

## بررسی رفتار حرارتی سنگ معدن دولومیت شهرضا

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**چکیده:** در این مقاله، رفتار حرارتی دولومیت شهرضا مورد بررسی قرار می‌گیرد. همچنین هیدراته شدن دولومیت کلسینه شده در دماهای مختلف مطالعه شده است. نتایج، سه قله گرماگیر در دماهای ۸۰۰، ۹۰۰ و ۱۰۵۰ درجه سانتیگراد را نشان می‌دهد که دو قله اول بترتیب مربوط به تجزیه کربنات منیزیم و کربنات کلسیم موجود در دولومیت، و قله سوم مربوط به تجزیه کلسیت آزاد است. نتایج همچنین نشان می‌دهند که درجه کلسیناسیون با افزایش دمای کلسینه کردن از ۸۰۰ تا ۱۴۰۰ درجه سانتیگراد، افزایش می‌یابد. درجه هیدراته شدن دولومی با افزایش دمای کلسیناسیون از ۸۰۰ تا ۹۰۰ درجه سانتیگراد به دلیل تشکیل فازهای آبگیر افزایش می‌یابد. اما، سرعت هیدراته شدن با افزایش بیشتر دمای کلسیناسیون کاهش یافته و در دمای کلسیناسیون ۱۴۰۰ درجه سانتیگراد ناچیز می‌شود که این موضوع می‌تواند ناشی از تفجوشی ذرات باشد.

**واژه‌های کلیدی:** دولومیت، تکلیس، هیدراته کردن، تفجوشی، رفتار حرارتی.



## An investigation on thermal behavior of Shahreza dolomite ORE

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**Abstract:** Thermal behavior of the Shahreza dolomite ore is investigated in this paper. The hydration of the calcined dolomite was studied as a function of the calcination temperature. The DTA results exhibit three endothermic peaks at 800, 900 and 1050 °C, corresponding to decomposition of  $\text{MgCO}_3$  and  $\text{CaCO}_3$ , both are present in dolomite and free calcite, respectively. The results also indicated that the degree of calcination is increased by increasing the calcination temperature from 800 to 1400 °C. As the calcining temperature increases from 800 to 900 °C, the hydration degree of the dolomite increases too because of more humid absorbing phases produced at higher temperature. However, the hydration degree declines with further increase in the calcination temperature and became negligible when the sample is calcined at 1400°C probably due to the sintering process occurred at elevated temperatures.

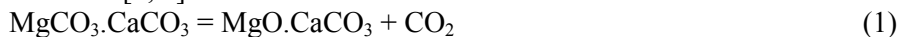
**Keywords:** Dolomite, Calcination, Hydration, Sintering, Thermal analysis.

## 1. Introduction

Dolomite is a double carbonate of calcium and magnesium ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ) which has a theoretical content of 45.7%  $\text{MgCO}_3$  and 54.3%  $\text{CaCO}_3$  [1]. Among different practical and industrial applications, dolomite is commonly used as a refractory material as well as in the magnesium production. As the product properties are considerably influenced by chemical analysis of the raw material and operating conditions, many researches have been focused on dolomite thermal behavior in recent years [2-4].

The first step in a carbonate mineral preparation is calcination and the terms dolomitic quicklime or dolime are sometimes used for calcined dolomite. Dead-burned dolomite or doloma is specially sintered form of dolomitic quicklime, which is heated to a high temperature to drive off all the carbon dioxide and to reduce the porosities to a level that will permit its use in refractory. Since the calcination reaction is highly endothermic, the rate of decomposition is probably controlled by the rate of heat transfer through the particles. Since the solid product is likely to be porous and permeable in texture, the gaseous product can easily escape. Sridhar et al. [5] and Chester [6] have found that the temperature at which dolomite is sintered, depends on its purity.

The thermal decomposition of dolomite occurs in two major steps: The first mass loss corresponds to the decomposition of  $\text{MgCO}_3$  and the second step is attributed to the decomposition of  $\text{CaCO}_3$  according to the following reactions [7, 8]:



The present investigation is aimed at optimization of the calcination behavior of the newly explored dolomite deposit of Shahreza.

