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A Comparative Study between the Historical Stones of Al-Namrud Monument in Iraq and the Fresh Stones Extracted from its Quarry Using TGA and XRD Analysis

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ABSTRACT

This study implies a characterization and comparison between the historical limestone and gypsum stones of Al-Namrud or (Calah) monument which located in the north of Iraq 37 km to the eastern south of Mosul city (eastern bank of the Tigris river) and those (fresh) extracted from Al-Mur hill which suppose to be its quarry (according to the historicity and archeology references). The aim of this study is the conviction of the veracity of these references depending on a number of complementary engineering techniques. These tests include physicochemical and mineralogical properties of fresh and historical stones , textural arrangement of particles (porosity and pore size distribution) by mercury porosimetry tests; water transfer properties by water retention curve test; bulk density at dry state by hydrostatic weighing method have been executed . Also a comparison between the fresh and historical stones has been carried out by *X-Ray* Diffraction ***(XRD)*** and Thermo Gravimetric Analysis (TGA). Results shows for the historical stone higher porosity and different pore size distribution, water transfer properties in comparison to the fresh stone .Also, a high match in the compositions of stone materials of both historical and fresh one reflect the rightness of the historicity and archeology references and their consideration of being Al-Mur hill the quarry of Al-Namrud monument.

Keywords: Historical Monuments, Multiscales Characterization, Al-Namrud Monument Quarry

دراسة مقارنة بين الحجارة التاريخية من نصب النمرود في العراق والأحجار المستخرجة من المحاجر الطازجة وذلك باستخدام تحليل TGA وXRD

الخلاصة

تعنى هذه الدراسة بتوصيف ومقارنة بين الحجر الجيري والجبس التاريخية من منطقة نمرود أو (كالح) الواقعة في شمال العراق 37 كم إلى الجنوب الشرقي من مدينة الموصل (الضفة الشرقية لنهر دجلة) وتلك (الطازجة) المستخرجة من تل المر الذي يفترض أن يكون المحجر لها (وفقا لعلم الآثار التاريخية والمراجع). والهدف من هذه الدراسة هو التأكد من صحة هذه المراجع اعتمادا على عدد من التقنيات الهندسية التكميلية. وتشمل هذه الاختبارات الخصائص الفيزيائية والكيميائية والمعدنية من الحجارة الطازجة والتاريخية، والترتيب النسيجي للجسيمات (المسامية وتوزيع حجم المسام) عن طريق اختبارات المسامية الزئبقية؛ خصائص نقل المياه بواسطة اختبار منحنى احتباس الماء ؛ الكثافة الظاهرية في الحالة الجافة بواسطة الطريقة الوزنية الهيدروستاتيكية. كما تم إجراء مقارنة بين الحجارة الطازجة والتاريخية عن طريق حيود الأشعة السينية (XRD) والتحليل الوزني الحراري (TGA). أظهرت النتائج ان للحجر التاريخي مسامية أعلى ومختلفة التوزيع من حيث حجم المسام،و خصائص نقل المياه بالمقارنة مع الحجر الطازج. كما وجد تطابق عالي في تركيبة المواد الحجرية لكلا التاريخية والطازجة واحدة تعكس صواب المراجع التاريخية والآثار باعتبار تلة المر هي المحجر لنصب النمرود.

INTRODUCTION

In the north of Iraq, beginning in the second millennium B.C., the Assyrian Empire developed great cities such as Nineveh, Korsabad, and Calah (Al- Namrud). The walls of Al-Namrud, located 37 km to the eastern south of Mosul city, were built with the clayey brick which provide a good isolation, then covered with a plates of green gypsum stones, while the ground was covered with a plates of limestone, also the outer major fence was built with limestone. The quarries of the stone elements (gypsum stone and limestone) which used in the construction of the monument were extracted from Eski-Mosul area in a place named locally by Al-Mur hill [4].

