REACTION PRODUCTS IN SYSTEMS OF CaMg(CO₃)₂-SiO₂-Ca(OH)₂-KOH-NaOH-H₂O AT TEMPERATURES BETWEEN 20°C and 60°C

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Abstract

Micro- to crypto-crystalline quartz exists always in dolomitic limestones. When the dolomitic limestones are used as aggregates of concrete, pore solutions mainly composed of K⁺, Na⁺, Ca²⁺ and OH⁻ ions may interact simultaneously with dolomite and micro- to crypto-crystalline quartz. To understand mechanism of alkali-silica-dolomite reactions in concrete, reaction products in systems of CaMg(CO₃)₂-SiO₂-Ca(OH)₂-KOH-NaOH-H₂O cured at 20°C, 38°C and 60°C were analyzed by X-ray diffraction (XRD), FT-Infrared spectroscopy (FT-IR), differential scanning calorimeter-thermo gravity (DSC-TG) and scanning electron microscope (SEM). Results show that magnesium derived from dolomite was mainly incorporated in brucite and silicon derived from micro- to crypto-crystalline quartz was in alkali-silica gel. No evident magnesium silicate gels were detected when concentration of OH⁻ was equal to or greater than 0.1mol/l. It is expected that magnesium silicate gels will not be formed accompanying with alkali-silica/dolomite reaction in concrete.

Keywords: reaction products, dolomite, quartz, alkali solutions

1 INTRODUCTION

In 1957, Swenson [1] investigated a case of concrete deterioration caused by an unusual reaction between alkalis and dolomitic limestones from Kingston, Ontario, Canada, which was then termed as

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alkali-carbonate rock reaction or alkali-carbonate reaction (ACR). Hadley [2] reported that although there were some forms of alkali-soluble silica in a few of dolomitic limestones tested, no obvious correlation was observed between reactive silica content and the expansion in alkali. Accordingly, he concluded that the expansion did not seem to be due to the classical alkali-aggregate reaction.

Chemical reaction for ACR was generally believed to be dedolomitization of dolomite attacked by alkali solutions [2-3]. As a result, brucite, calcite and alkali carbonate are formed. However, based on quantitative SEM-EDS analysis on reaction products of dolomitic rocks in field concretes from Canada or tested microbars of RILEM AAR-5, Katayama et al. [4-6] claimed that brucite resulting from dedolomitization might react with alkali-silica gels to form non-expansive Mg-silicate gels. Brew and Glasser [7] concluded that magnesium silicate hydrate gels with Mg/Si molar ratio of 0.67-1.0 might be formed by precipitation from solutions of Mg(NO₃)₂·6H₂O and Na₂SiO₃·5H₂O (Na/Si=1.0). Zhang et al. [8] investigated reaction products of mixtures of a lightly burned MgO and silica fume. Both brucite and magnesium silicate hydrate was detected at 28d in the mixture consisted of 20% MgO and 80% silica fume. The pH value was around 10.5 for the systems with brucite and magnesium silicate hydrate has been found in Portland cement pastes in which pH value is generally higher than 13.

For SEM-EDS analysis, characteristic X-rays in a zone of about 1µm width and 1µm thickness may be stimulated out by electron beam and probed by acceptor when accelerated voltage is about 15kV. Therefore, it is difficult to accurately identify the composition of a substance smaller than 1 µm in diameter or thickness by SEM-EDS analysis except that no other substances are mixed with the target substance. From this point of view, accuracy of some SEM-EDS analysis results reported by Katayama et al. [4-6] on Mg-silicate gels needs to be evaluated by other methods because Mg-silicate gels were less than 1µm. Micro- to crypto-crystalline quartz is always contained in dolomitic limestones [9]. This paper provides results on the reaction products of mixtures of dolomite with micro- to crypto-crystalline quartz in alkali solutions evaluated by XRD, FT-IR, DSC-TG and SEM. It is expected to clarify whether Mg-silicate gels are formed or not in dolomitic limestones soaked in alkali solutions.

