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Characterization and Determination the Optimal Conditions of Syrian Limestone, for Calcification and Extinguishing

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Abstract
In this study, Characterization of Syrian limestone was conducted from the area of Al-Musallamiya-Aleppo. The optimal conditions for calcination of the limestone sample were studied. Results indicated that the preferred conditions for calcination were depended on crashing the limestone sample of a diameter of 5 cm at 1200°C for 60 min. The optimal conditions for extinguishing the calcined limestone sample have also identified, where the highest yield was obtained at a liquid to the solid phase ratio (L/S) of 3: 1, at 75°C for 30 min reaction?. As a result, two highly important products have obtained in various industrial fields, calcium oxide and calcium hydroxide from local ore, which is widely available in large parts of the Syrian Arab Republic.

Keywords: Limestone, Calcination, Calcium Oxide, Calcium Hydroxide.

Introduction
Limestone is a calcite rock, consists mainly of calcium carbonate $CaCO_3$, calcite or aragonite, and may also contain a high percentage of magnesium carbonate (Dolomite), in addition to some other components in small quantities such as chloride, iron oxide hydrate, feldspar, and quartz [1-3].

Limestone, marble and calcium ($CaCO_3$) are the main component of calcite, which is one of the most widespread raw materials in nature. $CaCO_3$ is composed of 56% of CaO and 44% of CO_2. It also contains impurities such as Mg^{+2}, Fe^{+2}, Mn^{+2}, and sometimes Pb^{+2}, SO_4^{-2} are crystallized according to a cubic crystalline structure as in Figure 1 [1-5].

Aragonite consists of 56% CaO and 44% CO_2, with some impurities such as Fe^{2+}, Al^{3+}, Mg^{2+}, Mn^{2+}, SO_4^{2-}. Its crystalline structure differs from that for calcite, as aragonite takes the form of chains of carbonate roots CO_3^{2-} trigonometric, located above each other and associated with Ca^{2+} to form columns extending along the C axis, Figure 2 [1-3].

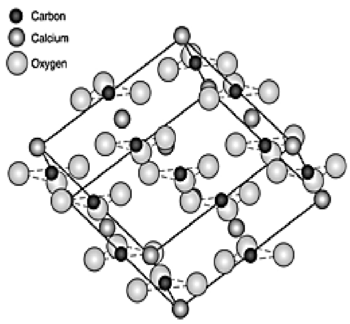

Figure 1: The crystal structure of calcite.

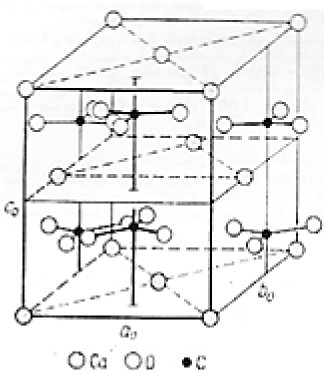

Figure 2: The crystal structure of aragonite.

Dolomite is composed of $CaCO_3.MgCO_3$, the crystalline form of trigonal crystals, whose crystals may be transparent as water.

Magnesium may be replaced with iron or manganese, thus, the color of dolomite will change into gray, brown, or red [1-3].

Uses of limestone and its derivatives in industry

The limestone compounds are used in many industrial fields. Limestone is used for the preparation of various types of cement, pyrotechnics, ceramics, glass and others [REFERENCES]. Calcium oxide is used in iron and steel plants to remove phosphorus and sulfur, in water treatment, in agriculture to modify the acidity of the soil or to cover the lack of calcium in the soil. As well as, Calcium oxide is used in the manufacture of a large number of organic and inorganic compounds [REFERENCES]. Calcium hydroxide is used to sterilize the cellars and animal breeding sheds, especially within the wetlands. Adding calcareous materials to marshes was used to inhibit all forms of microbes. it is also used to paint the trunks of light fruit trees to avoid dehydration [3].

Materials and Methods

Preparation of raw limestone

Collection of limestone samples: Limestone samples were collected from Al-Musallamiya area northeast of Aleppo, where reservoir reserves were estimated at 70 million tons [6]. Samples were collected as described in international methods (ASTM C-33) [Reference].

Primary treatment of limestone: limestone was cracked, washed with water to remove some impurities, and dried. The washed limestone was sorted into several different granular sizes 2, 3, 4, and 5 cm.

Characterization of calcareous limestonee

X-ray (XRF): 25 g of dry limestone was grinned in a crushing mill for 5 min. A weight of 10 g of the resulted grin was then mixed well with 3g of boron powder and placed in an aluminum mold. The sample was then pressed roughly 150 KN to obtain a disc of 30 mm diameter and a thickness of 5 mm.

Crystal Phases: phases were determined using XRD (2 θ: 10-70 A°), with a filter of nickel, Cu $K_{\alpha 1}$ radiation and wavelength (λ = 1.5405 ° A).

Infrared spectroscopy (IR): IR measurement was performed using the FT-IR spectrometer (JASCO 4100) within a range of λ 400-4000 cm^{-1}. A dry sample (heated up to 60°C) was compressed with KBr (1:200) at the value of 7ton / cm^2.