This work is a part of a research program aimed to make sure that Al-Mur hill location which located in Eski-Mosul area is the stone quarry of Al_Namrud monument (as the historicity and archeology references mentioned).This verification was come through an engineering complementary techniques: Water Retention Curve (WRC), mercury intrusion porosimetry, and X-ray diffraction (XRD) and Thermogravimetric (TGA) analysis limit the amount and type of the stone materials.

There are many monument locations spread in different parts in Iraq , among them are the most important historical monuments from tourist point of view are the following [7]:-

Samarra, Babylon, Hatra, Agargof, Al- Namrud, Ashur, Al-Madaen, Al-Akhezer castle, Ninevah , kish and Ur.

In Mosul city, more than 2000 historical locations(in both types Islamic and Assyrian) are located within the administrative boundary of the city [8]. These historical cities are constructed from materials collected from quarries located in different distance of the monument [9], but the majority of these quarries are extinction due to city growth especially the Islamic locations .The monuments which their quarries are known until now are the Assyrian monuments [4], since these monuments were submitted to many conservation processes since the fortieth of the last century by the Iraqi Official of Museum and Heritage [8].

EXPERINMENTAL PROGRAM

Characterization methods

A multi-scale characterization was conducted on the studied samples (historical and fresh) in order to identify stone properties.

Mineralogical characterization: XRD and TGA

X-ray diffraction patterns were obtained on powders of stone using Philips Apparatus with the K line of copper (λ_{Cu} = 1.5406 A) with 20 from 1.5° to 60°. In order to compare the obtained patterns, the main quartz reflection is used to scale the X-ray patterns intensities for all tested samples. In TGA test, the mass loss of a given sample is recorded under controlled temperature ramp. The apparatus used is a Setaram TG-DTG 92-16 electrobalance operating within the 20-1000°C range, with a heating rate of 100°C per hour and under argon atmosphere.

Porosity and pore size distribution tests

Bulk dry density was determined by hydrostatic weighing method which is based on the Archimede's principle on a sample saturated and submerged in a wetting fluid as water [1].

The mercury intrusion method was performed by applying pressure (up to 210 MPa) and monitoring continuously the intruded volume of mercury in the pores of the tested sample. The radii of pores were estimated using Young-Laplace equation. Theoretically, pores with a diameter between 350 μ m and 4 nm can be investigated with the apparatus used: a Poresizer 9320 porosimeter. Limestone and gypsum stone samples of about 1 cm^3 were dried at 105 °C and 70 °C for 24 hours and then tested.

Water Retention Curve (WRC)

The Water Retention Curve (WRC) defines the ability of the stone samples to store and/or release water .Commonly used together with the water content to estimate soil suction .This curve describes the relation between the percentage of moisture content, degree of saturation, percentages of relative humidity and at some times the volumetric water content of the stone and the matric potential (matric suction) under equilibrium conditions [6, 3, 5].

The WRC consists of three parts; each part is limited with a specified range of matric suction and these parts are:

Salt Solutions: This technique is used to study the water retention curve in the range of suction 2.7 MPa.

Osmotic Solution Method*:* This technique is used to study the water retention curve in the range of suction values between 0.1 MPa and 1.5 MPa.

Tensometric Plates*:* This technique is used to study the water retention curve in the range of suction values between 0.001 to 0.01 MPa.

RESULTS AND ANALYSIS

Characterization of the historic and fresh stone samples

Figure (1) shows the mercury intrusion porosimetry curves of the tested fresh and historic limestone stones. Total pore volume is higher in the historical stone than in the fresh limestone. Also, pore size distribution is shifting towards higher pore diameter in the historical stone. Table 1 detail the main parameters obtained from mercury porosimetry and from hydrostatic density method. The porosity determined by mercury porosimetry is 60% higher in the historical (34%) to that in the fresh stone (21%). Pore spaces having diameter more than 6 μm represent about two third of total pores in the historical (altered) sample while these pores represent initially (in the fresh stone) about one quarter of the total pores. Moreover, the average pore diameter is more than doubled; the bulk and the skeletal densities are decreased in the altered stone in comparison to the fresh stone. Moreover, porosities measured by mercury tests are lower to that measured by hydrostatic density method, 38% and 26% for the historical and fresh stone respectively. Finally, bulk density and skeletal density are lower in the historical than in the fresh stone. Mercury can't invade the small pores (<10 nm) and can't account the largest pores (>300 μm); i.e. this technique does not take into account all the pore volume and thus the measured porosity is lower than the real porosity.