2 MATERIALS AND METHODS

2.1 Materials

The dolomite used was powders less than 0.080mm produced by grinding dolostone from Zhangqiu, Shandong Province, China. The dolostone was mainly composed of 20-50µm dolomite in a mosaic texture.

The quartz powders used were less than 0.080mm made from chert from Jurong, Jiangsu province, China. The chert was composed of about 66vol% micro- to crypto-crystalline quartz, 15vol% quartz (larger than 50µm) and 19vol% dolomite, and was classified as alkali-silica reactive due to 0.221% expansion of ASTM C1260 accelerated mortar bars at 14d. The dolomite in chert powder was dissolved by 1:1 HCl.

Distilled water and chemically pure NaOH, KOH and Ca(OH)₂ were used.

2.2 Preparation and analysis of reaction products

Dolomite powders and quartz powders were homogeneously mixed and compacted into a cylinder in $\Phi 25 \text{mm} \times 35 \text{mm}$ by a pressure 34.3MPa in order to prevent powders to go around when alkali solutions were added. Three kinds of compacts were prepared in which the ratio of dolomite powders to quartz powders was 83.3%:16.7%, 66.7%:33.3% or 50.0%:50.0% by weight, respectively. The compact was then placed in a smaller PVC bottle which was unsealed and suspended in another bigger PVC bottle. The compact was placed in the smaller bottle so that powders would not be mixed with added solid Ca(OH)₂ during curing periods. Alkali solutions of 0.1, 0.5 and 1.0 mol/l, being typical concentrations of OH⁻ ions in the pore solutions of concretes, were prepared by chemical reagents in which the molar ratio of KOH to NaOH was 4:1. The alkali solutions were then added into the bigger PVC bottle until the smaller PVC bottle was fully filled with alkali solutions and weight ratio of alkali solution to compact was 50:1. When solid Ca(OH)₂ was added, it was placed in the bottom of the bigger PVC bottle. The bigger PVC bottles containing compact and alkali solutions were then sealed and placed in water baths kept at 20°C, 38°C and 60°C for 28d.

Solids from soaked compacts were separated from alkali solutions by quantitative filter papers and dried at 105°C. Some solids were placed in ethanol and dispersed by ultrasonic wave. Finer particles were separated from coarser particles based on differential settling rate. The obtained solids and finer particles were examined by ARL X'TRA X-ray diffractometer, Continum IR-Nexus 670 Infrared-Raman spectroscopy, Netzsch 204 differential scanning calorimeter-thermo gravity and Hitachi S4800 cold field scanning electron microscope.

3 RESULTS

3.1 XRD analysis

Calcite was formed in all mixtures of dolomite and quartz soaked in 0.1, 0.5 and 1.0 mol/l alkali solutions with and without Ca(OH)₂ at 20°C, 38°C and 60 °C for 28 days as shown in Fig. 1, Fig. 2 and

Fig. 3. Brucite was detected by XRD in the mixtures of composed of 83.3% dolomite and 16.7% quartz and of 66.7% dolomite and 33.3% quartz cured in 0.5 and 1.0 mol/l alkali solutions at 20°C, 38°C and 60°C for 28 days, and in the mixtures of 50.0% dolomite and 50.0% quartz cured in 1.0 mol/l alkali solutions at 38°C and 60°C for 28 days. No obvious brucite was detected by XRD in all the mixtures of dolomite and quartz soaked in 0.1 mol/l alkali solutions for 28 days, and in the mixtures of 50.0% dolomite and 50.0% quartz cured in 1.0 mol/l alkali solutions at 20°C for 28 days. No obvious brucite was detected by XRD in all the mixtures of dolomite and quartz soaked in 0.1 mol/l alkali solutions for 28 days, and in the mixtures of 50.0% dolomite and 50.0% quartz cured in 0.5 mol/l alkali solutions for 28 days and in 1.0 mol/l alkali solutions at 20°C for 28 days. Correspondingly, abundant dolomite and quartz in these mixtures were not altered. The reaction products formed in the mixtures were not changed by addition of Ca(OH)₂.

