area:

Table (2) shows the relatively higher fineness of Jeddah sample (3100 cm<sup>2</sup>/g), Wadi starah sample (3090 cm<sup>2</sup>/g) and Alkamel sample (3060 cm<sup>2</sup>/g) compared with the reference and other samples (3010-3020 cm<sup>2</sup>/g).

**Table 2. Surface area of OPC and raw minerals**

| Sample | Sample area | Surface area cm <sup>2</sup> /g |
|--------|-------------|---------------------------------|
| C      | Reference   | 3100                            |
| C1     | Osfan       | 3020                            |
| C2     | Alkamel     | 3060                            |
| C3     | Wadi Starah | 3090                            |
| C4     | Khulais     | 3020                            |
| C5     | Jeddah      | 3100                            |
| C6     | Alghowla    | 3010                            |

### Chemical composition of OPC and raw minerals

The XRF analysis in Table (3) indicates that the cement is composed mainly of CaO (63.50%) and SiO<sub>2</sub> (24.50%) with considerable contents of Fe<sub>2</sub>O<sub>3</sub> (4.02%) in addition to little contents of other constituents e.g., Al<sub>2</sub>O<sub>3</sub> (7.00%), MgO (0.08%), SO<sub>3</sub> (0.40%), Na<sub>2</sub>O + K<sub>2</sub>O (0.50%), and ignition loss (3.01%). According to the American classification, the cement used in this research work is ordinary portland cement, Type I [44].

**Table 3. Chemical composition of OPC**

| Chemical composition           | OPC % |
|--------------------------------|-------|
| CaO                            | 63.50 |
| SiO <sub>2</sub>               | 24.50 |
| Al <sub>2</sub> O <sub>3</sub> | 7.00  |
| Fe <sub>2</sub> O <sub>3</sub> | 4.02  |
| MgO                            | 0.08  |
| Na <sub>2</sub> O              | 0.25  |
| K <sub>2</sub> O               | 0.25  |
| SO <sub>3</sub>                | 0.40  |
| LOI                            | 3.01  |

Table (4) shows the chemical constituents of the raw minerals under study. It is clear from this table that the raw mineral of Osfan, Alkamel, Khulais, Jeddah, and Alghowala are consisting mainly of aluminosilicate minerals. They are mainly composed of silicon oxides, aluminum oxide and iron oxide as well as small amounts of other oxides such as calcium, magnesium, titanium, potassium and sodium, which means that these materials have a pozzolan nature. The table shows that Jeddah area is the highest in pozzolanity nature, the total oxides of silicon, aluminum and iron reaching 89.30%, followed by Alkamel area, reaching 88.26%, Osfan area

reaching 80.25%, Khulais area reaching (73.55%), and finally the Alghowla raw mineral reaching (67.52%). On the other hand, Wadi Satarh raw mineral differs in its chemical composition from the previous five raw minerals. It contains a relatively high percentage of calcium oxide (42.11%), in addition to an increase in the percentage of loss of ignition (31.73%) which indicates that it consists mainly of calcite mineral ( $\text{CaCO}_3$ ) which is an essential constituent of cement industry it also contains appreciable amount of silicon oxide (12.5%), aluminum oxide (5.12%) and iron oxide (3.11%), these indicating that it may also contain a percentage of kaolinite mineral ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ ), which is also one of the basic raw materials used in the cement industry in addition to limestone (calcite).

**Table 4. Chemical composition of the local mineral samples**

| Mineral area | Chemical composition (%) |                         |              |                         |              |                |                      |                       |       |
|--------------|--------------------------|-------------------------|--------------|-------------------------|--------------|----------------|----------------------|-----------------------|-------|
|              | $\text{SiO}_2$           | $\text{Al}_2\text{O}_3$ | $\text{CaO}$ | $\text{Fe}_2\text{O}_3$ | $\text{MgO}$ | $\text{TiO}_2$ | $\text{K}_2\text{O}$ | $\text{Na}_2\text{O}$ | LOI   |
| Osfan        | 52.18                    | 17.60                   | 1.51         | 10.47                   | 0.36         | 1.78           | 1.97                 | 4.31                  | 9.83  |
| Alkamel      | 53.1                     | 17.96                   | 3.77         | 17.19                   | 0.76         | 4.12           | 0.86                 | 0.81                  | 1.42  |
| Wadi Starah  | 12.06                    | 5.12                    | 42.11        | 3.11                    | 1.70         | 2.25           | 0.70                 | 1.22                  | 31.73 |
| Khulais      | 50.76                    | 9.65                    | 3.04         | 7.11                    | 4.22         | 2.64           | 2.11                 | 4.85                  | 15.62 |
| Jeddah       | 54.32                    | 18.86                   | 4.11         | 16.12                   | 0.41         | 2.65           | 0.32                 | 0.51                  | 2.70  |
| Alghowla     | 50.11                    | 14.65                   | 4.35         | 8.79                    | 4.11         | 2.54           | 2.23                 | 4.56                  | 8.66  |

Table (5) shows the chemical composition of the prepared cement mixes composed of each mineral sample (25 % wt.) with ordinary portland cement (75 % wt.), that calculated theoretically from the chemical analysis of cement and raw minerals. The table shows that mixtures C1, C2, C4, C5 and C6 are mainly composed of calcium oxide ( $\text{CaO}$ )  $\approx$  48% and  $\text{SiO}_2$  ranges from 21.39 - 31.96% ,  $\text{Al}_2\text{O}_3$  value ranges from 6.53 - 9.97% and iron oxide ( $\text{Fe}_2\text{O}_3$ ) from 3.80 - 7.31%, in addition to a small percentage of magnesium oxide ( $\text{MgO}$ ) ranging from 0.15 - 1.11%, titanium oxide ( $\text{TiO}_2$ ) from 0.46 - 1.03% , alkalis ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) which ranges from 0.80 - 2.12% and constant amount of sulfur dioxide ( $\text{SO}_3$ ) = 0.3% whereas the loss of ignition (LOI) ranges from 0.36 - 7.93%. The mix prepared using the sample (C3) differs from the previous samples, it possess a high percentage of ( $\text{CaO}$ ) reaching 58.15% , and relative high percentage of LOI reaching 7.93%. These compositions indicate that C1, C2, C4, C5 and C6 mixes are mainly aluminosilicates while C3 sample contains is mainly calcite ( $\text{CaCO}_3$ ).

**Table 5. Chemical composition of the prepared mix**

| Prepared mix. | Chemical composition (%) |                         |              |                         |              |                |   |      |
|---------------|--------------------------|-------------------------|--------------|-------------------------|--------------|----------------|---|------|
|               | $\text{SiO}_2$           | $\text{Al}_2\text{O}_3$ | $\text{CaO}$ | $\text{Fe}_2\text{O}_3$ | $\text{MgO}$ | $\text{TiO}_2$ | Alkalis<br>( $\text{K}_2\text{O} + \text{Na}_2\text{O}$ ) | LOI  |
| C1            | 31.42                    | 9.65                    | 48.003       | 5.64                    | 0.15         | 0.46           | 1.95  | 2.46 |
| C2            | 31.65                    | 9.74                    | 48.57        | 7.31                    | 0.25         | 1.03           | 0.80  | 0.36 |
| C3            | 21.39                    | 6.53                    | 58.15        | 3.80                    | 0.46         | 0.56           | 0.86  | 7.93 |
| C4            | 30.90                    | 8.91                    | 48.71        | 5.22                    | 1.09         | 0.64           | 2.07  | 2.17 |
| C5            | 31.96                    | 9.97                    | 48.56        | 7.05                    | 0.16         | 0.66           | 0.58  | 0.68 |
| C6            | 31.07                    | 7.663                   | 48.36        | 4.80                    | 1.11         | 0.66           | 2.12  | 3.91 |

### Mineralogical composition of OPC and raw minerals samples

Fig. 1 shows the main composition of OPC. The figure shows that OPC is composed mainly of calcium silicate ( $\text{Ca}_3\text{SiO}_5$  - 71.9 %) and calcium aluminum oxide ( $\text{Ca}_3\text{Al}_2\text{O}_6$  - 28.1 %).