Depending on the porosity classification [2] the fresh gypsum stone could be classified as sufficiently impervious while the historical gypsum stone was classified as a low porous to porous material. Also a difference in the porosity values has been noticed between the hydrostatic and mercury intrusion methods Table (2), this is attributed to the same reason mentioned in the case of fresh and historic limestone. Through the pore size distribution of both fresh and historical gypsum stones in Figure (2), two zones of pores are observed, the first zone is ranged from 6 pm to 200 pm where the amount of pores of the historical gypsum stones increased from the fresh one by 0.00116 mL/g, while the second zone is ranged from 3 pm to approximately 0.02 pm where the amount of the pores increased from the fresh gypsum stone by an amount of 0.03851 mL/g.

Figure (3a) shows the Water Retention Curve (WRC) of both fresh and historic limestone. The difference in the pore size distribution and porosity of both fresh and historical limestone reflect the difference in the ability for water retention.

In the zone of suction values (>2 MPa), the amount of the meso-micro pores for the fresh limestone was more than the historical one, also the capillary pressure (ability) to retain water inside the meso-micro pores for fresh limestone was approximately more, but in the zone (<2 MPa) the amount of the macro pores for historical limestone are more than the fresh one, thus a more amount of the water will easily fill the pore of the historical limestone. In the case of gypsum stones, Figure (3b), the WRC of the historical gypsum stone is above the fresh one; which reflects the high ability of the historical stone to retain the water inside its pores. This come through the high amount of the meso-micro pores which produce an ability to retain water inside the pores in the zone (more than 2 MPa), and this ability increases with the increase in the amount of the macro pores in the zone (less than 2 MPa) as compared with the fresh stone

Comparison between the fresh and historical stones

Figure (4) shows the X Ray Diffraction analysis (XRD) of both fresh and historic limestone. XRD analyses shows that the major mineralogical compositions are Calcite (CaCO3), silica (SiO2) in the form of quartz. Figure (5) shows the Thermo Gravimetric Analysis (TGA) of both fresh and historic limestone, the calcium carbonate was about 90% and 94% in the historical and fresh stones respectively. These two stones are practically pure limestone with some clay and siliceous impurities.

CONCLUSIONS

Characterization results shows a modification in the porosity properties and water retention ability for the historical stones as compared with the fresh one due to the degradation agents which the historic stones may submit to it the field within the Al-Namrud monument structure. In spite of these modification the stone materials remains the same as shown by the results of XRD and TGA analysis, where these analysis exhibit great match in the mineralogical component and their amounts but with a slight difference and some impurities due to the weathering agents in the field. Thus, this comparison between the fresh and historic stones using XRD and TGA techniques confirm what the historicity and archeology references mentioned about the quarry of Al-Namrud monument is Al-Mur hill in Eski-Mosul area.

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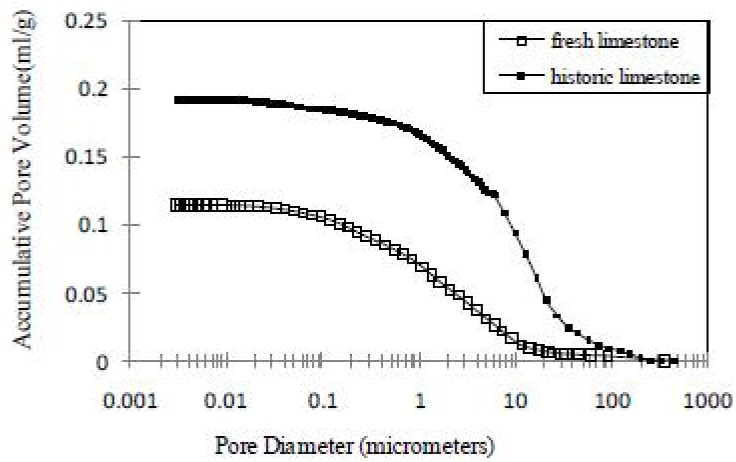
Table (1) Properties of the fresh and historic limestone.

