Physiochemical and Mechanical Analysis of Local Gypsum Deposits, East Benghazi, Libya

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ABSTRACT

The local gypsum deposits were investigated in order to determine their physical and chemical properties. General properties such as physical and chemical properties are tested using standard laboratory procedure. The raw gypsum has been produced by open pit mining technique. The study was conducted to evaluate the characteristics of gypsum from Al Mabrouk mining sites; one is a huge reserve with great thickness and two others with less thickness. Samples of gypsum from the studied sites were obtained and their physical and chemical properties were determined. They were calcined into plaster of Paris (P.O.P) in an oven between 105°C (221°F) and 200°C (392°F). The raw gypsum samples were analyzed to determine their chemical constituents using XRF technique. The major significant constituents such as Sulphur Trioxide (SO_3); Calcium Oxide (CaO); Magnesium Oxide (MgO); Sodium Oxide (Na_2O); Potassium Oxide (K_2O); Manganese Oxid (MnO); Titanium Oxide (TiO_2); Ferric Oxide ($Fe20_3$) and combined matter (Loss-on-ignition) were determined. Based on the previous tests the results confirmed that the investigated gypsum is suitable for several purposes e. g. cement manufacture, source sulphates, construction and production P.O.P for use in plasterboards.

Keywords: Gypsum, deposit, physiochemical, properties, plaster of Paris, changes chemical composition.

1 Introduction

The mineral gypsum precipitated some 100 to 200 million years ago when sea water evaporated. From a chemical point of view it is calcium sulphate Dihydrate ($CaSO_4.2H_2O$) deposited in sedimentary layers on the sea bed. Under high pressure and temperature gypsum turns into anhydrite ($CaSO_4$). In nature, gypsum and anyhdrite occur as beds or nodular masses up to a few meters thick. Gypsum is formed by the hydration of anhydrite. The depth of hydration can range from the surface of the deposit down to three hundred meters, depending on temperature and pressure, topography and the structure of the deposit. Anhydrite is often mined in conjunction with gypsum, but is comparatively limited in its technical applications. The content of gypsum in sedimentary rock varies from 75% to 95%, the rest being clay and chalk [1]. Gypsum is a common sulphate mineral of great commercial importance, it composes of hydrated calcium sulphate ($CaSO_4.\ 2H_2O$). It is a white mineral of calcium sulphate found in deposits in the earth crust. Gypsum is a less reflective, glass-like soft stone; which is of great importance for the manufacture of many industrial products. Gypsum is formed through geological processes, hence it occurs in nature in various forms. These forms can basically be grouped into two broad categories of rock gypsum and sand gypsum. Rock gypsum is described as having different colours ranging from transparent or white; sometimes grey, yellowish to red. Gypsite is gypsum mixed with sand and dirt [2]. Commonly used in many industries, gypsum ($CaSO_4 \cdot 2H_2O$) is a monomineral sulphate sedimentary rock, built almost exclusively from the mineral of the same name, with anhydrite, calcite and halite admixtures [3,4]. The crystal structure of gypsum depends mainly on the conditions in which the raw material transformations took place and a specific phase (temperature and pressure) was created [5-8]. Gypsum/anhydrite are produced from open-cast mines, or underground mines using pillar and stall mining methods, that give extraction rates of up to 75%. Gypsum is normally only screened to remove ‘fines’ (mainly mudstones), then crushed and finely ground. Gypsum/anhydrite for cement manufacture is supplied in crushed form for further fine grinding with cement clinker [6]. When Gypsum ($CaSO_4,2H_2O$) is ground to a powder and heated at 150° to 165° C, three-quarters of its combined water is removed producing hemi-hydrate plaster ($CaSO_4,1/2H_2O$), commonly known as the ‘Plaster of Paris’. When this powder is mixed with water the resulting paste sets hard as the water recombines to produce Gypsum again. This process can be repeated almost indefinitely, with important implications for recycling [7]. Gypsum is one of the oldest known minerals used in basic and construction materials. As far back as 7000 BC, gypsum was already used as a base for frescoes in the town of Catal Huyuk in Asia Minor [9]. Gypsum was also used in its natural form for sculptures and building blocks, as plaster and in the mortar of world-famous buildings such as the towers of Jericho, the Great Pyramid of Cheops or the Palace of Knossos [9]. The Romans knew about the advantageous properties of gypsum and spread the knowledge about its preparation to the area north of the Alps. Much of this knowledge during the Migration Period (400–700 AD). It was not until the architectural style of Romanticism that gypsum returned to the scene as a building material. Gypsum technology was further developed during the period of industrialization in the 19th century, which provided a clear distinction between gypsum dihydrate, hemihydrate and completely dehydrated anhydrite and the importance of different firing temperatures [9]. The world production of gypsum is in range of 140–160 million tons [10].

