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MECHANISM OF EXPANSION IN HARDENED CEMENT PASTES WITH HARD-BURNT FREE LIME

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ABSTRACT

The expansion characteristics of hard-burnt free lime in cement pastes were determined by measurements of free linear length changes in various periods. Hydration of lime in water and in alkali solutions was investigated to evaluate the influence of OH^- ions on the migration of Ca^{2+} ions from lime, the supersaturation of solutions for $Ca(OH)_2$ and the size as well as the dispersion of distribution of $Ca(OH)_2$ crystals formed. Based on the experimental results, an expansion mechanism of hydrating lime in cement pastes was proposed. It is found that OH^- ion in pore solutions may force $Ca(OH)_2$ to form in situ and promote the development of expansive forces. The expansion of hydrating lime is caused by the crystallization of $Ca(OH)_2$ crystals formed in situ.

Introduction

The expansion of hydrating free lime has been observed since ancient times. This property has been successfully utilized for various practical uses, such as demolition and shrinkage-compensation. The expansion, however, may bring about unsoundness of set cement pastes and give concrete engineering practice problems. These phenomena attract much attention and many studies about the expansive behavior of free lime have been done. It is generally assumed that hard-burnt free lime could cause delayed expansion in cement pastes or concrete and the expansion is due to the formation of $Ca(OH)_2$ from the hydration of lime [1,2]. However, the mechanism for the expansion is not fully understood.

The development of expansion in cement pastes during formation of a compound needs two essential conditions. One is that the compound must be confined and the other is that the compound may give rise to an expansive force to resist restraint. Yamazaki and Ramachandran et al [2,3] believed that the expansion was associated with the increase of solid volume during the hydration of lime. This hypothesis seems not to be quite reasonable. Hydration of a Portland cement clinker always accompanies a large increase of solid volume but no expansion occurs.

The hydration of C_3S, for example, would not cause any expansion although 1 cm^3 of C_3S hydrates to form 1.65 cm^3 of C-S-H gel (0.965cm^3) and $Ca(OH)_2$ (0.686cm^3). The expansion may be closely related to the position occupied by hydration products. When $Ca(OH)_2$ forms in voids or cracks, no expansion will be brought about, as mentioned by Idorn and Johansen et al [4,5]. However, $Ca(OH)_2$ forming in a restricted space may give expansion.

The origin of expansive forces is still controversial. Chatterji and Johansen et al [1,5] suggested that the expansive force was crystallization pressure based on the formation and growth of $Ca(OH)_2$ crystals. Lime hydrated to form colloidal $Ca(OH)_2$ and then these colloidal crystallites would grow into crystals. During this process of growth, a thrust was developed against constraining cement pastes, thereby causing expansion. On the other hand, Yamazaki and Sakakibara [6] proposed that the expansion was caused by dusting or swelling pressure resulting from the formation of massive tiny $Ca(OH)_2$. They found in experimental that the massive $Ca(OH)_2$ consisted of smaller microcrystals than about 0.1μm. Therefore, they claimed that it was difficult to support the opinion that expansive pressure of hydration of lime was caused by the growth of $Ca(OH)_2$ crystals.

Experimental

Lime was obtained by burning limestone at 1400°C for 1.5 hours and was ground to 5.5 percent residue on 0.080 mm sieve. Other materials used were a Portland cement (OPC), a white Portland cement (WC), a pulverized fly ash (PFA) and a granulated blast-furnace slag (BFS). Two blended cements were prepared by mixing the Portland cement with PFA and BFS, respectively. The replacement of cement by PFA or BFS was 30 percent. Cement with PFA is signed as OPC-PFA and cement with BFS as OPC-BFS. The chemical compositions and specific surface area of the materials are listed in Table 1.

Table 1 The chemical compositions and specific surface area of the materials

Materials	Chemical compositions (%)										Blaine
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Loss	Total	(cm^2/g)
OPC	20.72	4.91	4.23	61.39	0.97	1.90	0.20	0.65	2.70	95.77	3210
WC	21.52	0.11	4.74	64.40	0.38	1.86	0.15	0.09	5.60	98.85	3243
PFA	50.32	7.07	30.40	2.97	1.40	0.46	0.41	1.22	4.40	98.65	4435
BFS	35.52	3.24	11.08	38.82	9.07	0.40	0.34	0.55		99.02	4325
Limestone	0.72	0.09	0.11	54.43	0.08				43.38	98.80	

The cements incorporated with and without free lime were cast in 10x10x40 mm pastes with studs at two ends. Each set of paste consisted of six specimens. Immediately after being cast , the pastes were cured under normal conditions for 24 hours except that a group of OPC pastes with additions of alkali and gypsum were cured for 10 hours. Then they were demolded and measured original length by a spiral millimeter. The specimens were cured in moist chambers at ambient temperature.

