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Effect of porosity on carbonation and hydration resistance of CaO materials

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Abstract

CaO pellets with different porosity were carbonated at 700 °C in CO_2 atmosphere. The carbonation rate was controlled by the diffusion of CO_2, regardless of the difference in porosities. For the low-porosity pellet, carbonation reaction only occurred on the surface, with a dense $CaCO_3$ film thus formed, which combined well with the substrate material; while for the pellet of high-porosity, the carbonation reaction occurred simultaneously both on surface and inside pores, and each CaO grain was surrounded by $CaCO_3$ film that contained microfissures. Hydration test results showed that carbonation treatment could effectively improve the hydration resistance of CaO materials regardless of porosity, but the carbonated high-porosity pellet was prone to breakage due to poor combination between the carbonated CaO grains. Therefore, for the purpose to improve the hydration resistance by carbonation treatment, it is recommended that the CaO materials should be either with less appreciable apparent porosity or with a limited carbonation ratio for the high-porosity CaO material.

Keywords: A. CaO materials; B. Porosity; C. Carbonation treatment; D. $CaCO_3$ film; E. Hydration resistance

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1. Introduction

Lime has the properties of high melting temperature, low vapor pressure, and thermodynamic stability in the presence of carbon as well as high alkality, thus it has long been considered to use as the raw materials for high temperature ceramics (such as crucible and ceramic filter), refractories and metallurgical accessories (such as refining slag and tundish covering powder).[1–6] With the development of clean steel production, free lime containing materials have been becoming more and more important for increasing the service life and removing inclusions from molten steel.[7–11] It is considered that application of CaO containing materials is an essential direction for the development of metallurgical industries and other high temperature field.[12] However, the application of CaO containing materials have been inhibited due to their drawback of poor hydration resistance, and many studies on this subject had been carried out from quite a long time ago.[13–15]

Among all of the methods to improve the hydration resistance of CaO materials, carbonation treatment is considered to be "green", since no impurities are added into CaO materials so that their advantages are kept after $CaCO_3$ decomposes at high temperature. Another reason for calling this method "green" is that carbonation process can consume CO_2 which is friendly to environment. Therefore, the studies on improving hydration resistance of CaO materials by carbonation treatment have been conducted since 1970s.[16–19] However, most of these works focused on the carbonation conditions by using deadburned CaO clinker as starting material, and it has been concluded that the optimum carbonation temperature is around 700 °C.[16,17] In fact, besides the deadburned CaO clinker with high compactness used for refractory materials, there are also porous CaO materials, such as CaO filter and lightburned CaO for tundish covering powder, and it is more difficult to prevent these porous CaO materials from hydrating.[5] It is necessary to confirm the feasibility to improve these CaO materials by carbonation treatment. Therefore, the present work investigated the carbonation of CaO materials with different porosities. The influence of porosity on carbonation behavior and microstructure of CaO pellets as well as their hydration properties were discussed.

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2. Experimental

Reagent $CaCO_3$ powder (99.5% purity and average size of 10 μm) and lightweight $CaCO_3$ powder were used as starting materials. The lightweight $CaCO_3$ powder was prepared from precipitation reaction by bubbling CO_2 gas to aqueous solution of CaO (that was derived from heating reagent $CaCO_3$ powder at 900 °C), with average size less than 1 μm. The two kinds of powders were pressed to pellet sized of 20 mm × 20 mm × ~5 mm by CIP under pressure of 100 MPa, and then fired at 1500 °C for 4 h in an electric furnace to obtain CaO pellets with low- and high-porosities. To obtain the sintered CaO pellets with different porosities, the pellets pressed from lightweight $CaCO_3$ powder were also fired at 1250–1400 °C (with the temperature interval of 50 °C) for 4 h.

Then the obtained CaO pellets were led into a vertical alumina tube furnace kept at 700 °C, with mass change recorded continuously. CO_2 gas flowed into the tube furnace at the bottom and exited at the top with a rate of 0.4 L/min during the whole heating and cooling process. The flow of CO_2 was so slow that it did not disturb the measurement of mass change in the present experiment conditions.