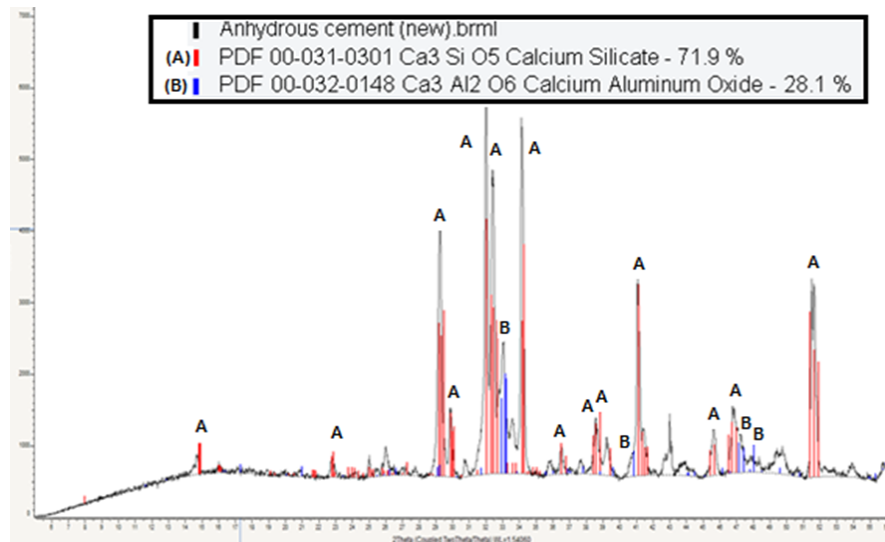


Fig. 1 XRD pattern of ordinary portland cement.

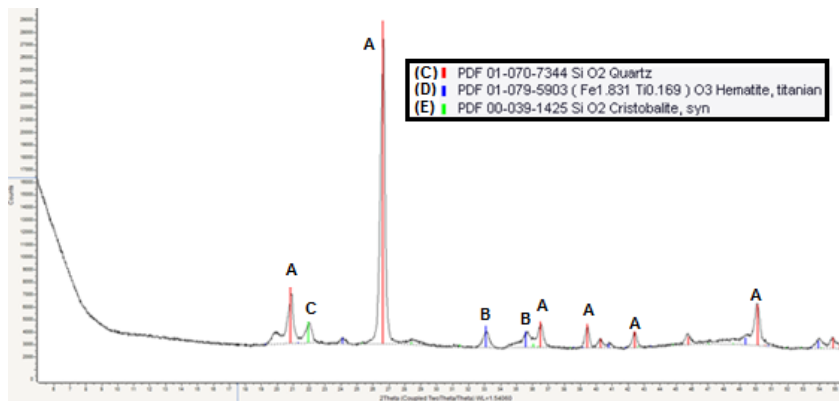


Fig.2a, XRD pattern of the natural minerals (Osfan mineral)

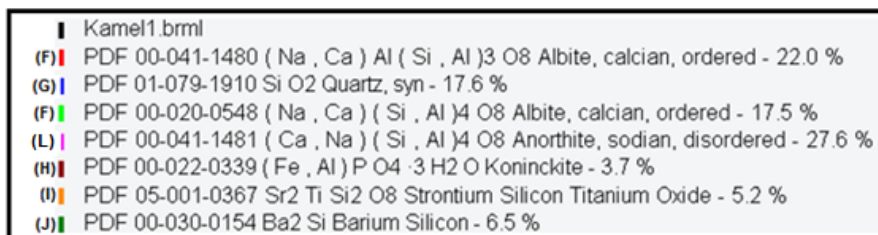


Fig.2b, XRD pattern of the natural minerals (Alkamel mineral)

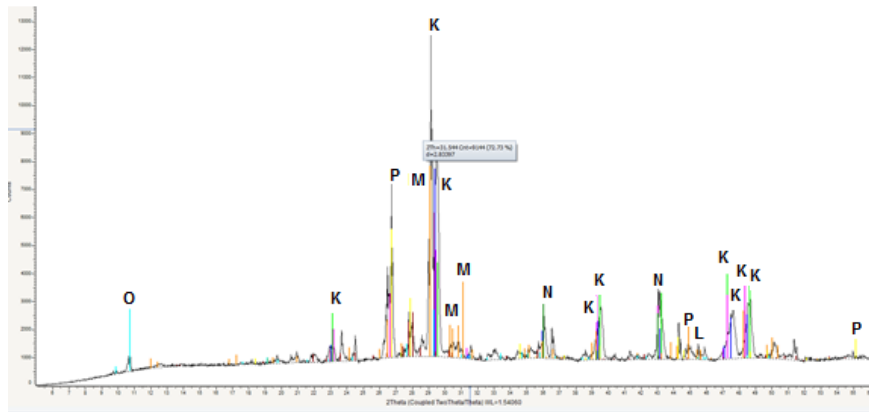
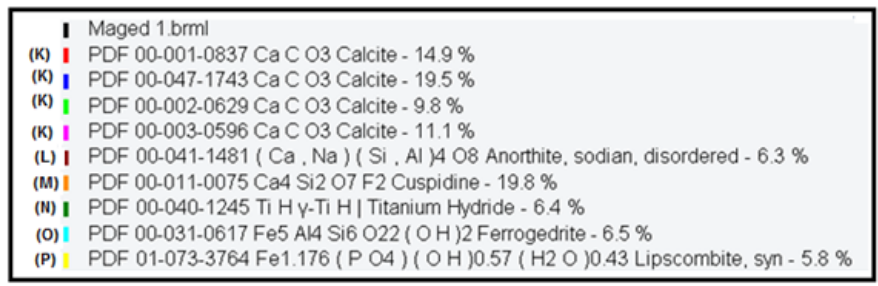


Fig.2c, XRD pattern of the natural minerals (Wadi starah mineral)

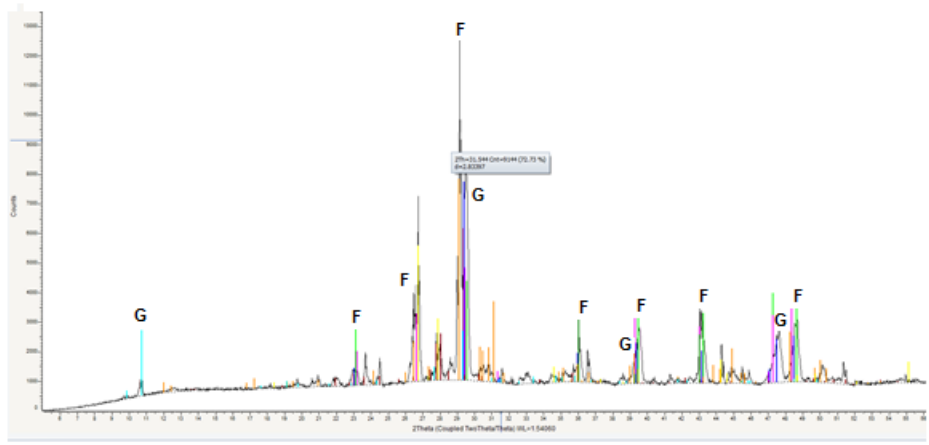
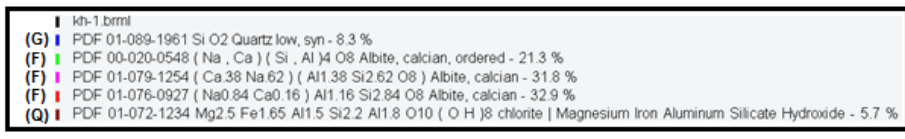
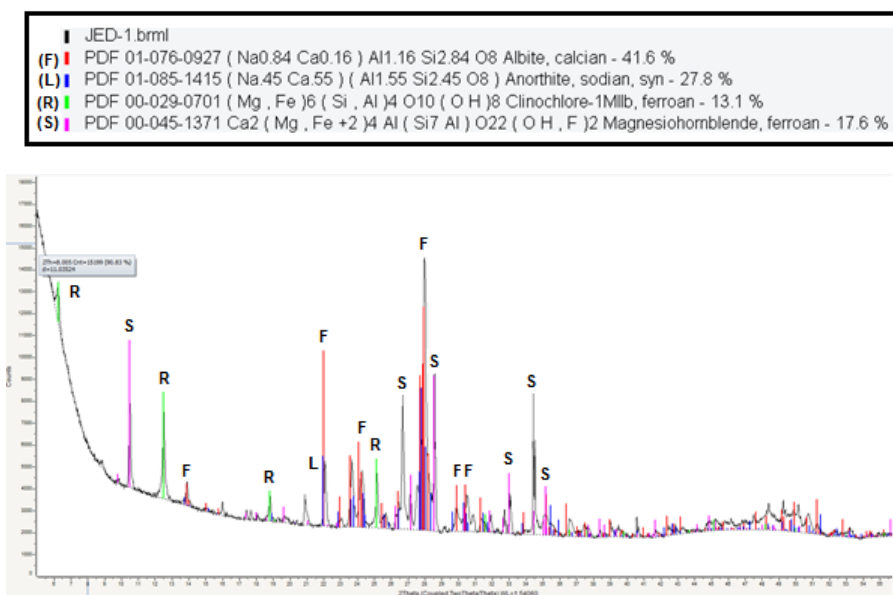
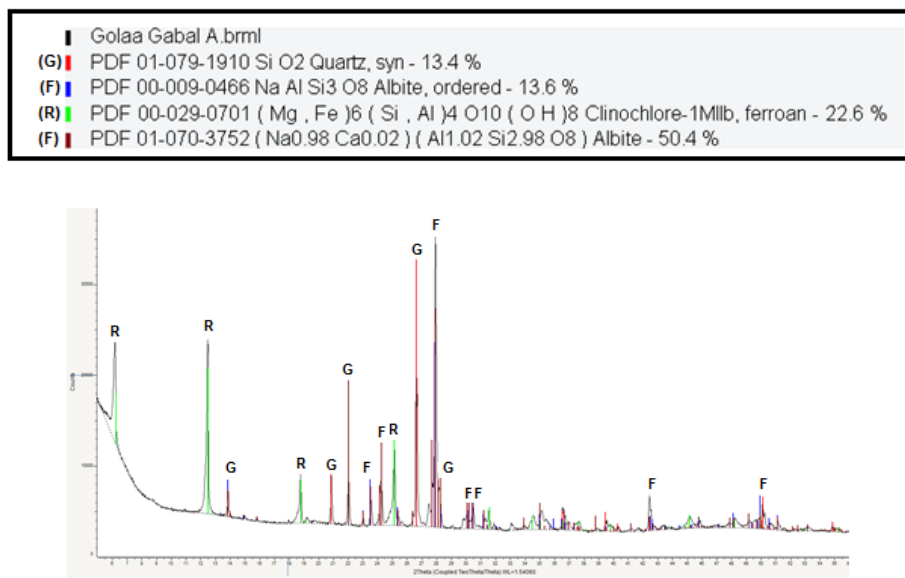