The concentrations of Ca^{2+} and OH^- ions in systems of lime-water and lime-NaOH solution were determined by chemical analysis.

Results and discussion

Expansion of free lime in set cement pastes

Hydration of free lime may cause distinct expansive characteristics in different cement pastes. Considering the disparity in deformation of cementitious matrices, the expansion due to the hydration of lime was obtained by free linear length change of a cement paste with addition of lime minus that of the corresponding cement matrix. This value of expansion reports the influence of a cement matrix on the expansive behavior of lime.

Fig. 1 gives the expansion caused by the hydration of 2 percent free lime incorporated in pastes of Portland cement (OPC), white Portland cement (WC) and blended cements with 30 percent of BFS (OPC-BFS) or PFA (OPC-PFA), which were cured at ambient temperature and 100 percent RH. It is shown that lime manifests the largest expansibility in OPC and the smallest expansibility in WC. Replacements of OPC by BFS and PFA may reduce the expansibility of lime. In this respect, PFA is more effective than BFS. Some similar results were obtained when the content of lime increased to 5 percent (Fig. 2). It was found, however, that both BFS and PFA increased the expansion of hydrating lime when the cements contained 5 percent of lime.

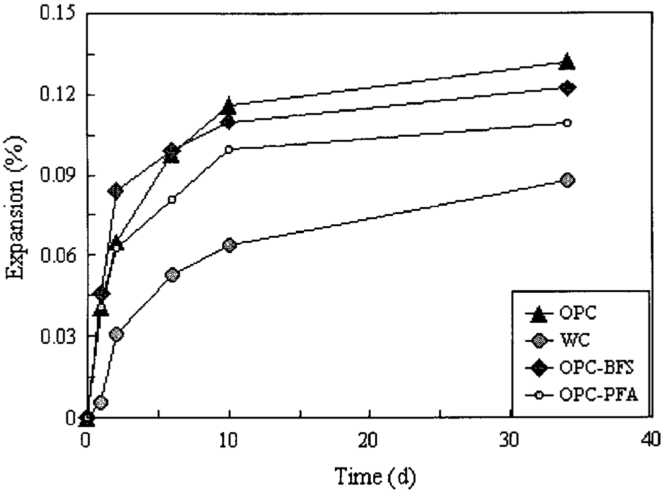

Fig. 1 Expansion caused by hydration of lime in cement pastes (lime=2 percent)

The development of expansion due to hydration of lime in set cement pastes depends mainly on the development of restraint and expansive force. Restraint tends to eliminate expansion, but expansive force contributes to expansion. The restraint is the tensile strength of cement pastes, which is proportional to the compressive strength. It is well known that replacement of OPC by BFS or PFA will decrease the early strength of cement pastes. At the same replacement, the strength of a cement paste blended with PFA is generally lower than that of one with BFS. In the case of 2 percent lime addition, the direct proportion of the expansion to the restraint reveals that the expansive force developed during the process of hydration of lime in OPC, OPC-BFS and OPC-PFA pastes is distinct. The expansive force in the three cement pastes follows: OPC>OPC-BFS>OPC-PFA. When the amount of lime added increases from 2 percent to 5 percent, the expansive force will be enhanced correspondingly. As a result, the weak pastes of OPC-BFS and OPC-PFA can not withstand the expansive force and expand