2 World Mine Production and Reserves

Gypsum and anhydrite occur all over the world and are usually easy to exploit. In global terms, around 50 % of the gypsum is used for the production of cement, 39 % for the production of plaster and stucco (which also includes wallboards) and around 10 % in agriculture. Due to its low price gypsum and gypsum products are not usually transported over long distances, which in the past prevented the recycling of gypsum waste. During the past few years better technologies were developed for the increased recycling of gypsum [9]. Table 1 presents the world production of gypsum by countries.

Table 1 *World production of gypsum by countries [10]*

Countries	Mine production (MT*)		Reserves (MT*)
	2018	2019	
United States	21,100	20,000	700,000
Algeria	2,500	2,500	NA*
Brazil	3,200	3,200	340,000
Canada	3,000	3,000	450,000
China	15,500	16,000	NA
France	3,000	3,000	NA
Germany	3,200	3,200	NA
India	2,700	2,700	37,000
Iran	16,000	16,000	NA
Japan	4,700	4,700	NA
Mexico	5,400	5,400	NA
Oman	7,000	7,000	NA
Pakistan	2,200	2,200	4,900
Russia	3,800	3,800	NA
Saudi Arabia	3,310	3,300	NA
Spain	7,000	7,000	NA
Thailand	9,300	9,300	1,700
Turkey	10,000	10,000	200,000
Other countries	20,000	21,000	NA
World total (rounded)	143,000	140,000	Large

* NA = Not available   *MT = million tons

3 Significance of Study and Problem Statement

The importance of this study can be summarized as Libya has a great quantities of raw materials estimated as millions of tons the raw materials characterized by the lower contents of impurities the most locations of these materials located on or nearby the highways the easy of transportation by trucks or belt conveyor to achieve the sustainable development and support the national income. These rocks haven't subjected in details studies and evaluation the study spotlight on the importance of these rock materials as a natural resource there is no available concerning data can be used as reference.

4 Objectives of Study

The main aim of this study is to focus on the assessment of the raw materials of local gypsum deposits required as a raw material for various industrial purposes particularly cement manufactures in the investigated locations throughout:

1. Study the chemical composition of raw materials.
2. Determination their characterizations and the potentiality as construction raw material.

3. Correlation between these raw materials and the standard ones to distinguish their quality.
4. Highlight on the raw materials as natural resources in Libya.
5. The study regards as preliminary one for more detail study later.

Figure 1 *Sidi Al Mabrouk (Site 1)*

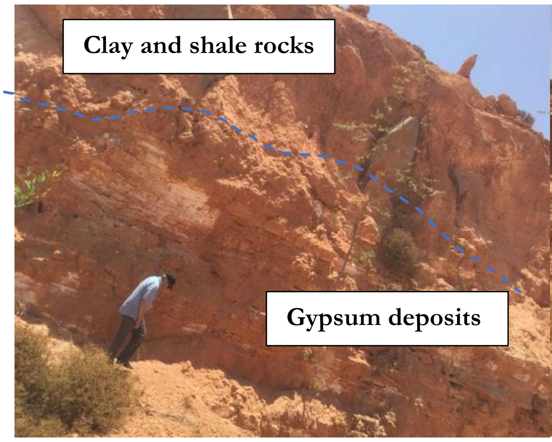

Figure 2 *Sidi Al Mabrouk (Site 2)*

Figure 3 *Sidi Al Mabrouk (Site 3)*

5 Materials and Methods

5.1 Location of Studied Sites

Gypsum deposits occur in different locations all over Libya with different amounts and reserves. This study has been carried out on the area including a high reserve of gypsum deposits namely Mabrouk quarry lies in the east Benghazi city e. g. Al Rajma and Sidi Mabrouk. Figure 2 a map illustrates the different location deposits of vaporits rocks such as gypsum and salts.