Fig.2d, XRD pattern of the natural minerals (Khulais mineral)





**Fig.2e, XRD pattern of the natural minerals (Jeddah mineral)**



**Fig.2f, XRD pattern of the natural minerals (Alghwla mineral)**

Fig. 2, XRD pattern of the natural minerals:  
a-Osfan mineral, b-Alkamel mineral , c-Wadi starah mineral ,  
d-Khulais mineral, e-Jeddah mineral, f-Alghowla mineral.

Fig. 2 (a, b, c, d, e, f) shows the X-ray diffraction (XRD) patterns of the used raw mineral powders collected from Osfan, Alkamel, Wadi Starah, Khulais, Jeddah and Al ghowla respectively. The data show that:

- Osfan sample composed of mainly of quartz mineral ( $\text{SiO}_2$ ), oxides of hematite titanium ( $(\text{Fe}_{1.83} \text{TiO}_{1.09}) \text{O}_3$ ) and cristobalite ( $\text{SiO}_2$ ).
- Alkamel sample composed mainly of albite calcian ( $\text{Na, Ca} \text{ Al (Si, Al)}_3 \text{O}_8$  - 37.5%, anthonite sodian ( $\text{Ca, Na} \text{ Al (Si, Al)}_4 \text{O}_8$  -27.6%), Konickite ( $\text{Fe, Al} \text{ PO}_4 \cdot 3\text{H}_2\text{O}$  -

3.75%), strontium titanium dioxide ( $\text{Sr}_2\text{Ti SiO}_8$  - 5.2%) and barium silicate ( $\text{Ba}_2\text{Si}$  - Barium silicate 6.5%).

- Wadi Starah sample composed of mainly calcium carbonate ( $\text{CaCO}_3$ -Calcite 55%), Ferrogednite ( $\text{Fe}_4\text{Al}_4\text{SiO}_6\text{O}_{22}(\text{OH})_{2-}$  6.5%), Cuspidine ( $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$ -19.8%) and Lipscombite ( $\text{PO}_4$ )  $\text{OH}_{(0.57)}\text{H}_2\text{O}_{(0.43)}$  - 5.8%) and titanium hydride (TiH- 6.4%).
- Khullais sample composed of quartz ( $\text{SiO}_2$  -8.3%), and magnesium iron aluminum silicate hydroxide ( $\text{Mg}_{2.5}\text{Fe}_{1.65}\text{Al}_{1.5}\text{Si}_{2.2}\text{Al}_{1.8}\text{O}_{10}(\text{OH})_8$ - 5.7%).
- Jeddah sample composed of albite calcian (Na, Ca) Al (Si, Al) $_3\text{O}_8$ -41.6%), anthronite sodian ( $\text{Ca}_{44}, \text{Na}_{55}$ ) ( $\text{Al}_{1.55}, \text{Si}_{2.45}\text{O}_8$ -27.8%) and clinocholre Ferraon ( $\text{Mg}, \text{Fe}$ ) $_6(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})$  as well as Magnesiohornbelende Ferraon ( $\text{Ca}_2(\text{Mg}, \text{Fe}^{2+})_4\text{Al}(\text{Si}_7\text{Al})\text{O}_{22}(\text{OHF}_2)_2$  - 17.6%).
- Alghwlaa sample composed of albite ( $\text{NaAlSi}_3\text{O}_8$ - 64%), Clinocholre Ferraon ( $\text{Mg}, \text{Fe}$ ) $_6(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_8$ - 22.6%) and quartz mineral ( $\text{SiO}_2$ - 13.6%).

### Cementing properties of the prepared cement pastes

#### *Water requirement (water of consistency)*

Using the optimum amount of mixing water during cement paste production is very sensitive since too little water leads to poor consideration and workability while too much water may result in porous matrix and hence weak mechanical properties after hardening.

Table (6) shows that different cement mixes consume different contents of water of consistency. Samples C5, C3 and C2 show relatively higher contents of water; 36, 34, 33 % respectively compared with the reference sample (28 %) and the other samples C4, C1 and C6 which recorded 31, 30 and 29 %, respectively. This is due to the relatively higher surface area of the raw minerals used in these mixes (3100, 3090 and 3060  $\text{cm}^2/\text{g}$ ) of C5, C3 and C2 compared with the reference sample (3100  $\text{cm}^2/\text{g}$ ) and other samples C4, C1 and C6 (3020, 3020 and 3010  $\text{cm}^2/\text{g}$ ).

**Table 6. Water consistency of OPC and cement pastes of minerals**

| Sample | Sample area | Standard water (%) |
|--------|-------------|--------------------|
| C      | Reference   | 28                 |
| C1     | Osfan       | 30                 |
| C2     | Alkamel     | 33                 |
| C3     | Wadi Starah | 34                 |
| C4     | Khulais     | 31                 |
| C5     | Jeddah      | 36                 |
| C6     | Alghowla    | 29                 |

#### *Setting time*

The initial setting time of ordinary portland cement was estimated at 48 minutes, while the initial setting time for the other pastes ranged from 50 to 55 minutes, while the final setting time of the reference sample C was up to 120 minutes. With minerals additions the final setting time ranging from 140-160 minutes as in Table (7). Thus, all the prepared cement pastes meet the requirements of ASTM C191, which require that the initial time of OPC should not be less than 45 minutes and the final setting time is not more than 375 minutes.

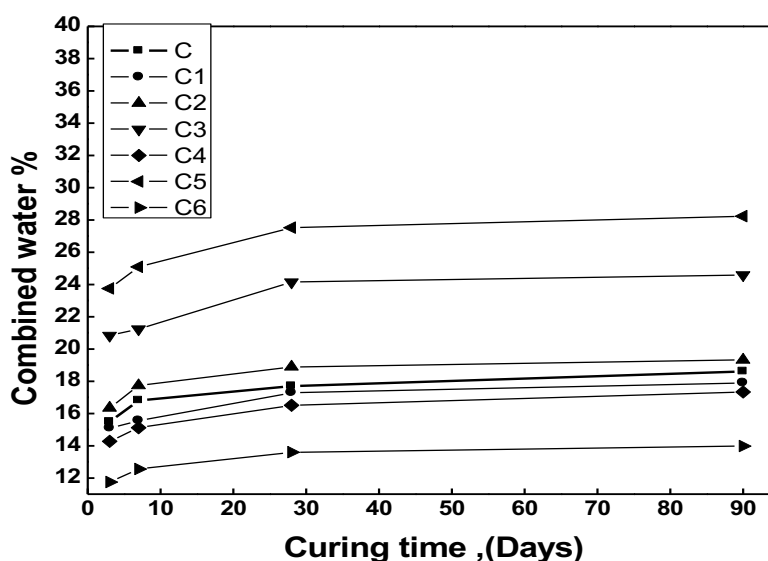
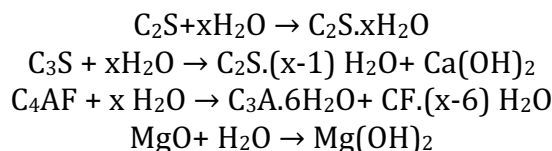
**Table 7. Setting time for cement pastes of different minerals**

| Sample | Setting time (min.)  |                    |
|--------|----------------------|--------------------|
|        | Initial setting time | Final setting time |
| C      | 45                   | 120                |
| C1     | 50                   | 140                |
| C2     | 52                   | 144                |
| C3     | 52                   | 145                |
| C4     | 54                   | 150                |
| C5     | 55                   | 160                |
| C6     | 53                   | 156                |