Fig. 4 shows XRD patterns of finer particles separated from the mixture of 50.0% dolomite and 50.0% quartz cured in 0.5mol/l alkali solution at 38°C for 28d and from mixture of 83.3% dolomite and 16.7% quartz cured in 0.1mol/l alkali solution at 38°C for 28d. There is characteristic diffraction peak of calcite and a diffusion peak at 2θ =25-31° in the finer particles of mixture of 50.0% dolomite and 50.0% quartz cured in 0.5mol/l alkali solution at 38°C for 28d. This diffusion peak may be caused by alkali-silica gels. Although it was not obviously found in the whole mixture of 83.3% dolomite and 16.7% quartz soaked in 0.1mol/l alkali solution at 38°C for 28d as revealed by Fig. 1, brucite was detected by XRD in the finer particles separated from the mixture as shown in Fig. 4. This may be due to a low content of brucite formed from dedolomitization. No characteristic peak at 2θ =35-39° of magnesium silicates reported by Brew et al. [7] were found in the finer particles in which reaction products were enriched.

Fig. 5 demonstrates the relationship between ratio of XRD intensity (in terms of integral area of strongest peak) of brucite to calcite and ratio of intensity (in terms of integral area of strongest peak) of calcite to dolomite in mixtures. The ratio of intensity of brucite to calcite ranged from 0.08 to 0.11 when the ratio of intensity of calcite to dolomite varied from 0.12 to 20.0. This little change of the ratio of intensity of brucite to calcite seems to indicate that the ratio of mass of brucite to calcite in mixtures was almost fixed. Both calcite and brucite formed were derived from dedolomitization of dolomite. Therefore, it may be concluded that brucite formed from dedolomitization was not significantly altered in the systems investigated.

3.2 IR analysis

FT-IR spectrums of the mixtures of dolomite and quartz cured in 1.0 mol/l alkali solutions for 28d are shown in Fig. 6 and Fig. 7. Table 1 lists vibration wavenumbers of related substances.

Vibration at 3690-3691cm⁻¹ is for O-H in brucite[10]. The characteristic vibrations 1418-1424 and 712cm⁻¹ belongs to C-O in calcite[11,12]. Vibrations 994-999 and 459-463 cm⁻¹ may be caused by Si-O in alkali-silica gels. Other vibrations may be contributed to either C-O in dolomite or Si-O in quartz[11,12].

Results show that newly formed products were calcite, brucite and alkali-silica gels in the three mixtures of 83.3% dolomite and 16.7% quartz, of 66.7% dolomite and 33.3% quartz and of 50.0% dolomite and 50.0% quartz soaked in 1.0 mol/l alkali solutions (molar ratio of KOH to NaOH was 4) at 20°C, 38°C and 60°C for 28d.

Fig. 8 demonstrates IR spectrums of finer particles separated from mixtures of 83.3% dolomite and 16.7% quartz and of 66.7% dolomite and 33.3% quartz soaked in 0.1 mol/l alkali solutions without $Ca(OH)_2$ at 20°C and 38°C for 28d. Vibration at 3690cm⁻¹ belongs to O-H in brucite[10]. This indicates that there is a low amount of brucite in mixtures cured in 0.1 mol/l alkali solutions.

No obvious vibrations at 1618-1622, 1040-1082 and 1014-1033cm⁻¹ for magnesium silicate gels as reported by Brew et al. [7] were detected by FT-IR in the mixtures tested.