## 2. Experimental procedure

The raw material studied in this research was a dolomite samples from Shahreza dolomite mine in Iran. The thin sections were studied using a Nikon E600POL polarized microscope. Various analysis such as differential thermal analysis (DTA, Linseis L81/1700) in a normal atmosphere and a heating rate of 10 °C/min, wet chemical analysis, X-ray diffraction (Philips PW1440) using  $\text{Cu-K}\alpha$  radiation, and X-ray fluorescence analysis and scanning electron microscopy (SEM, Cambridge Instruments S360) were employed to evaluate the characteristics of the samples. The dolomite sample was crashed using a jaw crusher and then milled by a ball mill.

The calcination was carried out in a muffle furnace with a heating rate of 3 – 4 °C/min in a temperature range of 800 to 1400 °C for a period of 1 to 10 hours. Hydration experiments were carried out on 5 gr calcined samples at room condition. Samples were weighed in definite time intervals using a digital Mettler balance with an accuracy of 0.01 gr.

### 3. Results and discussion

Figure 1 shows the photomicrograph of thin sections of the Shahreza dolomite ore. A calcite veinlet and iron rich regions can be seen in this figure. Other possible impurities could also be present in this ore. The wet chemical analysis of the sample is shown in Table I. Analysis of the X-ray diffraction pattern in Figure 2 confirms the presence of the calcite as a major impurity. Since theoretical magnesium oxide of the pure dolomite is 21.7%, the purity of the Shahreza dolomite sample which contains 21.15% of MgO is calculated to be 97%. According to the reactions (1) and (2), the weight of calcined dolomite is as follows:

$$m_2 = \frac{m_1 \times 100}{100 + 0.4924m_1} \quad (3)$$

In which,  $m_1$  and  $m_2$  are weights of dolomite before and after calcination, respectively.

Also, the calcination degree is generally calculated as the ratio of the weight change in practical dolomite calcination to the weight change in a theoretical complete calcination condition. Therefore, the calcination degree would be as follows:

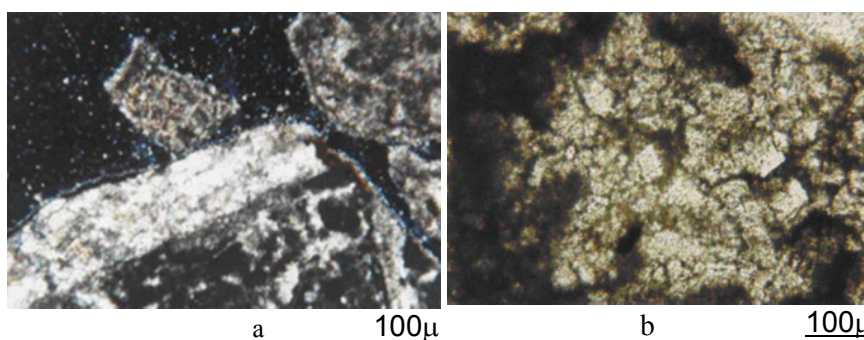
$$\% \text{ Calcination} = \frac{m_1 - m_2}{0.4924m_1} \times 100 \quad (4)$$

Decomposition of the dolomite sample was studied using DTA from ambient temperature up to 1400 °C. Figure 3 illustrates the DTA trace, which reveals three endothermic peaks at about 800, 900 and 1050 °C. As can be seen, the major part of the dolomite decomposes up to 1050 °C.

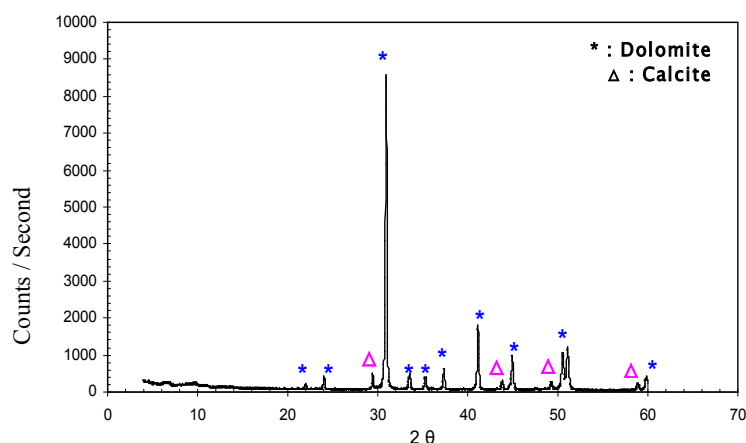
**Table I** Chemical analysis of the Shahreza dolomite ore (wt %).