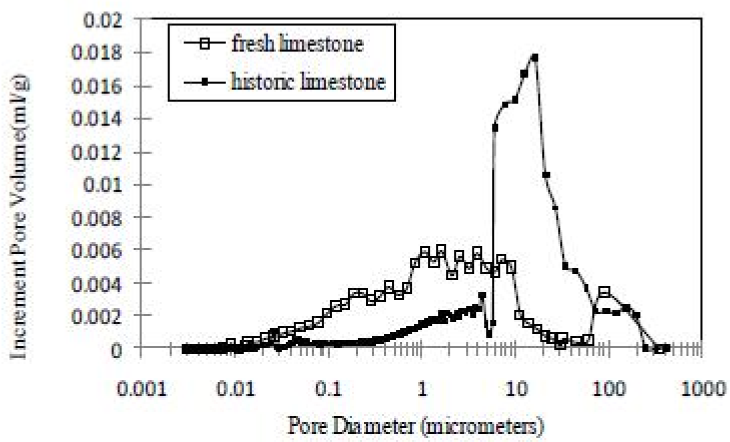
	Historic limestone	Fresh limestone
Bulk density(gmcm^3)	1.71	2.04
Skeletaldensity(gm/cm^3)	2.58	2.66
Porosity by hydrostatic method(%)	38	26
Porosity by mercury intrusion(%)	34	21
% of pores having>6µm	65	25
% of pores having<6µm	35	75
Average Pore diameter(µm)	0.73	0.28

Table (2) Properties of the fresh and historic Gypsum stone.

	Historic Gypsum stone	Fresh Gypsum stone
Bulk density(gmcm^3)	2.13	2.25
Skeletaldensity(gm/cm^3)	2.35	2.28
Porosity by hydrostatic method(%)	10.5	1.6
Porosity by mercury intrusion(%)	9.5	1.2
% of pores having>6µm	13	100
% of pores having<6µm	87	0
Average Pore diameter(µm)	4.4	0.12