3.3 DSC-TG analysis

Fig. 9 gives DSC-TG result of mixture composed of 66.7% dolomite and 33.3% quartz cured in 0.5 mol/l alkali solution at 20°C for 28d. The endothermic peak at about 400°C is caused by dehydration of brucite. Endothermic peaks at 770-790°C and about 880°C are due to decomposition of MgCO₃ in dolomite and CaCO₃ in calcite formed from dedolomitization and unreacted dolomite, respectively. Table 2 lists content of brucite, calcite and dolomite in the mixtures calculated according to loss of the mixtures at 400, 770-790 and about 880°C. Molar ratios of brucite to calcite in the mixtures were 0.9-1.1.

3.4 Fe-SEM analysis

Fig. 10 shows morphologies and compositions of calcite, brucite and alkali-silica gels in mixture of 66.7% dolomite and 33.3% quartz cured in 0.5 mol/l alkali solutions at 38°C for 28d. One to three µm calcite formed is mainly composed of Ca, C and O. Less than 1µm brucite was mainly composed of Mg and O. Elements Si, K, Ca and C in brucite detected by EDS may come from other substances closely near small particles of brucite. Less than 0.2µm fibre-like alkali-silica gels are dominated by Si and O. They also contain a small amount of K, Na, Ca, Mg and C. The elements Mg and C in alkali- silica gels detected by EDS may come from other substances.

4 DISCUSSION

Calcite was detected by XRD in all mixtures of dolomite and quartz soaked in 0.1, 0.5 and 1.0 mol/l alkali solutions. This product was derived from dedolomitization of dolomite in alkali solutions. According to Hadley [2], brucite would also be produced by dedolomitization. However, brucite was detected in some mixtures of dolomite and quartz which were soaked in alkali solutions with higher concentrations of OH^{-} ions, contained more dolomite or were cured at a higher temperature as shown in

Fig. 1, Fig. 2 and Fig. 3. When coarser particles were separated from the mixture of 83.3% dolomite and 16.7% quartz soaked in 0.1 mol/l alkali solution at 38°C for 28 days, brucite was detected by XRD in the obtained finer particles as shown in Fig. 4.

FT-IR results indicate that reaction products in the mixtures of dolomite and quartz immersed in alkali solutions were calcite, brucite and alkali-silica gels as demonstrated in Fig. 6, Fig. 7 and Fig. 8. O-H stretching vibration at 3690cm⁻¹ for brucite was detected by FT-IR in the finer particles separated from the mixtures in which no evident brucite was probed by XRD as shown in Fig. 8.

The ratio of XRD intensity (in terms of integral area of strongest peak) of brucite to calcite in the mixtures was about 0.10. The molar ratio of brucite to calcite was approximately 1.0 according to DSC-TG results. These seem to imply that brucite derived from dedolomitization was not significantly altered in the mixtures.

No magnesium silicate gels were obviously detected by XRD and FT-IR in the mixtures of 50.0%-83.3% dolomite and 16.7%-50.0% quartz soaked in 0.1, 0.5 and 1.0 mol/l alkali solutions at 20°C, 38°C and 60°C. Therefore, it is expected that reaction between brucite from dedolomitization and quartz or alkali-silica gels from ASR of quartz will not take place in concrete in which ASR or dedolomitization may proceed to an unusual degree.

5 CONCLUSIONS

Reaction products in the mixtures of 50.0%-83.3% dolomite and 16.7%-50.0% quartz soaked in 0.1, 0.5 and 1.0 mol/l alkali solutions and cured at 20°C, 38°C and 60°C for 28d were calcite, brucite and alkali-silica gels. No magnesium silicate gels were detected in the mixtures of dolomite and quartz soaked in alkali solutions with 0.1 mol/l of OH⁻ ions or more. This seems to indicate that the products of ACR will not be affected by ASR and ASR expansion will not be reduced through a mechanism proposed by Katayama et al. [4] in concretes.