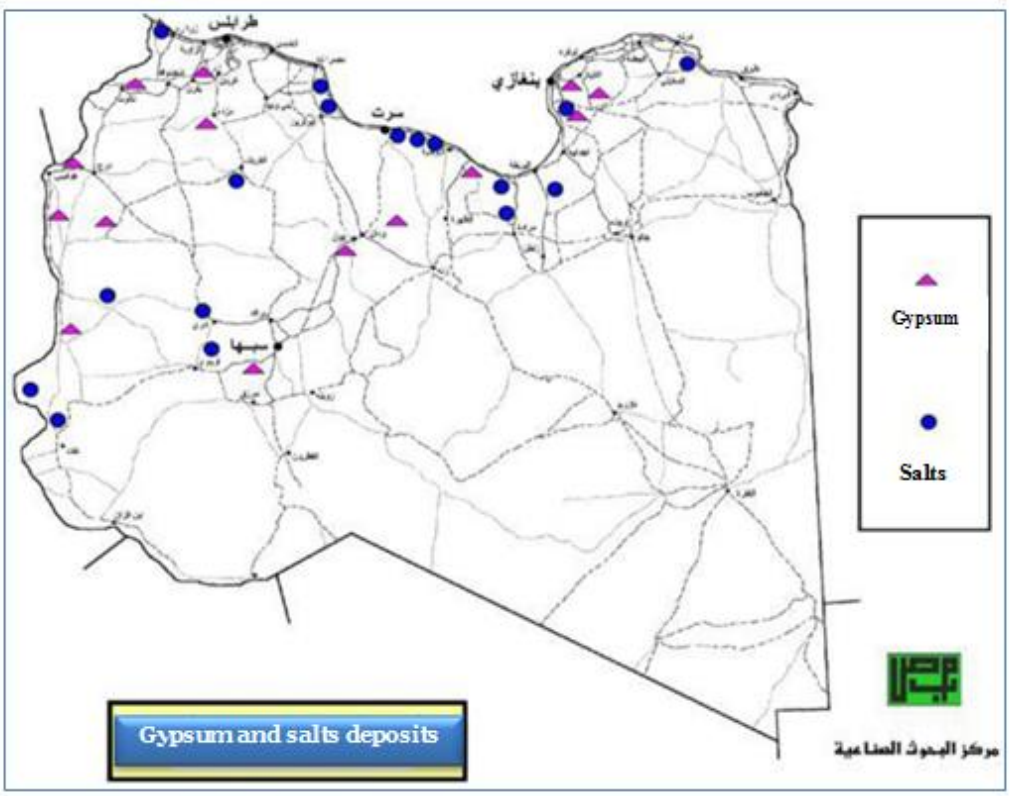

Figure 4 *Location map of gypsum and salts deposits [11]*

Figures 5 & 6 a satellite images show the location of the studied area and their investigated sites at Al Mabrouk quarry.

