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Dolomite used as raw material to produce MgO-based expansive agent

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Abstract

In this paper, the manufacture of MgO-based expansive agent using dolomite as raw material was studied. The decomposition of dolomite was discussed at first by DTA-TG analysis and on the crystalline view. On the characteristics of decomposition of dolomite, the authors think it is possible to use dolomite as raw material, but the silica-bearing mineral is considered to combine the CaO released from dolomite to form silicate. The phases of MgO-based expansive agent are mainly MgO, C_2S and a little amount of CaO. The expansion of resulting expansive agents by autoclaving testing and hot water curing at 80 °C shows that the MgO-based expansive agents have desired expansion. If the burning temperature and burning time, dosage in cement are controlled according to the requirement of concrete construction, the MgO-based expansive agent can be used to compensate the shrinkage as designed.

Keywords: Dolomite; MgO; Expansion

1. Introduction

Shrinkage cracking occurs in constructions frequently. The cracks would be the pathway of water and harmful substances into concrete resulting in destruction of concrete. Several of measures to be developed to eliminate the shrinkage cracking; the one of these is using expansive agents to compensate the shrinkage of concrete. The expansion based on CaO, MgO and AFt have been studied [1–4]. Of these, the authors are interested in MgO-based expansive agents, especially in those burned at lower temperature than that of ordinary Portland cement.

MgO reacts with water to form $Mg(OH)_2$ that causes volume expansion about 118%. The "dead burned" MgO reacts with water very slowly; that causes the expansion to take place after the solidification of cement. Thus, the content of MgO in ordinary cement is restricted to less than 5%, and can be 6% if cement is sound examined by autoclaving testing in cement standards in many countries. Mehta and Pritz [5] proposed that high-MgO cement can be used to compensate shrinkage. A successful case is the Baishan Dam constructed in 1973 in China. In fact, at that time, high-MgO cement was not chosen specially. Some years later, it was found no impenetrating cracking was observed in this dam, then in turn to investigate the reason, and finally considered that the main effect is the high content MgO (4.5% ca.) contained in the cement. For various constructions, to get the cement with suitable content of MgO to obtain the required expansion rate and expansion ratio are much difficult. The authors of this paper are trying the technique of adding MgO (usually called as MgO expansive agent) to Portland cement to get the desired expansion to meet the requirement of construction.

MgO expansive agents are usually produced by firing magnesite at 800–1200 °C. But considering the reserves of magnesite and the producing technique, as well as construction far from the producing plant, the possibility of using the other magnesium-bearing minerals, such as dolomite, as raw materials to produce MgO has been

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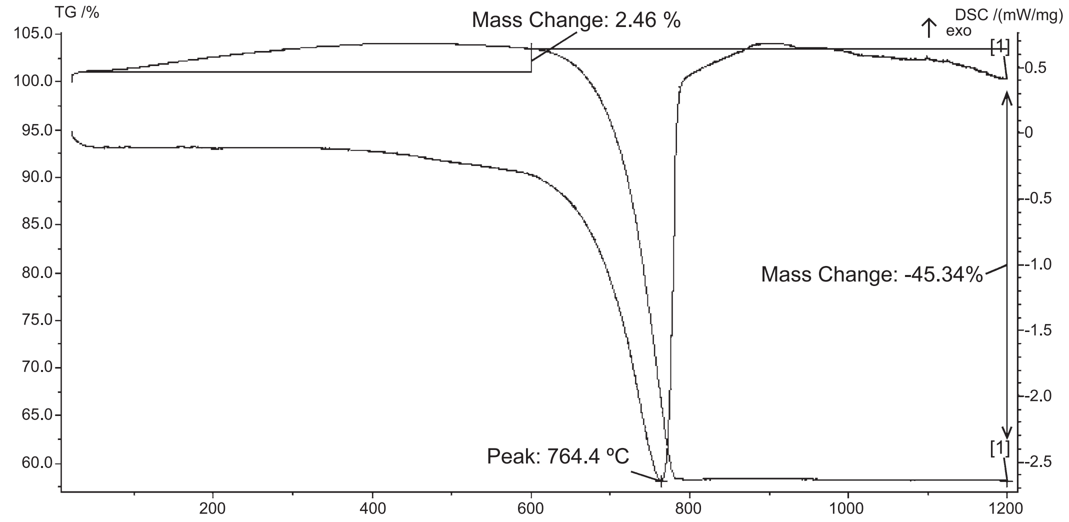