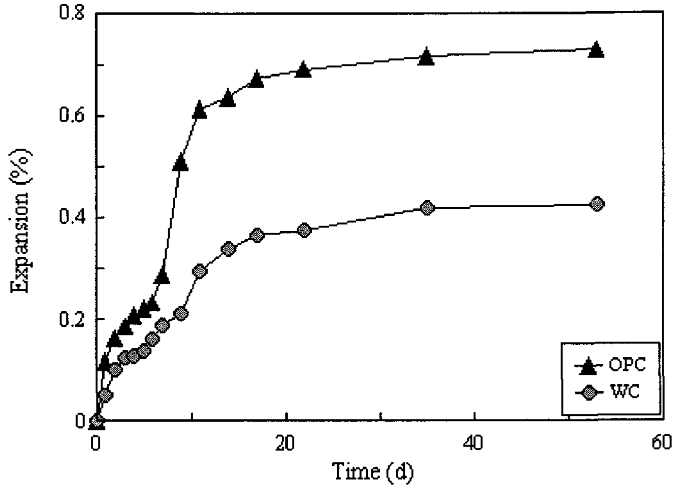

Fig. 2 Expansion vs time of hydration of lime in cement pastes (lime=5 percent)

unusually. This unusual expansion may be due to the poor coordinate of the development of restraint and expansive force.

The strength of OPC pastes develops approximately as that of WC pastes. The difference of expansion of hydrating lime in them indicates that the OPC paste is more conducive to the development of expansive force than the WC paste.

With respect to OPC, OPC-BFS, OPC-PFA and WC pastes, they resemble in solid phases and differ in pore solutions, which are composed of OH^-, K^+, Na^+ and a few other ions, such as Ca^{2+}, AlO_2^-, SO_4^{2-}, SiO_4^{4-}[7]. It may be the pore solution that causes the discrepancy in the expansive force. It is generally accepted that the addition of BFS or PFA will decrease the concentration of OH^- and alkali metal ions in the pore solutions and PFA usually plays a more effective role than BFS. In addition, BFS or PFA tends to react with $Ca(OH)_2$, which may decrease the content of $Ca(OH)_2$ from hydration of cement clinkers or free lime. Because the pozzolanic reaction proceeds very slowly, the consumption of $Ca(OH)_2$ derived from free lime in the early stage may be negligible. As compared to the OPC paste, the concentrations of OH^- and alkali metal ions in the pore solution of the WC paste are lower due to the lower alkali content of WC (Table 1). From the experimental results and discussion above, It seems to deduce that OH^- or alkali metal ions may promote the development of expansive force.

To examine the deduction, solid NaOH reagent was added to mix water to elevate the alkali content of WC and OPC. The amounts of solid NaOH added were 0, 0.14, 0.28, 0.42 and 0.56 percent Na_2O equivalent, respectively. Fig. 3 demonstrates the results from WC pastes with 5 percent lime. It is obvious that an adequate amount of alkali may increase the expansion resulting from the hydration of lime. As is the case for 5 percent lime in OPC pastes (Fig. 4) which were added with 6 percent gypsum and demolded at 10 hours after being cast so that the degree of hydration of lime was reduced when demolding [2]. The influence of alkalies on the expansion of lime was more stronger in WC pastes than in OPC pastes. This may be associated with the difference in alkali content of the two cements (Table 1). However, it was observed in experimental that, when further more alkali was incorporated, the expansion of lime both in WC and OPC pastes would decrease. It is assumed that alkalies may accelerate the hydration of Portland cements and the development of early strength of cement pastes. Therefore, the hydration of lime in cement pastes with higher strength caused a larger expansion. This indicates that the alkalies added contributed to the expansive force. Besides, alkalies may promote the concentrations of OH$^-$ and alkali metal ions in pore solutions of cement pastes[7]. So the expansive force is proportional to the concentrations of OH$^-$ and alkali metal ions in the pore solutions. Considering that the alkali metal ions are not involved in the hydration of lime and that the concentration of OH$^-$ ion is well corresponding to that of alkali metal ions, we may suggest that the expansive force is , to some extent, dependent on the concentration of OH$^-$ ion. The higher the concentration of OH$^-$ ion, the larger the expansive force is developed. Alkalies may also affect the kinetics of hydration of lime, which is associated with the content of unhydrated lime at the demolding time and the rates of nucleating and growing of $Ca(OH)_2$ crystals. The intersection of these effects of alkalies is complex and needs to be further investigated.