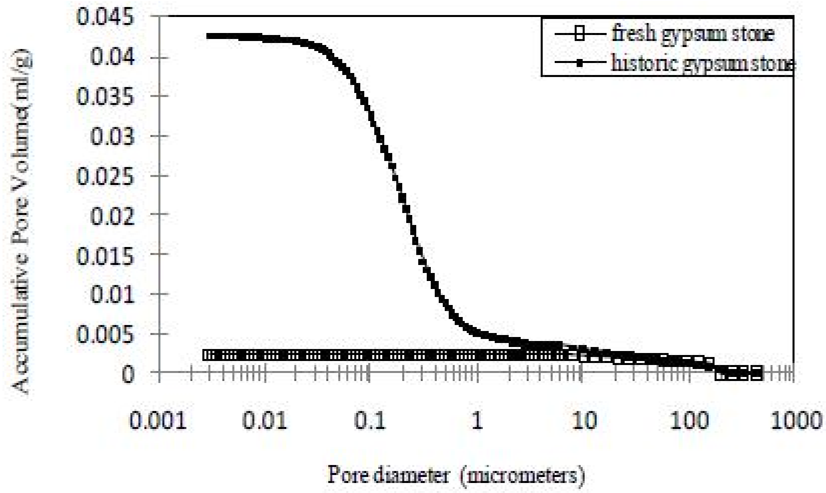


a. Cumulative pore volume

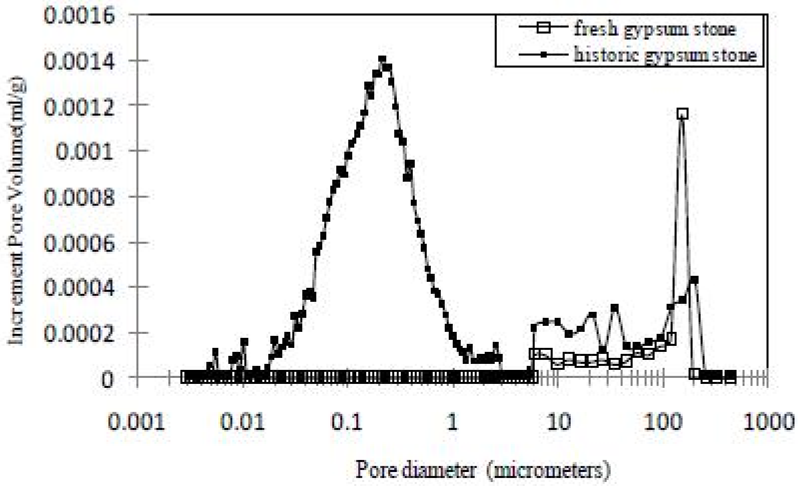


b. incremental pore volume

Figure (1) Mercury intrusion porosimetry results of the Historical and fresh limestone showing cumulative pore Volume (above) and incremental pore volume (Lower).



a. Cumulative pore volume



b. incremental pore volume

Figure (2) Mercury intrusion porosimetry results of the historical and fresh Gypsum stone showing cumulative pore volume (above) and incremental pore volume (Lower).