Figure 5 *Satellite image for the location of study are (Mabrouk quarry)*

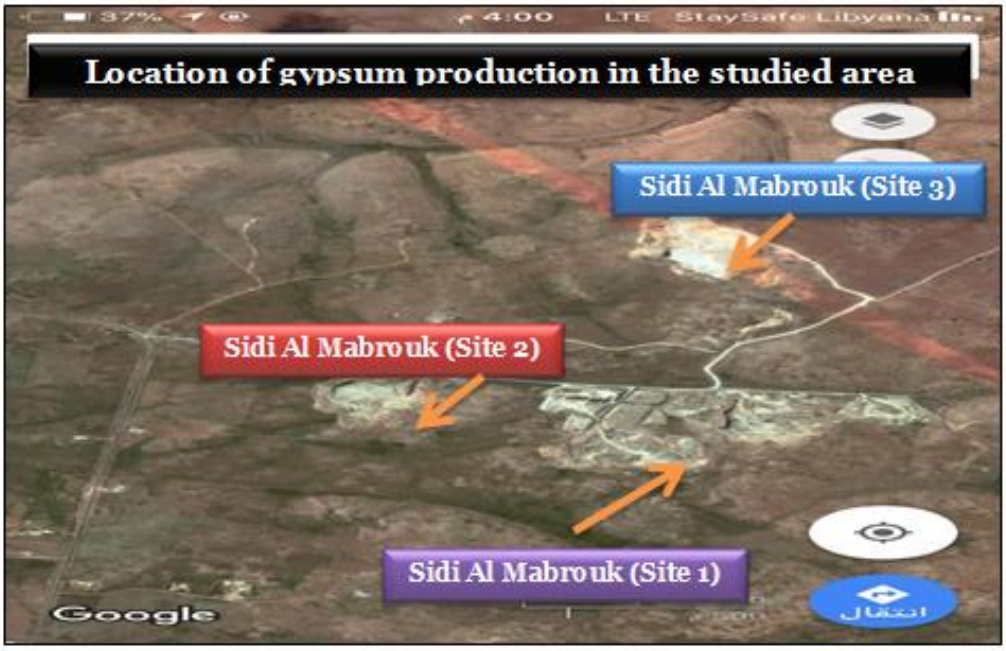

Figure 6 *Satellite image for the study sites at Al Mabrouk quarry*

On the other hand, Figures 5 through 7 photos show the gypsum face cuts at the investigated three sites of Al Mabrouk quarry.

5.2 SAMPLES COLLECTION

The extraction and exploitation of gypsum in the studied area is mainly carried out by open pit methods (Figure 7).

Figure 7 *Open cast mining process in the investigated locations*

To assessment the quality of the gypsum as raw material for the different applications, the raw gypsum samples were brought from the locations of studied sites represented by the three sites, three samples of each site (Figure 6). These samples were subjected to the chemical analysis and physical tests to determine their characterizations. All tests have been carried out in Libyan National Cement Company at Al Fataih area to determine the different constituents using XRF technique.

Figure 8 *The collected samples from Al Mabrouk quarry*

Sample of gypsum from the sites were crushed to fine particles in stages. The final crushing resulted in flour like texture. The powder was loaded into kettles and calcined at about 105°C (221°F), a temperature reasonably above the minimum temperature necessary for calcinations as reported by Coburn [12]. The result obtained from each sample was added and an average result obtained.

5.3 Formation of the Plasterboards

The Plasterboard panel consists of a layer of gypsum plaster sandwiched between two layers of paper. The raw gypsum, $CaSO_4.2H_2O$, was heated to drive off the water then slightly re-hydrated to produce the hemihydrate of calcium sulphate ($CaSO_4. 1/2H_2O$).

5.4 Sample Analysis

The gypsum samples were dried under naturally conditions and later soaked in tap water for 24 hours to reduce impurities such as clay within the gypsum. The gypsum minerals were placed on wire mesh on three steps in an oven in order to allow free circulation of heat in the oven. The temperature of the oven was regulated at 105^oC as a preliminary test for 24 hours.

5.5 Mechanical Properties Measurements

5.5.1 Compressive Strength

Compressive Strength test have been carried out on three samples that representing the three studied sites for the investigated P.O.P specimens. After calcination process and grinding the samples were moulded with a dimensions $200 \times 100 \times 20$ mm. The compressive results revealed a relative variation between the investigated sits as shown in Table 2.

Table 2 *Compressive strength of board samples*

Location	Sample average volume (mm)	Failure load (KN)	Compressive strength (KN/ mm^2)
Site (1)	200 × 100 × 20	11.75	0.588
Site (2)	200 × 100 × 20	12.14	0.607
Site (3)	200 × 100 × 20	12.89	0.645

5.5.2 Modulus of Rupture

Munai [13] presented an explanatory study gives a mathematical formula could be used to estimate the modulus of rupture as following:

$M = 3WL/2bd^2$

where, Lbd sample dimensions and the failure load by KN.

Three samples represented the three studied locations were subjected to examination and the results were presented in Table 3.