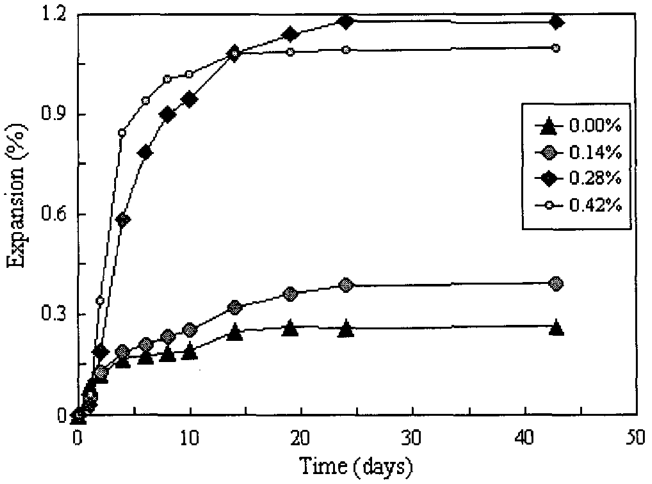

Fig. 3 Expansion resulting from the hydration of 5 percent lime in WC pastes added with 0, 0.14, 0.28 and 0.42 percent Na_2O equivalent

By using the data of Shi[8] and assuming that the tensile strength of cement pastes is one tenth of their compressive strength[9] , the expansive force from hydration of free lime in a Portland cement paste and a blended cement paste with 23 percent PFA can be calculated. It is 11.87 MPa in the Portland cement and 10.26 MPa in the blended cement at 3 days. These data further confirm the conclusion above.

Hydration of lime in liquids

This section tries to study some phenomena on the hydration of lime in water and NaOH solutions. They include migration of Ca^{2+} and OH$^-$ ions, saturation of liquid to $Ca(OH)_2$ and size of $Ca(OH)_2$ formed. The study was emphasized on the role of NaOH solution in the hydration of lime based on the consideration that the pore solutions of cement pastes are essentially alkali solutions and the concentration of OH$^-$ ions affects the expansive force due to the hydration of lime.

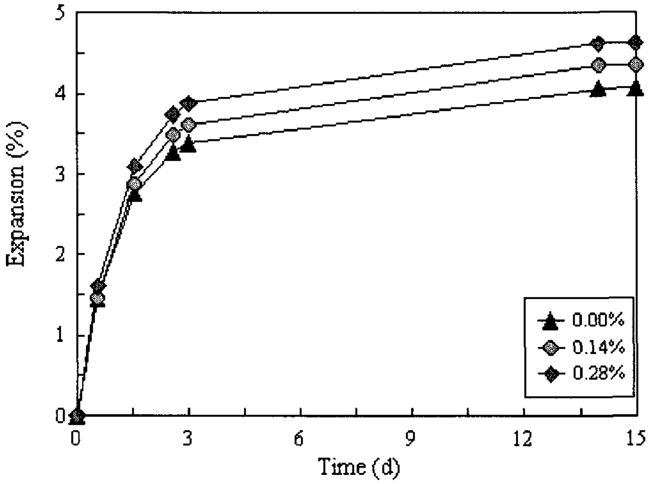

Fig. 4 Expansion caused by the hydration of 5 percent lime in OPC pastes added with 6 percent gypsum and with 0, 0.14, 0.28 percent Na_2O equivalent

First, a certain amount of deioned water or 1 M NaOH solution was slowly and carefully added to a container in which a thick layer of lime powder had been placed. Then the container was sealed to prevent the liquid from carbonation. The liquid was drawn out and chemically analyzed after the container was set quietly for 7 hours. Table 2 lists the results. It is observed that the migration of Ca^{2+} ion derived from lime was, to some extent, confined in a liquid with high concentration of OH^- ion, but the migration of OH^- ion seemed to be independent of the distance from the interface of lime-liquid systems. The concentration product for $Ca(OH)_2$ ($Ksp=[Ca^{2+}][OH^-]^2$) decreased with the increase of the distance from lime particles, especially in NaOH solution.

Secondly, the lime powder was mixed with deioned water or 1 M NaOH solution by liquid:lime ratio 300. The liquids were continuously stirred for certain periods. The solutions filtered from the suspensions were then sustained to chemical analysis. The results are illustrated in Fig. 5, in which Ksp represents the concentration product for $Ca(OH)_2$ at the actual state; Ksp,eq. means that at equilibrium. The ratio of Ksp/Ksp,eq. may be used as an estimation of saturation. The suspensions were both supersaturated with respect to $Ca(OH)_2$. However, the supersaturation is larger in 1M NaOH solution than in deioned water, especially at early stage. This is confirmed by the chemical analysis on solutions in the static systems of lime-liquid (Table 2).