| MgO   | CaO   | L.O.I* | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | Na <sub>2</sub> O | K <sub>2</sub> O | MgO/CaO |
|-------|-------|--------|------------------|--------------------------------|--------------------------------|-------------------|------------------|---------|
| 21.15 | 32.38 | 45.68  | 0.39             | 0.19                           | 0.21                           | 0.04              | 0.04             | 0.65    |

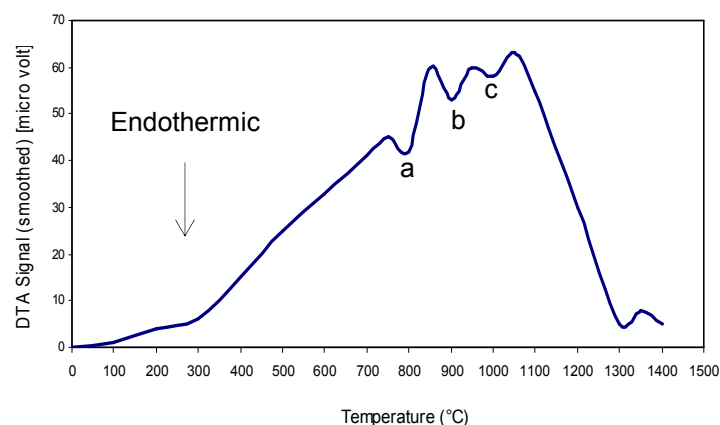
\*Loss of Ignition



**Figure 1** photo microscop of the Shahreza dolomite ore indicating (a) a calcite veinlet (white lath), and (b) iron rich regions (dark areas).



**Figure 2** X-ray diffraction pattern of the Shahreza dolomite ore.



**Figure 3** DTA trace of the Shahreza dolomite ore.

Under the action of thermal energy, dolomite undergoes two characteristic transformations. The first transformation (peak a) consists of the magnesium carbonate decomposition, which begins at about 800 °C [9]. The second transformation (peak b) consists of the decomposition of calcium carbonate which begins immediately after completion of the magnesium carbonate decomposition, and continues up to 1050 °C [9].

The third peak (c) on the DTA analysis curve might be related to the decomposition of the extra calcium carbonate (calcite) which its presence was detected by X-ray diffraction (Figure 2). When the ratio of  $\text{MgCO}_3$  to  $\text{CaCO}_3$  in a dolomite is smaller than 1, it contains extra calcium carbonate, and is called as calcitic dolomite. Two thermal effects appeared, in the range of thermal decomposition of calcium carbonate. As a matter of fact, this is an endothermic reaction with a double peak. The first one corresponds to the calcium carbonate bonded in the dolomitic lattice, and the second one, to the calcium carbonate of the calcite type. This scenario seems to be in agreement with the X-ray diffraction results as shown in Figure 4. Figure 4(a) shows

peaks of the remained dolomite and calcite phases after calcination at 800 °C, which are not present after the calcination at 1100 °C (Figure 4b).

Figure 5 shows variation of the calcination degree as a function of temperature. As the calcination temperature increases from 800 to 950 °C, the calcination degree increases from 63 to 96.4% and more CO<sub>2</sub> gas evolves. The results of wet chemical analysis of the calcined products are summarized in Table II, which confirms the calculated calcinations degree. Tables I and II, show that the ratio of MgO/CaO is increased by increasing the calcinations temperature due to the higher calcinations rate of MgCO<sub>3</sub>. Relatively low amount of CaO at calcinations temperature at 1400 °C is probably relate to the existence of free calcite in the dolomite sample.