Table 3 *Compressive strength of board samples*

Location	Sample average volume (mm)	Failure load (KN)
Site (1)	200 × 100 × 20	0.40
Site (2)	200 × 100 × 20	0.43
Site (3)	200 × 100 × 20	0.46
Failure load average (KN)		0.43

$M = 3WL/2bd^2$

$L = 80$ mm, $b = 100$ mm, $d = 10$ mm

$W = 0.43$ KN

Modulus of rupture = $3 \times 0.43 \times 10^3 \times 80/2 \times 100 \times 10^2 = 5.16$ N/mm^2

ASTM – C-59, (1990) recommended that the minimum value of bearing strength for Plaster Of Paris is 267 N, and 455 N for flexural strength. Accordingly, the obtained result of the investigated samples is 516 N which greater the recommended value of ASTM – C-59, (1990).

6 Results and Discussion

The gypsum ore deposits occur in a huge amounts and high reserves. The thickness varies from site to another ranging from a few meters to more than 20 meters of the outcrops beds (Figure 9). Generally overlain by clay rocks or sometimes calcareous ones. The area have irregular land morphology depending on the lithology and tectonics of the region. The rock outcrops are common on the upper slopes. Weathering products cover the lower slopes. Peaks around the region are generally W-E and sometimes NW-SE trending. The climate is an east Mediterranean one. In the region, the summer is mild and humid and the winter is mild and wet. Precipitation occurs mostly in the form of rainfall, intensifying winter.

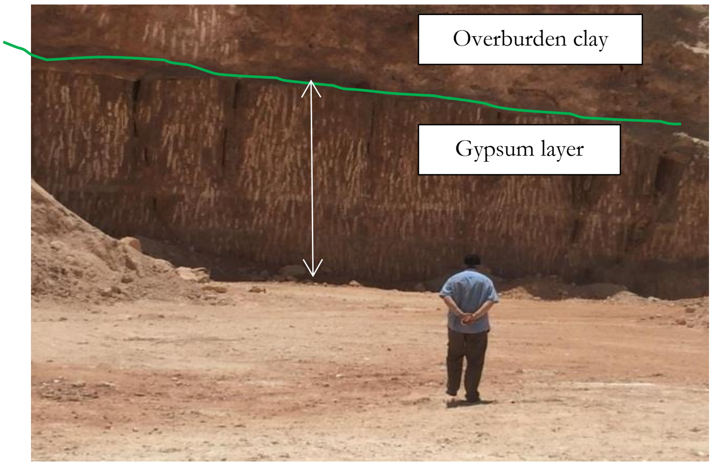

Figure 9 *Thickness variation of gypsum depsites*

Generally, in the point of view of the previous geological studies, Libya has beendivided into four main regions as following:

1. Northwestern region: include Tripoli area, Al Jofra coastal plain, Nafossa mountain, Hamada basin and northern Gargaf elevations.
2. Northcentral region: include Sirte basin and Al Jofra area.
3. Northeastern region: made up of Cyrinica area, Al Jabal Al Akhadar, Al Sarir and Al Jaghboub.
4. Southwestern region: represented by Fazan area and Merzq basin.

This study has been performed on the local gypsum deposits in north east Benghazi city which belonging to the Northeastern region which covered by a succession of clay and limestone rocks which go back to the Tertiary of Cenozoic Era, representing by Al Faidiyah formation.

6.1 Chemical Analysis

Three samples from different from each quarries were ground to fine powder using mortar and pestle to prepare for chemical analysis. Tables 5 through 7 provide the results of chemical analysis for the studied locations.

Table 5 *Chemical composition of three gypsum samples for site (1)*

Chemical compound	Chemical composition (Wt. %)			Average ($\bar{x}$)
	Sample (1)	Sample (2)	Sample (3)	
SO_3	43.40	44.19	42.99	43.52
CaO	23.06	23.90	22.96	23.30
MgO	1.45	1.49	1.50	1.48
K_2O	0.33	0.30	0.29	0.31
Na_2O	0.21	0.25	0.26	0.24
MnO	0.033	0.32	0.30	0.217
TiO_2	0.050	0.045	0.052	0.049
Fe_2O_3	0.25	0.20	0.21	0.22
Cl	0.0050	0.0042	0.0056	0.0049
L.O.I.*	33.40	29.20	30.53	31.043
$\sum$	99.19	99.70	99.10	99.33