The samples were characterized by bulk density and apparent porosity, X-ray diffraction (XRD, Cu target, 20 kV and 20 mA), scanning electron microscopy (SEM), and hydration resistance. The bulk density and apparent porosity of samples before and after carbonation were measured by immersion method in kerosene under vacuum using Archimedes' principle and calculated according to Eqs. (1) and (2):

$$\text{Bulk density} = \frac{m_1 d}{m_3 - m_2}\ (\text{g/cm}^3) \tag{1}$$

$$\text{Apparent porosity} = \frac{m_3 - m_1}{m_3 - m_2} \times 100\% \tag{2}$$

where m_1 is the mass of dried sample in air (g), m_2 is the mass of a sample in kerosene (g), m_3 is the mass of a sample with free bubbles on the surface (g), and d is the density of kerosene (g/cm^3).

The hydration resistance of the sample was evaluated by measuring the mass gain after soaking the pellets in a chamber kept at 70 °C and 90% relative humidity.

3. Results

3.1. Carbonation properties

Table 1 shows the porosity and relative density of the CaO pellets before and after carbonation treatment. After firing at 1500 °C for 4 h, the relative density of CaO pellet sintered from reagent $CaCO_3$ was 70% and its apparent porosity was 27% (hereafter called high-porosity pellet). The relative density was calculated by comparing bulk density of the pellet as the fraction of its theoretical density that was calculated from a fractional summation of the theoretical densities of cubic CaO ($3.346\ \text{g/cm}^3$) and hexagonal $CaCO_3$ ($2.710\ \text{g/cm}^3$) according to Eq. (3):

$$\text{Theoretical density} = \frac{m_{CaO} + m_{CaCO_3}}{m_{CaO}/3.346 + m_{CaCO_3}/2.710} \tag{3}$$

where m_{CaO} and m_{CaCO_3} are the mass of CaO and $CaCO_3$ in the pellet, respectively.

Table 1
Relative density and apparent porosity of the low- and high-porosity CaO pellets before and after carbonation treatment

Sample	Relative density (%)		Apparent porosity (%)	
	Before	After	Before	After
High-porosity	70	86	27	0.5
Low-porosity	95	95	0.2	0

After carbonation treatment, the relative density of the high-porosity sample increased obviously, and almost all of the open pores turned to the closed ones. The relative density increased to 86% and the apparent porosity decreased significantly to 0.5%. But for the pellet sintered from lightweight $CaCO_3$, its relative density was 95% and the apparent porosity was 0.2% (hereafter called low-porosity pellet). After carbonation treatment, there was little change in relative density and the apparent porosity disappeared.

Fig. 1 shows the mass change of the low- and high-porosity pellets against carbonation time. The mass change was expressed by the percentage of mass gain to the original mass. The mass gain increased gradually and reached a plateau indicating completion of the carbonation process. The mass gain was only 2% for the low-porosity pellet, whereas it was about 14% for the high-porosity one. For both samples, a parabolic relationship between mass gain and carbonation time is observed. This result indicates that for both the low- and high-porosity CaO pellets, the carbonation reactions were controlled by the diffusion process.[20]

Fig. 2 shows the changes of relative density and apparent porosity of CaO pellets sintered at 1250–1400 °C for 4 h and subsequently carbonated at 700 °C for 24 h. It is observed that the relative density increased and apparent porosity decreased with increase of firing temperature. After carbonation treatment, the relative density of all samples increased appreciably, with the disappearance of the apparent porosity.

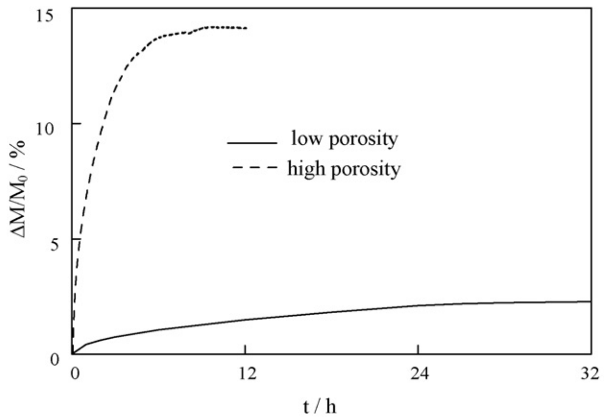

Fig. 1. Values of mass gain against carbonation time kept at 700 °C. M is the original mass of the sample and ΔM is the mass gain after carbonation treatment.