**Chemically combined water**

Fig. 3 shows a gradual increase in the content of combined water as the curing time increases; 3, 7, 28 and 90 days. From the figure it is shown that samples C5, C3 and C2 have relatively higher contents of combined water (23.75-28.23%), (20.84-24.59%), (16.34-19.31%), respectively compared with reference sample (C) which recorded only (15.59-18,00%), whereas the samples C1, C4 and C6 showed relatively lower contents of chemically combined water, (15.18-17.89%), (14.48-17.62%) and (11.75-13.98 %), respectively. This also correlated with the relatively higher the surface area of C5, C3 and C2 with that consume relatively higher contents of water.

The increase of percentage of chemically combined water from 3 to 7, 28 and 90 days for all samples, reflecting the increasing of the reaction of water with cement as the curing time increased due to more opportunities for water interaction with cement granules. The components of ordinary cement (OPC) interact with water according to the following equations:



**Fig.3 Chemically combined water of the hardened cement pastes.**

### Heat of hydration

Fig. 4 shows a gradual increase in the heat of hydration of hardened paste as the curing time increases; 3,7,28 and 90 days. It is shown that samples C5, C3 and C2 have relatively higher values of heat of hydration (81-97 cal/g), (77-94 cal/g) and (75-90 cal/g), respectively compared with the reference sample (C) which recorded (70-85 cal/g), whereas samples C1, C4 and C6 show relatively lower values of heat of hydration compared with the reference sample they recorded (64-79 cal/g), (60-77 cal/g) and (55-69 cal/g), respectively.

This behavior is correlated with the chemically combined water i.e., increasing the chemically combined water in C5, C3 and C2 means more progressive of cement hydration and hence a relatively higher amount of heat evolved due to hydration process and vice-versa, lower content of chemically combined water of C1, C4 and C6 results in a relatively decrease in their heat of hydration.

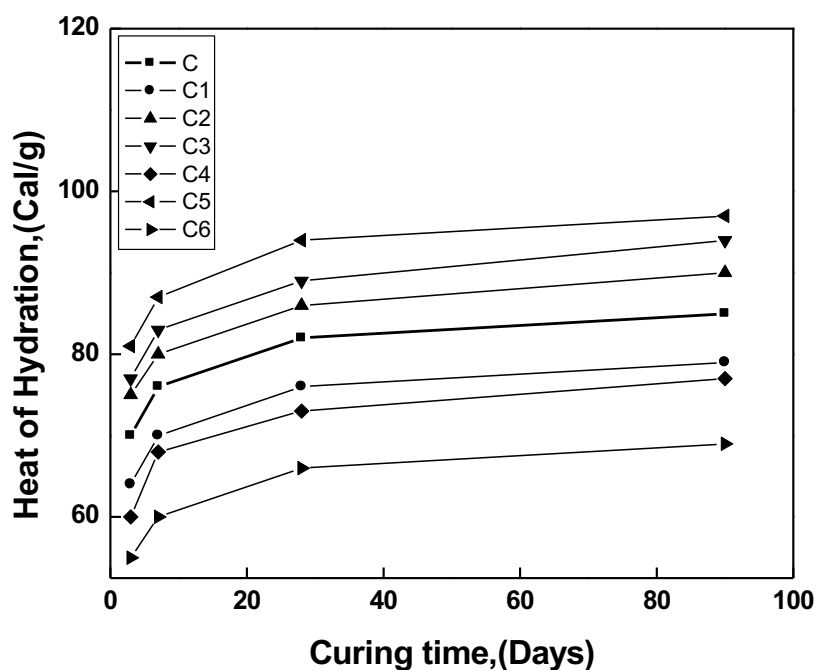


Fig.4, Heat of Hydration hardened cement pastes

### Bulk density and apparent porosity

Fig. 5 shows the data of bulk density values of the hardened cement pastes with different minerals additions while (Fig. 6) shows their apparent porosity percentages. A gradual increase in the bulk density values corresponded with a gradual decrease in apparent porosity percent is observed as the curing time (age of hydration) increases from 3 to 7 to 28 to 90 days, the higher values of bulk density were recorded by samples C5, C3 and C2, (1.61-1.96 g/cm<sup>3</sup>), (1.66-1.84 g/cm<sup>3</sup>) and (1.65-1.84 g/cm<sup>3</sup>), respectively compared with the reference sample (C) that recorded (1.61-1.84 g/cm<sup>3</sup>) whereas the remaining samples C1, C4 and C6 show relatively lower values in bulk density than the values for the control sample (1.58-1.78 g/cm<sup>3</sup>), (1.56-1.77 g/cm<sup>3</sup>) and (1.52-1.70 g/cm<sup>3</sup>), respectively.

Samples C5, C3 and C2 which recorded relatively lower percentages of apparent porosity; (15.02-10.41%), (16.25-12.75%) and (17.40-13.96 %), respectively compared with the reference sample (24.11-14.39%) while samples C1, C4 and C6 show relatively higher apparent porosity percentages (17.89 -15.58 %), (24.67 -16.24 %) and (28.58-17.99 %),

respectively. These results are in accordance with the chemically combined water contents and heat of hydration.

These results can be attributed to the variation of chemical and mineral composition of these samples, and also to the difference in the percentage of chemically combined water, that necessarily reflected on the characteristics of the samples (bulk density and apparent porosity). In addition, the relative increase in surface area for the sample C5, C3 and C2, which resulted in a relative increase in the standard water quantity used for the preparation of cements pastes gives a greater chance for the interaction of the cement mixture with the water and then increasing the hydrated products that fill the pores and voids in the cement paste, resulting in a relative increase in its bulk density and a relative decrease in its apparent porosity compared with the reference sample and other cement mixes (C1, C4 and C6) [1].

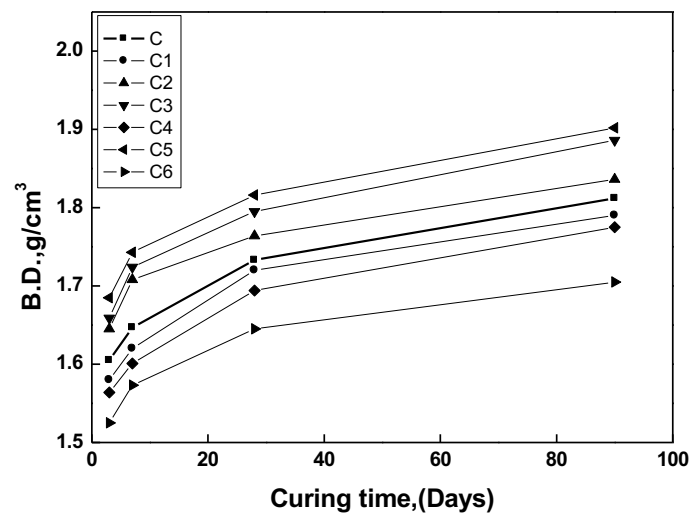


Fig.5, Bulk density of the hardened cement pastes

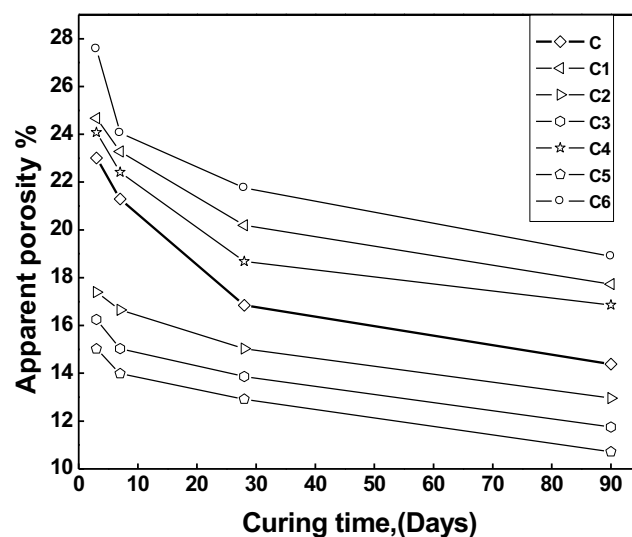
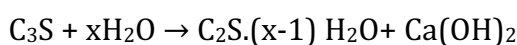


Fig. 6. Apparent porosity of the hardened cement pastes

### Compressive strength of the hardened cement pastes

The results shown in (Fig. 7) indicate a noticeable improvement in the compressive strength of the hardened cement for the samples C5, C3 and C2; (90-125 kg/cm<sup>2</sup>), (80-120 kg/cm<sup>2</sup>) and (75-113 kg/cm<sup>2</sup>), respectively compared with the reference sample (60-110 kg/cm<sup>2</sup>). A noticeable decrease in the compressive strength values are observed for the samples C1, C4 and C6 when compared with the reference sample (C). The results show also that C5 sample exhibits the highest compressive strength values followed by sample C3 which in turn is relatively higher than C2 sample. A noticeable improvement in compressive strength is observed as the curing time (age of hydration) increases from 3 to 7 to 28 days, beyond which (at 90 days) the improvement in strength is less significant.