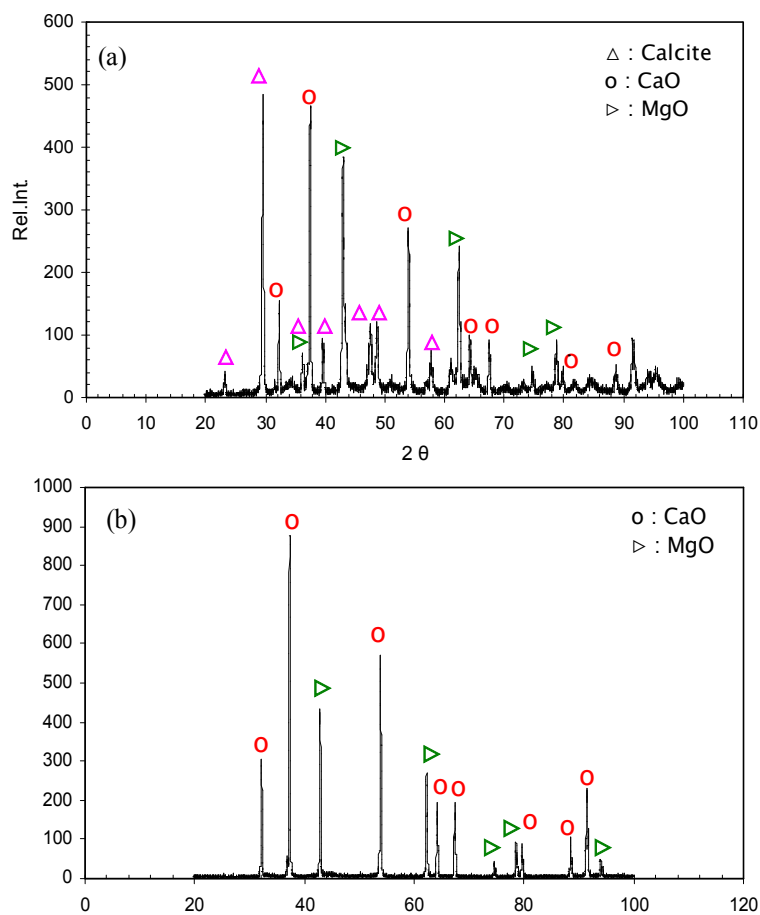
The sample calcined at 1400 °C was considerably different with others in appearance, porosity and color. This could be due to the possibility of sintering process at this temperature. Sintering is the mechanism by which solid particles coalesce when heated to temperatures below their melting point. Consequently, the sintering process causes the loss of surface area as well as porosity [4]. Figure 6 shows the scanning electron micrographs of the samples calcined at 1150 and 1400 °C.

In contrast to the sample calcined at 1150 °C in which the individual particles are clearly visible, other samples calcined at 1400 °C: there for sintering phenomenon could be seen, and the particles have merged together and formed a continuous texture. This might be due to the formation of glassy phases on the surface of particles produced at higher temperature. Presence of impurities such as K<sub>2</sub>O, CaO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, favors the formation of these phases [6]. According to Figure 5a, complete calcination has not been achieved at 1400 °C and the calcination degree is less than 100%. This is due to the sintering process and formation of the glassy phases which prevent the CO<sub>2</sub> to exit freely and impede the calcination process.

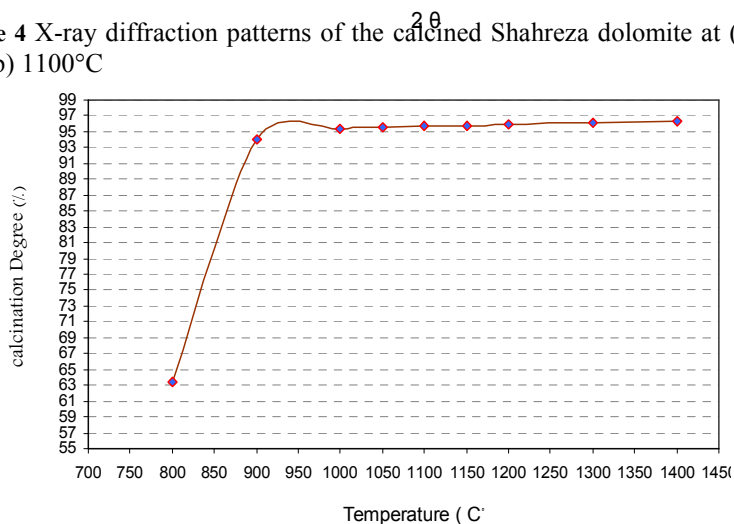
Kinetic constant of the reaction ( $k$ ) was calculated using the rate of weight loss at different calcination temperatures of fine dolomite particles (-200 mesh) at 800, 950, 1050 and 1150 °C. Using Arrhenius equation and by plotting values of  $\ln(k)$  against  $1/T$  a straight line was obtained (Figure 7), and the value of slope being  $-Q/R$ . The relevant activation energy would be 16.7 kcal, which confirms that the calcination is mainly controlled by chemical reactions. For coarse dolomite particles (+ 200 mesh) the calcination activation energy was calculated in the same temperature range as 7.4 kcal which indicates a mixed control of chemical reaction and diffusion for this type of dolomite particles.