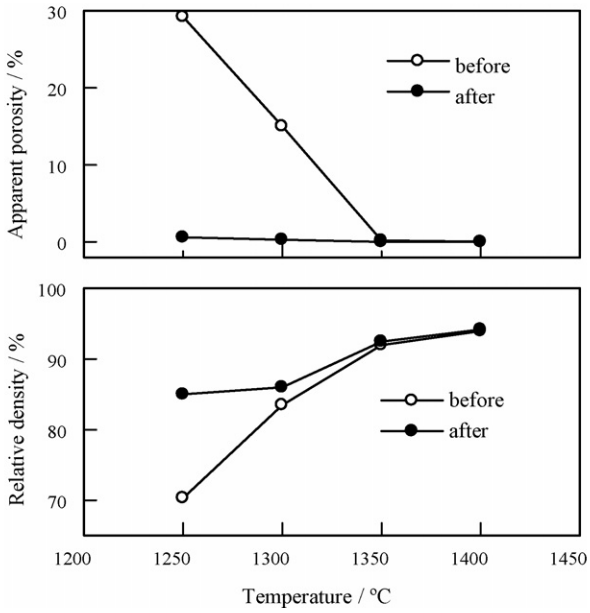

Fig. 2. Changes of relative density and apparent porosity of CaO pellets sintered under different temperatures and then carbonated at 700 °C for 24 h.

3.2. Phase composition and microstructure

Fig. 3 shows XRD patterns of the low- and high-porosity CaO pellets after carbonation treatment. $CaCO_3$ (calcite) was identified in both samples, indicating the formation of $CaCO_3$ after carbonation treatment. The intensity of the formed $CaCO_3$ in the high-porosity sample was much stronger than that in the low-porosity one, indicating the amount of the formed $CaCO_3$ in the high-porosity sample was more than that in the low-porosity one. For both the low- and high-porosity pellets, CaO was still the main phase after carbonation treatment.

Fig. 4 illustrates the microstructure of the low-porosity pellet before and after carbonation treatment. It is observed that the low-porosity pellet was only carbonated on the surface, with a dense $CaCO_3$ film about 2 μm in thickness formed. It is also observed that the $CaCO_3$ film combined well with the substrate CaO material. This result is correspondent to the previous works.[16,17] But different from the low-porosity sample, the high-porosity pellet was carbonated both on the surface and in the pores, with each CaO grain being encompassed by the formed $CaCO_3$ film. In addition, microfissures were observed in the formed $CaCO_3$ film (Fig. 5).

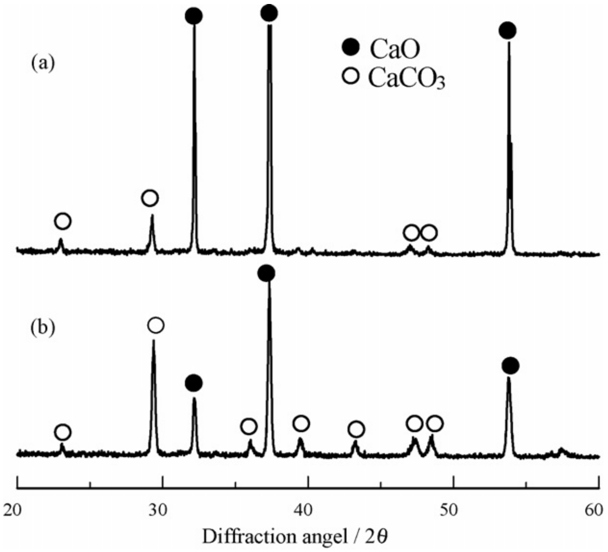

Fig. 3. X-ray surface diffraction patterns of the low- and the high-porosity pellets carbonated at 700 °C: (a) high-porosity and (b) low-porosity.

3.3. Hydration properties

Fig. 6 illustrates the relationship between mass change and hydration time kept at 70 °C and 90% relative humidity for both the low- and high-porosity pellets with and without carbonation treatment. The mass gain was expressed by the percentage of mass gain to the original mass of CaO pellets. The arrows represent the time when the pellets broke during hydration process. It shows that carbonation treatment significantly improved the hydration resistance of both the low- and high-porosity samples, with the formation of an induction period (during which there was no appreciable mass change).[18] For the low-porosity pellet, the hydration reaction proceeded from surface to inside gradu-