The results of the compressive strength are in a well accordance with those of chemically combined water, heat of hydration and sintering properties. The improvement in compressive strength of C5 and C3 samples are due to the pozzolanic nature of minerals involved in these mixes which assists hydration process according to the following equations;



The improvement of compressive strength of C3 sample is due to its higher contents of calcite which acts as a good filler resulting in improved sintering properties and hence mechanical properties [45,46].

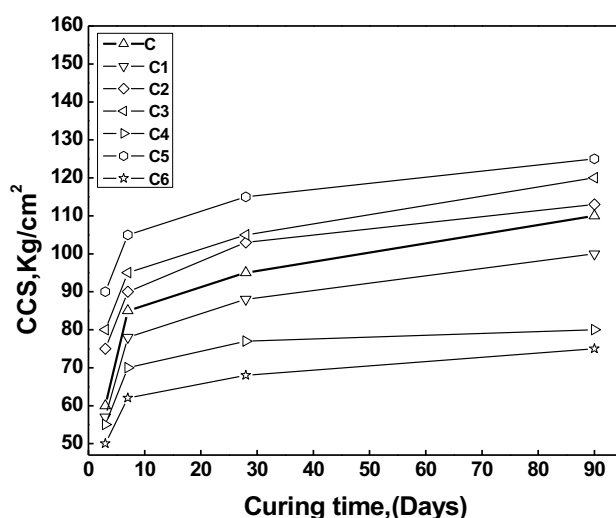
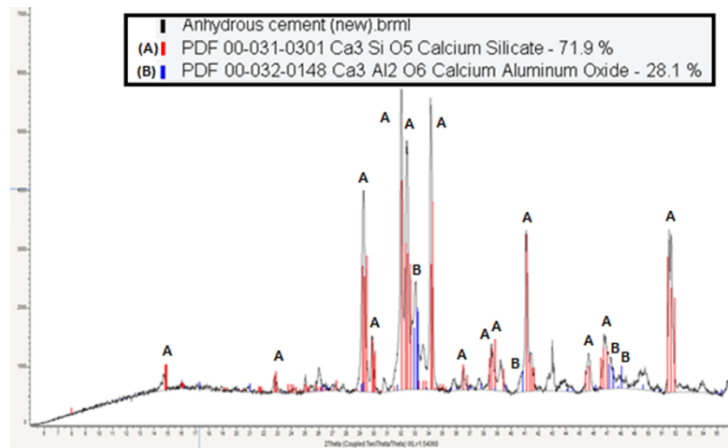


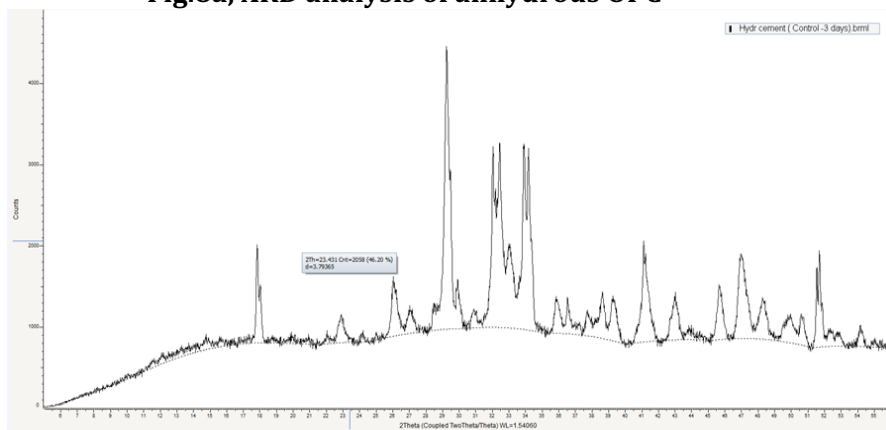
Fig. 7 Compressive strength of the hardened cement pastes

### Phase composition of the hydrated cement pastes:

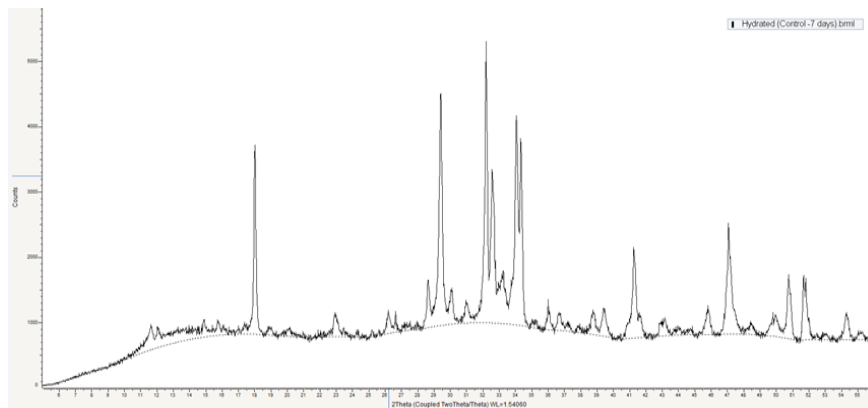
Fig.8(a, b, c, d, e) shows the mineral composition of the hydrated cement compared to anhydrous OPC sample. Figure (8a) shows the results of X-ray diffraction analysis of anhydrous (OPC), which is composed of a mixture of tri-calcium silicate (Ca<sub>3</sub>SiO<sub>5</sub>- 71.90%) and tri-calcium aluminate (Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>- 28.10%). Figure 8 (b, c, d, e) shows the results of the X-ray diffraction analysis of the hydrated cement (reference sample C) after 3, 7, 28, 90 days of hydration, from the figures new peaks characterizing portlandite mineral Ca (OH)<sub>2</sub>, are observed after 3 days of hydration (Fig.8b), their intensity increases as the age of hydration increases from 3 to 90 days (Figs.8b-8c). On the other hand, the intensity of the anhydrous minerals (tri-calcium silicate and tri-calcium silicate aluminate) decreases as the age of hydration increases. This is reflecting the progress in cement hydration with time and thus appreciable improvement in the physical, chemical and cementing properties of cement when increasing curing time.