**Table II** Chemical analysis of the Shahreza calcined dolomite at different temperatures (wt %).

| Temperature (°C) | MgO (%) | CaO (%) | L.O.I (%) | MgO/CaO |
|------------------|---------|---------|-----------|---------|
| 800              | 32.89   | 49.22   | 16.92     | 0.67    |
| 1150             | 39.98   | 58.28   | 1.87      | 0.69    |
| 1400             | 40.67   | 57.87   | 0.7       | 0.70    |

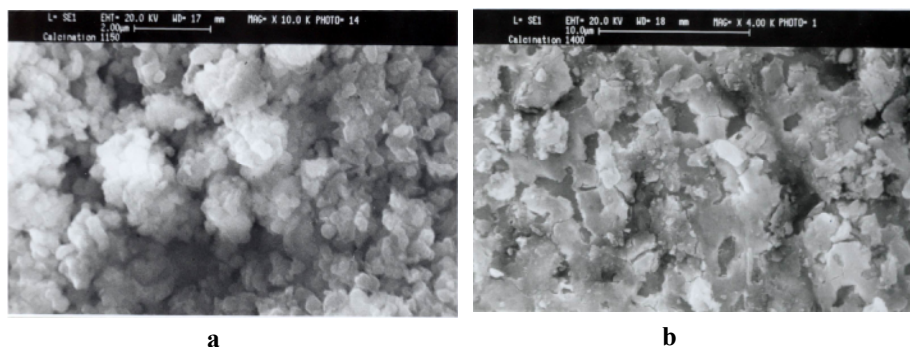


**Figure 4** X-ray diffraction patterns of the calcined Shahreza dolomite at (a) 800 °C and (b) 1100 °C

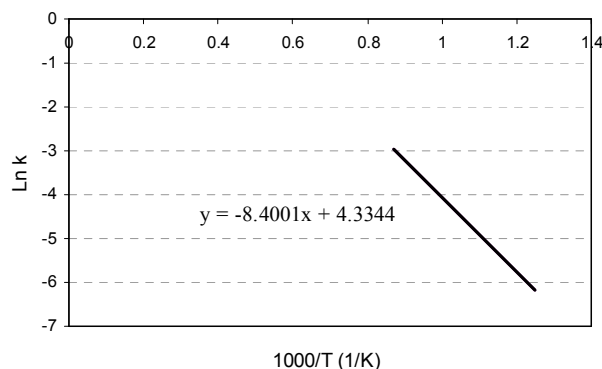


**Figure 5** Shahreza dolomite calcination degree – temperature relationship.





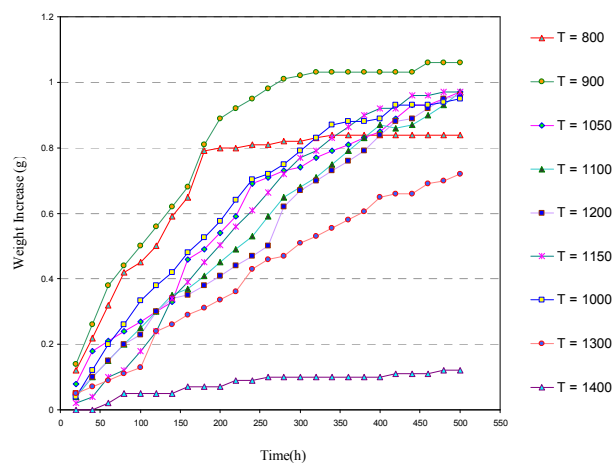
**Figure 6** Secondary electron images of the Shahreza dolomite calcined at (a) 1150 °C and (b) 1400 °C.