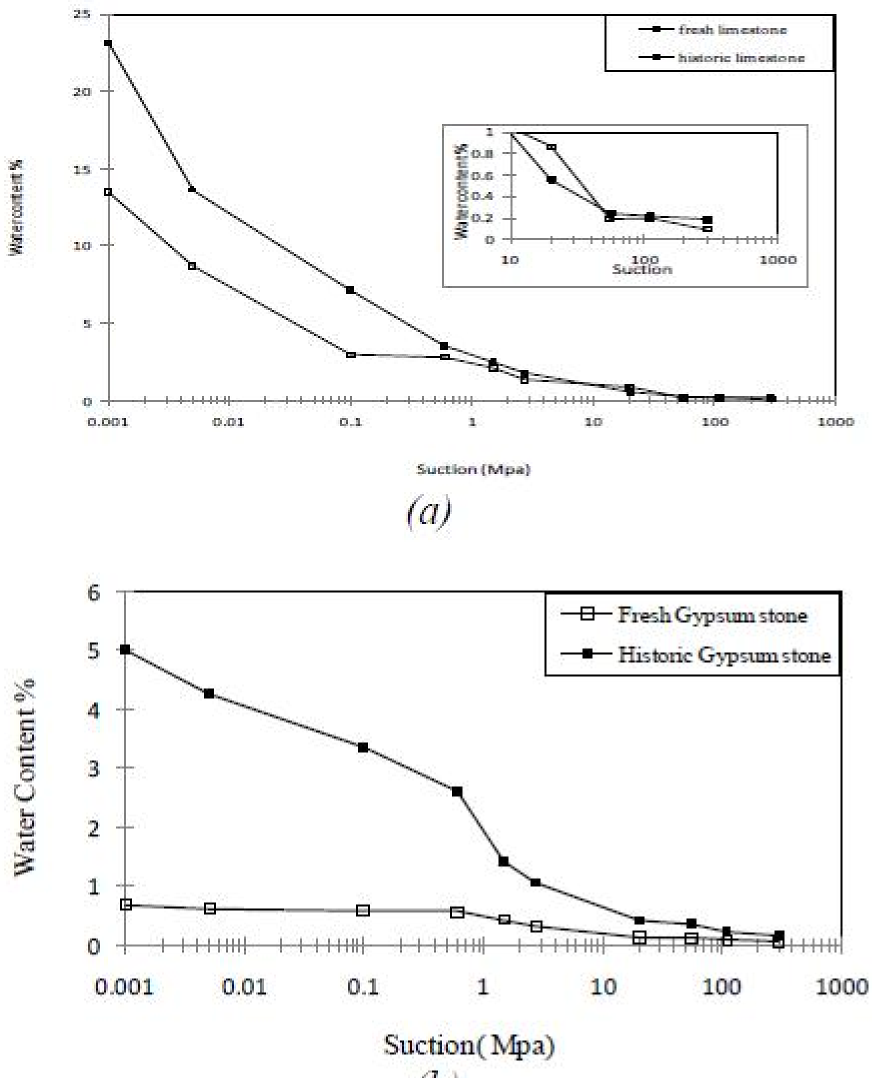
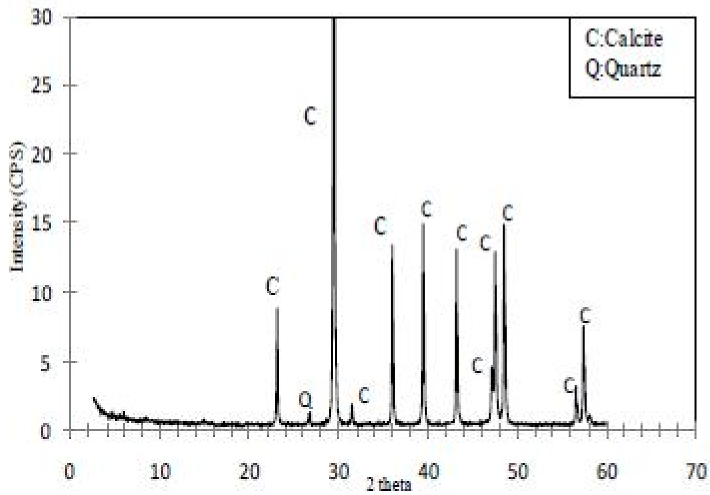
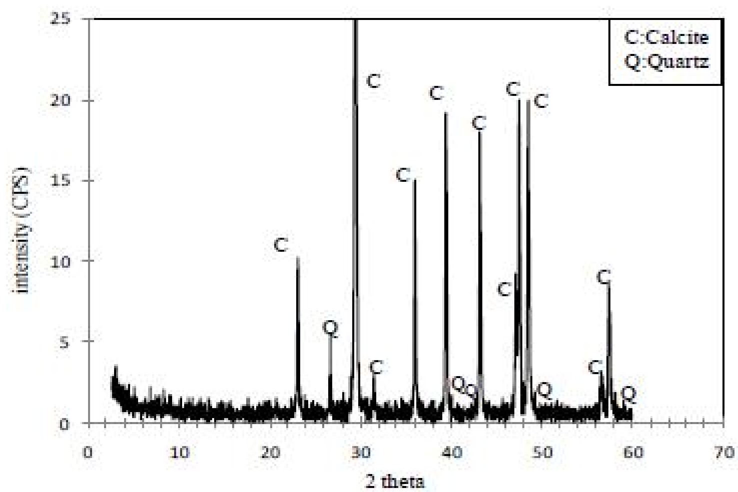


Figure (3) The Water Retention Curve (WRC) of: (a) fresh and Historic limestone. (b) Fresh and historic gypsum stone.



(a)



(b)

Figure (4) XRD of (a) fresh limestone. (b) historic limestone.