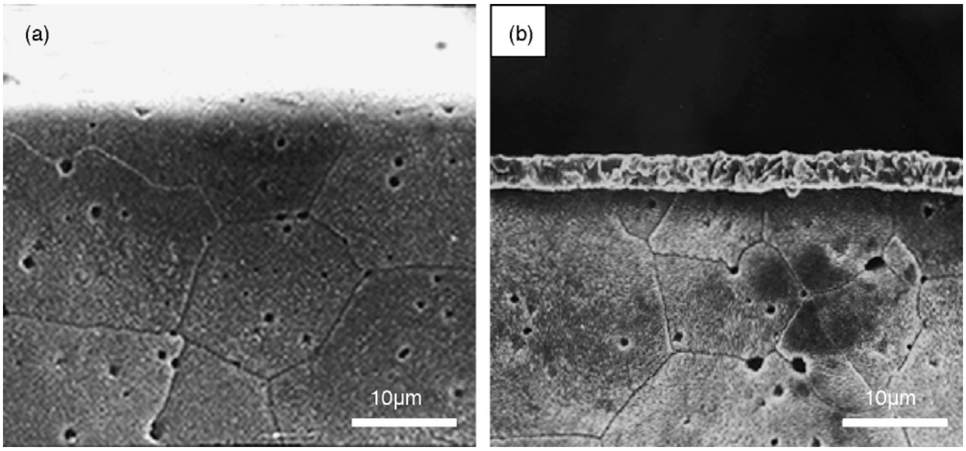

Fig. 4. Fractured surfaces of the low-porosity pellet: (a) before and (b) after carbonation treatment.

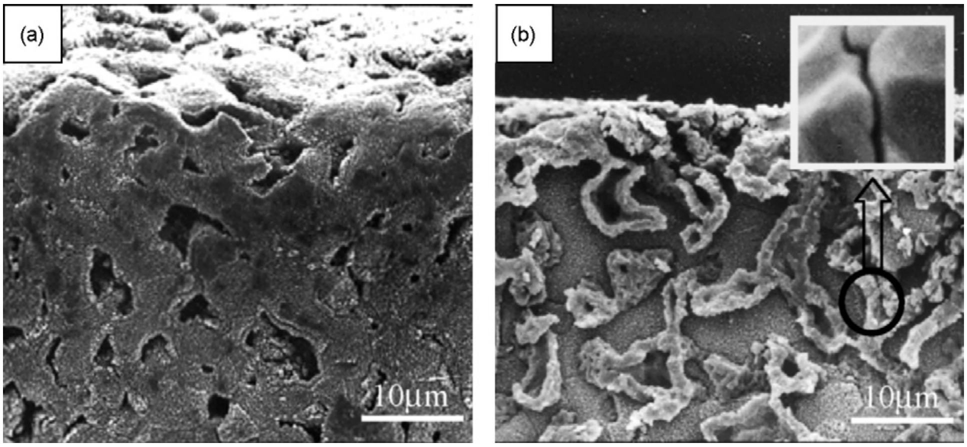

Fig. 5. Fractured surfaces of the high-porosity pellet: (a) before and (b) after carbonation treatment.

ally, with appreciable interface between the hydrated and unhydrated part. For the orientated growth of the formed $Ca(OH)_2$ and anisotropic volume expansion when CaO was hydrated,[21] cracks were observed at the corner (Fig. 7). After carbonation treatment, a long induction period of 7 days formed and the sample did not break after soaking for 21 days, with mass gain of about 22% that was a little more than that of the uncarbonated one (20%).