L.O.I.* = loss on ignition

Table 6 *Chemical composition of three gypsum samples for site (2)*

Chemical compound	Chemical composition (Wt. %)			Average ($\bar{x}$)
	Sample (1)	Sample (2)	Sample (3)	
SO_3	43.43	43.16	42.40	42.99
CaO	22.82	21.96	20.99	21.92
MgO	1.07	1.02	1.15	1.08
K_2O	0.25	0.22	0.19	0.22
Na_2O	0.21	0.19	0.24	0.213
MnO	0.024	0.030	0.032	0.028
TiO_2	0.0037	0.0031	0.002	0.0029
Fe_2O_3	0.22	0.26	0.31	0.26
Cl	0.0040	0.0039	0.0044	0.0041
L.O.I.	30.93	32.19	33.80	32.31
$\sum$	98.96	99.02	99.12	99.03

Table 7 *Chemical composition of three gypsum samples for site (3)*

Chemical compound	Chemical composition (Wt. %)			Average ($\bar{x}$)
	Sample (1)	Sample (2)	Sample (3)	
SO_3	42.70	41.15	40.12	41.32
CaO	22.66	24.16	25.01	23.94
MgO	1.12	1.19	1.21	1.17
K_2O	0.33	0.35	0.41	0.36
Na_2O	0.19	0.28	0.30	0.26
MnO	0.026	0.032	0.031	0.029
TiO_2	0.040	0.044	0.046	0.043
Fe_2O_3	0.22	0.290	0.310	0.273
Cl	0.004	0.0091	0.0062	0.0064
L.O.I.	31.80	31.37	31.58	31.58
$\sum$	99.09	98.88	99.02	98.99

The gypsum samples were dried under naturally conditions and later soaked in tap water for 24 hours to reduce impurities such as clay within the gypsum. The gypsum minerals were placed on wire mesh on three steps in an oven in order to allow free circulation of heat in the oven. The temperature of the oven was regulated at 105°C as a preliminary test for 24 hours. Only partial transformation to hemihydrates was observed. To achieve the required calcination of gypsum, the temperature was raised to about 200°C (392°F) for another 24hours. The calcined gypsum was brought out and the mineral was observed to become completely whitish in physical presentation. The same process was carried out for the second batch of calcination. In order to achieve smooth and homogenous finish to the board surface, the calcined mineral was ground and 200µm sieve was used to obtain fine powder. The powder was then placed into clean polythene bag to avoid moisture absorption. The average chemical composition of the investigate gypsum is shown in Tables 8, while Table 9 gives the chemical composition of the plaster in percentage by weight. Tables 10 and 11 give comparison of the chemical composition of the studied gypsum and its plaster with those of pure gypsum respectively.

Table 8 *Chemical composition of plaster of site (1)*

Chemical compound	Chemical composition (Wt. %)			Average ($\bar{x}$)
	Sample (1)	Sample (2)	Sample (3)	
SO_3	54.12	55.16	53.77	54.35
CaO	26.90	27.02	25.97	26.63

H_2O	16.10	15.02	19.33	16.82
$\sum$	97.12	97.2	99.07	97.80

Table 9 *Chemical composition of plaster of site (2)*

Chemical compound	Chemical composition (Wt. %)			Average ($\bar{x}$)
	Sample (1)	Sample (2)	Sample (3)	
SO_3	53.41	54.16	53.62	53.73
CaO	25.66	26.14	24.88	25.56
L.O.I.	19.87	18.88	20.22	19.66
$\sum$	98.94	99.18	98.72	98.95

Table 10 *Chemical composition of plaster of site (3)*

Chemical compound	Chemical composition (Wt. %)			Average ($\bar{x}$)
	Sample (1)	Sample (2)	Sample (3)	
SO_3	53.10	52.19	52.77	52.69
CaO	24.19	25.84	25.98	25.34
L.O.I.	21.74	20.12	21.40	21.09
$\sum$	99.03	98.15	100.15	99.11

Table 11 *Comparing average gypsum and plaster chemical composition with pure gypsum*