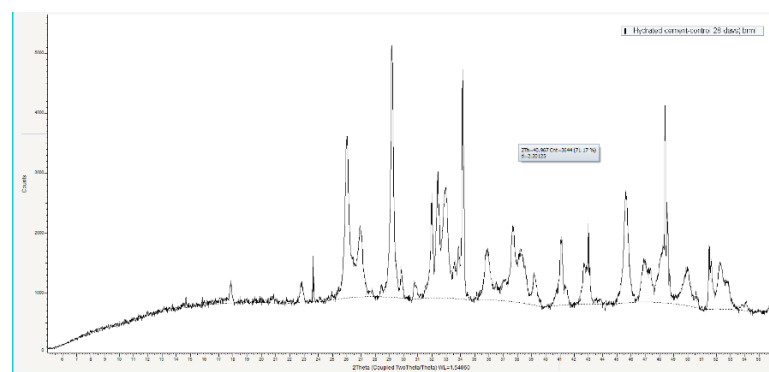
**Fig.8a, XRD analysis of anhydrous OPC**



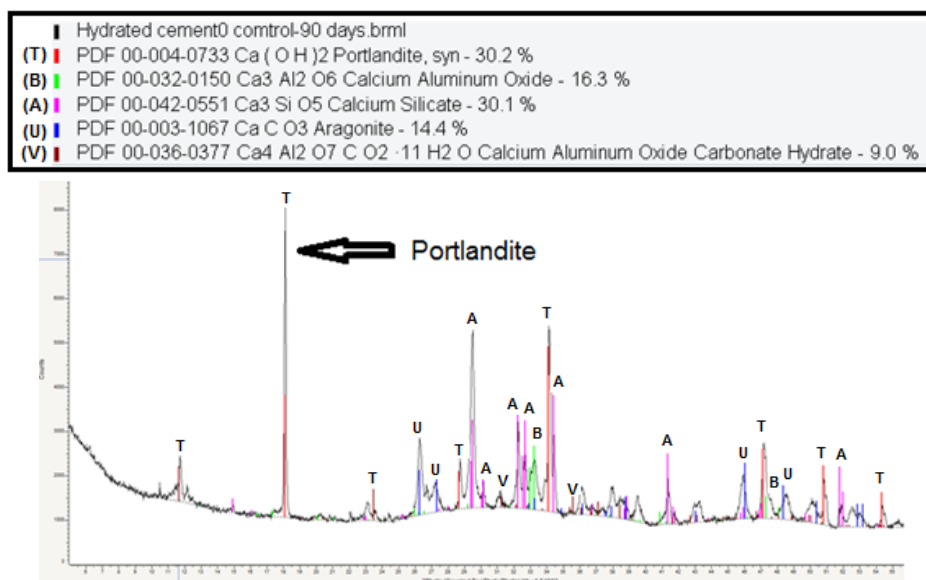
**Fig.8b, XRD analysis of hydrated hardened OPC at 3 days curing time**



**Fig.8c, XRD analysis of hydrated hardened OPC at 7 days curing time**



**Fig.8d, XRD analysis of hydrated hardened OPC at 28 days curing time**



**Fig.8e, XRD analysis of hydrated hardened OPC at 90 days curing time**

A comparison of XRD analysis results of hydrated hardened pastes at fixed age (90 days) of hydration (Figs. 9a - 9e) show the following:

- 1) The appearance of some peaks for the anhydrous minerals that present in the anhydrous cement with a relative low intensity compared to their intensities in the anhydrous cement. These minerals are tri-calcium silicate ( $\text{Ca}_3\text{SiO}_5$ ), tri-calcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ), calcite ( $\text{CaCO}_3$ ), larnite ( $\text{Ca}_2\text{SiO}_4$ ), quartz ( $\text{SiO}_2$ ), hatronite ( $\text{Ca}_3\text{SiO}_4 \cdot \text{O}$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), calcium aluminate silicate ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), di-calcium silicate ( $\text{Ca}_2\text{SiO}_3$ ) and spurite- $\text{Ca}_3(\text{SiO}_4)\text{CO}_3$ .
- 2) The appearance of new peaks characterizing portlandite mineral  $\text{Ca}(\text{OH})_2$ , which is one of the main hydration products of cement (Fig.8e). The progress in the process of hydration of cement and other mixes is due to the formation of the hydrated minerals involving portlandite  $\text{Ca}(\text{OH})_2$  and other hydrated minerals namely; gismondine ( $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ ), hydrated calcium silicate ( $\text{Ca}_{1.5}\text{SiO}_{3.5} \cdot x\text{H}_2\text{O}$ ), hydrated calcium silicate ( $\text{Ca}_2\text{SiO}_{4.0} \cdot 3\text{H}_2\text{O}$ ), Jafite ( $\text{Ca}_6(\text{Si}_2\text{O}_7)\text{OH}_6$ ) and rosenharite ( $\text{Ca}_3\text{Si}_3\text{O}_9 \cdot \text{H}_2\text{O}$ ).
- 3) The decrease in the intensity of the peaks of the anhydrous minerals and increase in the intensity of the peaks for these minerals by increasing the hydration ages from 3 to 7 to 28 and 90 days of the prepared samples, reflects the progress in the process of hydration of cement as the curing time increases because of the more opportunities for the interaction of cement granules with water which explains the increase in the percentage of chemically combined water and hence the improvement in the mechanical and sintering properties of the cement mixes at later age of hydration.
- 4) The observed high intensity of portlandite mineral peaks (hydrated cement products) in the samples C5, C3 and C2 as in (Fig. 9d,9c and 9b), respectively and the significant improvement in the percentage of chemically combined water and heat of the hydration showing the characteristics of the sintering properties (increase in bulk density and the decrease of the apparent porosity), and also improvement of the mechanical properties of these samples compared to the reference samples and the remaining samples under the study.



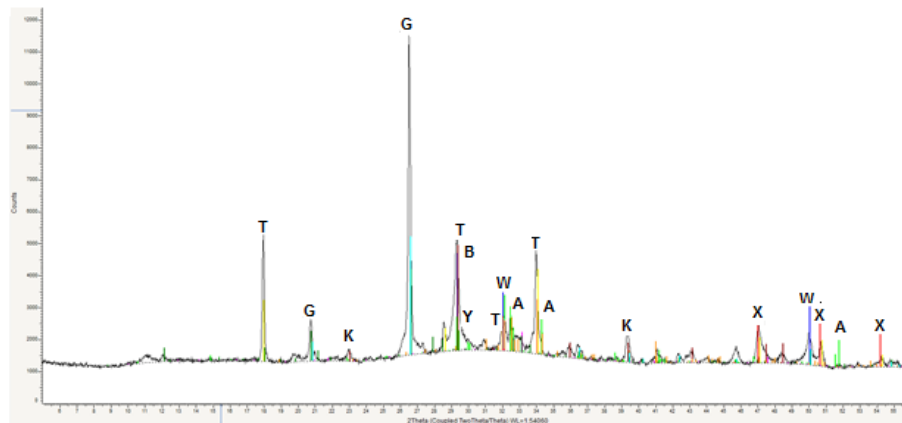
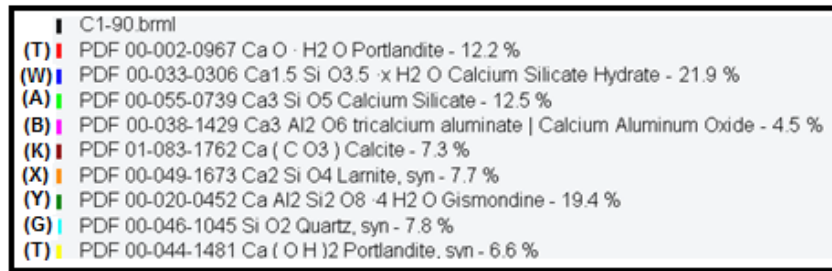


Fig.9a, XRD analysis of hydrated paste with C1 at 90 days curing time

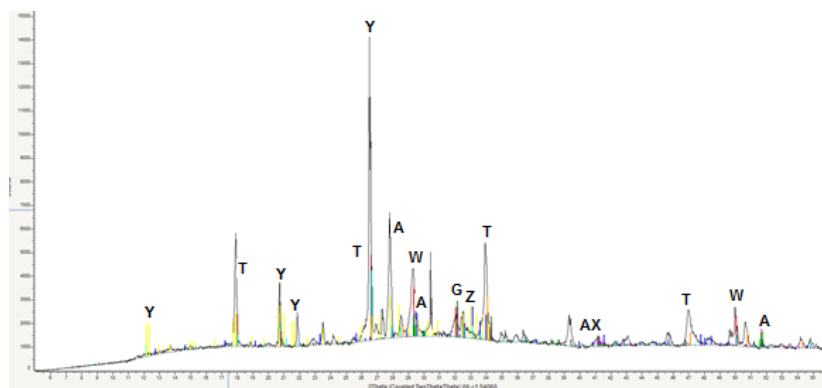
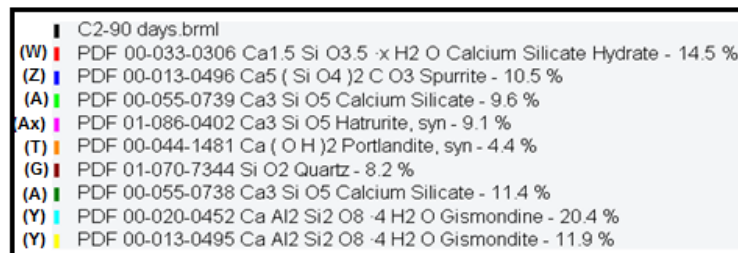