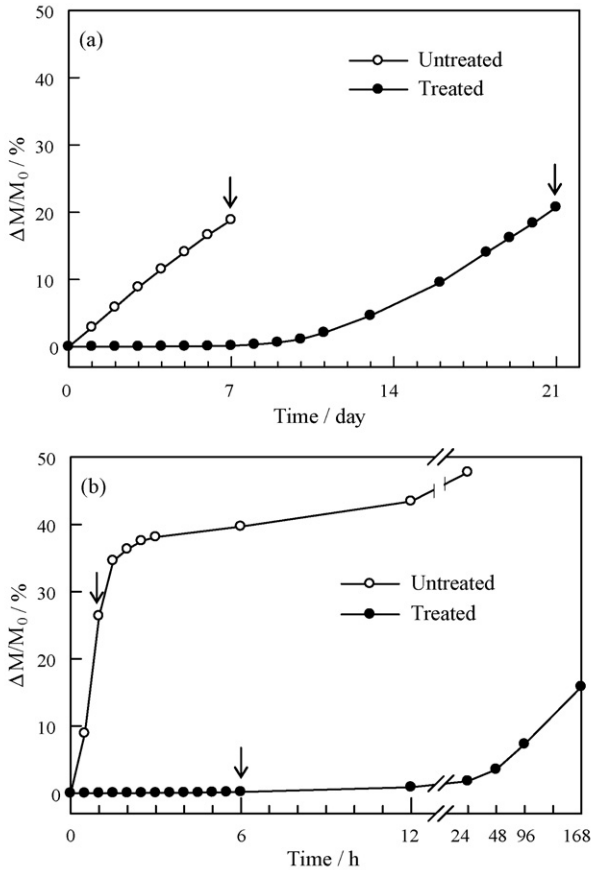

Fig. 6. Mass gains of: (a) the low- and (b) the high-porosity CaO pellets with time soaking at 70 °C and 90% RH. M is the original mass of the sample before hydration test and ΔM is the mass change after hydration test.

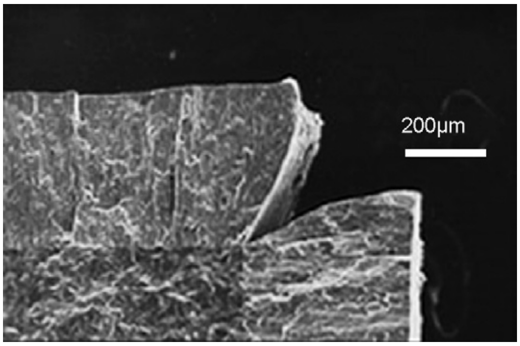

Fig. 7. Microstructures of CaO pellet after soaking at 70 °C and 90% humidity for 96 h.

But for the carbonated high-porosity pellet, there was only a short induction period of about 12 h. The interesting result was that the pellet broke to several pieces after hydration test for only 6 h. This time was within the induction period. Even after the induction period, the hydration reaction still proceeded at a low rate, and the mass gain was only about 2.5% after 24 h. Then with hydration time increasing, the broken pieces further turned to much smaller size gradually, and finally turned to fine powders. From these results, it is considered that the carbonated low- and high-porosity pellets were hydrated in different mechanisms.

Fig. 8 shows the hydration test result of the carbonated CaO pellets with different apparent porosity. It is found that although there was little apparent porosity for all the carbonated pellets, the time of the carbonated CaO pellet to break was abruptly decreased with increase of the apparent porosity of the original CaO pellet, even with a very limited mass gain. From this result, it is considered that the breakage of the carbonated CaO pellet was closely dependent to apparent porosity or compactness of the sintered original CaO pellet.

4. Discussion

4.1. Carbonation properties and microstructure

From the curves of mass gain and microstructure observation, it is considered that the CaO materials with different porosity

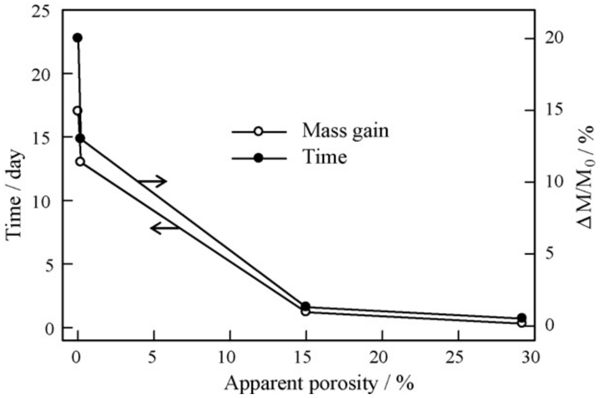

Fig. 8. The dependence of apparent porosity on the time of the carbonated CaO pellets to break and its mass gain during hydration process.

were carbonated in different mechanisms, as shown in Fig. 9. For the pellet without apparent porosity, CO_2 gas could not flow into the sample and thus the carbonation reaction only occurred on the surface, with a thin and dense $CaCO_3$ film formed on the surface. It is calculated that the molar volume of $CaCO_3$ (36.9 cm^3/mol) is larger than that of CaO (16.7 cm^3/mol), and there is a large volume expansion when CaO converts to $CaCO_3$, with the generation of stress between the formed $CaCO_3$ and the uncarbonated CaO grains. But for the amount of the formed $CaCO_3$ was limited when the low-porosity pellet was carbonated, the stress between the formed $CaCO_3$ and the substrate CaO grains was not so severe to form microfissures. Therefore, there was no microfissures were observed in the $CaCO_3$ film which combined well with the substrate CaO materials. It is unnecessary to concern for the formation of microfissure when the CaO materials of low-porosity were carbonated.