Chemical compound	Pure gypsum (wt. %)	Gypsum (wt. %)			Pure gypsum plaster (wt. %)	Gypsum plaster (wt. %)		
		Site (1)	Site (2)	Site (3)		Site (1)	Site (2)	Site (3)
$CaSO_4$	79.20	72.24	71.16	69.67	93.50	90.12	88.66	87.54
$2H_2O$	20.95	26.57	27.95	29.33	6.50	9.05	10.14	10.98
$\sum$	100.15	98.80	99.11	98.99	100.00	99.17	98.80	98.52

Figure 10 gives a comparison between the local investigated gypsum samples and the standard pure one; while Figure 11 depicts the comparison between the studied gypsum plaster samples and the pure gypsum plaster. Both of them display no much difference which indicate that the local gypsum has good characterizations. It was recommended by Singer [13] that pure gypsum should have about 93. 8% $CaSO_4$ and 6.2% H_2O while the American Standard of Testing Materials (ASTM) – C-59 (1990) recommends 85% minimum of dehydrated purity. Thus, sites 1, 2 and 3 are 90.12%, 88.66% and 87.54% respectively have met the ASTM – C – 59 [14] requirements.

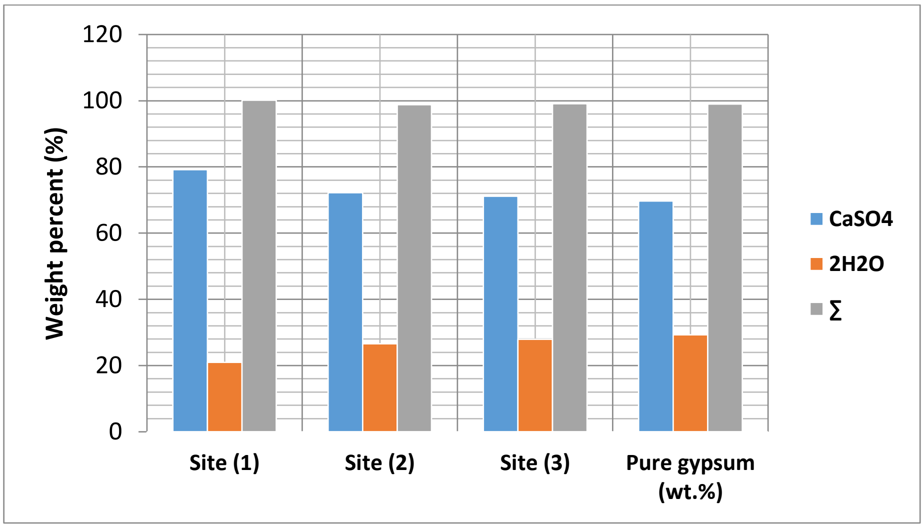

Figure 10 *A comparison between local gypsums and standard one*

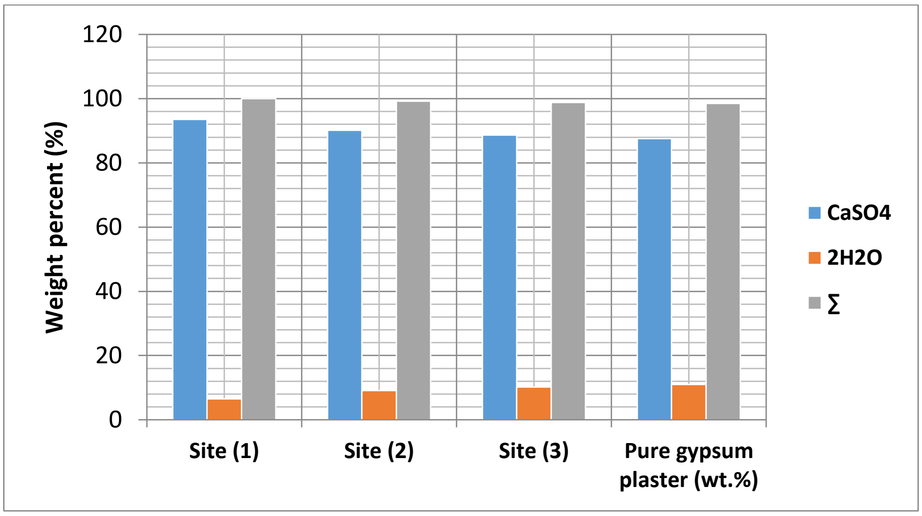

Figure 11 *A comparison between local gypsum plaster and the pure gypsum plaster*