Fig. 1. DTA-TG curves of dolomite.

considered. A part of researches are introduced in this paper.

2. Mineral dolomite and its decomposition

Dolomite is a kind of primary sediment mineral and has a widespread geologic distribution. Its chemical formula is written as $CaMg(CO_3)_2$, with the chemical composition in oxide by weight percent CaO 29.46 wt.%, MgO 20.65 wt.% and loss on ignition 46.88% used in this research.

The decomposition of dolomite was studied by DTA-TG analysis. The curves in Fig. 1 show that dolomite starts to decompose at about 590 °C and finishes its decomposing process at about 900 °C. The weight loss corresponding to the endothermic valley in DTA curve is about 45.34% that is attributed to the giving off CO_2. Comparing to the loss on ignition 46.88% by chemical analysis, decomposition of dolomite till about 900 °C is nearly completely.

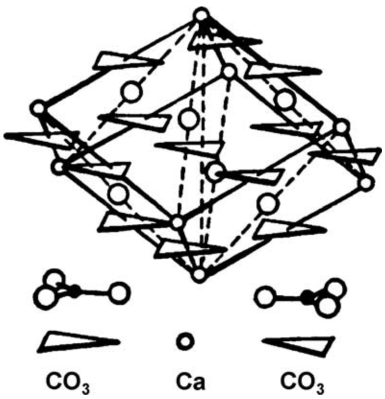


Fig. 2. Crystal structure of calcite.

The resulting products from decomposition of dolomite are MgO and CaO. The reaction equation can be simply written as following,

$$CaMg(CO_3)_2 = MgO + CaO + CO_2\uparrow$$

Although only one broad endothermic valley appears in DTA testing, actually the decomposition of dolomite includes two stages [6,7]. MgO forms at first when heating the dolomite above 590°C according to the reaction:

$$CaMg(CO_3)_2 = MgO + CaCO_3 + CO_2\uparrow$$

Then the decomposition of $CaCO_3$ follows when the heating temperature is increased:

$$CaCO_3 = CaO + CO_2\uparrow$$

The crystal structure of dolomite is the same as calcite shown in Fig. 2. The crystal structure of calcite, belongs to trigonal system and R3C of space group, where trigons represent CO_3 group. If Mg replaces a half of Ca, and by the segregation of Ca and Mg in distinct lattice planes, the structure is of dolomite, where the planes are oriented to the c-axis. The cation ordering results in a reduction of symmetry relative to calcite from R3C to R3 space group. Each cation is octahedrally coordinated by six oxygen atoms, which are themselves threefold coordinated with a calcium, magnesium, and carbon atom.

The lattice parameters of ideal dolomite are a_0=0.48069 nm, c_0=1.60034 nm. Above 590 °C, the bonds of –O–C–(I) in Mg–CO_3 (Fig. 3) start to break up, give off CO_2 and