Table 2 The concentrations of Ca^{2+} and OH^- ions in liquids and the concentration product for $Ca(OH)_2$

System	Distance from the interface	Concentrations of ions (M)		Ksp
		$[Ca^{2+}]$	$[OH^-]$	
Lime-deioned water	0-1 cm	0.0257	0.0516	6.83×10^{-5}
	1-2 cm	0.0245	0.0495	5.99×10^{-5}
Lime-1 M NaOH Solution	0-1 cm	0.0022	1.0130	2.23×10^{-3}
	1-2 cm	0.0011	1.0051	1.10×10^{-3}

Thirdly, the lime powder was dispersed on a slide by either deioned water or 1M NaOH solution. The slides then were laid in a sealed moist chamber. At the age of 18 hours, the samples on the slides were examined with an optical microscope. It was found that lime soaked in water hydrated to form 2-4 μm $Ca(OH)_2$ crystals, which were either scattered or gathered. $Ca(OH)_2$ crystals formed by lime soaked in NaOH solution were 0.5-2 μm and mainly in a gathered state.

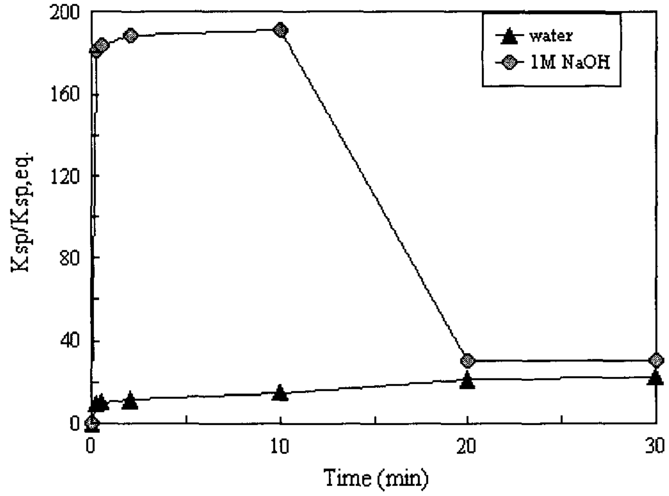

Fig. 5 The saturation of liquids mixed with lime with respect to $Ca(OH)_2$

Briefly, alkalies may force Ca^{2+} ions to locate near the surfaces of lime particles, give rise to a large nucleating supersaturation for $Ca(OH)_2$ and lead the formation of fine $Ca(OH)_2$ gathered. Because alkalies decrease the solubility of $Ca(OH)_2$, i.e. the concentration of Ca^{2+} ions, the driving force of migration is weakened. Consequently, Ca^{2+} ion exists principally near the lime particles. The high concentration of OH^- ions and the locally distributed Ca^{2+} ions guarantee a high supersaturation for $Ca(OH)_2$ around lime. The high supersaturation may give rise to a large nucleating rate, thus to many crystallizing centers. In consequence, fine crystals of $Ca(OH)_2$ are formed, which gather on the surfaces of lime particles or nearby. On the other hand, OH^- ion tends to minimize the recrystallization of fine crystals of $Ca(OH)_2$, thus maintains the size and location of $Ca(OH)_2$ crystals.

Mechanism of expansion

Formation of $Ca(OH)_2$ during the hydration of lime

The formation of $Ca(OH)_2$ by the hydration of cement clinker minerals in hardened cement pastes is not considered to cause expansion. In contrast, the formation of $Ca(OH)_2$ resulting from the hydration of free lime may bring hardened cement pastes to expand although the magnitude of expansion varies with different cement pastes as identified in Fig. 1 to 4. This disagreement may be closely related to the characteristics of $Ca(OH)_2$ formed, such as the position occupied and the dispersion of distribution. The former $Ca(OH)_2$ crystals disperse throughout the system and are not confined. Thus, the growth of them accompanies no expansion. The latter $Ca(OH)_2$ particles do not try to fill up the pore space. They are restricted by OH^- ions in the pore solutions and gathered in confined regions near the surfaces of lime grains as mentioned above. Because the solid volume is almost doubled during the hydrating of lime to form $Ca(OH)_2$ and the fine crystals of $Ca(OH)_2$ formed inevitably enclose many voids which may act as a solid to increase the solid volume, the gathered crystals of $Ca(OH)_2$ will contact with the surroundings consisted of hydrates after a certain period of hydration. From then on, the expansive force will be built up and cause the cement pastes to expand. When pore solutions of cement pastes are concentrated on OH^- ions, the fine $Ca(OH)_2$ crystals formed are highly confined and fill efficiently up the interface zones between lime and hydrates. Therefore, a large expansion occurs. When the pore solutions are of low alkalinity, some of $Ca(OH)_2$ crystals produced by the hydration of lime may form in the pore space due to the long-distance migration of Ca^{2+} ions. This will decrease the expansion.