Fig.9b, XRD analysis of hydrated paste with C2 at 90 days curing time

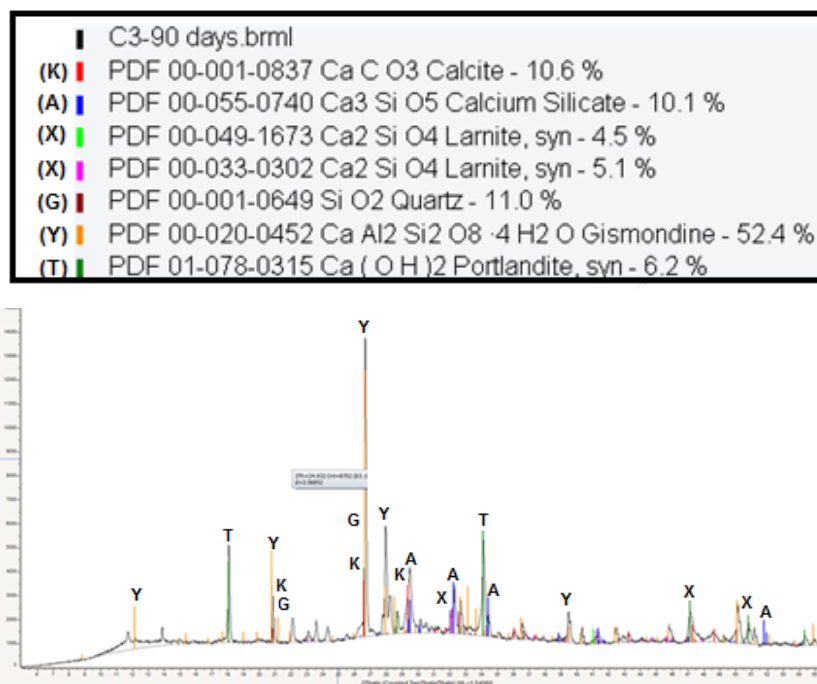


Fig.9c, XRD analysis of hydrated paste with C3 at 90 days curing time

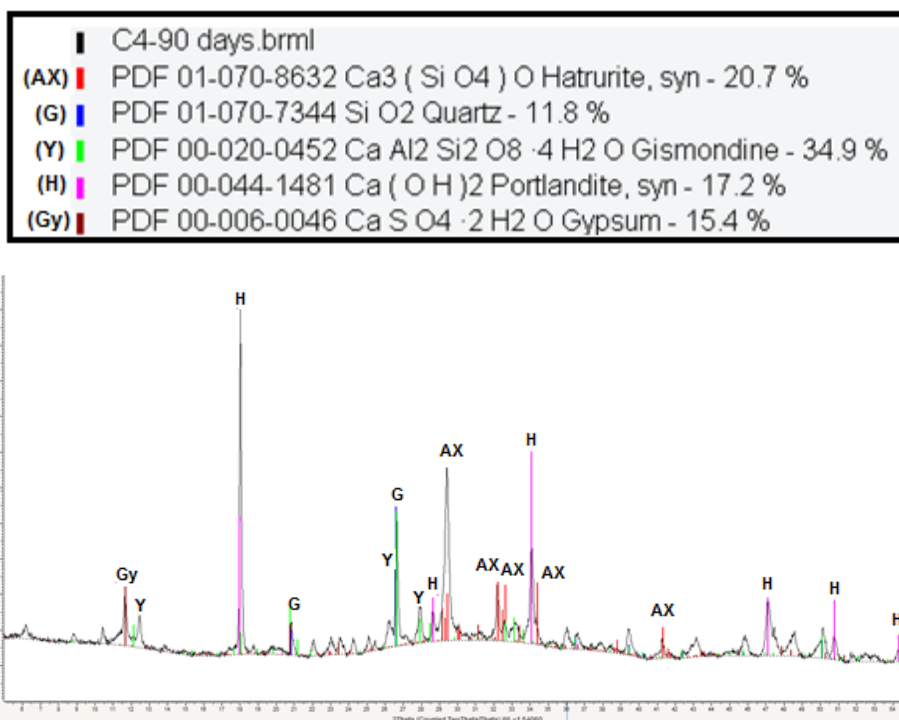


Fig.9d, XRD analysis of hydrated paste with C4 at 90 days curing time

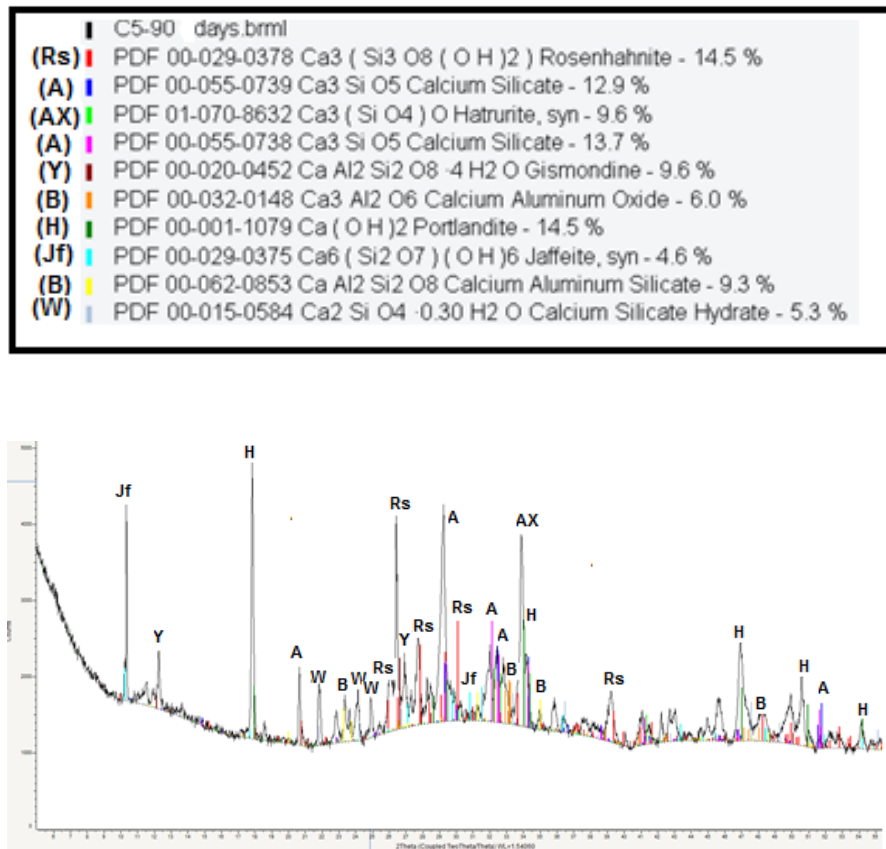


Fig.9e, XRD analysis of hydrated paste with C5 at 90 days curing time

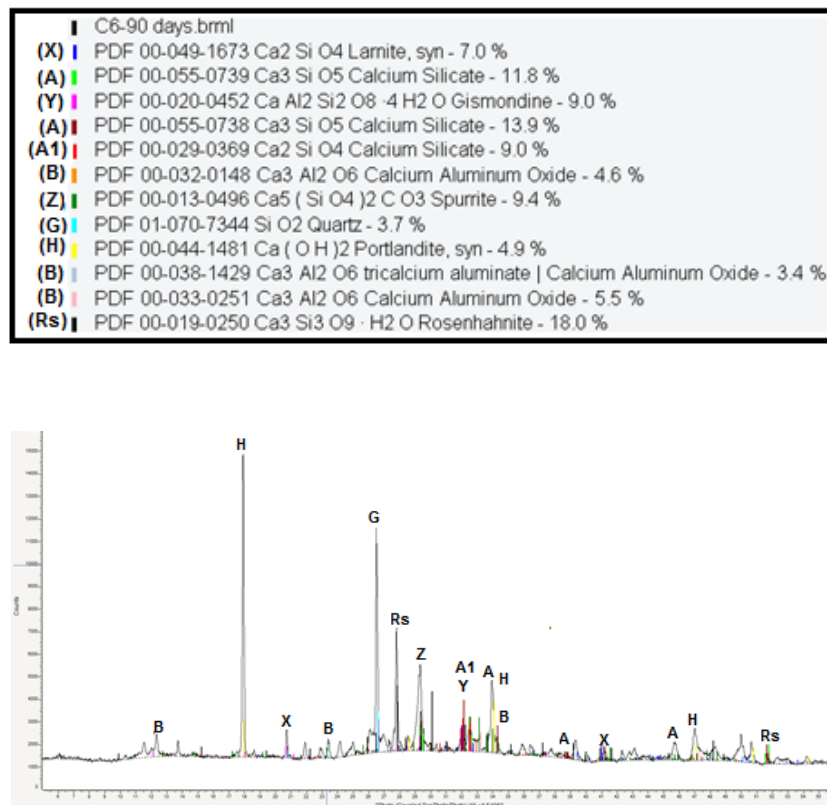


Fig.9f, XRD analysis of hydrated paste with C6 at 90 days curing time

### SEM for the hydrated cement pastes

The microscopic structure of all hardened cement samples was examined after 90 days of hydration using a scanning electron microscopy (SEM).