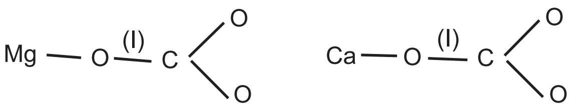
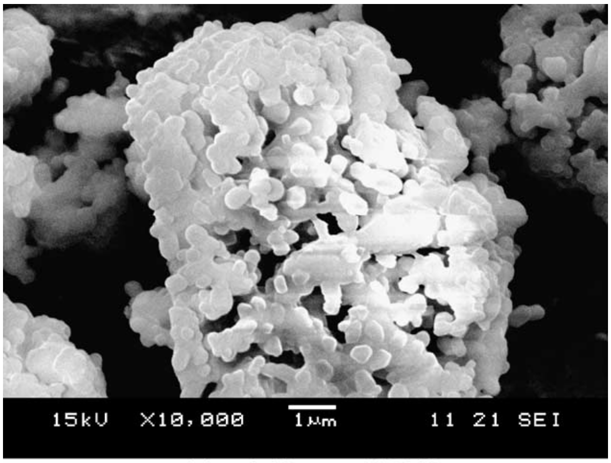
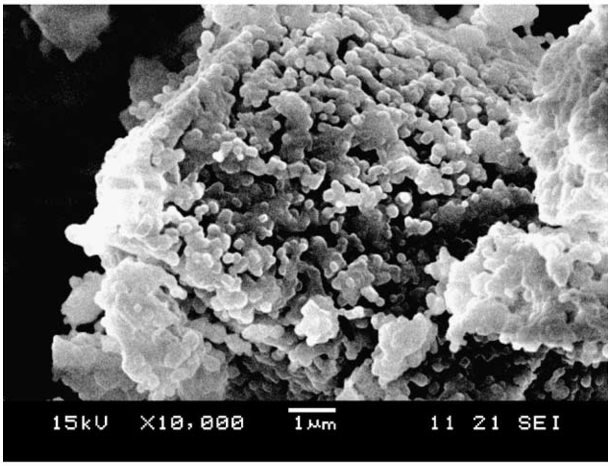


Fig. 3. Bonds in Mg–CO_3 and Ca–CO_3.



(a) calciting at 1150ºC



(b) calciting at 1200ºC

Fig. 4. SEM observation photographies: (a) calciting at 1150 °C, (b) calciting at 1200 °C.

keeps one O atom at the site of CO_3 group, forms the bonds Mg–O.

The ideal crystal structure of MgO belongs to facial cubic system and Fm3m space group. The lattice parameter is a_0=0.4203 nm. Comparing the lattice parameters of dolomite with that of MgO, it is obvious that the bonds are shortening gradually during the bonds of Mg–CO_3 changing to Mg–O. At the same time the angles are also in adjusting process. The crystal structure of resulting MgO is whether perfect or not depends greatly on the heating temperature and time. That also affects the chemical activity of MgO, which refers to the reaction rate of MgO with water. The lower temperature and shorter time, the higher is the chemical activity of MgO.

The SEM observation confirms that the bigger particles are got at lower temperature than those at higher temperature. In Fig. 4, it can be seen that MgO particles formed at 1150 °C are about 0.5 μm, those formed at 1200 °C are about 0.3μm. The reason is that MgO formed at low temperature is with loose not compact structure, in other words, the crystal structure is with much more defects.

At higher temperature, the bond of –O–C–(I) in Ca–CO_3 (Fig. 3) also starts to break up into Ca–O and forms CaO. From the DTA analysis, the endothermic peak is at 764.4 °C, lower than the decomposition temperature of limestone at which is about 850 °C in general. The phenomena can be explained that the forming of MgO at lower temperature destroys the structure of dolomite, and decrease the decomposition energy. The CaO formation process is thought very similar with that of MgO discussed above.

3. MgO-based expansive agent

MgO from decomposition of dolomite is interested mostly in this research, but the nearly same amount of CaO formed in decomposition of dolomite has to be considered when using dolomite as the raw material of expansive agents. Because CaO is also an expansive component which can produce great expansion at early age. To compensate the shrinkage of concrete at early age, a little amount of CaO is thought to be necessary. But most of CaO has to be considered to combined by silica-bearing materials to form silicate phase such as belite, which can hydrate as same as that in cement.