6.2 Setting Time

The plaster of Paris has a very short setting time which sometimes limits its usefulness, in some conditions like in buildings; however, the short setting time is a useful property. The optimum setting time is usually determined by the user's needs and convenience which can also be controlled through the use of additives. Table 12 shows the setting time of various mixes.

Table 12 *Setting time of calcined plaster with different water ratios*

S/N	Water ratio (ml)/dry plaster (g)	Pouring time (sec)	Setting time (sec)
1	150/350	19.0	370
2	160/350	24.0	485

3	170/350	29.0	498
4	180/350	34.0	530
5	190/350	38.0	565
6	200/350	41.0	610

The findings were obtained in Table 10 reveal that, as the quantity of water increased so did the setting time. Although 200 ml of water was poured in 41.0 seconds, 3 seconds less than the pouring time of 190ml, a longer time of 610 seconds was recorded as the setting time for the 200ml as against that of the 190 ml (565 seconds). This shows that the setting time is dependent upon the water content rather than the pouring time as illustrated in Figure 12.

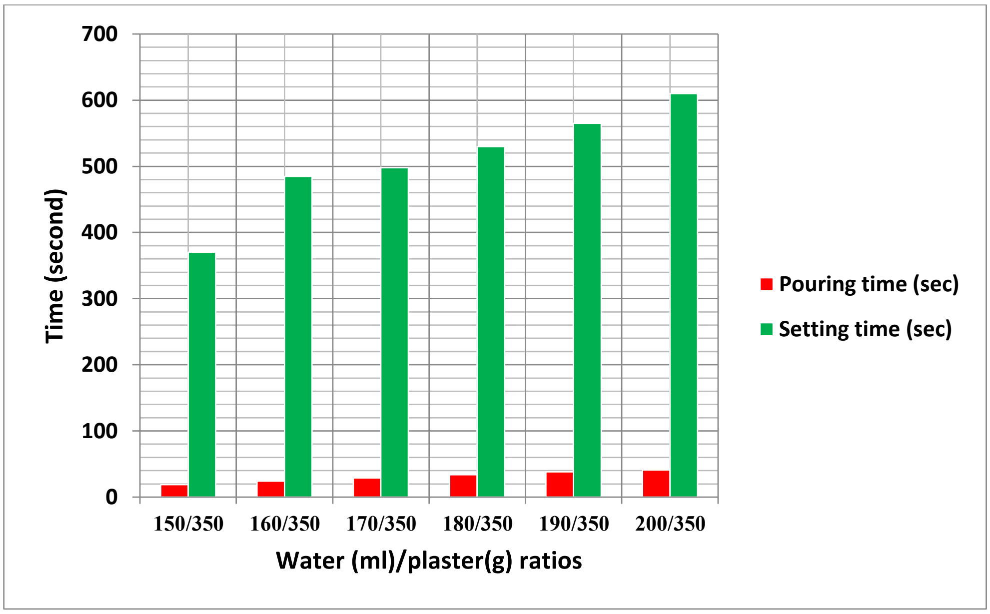

Figure 12 *Relationship between water/plaster ratios and time*

7 Conclusions

The varieties of gypsum minerals investigated in this study that based on the results of the physical and chemical analyses, it can be concluded that studied local gypsum has satisfied the requirement of good gypsum. The tests carried on the gypsum and plaster produced revealed that the gypsum is suitable for the production of quality calcium sulphate, hemihydrate ($CaSO_4.1/2H_20$) which is termed Plaster Of Paris (P.O.P). The ability to control the time of rehydration by addition of retarders or accelerators offers the huge and diverse nature of industrial applications in medicine, art, ceramics, building and construction among others. On the other hand, the mechanical testing of Plaster Of Paris samples revealed an acceptable characterization for construction purposes according to the recommended value of ASTM – C-59, (1990).

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