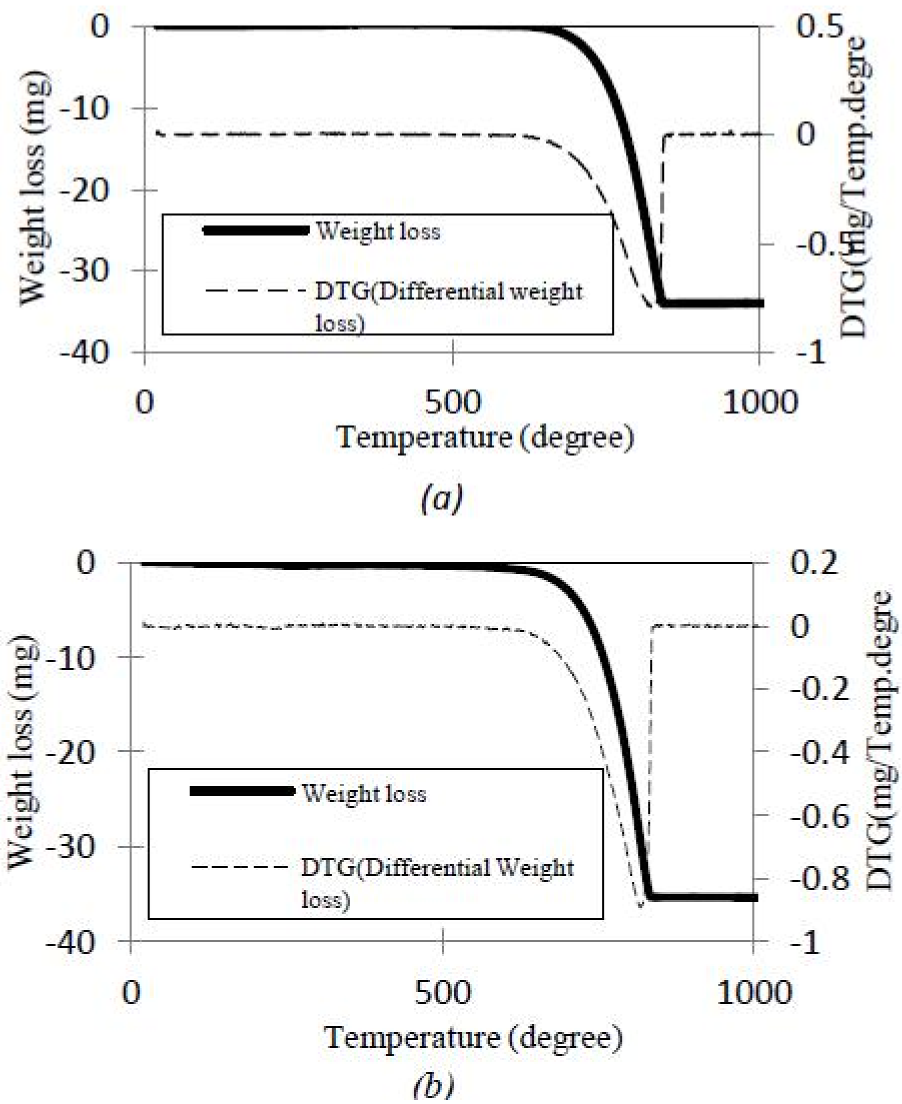
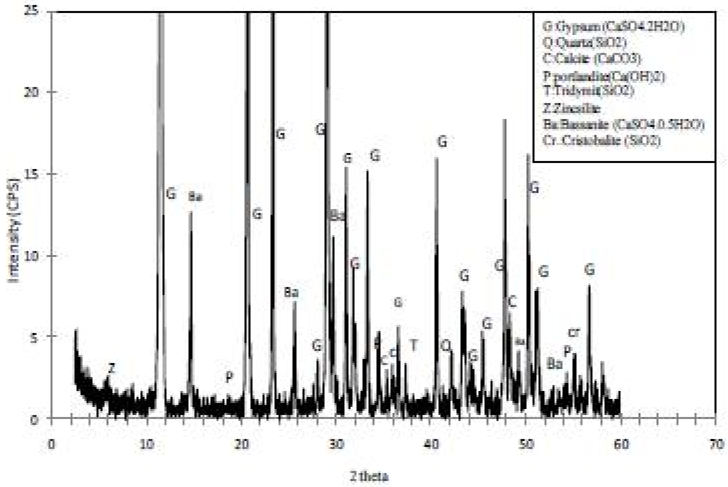
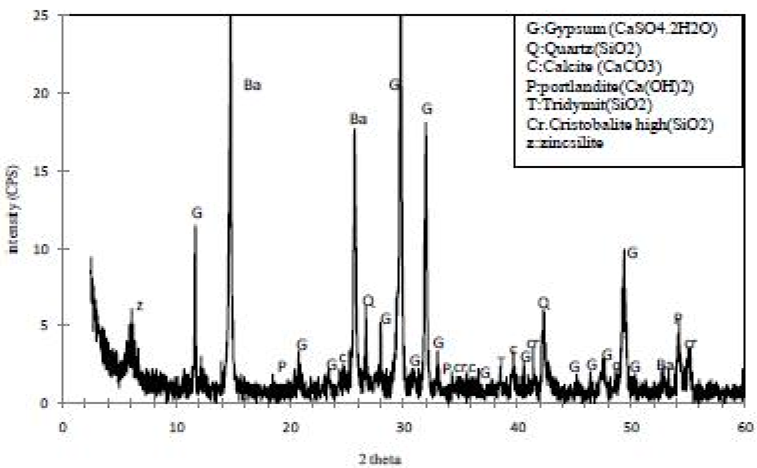