3.1. Making of MgO-based expansive agent

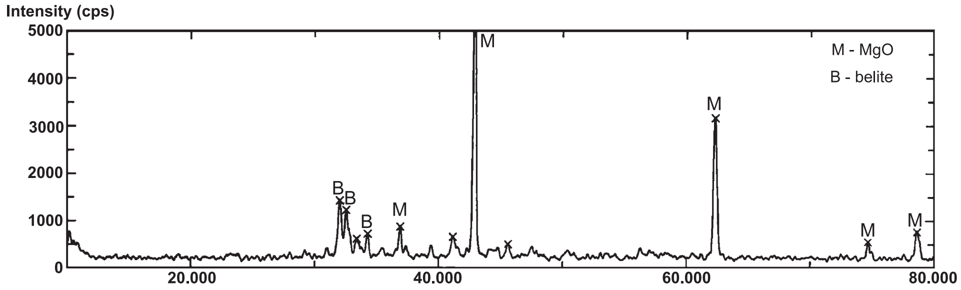
Based on above discussion, dolomite and silica-bearing mineral SERP were chosen as main raw material in this experiment, the magnesium rich mineral MAG is also used to improve the MgO content in expansive agents to about 50% by weight, their chemical composition are listed in Table 1.

The raw materials were ground to pass the 0.150-mm sieve respectively, then mixed according to the designed proportion, pressed to blocks in 70×70×10 mm after adding a little amount of water, dried at 105 °C for 6 h then burned at 1150–1250 °C for 0.5–1.5 h in laboratory electric furnace, quenched in air.

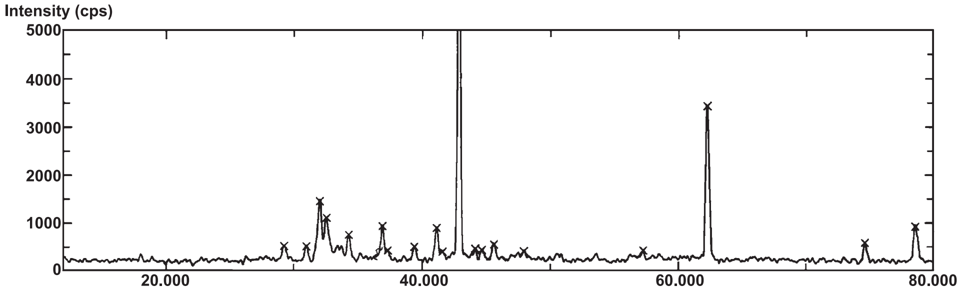
The clinkers were examined using X-ray diffraction analysis (Rigaku, 40 kV×40 mA, CuKα, 10 °/min). The patterns shown in Fig. 5 indicate that the main phases of expansive agent are MgO, C_2S and a little amount of CaO when the raw meal were burned at 1150, 1200 and 1250 °C.

Table 1
Chemical composition of raw material

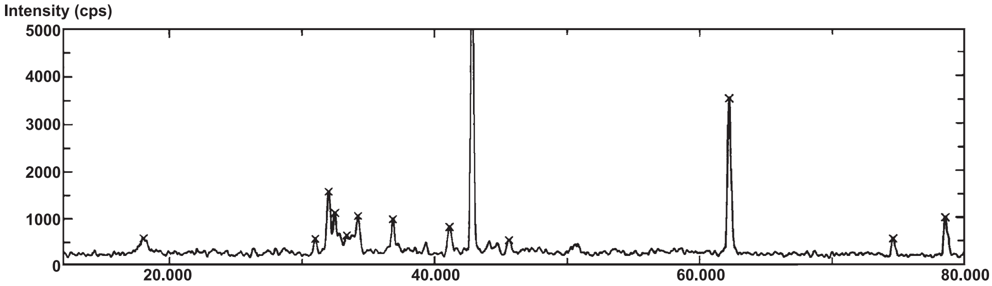
Chem. composition (wt.%)	Raw materials		
	Dolomite	SERP	MAG
CaO	29.46	1.36	0.88
MgO	20.65	39.02	46.88
Fe_2O_3	0.16	6.54	0.34
Al_2O_3	0.21	1.54	0.16
SiO_2	0.38	8.15	0.12
LOI	46.88	12.73	51.29



(a) 1250ºC



(b) 1200ºC



(c) 1150ºC

Fig. 5. XRD patterns of clinkers burned at 1100–1250 °C for 1 h: (a) 1250 °C, (b) 1200 °C, (c) 1150 °C.

