SYNTHESIS OF ULTRA FINE GRAIN MAGNESIUM CARBONATE PART 1. CALCINATION BEHAVIOUR OF INDONESIAN DOLOMITE

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Intisari

PEMBUATAN MAGNESIUM KARBONAT BERUKURAN ULTRA HALUS BAGIAN 1. PERILAKU KALSINASI DOLOMIT INDONESIA. Cadangan dolomite banyak terdapat di berbagai tempat di Indonesia. Cadangan terbesar terdapat di Provinsi Jawa Timur. Pada saat ini di Indonesia dolomit hanya dipergunakan sebagai pupuk, walaupun sebenarnya dolomit dapat diproses untuk menghasilkan magnesium karbonat berukuran ultra halus yang biasanya digunakan sebagai bahan baku untuk obat dan sebagai filler dalam industri farmasi dan industri cat. Dolomit mengandung 26,4% magnesium oksida dan 63,42% kalsium oksida. Kalsinasi adalah langkah pertama dari rangkaian proses untuk mendapatkan magnesium oksida atau magnesium karbonat dari dolomit. Pada penelitian ini, dolomit dari Madura telah dikalsinasi menggunakan tungku muffle. Reaksi dekomposisi terjadi pada temperatur 730-890 ^oC. Variabel yang paling berpengaruh adalah temperatur dan waktu kalsinasi. Pada temperatur 600-700 ^oC, reaksi dekomposisi berjalan sangat lambat dan hasil kalsinasinya pun rendah. Tetapi pada temperatur 800 ^oC, hasil kalsinasi yang didapat sangat tinggi walaupun laju dekomposisinya masih rendah. Dan pada temperatur 900 ^oC dan temperatur di atasnya, laju dekomposisi dan hasil kalsinasi mencapai maksimum.

Kata kunci : Dolomit, Magnesium Oksida, Kalsinasi, Ultra fine grain

Abstract

SYNTHESIS OF ULTRA FINE GRAIN MAGNESIUM CARBONATE PART 1. CALCINATION BEHAVIOUR OF INDONESIAN DOLOMITE. *Dolomite deposits can be found in many places in Indonesia. The larger deposit is located in East Java provence. Dolomite is mainly and recently used only as fertilizer, but it can be processed to obtain ultra fine grain magnesium carbonate that can be used as raw materials for drugs and fillers in pharmacy and coating industry. Dolomite contains 26,4% magnesium oxide and 63,42% calcium oxide. The calcination is the first important step in obtaining magnesium oxide or magnesium carbonate from dolomite. In this recent research, dolomite from Madura has been calcined by using a muffle furnace. The decomposition reaction temperature has detected to take place at temperature range 730-890 ^oC. The most important variable in dolomite calcination are temperature and time. At 600-700 ^oC, the decomposition rate is very slow and the result is very poor. But at 800 ^oC, although the decomposition rate is still slow but the result is maximum. At 900 ^oC and beyond, the decomposition rate is very high and the result is maximum. The result is magnesium and calcium oxide that is not bound chemically.*

Keywords : Dolomite, Magnesium oxide, Calcination, Ultra fine grain

INTRODUCTION

Magnesium based materials is widely used as raw materials for many purposes such as fertilizer, drugs, and various industrial fillers[1-2]. The type of magnesium based materials used in certain industry depends on the chemical compositions, purity and grain size. For example, the magnesium based material used in fertilizer industries is merely ore containing magnesium like dolomite and magnesite without any chemical treatment[3], whereas in drugs and industrial filler, only high purity and small size magnesium carbonate is used[4-5]. The prices among magnesium based materials are also very different. The price of magnesium based materials that are used as fertilizer is very cheap; it never exceeds 0.1 US Dollar per kg. In contrast, the price of chemically treated magnesium based materials, in which its purity is very high and its size is very small, can reach 40 USD per kilogram[6].

The deposit of dolomite in Indonesia is very abundant. Dolomite can be found in various amount and elemental composition at Sumatra, Java, Madura, Sulawesi and Papua Islands. The biggest deposit of dolomite can be found at Lamongan and Madura, East Java[7]. Nowadays, dolomite coming from this region is still conventionally used as fertilizer[8]. On the other hand, ultra fine grain magnesium carbonate used as raw material for drugs and filler in industries is still imported from abroad. Dolomite can be processed to obtain ultra fine grain magnesium carbonate. Among unit operation in this process, calcination is the first important step of process. The successful of calcination determines the yield of magnesium carbonate product at the end line of the process. Therefore, this paper deals with the analysis of calcination behaviour of dolomite.