But for the pellet with apparent porosity, the CO_2 gas could easily flow to the inside of the sample, and thus carbonation reaction occurred in all open pores, with each CaO grain surrounded by $CaCO_3$ films. When the $CaCO_3$ films formed inside the pores, CO_2 gas had to pass through these films to maintain the reaction proceeding. Thus, though the carbonation reaction occurred inside all pores, the carbonation rate was still controlled by the diffusion of CO_2 through these formed $CaCO_3$ films around CaO grains. With increase of the thickness of the formed $CaCO_3$ film and decrease of apparent porosity, the diffusion of CO_2 became so difficult that the carbonation reaction tended to cease. Since the reaction specific area of the high-porosity pellet was much larger than that of the low-porosity one, its carbonation rate was much fast than that of the low-porosity one, with a much more mass gain (Fig. 1). With the formation of the large amount $CaCO_3$ and the volume expansion, the stress between the formed $CaCO_3$ film and CaO grains was so severe that microfissures would form (Fig. 4). It is considered that the formation of these microfissures degraded the combining strength between the carbonated CaO grains.

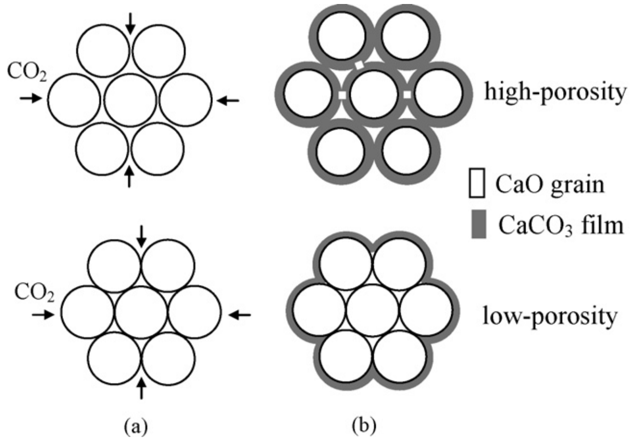

Fig. 9. Carbonation models of CaO pellets: (a) before and (b) after carbonation treatment.

Therefore, in order to prevent microfissure forming when the CaO materials is carbonated, the following two ways are recommended: one is that the pellet should be without appreciable apparent porosity and thus to ensure the carbonation reaction occurring on the surface; the other is to control the formed $CaCO_3$ amount, in another words, to control the carbonation ratio when the CaO materials with high-porosity is carbonated.

4.2. Hydration properties

Since the diameter of H_2O molecule (0.151 nm) is smaller than that of CO_2 molecule (0.232 nm), water vapor could still pass through $CaCO_3$ film although the carbonation reaction ceased owing to CO_2 diffusion. Therefore, carbonation treatment could effectively improve hydration resistance of CaO materials, but it could not inhibit CaO hydrating completely. For the low-porosity pellet, a long induction period of 7 days formed owing to the formation of dense $CaCO_3$ film after carbonation treatment. The time of the induction period is considered to be dependent to the thickness and the compactness of the formed $CaCO_3$ film. In fact, since the hydration reaction was conducted under the condition of 70 °C and 90% relative humidity, the hydration rate was several decade times to normal climate condition.[22] Thus an induction period of 7 days means that the carbonated CaO materials could be safely stored for more than 1 year. Therefore, it is considered that carbonation treatment could almost completely prevent CaO materials from hydrating during storage period. In addition, whether carbonated or not, the hydration process of the low-porosity pellet proceeded from surface to inside. The breakage of the pellet was due to the volume expansion with the hydration reaction proceeding, and thus the mass gains were equivalent when the carbonated and uncarbonated samples broke. Therefore, it is considered that carbonation treatment is suitable for improving hydration resistance of compact CaO materials, without concerning for the materials over carbonated.