Expansive force

The formation of $Ca(OH)_2$ in situ makes the particles of $Ca(OH)_2$ be restricted. This only meets one of the essential conditions for producing expansion. The other condition is that the confined crystals of $Ca(OH)_2$ could develop an expansive force to push away the restraint.

Nowadays, there are two major hypotheses on the driving force of expansion: crystallization pressure and swelling pressure. The swelling pressure is caused by the repulsion of inter particles absorbed with water molecules. It depends on the ability of the particles to imbibe water. A strong absorption of water may provide a high swelling pressure. Fig. 6 demonstrates the content of water absorbed by fine $Ca(OH)_2$ crystals from the hydration of lime. An increase in the content of imbibed water with increased specific surface area of $Ca(OH)_2$ is observed in the low surface area region, but at higher surface area the water content tends to become independent of the area. The maximum content of water imbibed by $Ca(OH)_2$ crystals may be comparable with that absorbed by C-S-H gel, but is much lower than the content of water absorbed by alkali-silica gel (Fig. 6). It should be mentioned that the content of water imbibed by $Ca(OH)_2$ crystals and alkali-silica gel shown in Fig. 6 includes a few amounts of pore water. Therefore, the swelling pressure resulting from the fine crystals of $Ca(OH)_2$ may be similar to that caused by C-S-H gel and further less than that of

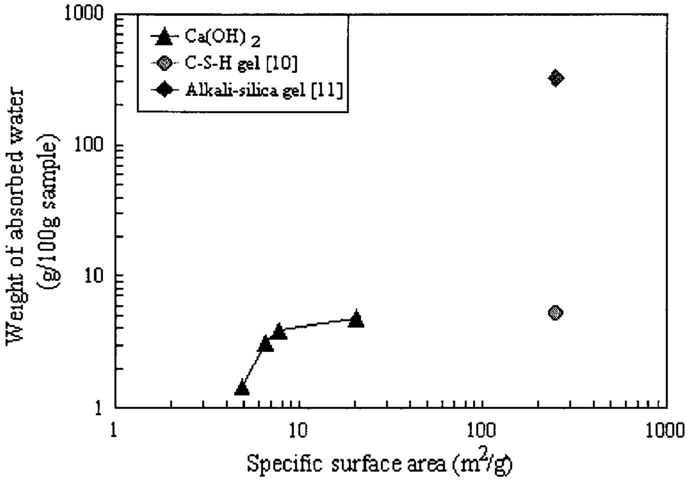

Fig. 6 Water content absorbed by $Ca(OH)_2$ crystals, C-S-H gel and alkali-silica gel (the data for gel are derived from references 10 and 11, respectively)

alkali-silica gel. Alkali-silica gel may produce a swelling pressure up to 13.79 MPa in mortars, whereas the expansibility of C-S-H gel is very limited [10]. From this, the swelling pressure of fine $Ca(OH)_2$ crystals may also be very limited.

The expansive force developed by fine crystals of $Ca(OH)_2$ may be as high as 90 MPa[6]. This shows that a strong expansive force must exist except for the swelling pressure. The force is the crystallization pressure, which is aroused by the growth of confined $Ca(OH)_2$ crystals. The energy to force $Ca(OH)_2$ crystals to grow against resistance comes from the free energy reduction of the hydration reaction of lime. The development of crystallization pressure relys on the supersaturation of pore solutions for $Ca(OH)_2$ and the restraint. A high supersaturation and a large restraint will stimulate a high crystallization pressure. However, a large expansion is correspondent to a high crystallization pressure or a small restraint.

Conclusions

The expansion of hydrating lime is caused by the crystallization of $Ca(OH)_2$ crystals formed in situ. The concentration of OH^- ion in pore solutions of cement pastes controls the expansion by affecting the positions occupied by $Ca(OH)_2$ crystals produced and the crystallization pressure.

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