EXPERIMENTS

Dolomite was obtained from a local mining site in Madura. The ore was ground prior characterization and processing. The average size of ground dolomite is around 1 cm. The ground dolomite was characterized by using x-ray fluorescence (XRF) and x-ray diffraction (XRD) to reveal the chemical composition and phases. The behaviour of the dolomite at elevated temperature was characterized through thermo gravimetric-differential thermal analyzer (TG-DTA) test. The calcination of the as-received dolomite was conducted in a muffle furnace in air atmosphere for 10 hours. The calcined sample was weighted, and then it was characterized through XRD and SEM-EDS (scanning electron microscope-energy dispersive spectroscopy) to reveal phases and the changes in elemental composition.

RESULT AND DISCUSSION

The composition of dolomite obtained from Madura is shown in Table 1. It can be seen that the ratio of CaO/MgO in Madura dolomite is about 2.4. This value is higher than standard dolomite which has ratio of CaO/MgO = 1.2. The large amount of calcium carbonate makes this dolomite classified as calcium carbonate dolomite. Other compounds that can be found in this dolomite are the oxide of sodium, aluminum, silicon and iron. Iron in dolomite determines the color appearance of dolomite. The high content of iron leads to the yellowish color.

Table 1. Composition of the as-dried dolomite

No	Compound	% Weight
1	CaO	63.42
2	MgO	26.39
3	Na_2O	5.93
4	SiO_2	1.20
5	Al_2O_3	0.86
6	Fe_2O_3	0.74

The only compound that can be found in dolomite ore from Madura is dolomite phase ($CaMg(CO_3)_2$), as shown in Fig 1. Although the content of calcium oxide is quite high, which can lead to the conclusion that there might be free calcium oxide in the as received sample, in reality there is no free calcium oxide can be found. Thus, it can be assumed that the entire calcium oxide molecule is bound into Ca-Mg-C-O network. Meanwhile, other oxides in this dolomite cannot be detected by XRD due to very low content.

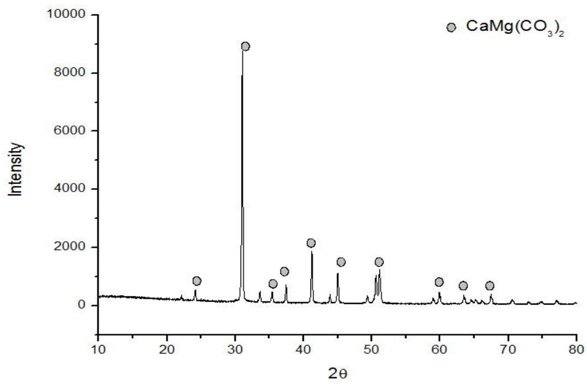

Fig 1. XRD patterns of the as-received dolomite from Madura

Fig 2 shows the comparison of XRD patterns of Madura dolomite and artificial dolomite obtained from the manufacture. It can be seen that both dolomite has the same 2θ location of almost entire peak of intensity. At least, the 2θ location of three major peaks are the same (at 2 θ = 31.02; 41.23; and 51.09). All these analysis show that Madura dolomite, as raw materials used in this experiment, contains dolomite phase resemble to artificial dolomite.

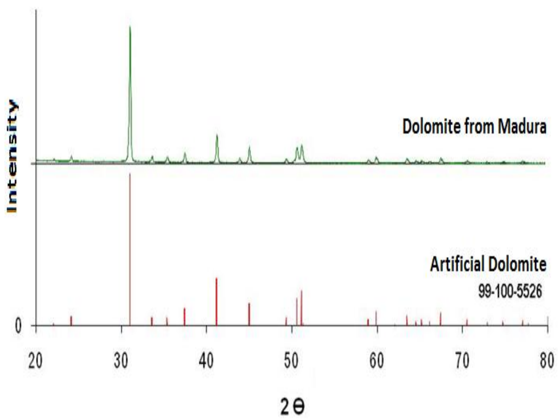

Fig 2. Comparison of XRD patterns of the as-received dolomite from Madura and artificial dolomite