The SEM observation of clinkers is shown in Fig. 6. EDS analysis indicates that the particles marked are MgO. The particles of MgO are about 1 μm. The small and round particles are C_2S that are about 0.5 μm.

3.2. Expansion of MgO-based expansive agent

The expansion of MgO-based expansive agents was tested by two methods. The one was the autoclaving test according to GB/T750-92. Another was to test the expansion of cement paste under curing condition at 80 °C in water.

The expansive agents were ground to pass the 0.088-mm sieve by lab mill. Cement P.II 52.5 produced by Jiannan-Onoda Cement was used. The expansive agent was replacing the cement amount by weight percent. Water content in cement pastes was as the results of consistency testing. The pastes were casted in 10×10×40 mm, demolded after 24±2 h cured at 20±2 °C and 90% RH, then autoclaving test and hot water curing test were carried out.

The relationship of autoclaving expansion with the replacing amount of cement by the MgO-based expansive agent prepared at 1200 °C for 1 h is listed in Table 2. The data in Table 2 are that the expansion increases with the increasing of dosage of expansive agent replacing of cement. The expansion of pastes are 0.145%, 0.318% and 2.122% when the dosage of expansive agent are 4%, 6% and 8%, respectively. They are much larger than the cement paste without MgO-based expansive agent.

Fig. 7 shows the expansion of pastes with or without MgO-based expansive agent prepared at 1200 °C for 1 h cured at 80 °C in water. The results indicate that the control cement pastes keep in shrinkage till 180 days, and the shrinkage rate decreases after 60 days. Under the same curing condition, replacing 6% cement by expansive agent by weight can compensate the shrinkage better, the expansion values are positive, in other words, the cement pastes keep in microexpansive state. But when increasing the dosage of expansive agent to 8% and 10%, the expansion of pastes are too lager and the rate are also fast within 3 to 14 days, although the expansion after 28 days keeps stable. Based on this fact, authors suggest that it must be carefully to control the expansion of MgO-based