Differential Thermal Analysis: The thermodynamic behavior of the calcareous limestone was determined using the Linseis 851 DTA. Heat was applied gradually on a quantity of crushed limestone at a constant time (10°C/min), starting from room temperature up to 1400°C. After that, the sample was slowly cooled up to a room temperature.

Study the optimal conditions for calcification of limestone

To determine the best conditions for calcification of limestone: the following were investigated:

- Effect of particle size
- Effect of temperature
- Effect of calcination time.

The weight loss was calculated to determine calcination coefficient according to the following:

$CaCO_3$	$\xrightarrow{\Delta}$	CaO	+	CO_2
100g/mol		56g/mol		44g/mol
X_1		X_2		X_3

The calcination output is calculated by the following ratio: $R\% = \frac{X_4}{X_3} \times 100$

X_1: weight of the sample (g) before calcination.
X_2: weight of the sample (g) after calcination.
X_3: weight loss (theoretical value) (g).
X_4: weight loss (practical value) (g).

Study the optimal conditions for the extinguishing of calcium oxide

To determine the best conditions for the extinguishing of the resulted calcium oxide, the following were studied:

a. Effect of the ratio of liquid to solid (L/S) on coefficient extinguishers.
b. Effect of the temperature on coefficient extinguishers

c. Effect of the time on coefficient extinguishers.

The coefficient extinguishers were calculated based on the increase in weight that reflects the ratio of the conversion from the formula of CaO to the formula of $Ca(OH)_2$.

Results and Discussion

Specifications of calcareous limestone

Chemical analysis

Chemical analysis of calcined limestone (after washing) is shown in Table 1. Results indicated that the limestone contained a high percent of CaO 55.64%, a low percent of associated impurities, mainly, magnesium oxide 0.14% and iron oxide 0.05%.

Table 1: Chemical analysis of calcined limestone.

%	Compound
0.06	SiO_2
0.12	Al_2O_3
0.05	Fe_2O_3
55.64	CaO
0.14	MgO
0.03	SO_3
0.02	K_2O
0.01	Na_2O
43.47	LOI

Phase structure

The XRD spectrum in Figure 3 show that calcareous limestone was mainly contained a pure $CaCO_3$ of calcite type. Additional small peaks could be attributed to a little amount of some secondary compounds, such as hematite (Iron oxide) and quartz, corresponds to the result of chemical analysis, these results were obtained by comparing the sample spectra studied with the reference x-ray spectroscopy [5, 7].

IR spectrum

Figure 4 shows the FT-IR spectra of the studied limestone. Peaks at 874.56, 1400, 1430.52, 1633.09, 1798.3, 2511.83, and 2981.41 cm^{-1} were corresponded to reference peaks of calcite (876 ,1422, 1431, 1636, 1786, 1792, 1798, 2516, 2570, 2873, 2982) cm^{-1}, which indicated calcite forms calcareous limestone. A Peak at 874.5cm^{-1} was due to the vibration of the C=O, a peak at 1430 cm^{-1} was due to the atmospheric vibration of the bond CO_3^{2-} , peaks at the 1636, 1786, 1792 cm^{-1} were due to the oscillatory vibration of the association C=O and peaks at 2516, 2570, 2873, 2982 cm^{-1} were due to the vibration of the O-H bond [5, 7].

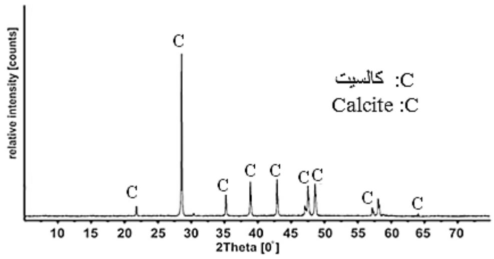

Figure 3: XRD spectrum of calcined limestone.

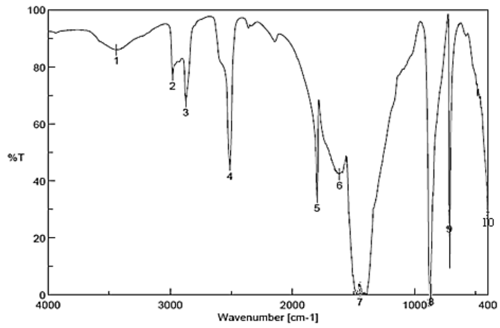

Figure 4: FT-IR diagram of the studied limestone.

Thermal behavior

The DTA of the calcined limestone sample is shown in Figure 5. Results demonstrated the existence of a peak at 830°C caused by a breakdown of calcium carbonate and its conversion into calcium oxide, in addition to some impurities and a release of carbon dioxide$_{(g)}$, according to the following reaction:

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

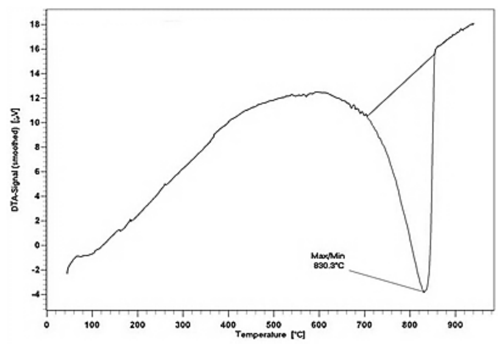

Figure 5: The DTA curve for calcined limestone.