The response of as received dolomite to temperature change is tested through TG-DTA. The result is shown in Fig 3. At low temperature zone (at about room temperature to 700 °C), TG curve shows that there is no weight change in sample. This means that at this temperature zone, there is no chemical reaction takes place. Therefore, the changes of DTA curve as shown in this figure is might be merely a crystallographic transformation. The significant change in TG and DTA curve can only be found at temperature range of 730 – 890 °C. Obviously, at those temperature ranges the calcination reaction has taken place. The result of this TG-DTA test will be the basis of calcination process.

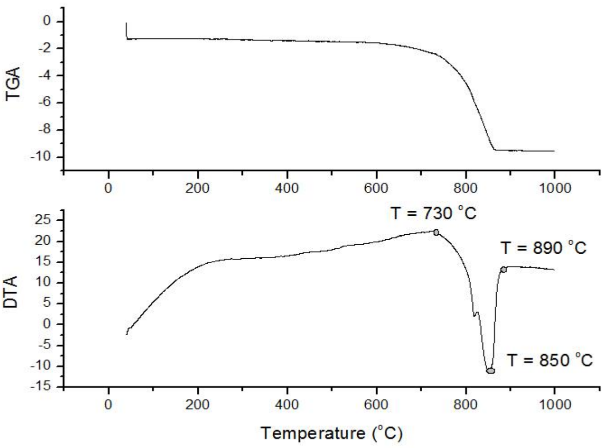

Fig 3. TG-DTA Pattern of the as-received dolomite

The calcination has been conducted at various temperatures. Based on TG-DTA, the experimental temperature was set at range of 600 – 1000 °C. The excess of 100 °C to the upper and lower temperature limit, which has been determined through TG-DTA, is meant to obtain complete prove of dolomite behavior. Since the calcination reaction is actually the release of carbon dioxide, there must be weight reduction during heating. Fig 4 shows the weight reduction of calcined dolomite at different temperature and time. At lowest temperature, 600 °C, the weight reduction is very low. It is only about 5 % weight reduction at 600 °C. It is mainly contributed by water evaporation. At higher temperature, 700 – 800 °C, the reaction become rapid with an increasing in temperature; and the time needed to obtain a certain amount of weight reduction is sharply reduced. For example, at 700 °C, the time needed to reduce weight down to 10% is 450 minutes, whereas that at 800 °C is only 90 minutes.

Thus by increasing temperature 100 °C, one can obtain weight reduction 5 times.

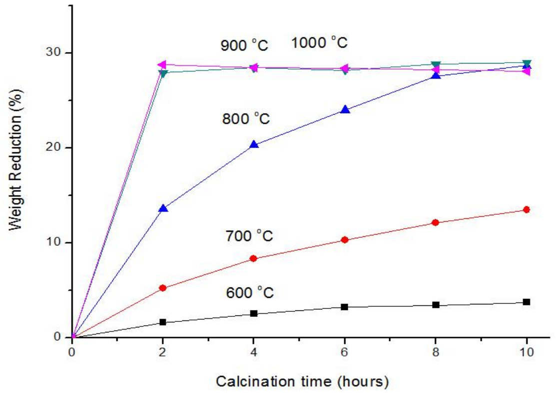

Fig 4. Weight reduction of calcined dolomite as the function of temperature and time

The weight reduction means the change of the percentage of elements left in calcined dolomite. As carbon and oxygen leaves the dolomite, the weight percentage of other elements increases. By using the energy dispersive spectrum in SEM-EDS equipment, one can roughly calculate the weight percentage or atomic percentage of elements in a material. By using the same equipment, a measurements of elements in calcined dolomite at various temperature and time has been done. The result is shown in Fig 5. As has been predicted, the weight percentage of carbon and oxygen decreases with an increasing in temperature. In opposite direction, the weight percentage of other elements increases with an increasing in temperature. It is interesting to find that the decreasing of weight percentage of carbon and oxygen stops at 800 °C. The increasing of temperature beyond 800 °C gives no siginificant change in weight percentage of these elements. On the other hand, the significant increasing of magnesium and calcium weight percentage also stops at 800 °C. This experiment is conducted for 10 hours. As can be seen in previous figure (Fig 4) the final weight reduction of sample at 800, 900 and 1000 °C after 10 hours calcination are the same. These three samples shows weight reduction 29 %. Thus, the results of analysis shown in Fig 4 is obviously agree with that in Fig 5. And both analysis (Fig 4 and 5) are also agree with TG-DTA shown in Fig 2, which shows that 800 °C is in the range of the DTA valley which indicates that chemical reaction has taken place.