Figs. 10(a- g) shows the images of the scanning electron microscope of the reference sample (C) and other cement mixes (Figs.10 b-g). The figures show that the matrices of C5, C3 and C2 are more tightened and less porous (Figures 10.f, 10.d and 10.c) compared with the matrix of the reference sample (Fig.10.a). The matrices of C6, C4 and C1 samples (Figs. 10.g, 10.e and 10.b) are less compact and contain some pores and voids in their microscopic structure compared with the reference sample. This is reflected from the relatively higher content of hydration products in C5, C3 and C2 appear in the photos as white crystals which fill pores and cavities resulting in well compact microstructure. This reflects the increase in bulk density and the decrease of the apparent porosity and hence the increase in the mechanical properties of these samples. On the other hand, the relatively lower compact of hydration products of C1, C4, and C6 makes them insufficient to close all the pores and voids leaving a less compact microscopic structure resulting in relatively poor sintering and hence relatively lower mechanical properties [1,2,47-48].

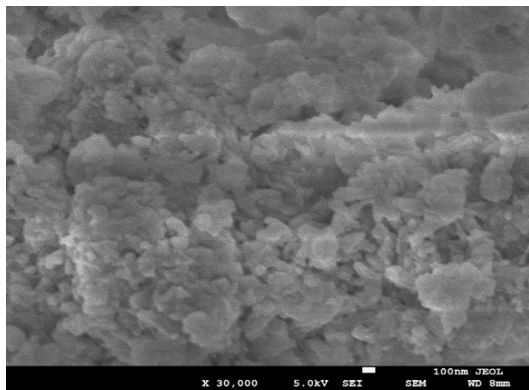


Fig.(10a), C

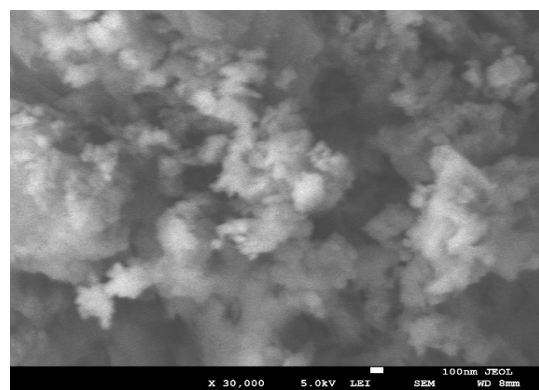


Fig.(10b), C1

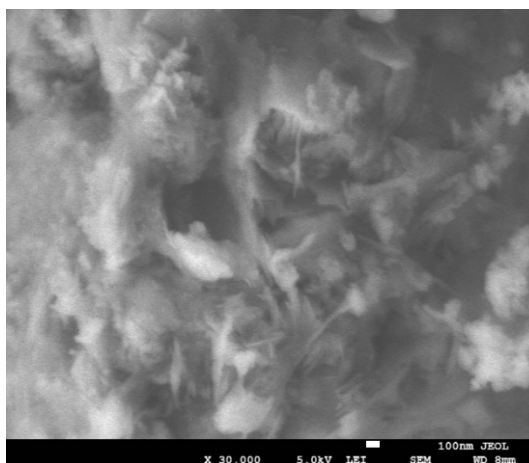


Fig.(10c), C2

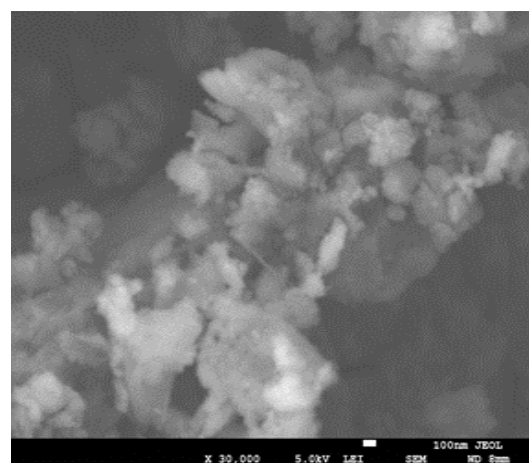


Fig.(10d), C3

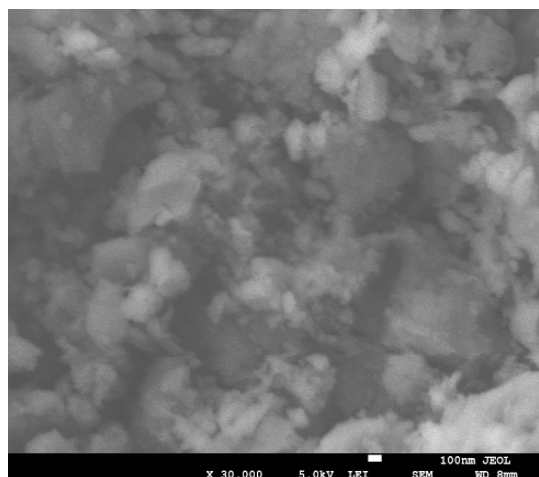


Fig.(10e), C4

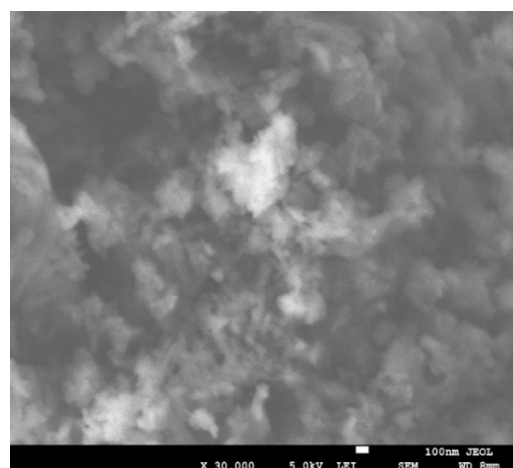


Fig.(10f), C5

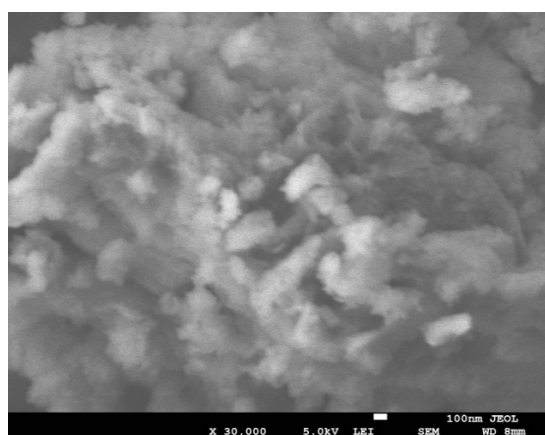


Fig.(10g), C6

Fig. 10 (a, b, c, e, f, g): SEM hydrated for 90 days hardened cement samples

M. Ahiduzzaman [45] and B. King, A [49] attributed the improvement of the mechanical properties to the pozzolanic nature of the cement additives which react with the portlandite mineral,  $\text{Ca(OH)}_2$ , released as a side product of cement hydration resulting in further yield of the main hydration product (calcium silicate hydrate, C-S-H) which plays the main role of hardening. Zhang et al. [50], Qijun et al. [51] and Cisse & Laquerbe [52] supported these findings. E.C. Beagle [53] suggested that the improvement in physicomechanical properties of the cement modified with some natural or artificial wastes is due to the higher pozzolanicity and filler effect of the added additives. Rukzon et al. [54] attributed this to the relatively fine particles of additives which segments the large pores in the cement paste and hence increases the nucleation sites resulting in a permeable paste due to refined pores. Farah Alwani et al. [55] proposed the two mechanisms i.e. pore refinement and pozzolanic activity as reasons for the improvement of mechanical properties.

## CONCLUSION

This study demonstrated the possibility of usage of some local minerals from western area in Kingdom of Saudi Arabia as a partial replacement of OPC. A partial replacement (25 wt.%) of local mineral materials to OPC results in improved cementing, chemical, sintering and mechanical properties of the products. The improvement takes the following order (C5) Jeddah sample > (C3) Wadi Starah > (C2) Alkamel sample > (C) Reference sample > (C1) Osfan sample >

(C4) Khulais sample > (C6) Algowala sample which correlated with their mineral composition and surface area and hence the rate of hydration.

### ACKNOWLEDGEMENT

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