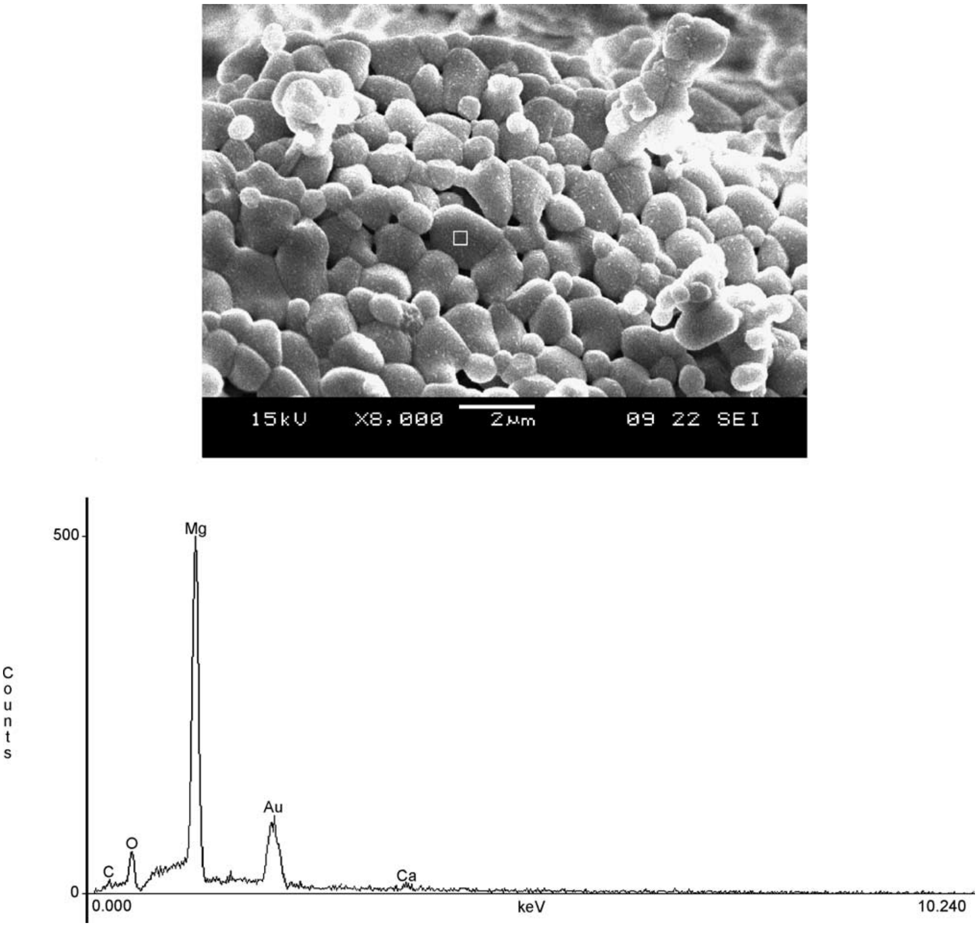


Fig. 6. SEM and EDS of expansive agent burnt at 1200 °C for 1 h.

expansive agent. The making condition (including proportion of raw meal, burning temperature and burning time) must be decided according to the actual situation of construction.

4. Conclusions

Based on above discussion, we propose that mineral dolomite can be used as raw material to produce MgO-based expansive agents to compensate the shrinkage of cement and concrete. To combine the CaO from decomposition of dolomite, silica-bearing mineral has to be used to adjust the amount of CaO existed in expansive agent to control the expansion at early age. To meet the requirement of various constructions, MgO-rich mineral is also considered to adjust the amount of MgO in expansive agents. The main phases of MgO-based expansive agents are MgO, C_2S and a little amount of CaO. The expansion of pastes depends on the making condition and dosage of MgO-based expansive agents greatly. MgO particles burned at lower temperature are bigger than those at high temperature, and resulting in

Table 2
Expansion of MgO-based expansive agent prepared at 1200 °C for 1 h

Dosage of expansive agent in cement (wt.%)	Expansion after autoclaving (%)
0	0.021
4	0.145
6	0.318
8	2.122

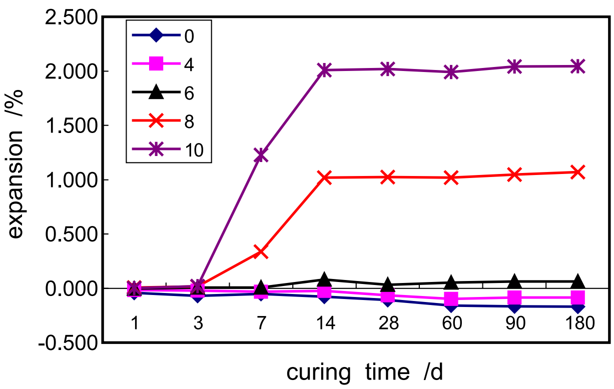


Fig. 7. Expansion of pastes with 0%, 4%, 6%, 8% and 10% expansive agent replacing of cement cured at 80 °C in water (burned at 1200 °C for 1.0 h).

expansion at early age. With the burning temperature increasing, the expansion is increasing but the expansion time delays. If the burning temperature and burning time, dosage in cement are controlled well according to the requirement of concrete construction, the MgO-based expansive agent can be used to compensate the shrinkage as designed.

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