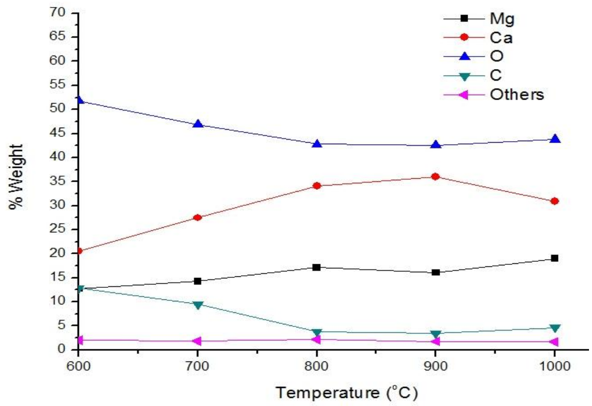

Fig 5. The weight percentage of elements in calcined dolomite

Fig 6 shows the XRD patterns of dolomite calcined at different temperature. At 700 °C, the decomposition reaction of dolomite seems to take place. But suppprisingly, it is found that the only free carbon phase in this sample is magnesium oxide, whereas the calcium related compound that can be found is calcium carbonate. The free carbon compound of calcium oxide starts to form at 750 °C. This means that the decomposition energy calcium carbonate is slightly higher than that of magnesium carbonate. By using the XRD patterns in Fig 6, the calcination reaction should be written as follows:

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgCO_3 \quad (1)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H = 179 \text{ kJ/mol} \quad (2)$$

$$MgCO_3 \rightarrow MgO + CO_2 \quad \Delta H = 118 \text{ kJ/mol} \quad (3)$$

Both calcination reaction of calcium and magnesium carbonate are endothermic reaction, as indicated by positive value of both enthalpy. But although both can be decomposed at high temperature, the enthalphy of calcium carbonate decomposition is higher than that of magnesium carbonate. Therefore it is reasonable why at 700 °C magnesium oxide has form at the first place rather than magnesium oxide.

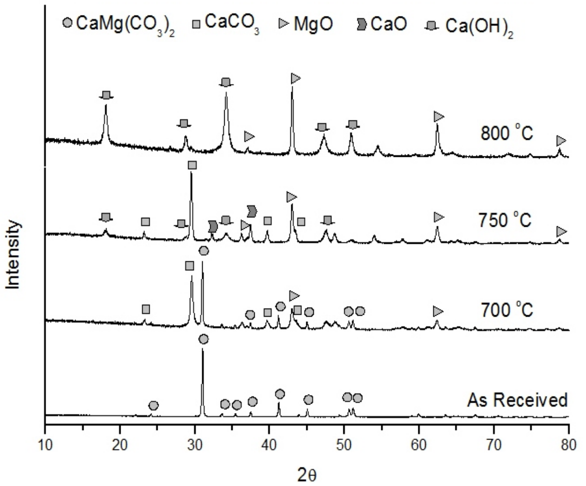

Fig 6. XRD patterns of dolomite calcined for 10 hours at different temperature

CONCLUSION

Dolomite from Madura contains 26.4% magnesium oxide and 63.42% calcium oxide. The phases of magnesium calcium bicarbonate in natural dolomite from Madura resembles that in artificial dolomite. The temperature range of dolomite decomposition is 730-890 °C. The reduction of weight increases with an increasing in temperature. The weight reduction depends on temperature and time. At 600-700 °C, the decomposition rate is very slow and the result is very poor. But at 800 °C, although the decomposition rate is still slow but the result is maximum. At 900 ^{o}C and beyond, the decomposition rate is very high and the result is maximum. The result is magnesium and calcium oxide that is not bound chemically.

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RIWAYAT PENULIS

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