Optimal conditions for calcification of calcareous limestone

Effect of particle size on calcination yield

To determine the effect of granular size on calcification, the calcination was performed at 1100°C for 60 min where different particle sizes were used (2-3-4-5) cm. The calcination yield% is shown in Table (2).

Table 2: Effect of particle size on the calcination yield of the limestone.

Calcination yield (%)	Particle size (cm)
97.14	2
96.88	3
96. 05	4
95.71	5

The largest particle size (5 cm) could consider the best for industrial and economical applications, due to law cost and less yield of calcification (less than 2% when compared with a particle size of 2 cm). On the other hand, a particle size of 5 cm is the most suitable size for gas release, where particles fill the spaces between granules and thus, protect the furnace from explosion during calcification process.

Effect of temperature on the calcination yield

A particle size of 5 cm was heated up to (900-1000-1100-1200-1300) ºC for 60 min.
Table (3) showed the effect of temperature on the calcination yield of a granular size of 5 cm for a fixed time (60 min).

Table 3: Effect of temperature on the calcination yield.

Calcination yield (%)	Temperature (℃)
88.94	**900**
93.11	**1000**
95.71	**1100**
98.11	**1200**
98.50	**1300**

The value of the calcination was proportional to the temperature, where the values have significantly increased as the temperature elevated from 900 ° C up to 1300 ° C. Above this, the calcination yield can be decreased due to the recrystallization of the crystals according to the theory of Mori.

Effect of time on the calcination yield

In order to study the effect of time on the calcination yield of the calcined limestone sample, the following conditions were applied: Particle size 5 cm, temperature was 1200ºC, time (30-60-90-120-180) min. Table (4) shows the effect of time on calcination yield.

Table 4: Effect of time on the calcination yield.

Calcination yield (%)	Time (min)
92.54	30
98.11	60
99.01	90
99.21	120
99.30	180

Calcination yield was proportional to the time of the calcination process, where the value increased significantly when the calcination time increased from 30 min to 60 min.
Extend the calcination time more than 60 min was economically inefficient due to little effect on the yield. The rate highest percentage of disintegration was 98.11% by 60 min, which indicated that the disintegration of limestone was almost complete. Therefore, the optimal time for calcification of calcareous stone can be considering 60 min.

Optimal conditions to extinguish produced of calcium oxide

Effect of the ratio of liquid to solid (L/S)

To determine the best (L/S) ratio on the extinguish yield, the following conditions were applied: temperature 25ºC, time 30 min, ratio (L/S): (4:1) - (3:1) - (2:1) - (1:1). Table (5) shows the effect of change in the ratio (L/S) on the extinguish yield, where the yield increased as the (L/S) increased. For 1:1 of (L/S), the yield was low, due to the evaporation of water under high heating of extinguish process. The best ratio was (3:1) because of a high correlated yield, up to 91%.

Table 5: Effect of the ratio of liquid to solid (L/S) on the extinguish yield.

Extinguish yield (%)	(L/S)
71	1/1
89	2/1
91	3/1
٩٢	4/1

Increasing the ratio of (L/S) to a higher value has no effect on the extinguish yield. Besides, the required amount of water will be more, which needs more effort to isolate and dry the calcium hydroxide. Therefore, we suggest here to avoid a ratio of L/S above 3:1.

Effect of temperature

The (L/S) ratio of 3:1 was employed to study the effect of different temperatures (25-50-75-90) ºC on the extinguish yield%, for 30 min reaction. Table (6) shows the effect of temperature on the extinguish yield%, where its elevation was correlated with increasing the temperature. However, at 75ºC, the reaction produced the highest yield (96%). Above that, low increase in the yield has observed

Table 6: Effect of temperature on the extinguish yield.

Extinguish yield (%)	Temperature (℃)
91	25
94	50
96	75
97	90

Effect of Time

The (L/S) ratio of 3:1 was employed to study the effect of different times (10, 20, 30, and 40ºC) on the extinguish yield%, at 75ºC for 30min reaction.

Table (7) shows the effect of time on the extinguish yield, where the yield % has significantly increased over time. The highest yield (98%) was observed after 40 min reaction.

Table 7: Effect of time on the extinguish yield.

Extinguish yield (%)	Time (min)
87	10
92	20
97	30
98	40

However, the increase in yield% after 30 min was nonsignificant.

Conclusions

Results of comprehensive characterizations of the limestone sample showed that it was a highly pure calcite, although a small percentage of impurities. Additionally, a calcification of calcareous sample with a particle size of 5 cm under 1200ºC for 60 min was optimal to obtain the highest yield%. Whilst, the highest yield% for extinguishing the calcined limestone sample was required 3:1 ratio of L/S under 75ºC for 30 min.

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