Figure (5) TGA of (a) fresh limestone. (b) historic limestone.



(a)



(b)

Figure (6) XRD of (a) fresh gypsum stone.
(b) Historic gypsum stone.

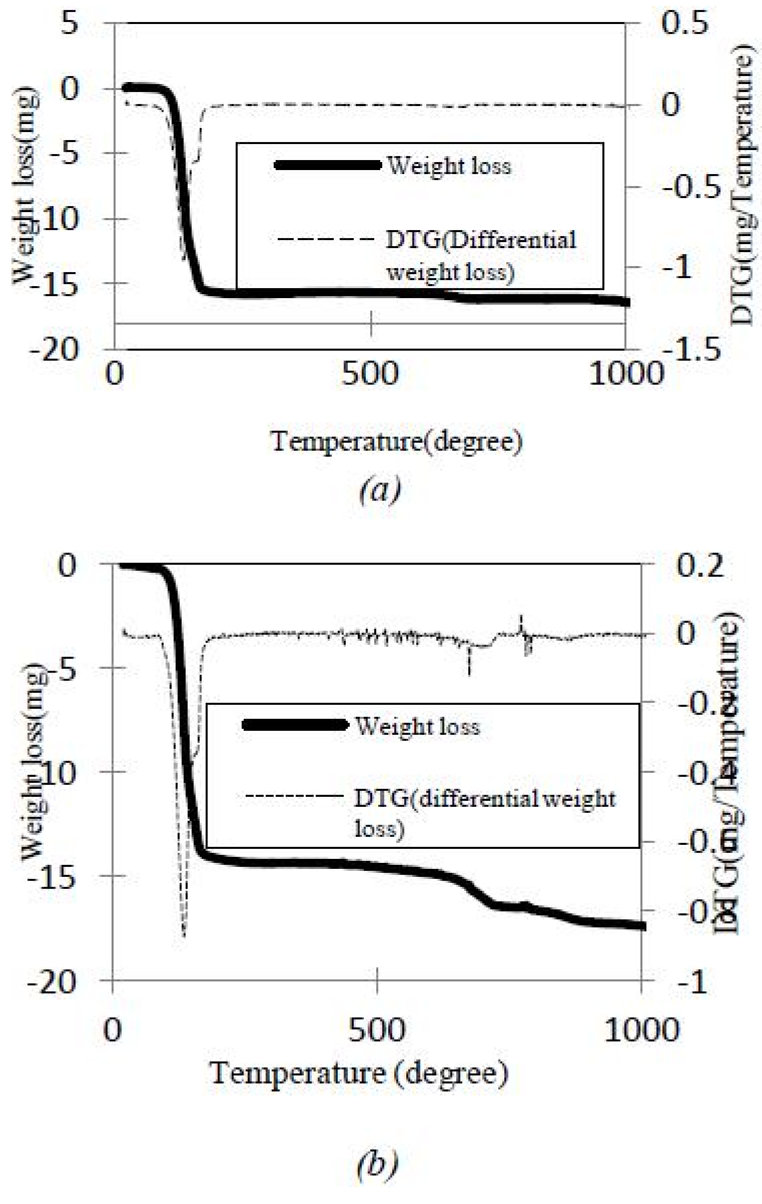


Figure (7) TGA of: (a) fresh gypsum stone, (b) Historic gypsum stone.