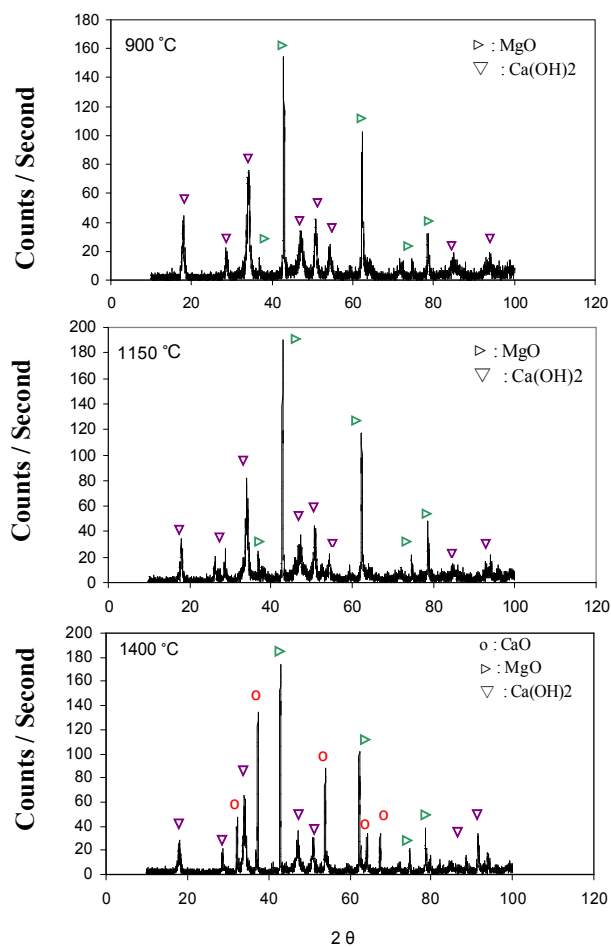
**Figure 7** Kinetics constant against reversed temperature plotted for fine dolomite particles.

The hydration experiments showed that the dolime hydration degree is strongly influenced by the calcination temperature. Shi et al. [10] has also reported similar results for hydration of the free lime. The hydration degree of the dolime was increased by increasing the calcination temperature from 800 to 900 °C due to higher amount of humid absorbing phases obtained at higher calcination temperature (Figure 8). However, the hydration degree declines with further increase in the calcination temperature and becomes negligible for the sample calcined at 1400 °C. Particle coarsening and sintering process which results in the formation of glassy phases and reduction of porosities, as observed in SEM images, could be responsible for this behavior.

Figure 9 shows the XRD patterns of the samples calcined at 900, 1150 and 1400 °C and hydrated afterwards. These patterns reveals the formation of  $\text{Ca}(\text{OH})_2$  in the samples.  $\text{Mg}(\text{OH})_2$  was not detected probably due to the kinetically reasons. Also, this may be attributed to the early decomposition of  $\text{MgCO}_3$  during the calcination process, which provides more opportunity for MgO particles to coalesce each other during further calcining. This could decrease the porosities within the MgO particles and hence tendency for hydration.



**Figure 8** Hydration behavior of Shahreza dolomite calcined at various temperatures.



**Figure 9** X-ray diffraction patterns of hydrated dolime samples calcined at 900, 1150 and 1400 °C.

#### 4. Conclusions

- 1- Characterization of the Iranian Shahreza dolomite by various analysis techniques indicated 97% purity and the major impurity was detected to be calcite.
- 2- The DTA results indicated three endothermic peaks at 800, 900 and 1050°C which are related to the decomposition of  $\text{MgCO}_3$  and  $\text{CaCO}_3$  both present in dolomite and the free calcite, respectively.
- 3- The temperature promotes the calcination behavior of Shahreza dolomite. However, at elevated temperatures, such as 1400 °C, sintering of the material impedes the calcination rate and increases the hydration resistance of the calcined dolomite.

#### Acknowledgment

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