For the uncarbonated CaO pellet with high apparent porosity, the water vapor easily flowed to the inside of the pellet, thus the hydration reaction occurred in the whole sample at the same time and a high hydration rate was obtained, which led to the pellet soon breaking to fine powder due to the abruptly volume expansion caused by hydration reaction. Similar to the low-porosity sample, the formation of dense $CaCO_3$ film after carbonation treatment effectively retarded occurrence of the hydration reaction, with the formation of an appreciable induction period.

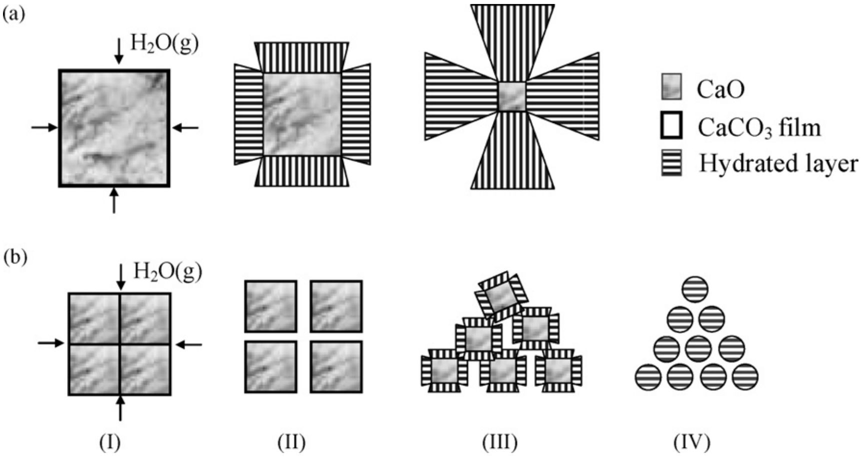

Fig. 10. Hydration models of the carbonated: (a) low- and (b) high-porosity CaO pellets.

As described above, the combination between the carbonated CaO grains was very weak due to the formation of microfissure when the carbonation ratio is too large, and it became much weaker when the pellet hydrated. Therefore, for the carbonated pellet of high-porosity, the breakage was so sensitive to the apparent porosity that the carbonated pellet would break even with a very small amount of CaO hydrated (Fig. 8). After the carbonated pellet broke, the $CaCO_3$ films around CaO grains still effectively inhibited the hydration reaction, so that the time of the pellet to break was shorter than the induction period (Fig. 6). Therefore, it is considered, for the carbonated high-porosity pellet, its breakage was not for the volume expansion with hydration proceeding, but mainly for the poor combination between the carbonated CaO grains. For this reason, compared with the low-porosity pellet, the carbonated high-porosity one was hydrated in a different mechanism, as shown in Fig. 10. A more stage formed during hydration process. It firstly broke to several pieces, and further turned to much smaller size gradually with hydration time increasing. Thus, it is considered, the following two ways to prevent the carbonated CaO materials easily breaking are recommended: one is that the original CaO pellet should be with less appreciable apparent porosity and thus to ensure the carbonation reaction occurring on the surface; the other is to control the formed $CaCO_3$ amount, in another words, to control the carbonation ratio to avoid “over carbonated” when the high-porosity CaO materials are carbonated.

5. Conclusion

Based on the above results, in order to improve the hydration resistance of CaO materials by carbonation treatment, the followings are concluded:

(1) The high-porosity CaO materials were carbonated with a higher rate compared to the low-porosity one. The carbonation processes were controlled by the diffusion of CO_2 through the formed $CaCO_3$ film, regardless of the porosity.
(2) The high-porosity CaO materials was carbonated both on the surface and in the pores, with each CaO grain being encompassed by $CaCO_3$ film containing microfissures; whereas the low-porosity one was only carbonated on the surface, with the formation of a dense $CaCO_3$ film that combined well with the uncarbonated CaO materials.
(3) The breakage of carbonated low-porosity pellet was due to the volume expansion caused by hydration reaction, whereas it was mainly due to the poor combination between the carbonated CaO grains for the high-porosity one.
(4) Carbonation treatment effectively improved the hydration resistance of CaO materials, with formation of appreciable induction period, regardless of porosity. For the low-porosity pellet, the induction period reached to 7 days. However, since the carbonated CaO materials of high-porosity would easily break due to the poor combination between the carbonated CaO grains caused by formation of microfissures, it is necessary to control the carbonation ratio to avoid “over carbonated”.

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