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No	Vibrations	Wave number /cm ⁻¹	Substance		
1	О-Н	3690-3691s(str), 3417-3418 s(H-bond, str) 1629-1639s(bdg)	Brucite[10]		
2	C-O	2894-2896w, 2524-2525w, 1798-1822w, 875-880 s (bdg)	Dolomite,calcite [11,12]		
		1438-1439 s (str), 727-729 s (bdg)	Dolomite[11,12]		
		1418-1424 s (str), 712 s (bdg)	Calcite[11,12]		
3	Si-O	1168-1171w, 1082-1088 s (str)	Ω uortz[12]		
		797-799 s, 777-779s, 691-696s, 515w, 459-463 s (bdg)	Qualtz[12]		
		994-999s, 459-463s (bdg)	ASR gel		

Table 1 Wave numbers of mixtures cured in 1.0 mol/l alkali solutions at 20°C, 38°C and 60°C for 28 days

Note: s-strong; m-medium; w-weak; str-stretching vibrations; bdg-bending vibrations.

Table 2 Contents of brucite and calcite in mixtures soaked in 0.5mol/l alkali solutions calculated according to DSC-TG results

		Mass loss /wt%			Mass fraction /wt%			Molar ratio
No	Sample	H ₂ O	CO ₂ at	CO ₂ at	Brucite Calcite	Coloita	Dolomita	of brucite to
			770-790 °C	880°C		Dolollite	calcite	
1	66.7%D+33.3%Q	0.00	8.5	10.3	2.9	5	36	1.0
	20 °C & 0.5mol/l	0.90						
2	66.7%D+33.3%Q	0.05	9.5	12.2	3.1	6	40	0.9
	38°C & 0.5mol/l	0.95						
3	83.3%D+16.7%Q	1.65	12.2	15.7	5.3	8	51	1 1
	38°C & 0.5mol/l	1.65						1.1



(a) in alkali solutions with solid Ca(OH)₂
(b) in alkali solutions without Ca(OH)₂
Figure 1: XRD patterns of mixtures of 83.3% dolomite and 16.7% quartz soaked in 0.1, 0.5 or 1.0 mol/l alkali solutions (molar ratio of KOH to NaOH was 4) and cured at 20°C, 38°C and 60°C for 28d D-dolomite, Q-quartz, C-calcite, B-brucite







(a) in alkali solutions with solid Ca(OH)₂
(b) in alkali solutions without Ca(OH)₂
Figure 3: XRD patterns of mixtures of 50.0% dolomite and 50.0% quartz soaked in 0.1, 0.5 and 1.0 mol/l alkali solutions (molar ratio of KOH to NaOH was 4) cured at 20°C, 38°C and 60°C for 28d D-dolomite, Q-quartz, C-calcite, B-brucite



Fig. 4: XRD patterns of finer particles in mixtures of 50.0% dolomite and 50.0% quartz and of 83.3% dolomite and 16.7% quartz cured at 38°C for 28d D-dolomite, Q-quartz, C-calcite, B-brucite

Fig. 5: Ratio of XRD intensity of brucite to calcite vs ratio of intensity (in terms of integral area of strongest peak) of calcite to dolomite in mixtures soaked in alkali solutions for 28d



(a) Mixtures of 83.3% dolomite and 16.7% quartz (b) Mixtures of 66.7% dolomite and 33.3% quartz Figure 6: FT-IR patterns of mixtures soaked in 1.0 mol/l alkali solutions at 20°C and 60°C for 28d





Fig. 8: FT-IR spectrums of finer particles in mixtures of 83.3% dolomite and 16.7% quartz and of 50.0% dolomite and 50.0% quartz soaked in 0.1 mol/l alkali solutions without Ca(OH)₂ at 20 °C and 38°C for 28d



Figure 9: DSC-TG result of mixture composed of 66.7% dolomite and 33.3% quartz cured in 0.5 mol/l alkali solution at 20°C for 28d



(c) Alkali-silica gels

Figure 10: Morphologies and compositions of calcite, brucite and alkali-silica gels in mixture of 66.7% dolomite and 33.3% quartz cured in 0.5 mol/l alkali solutions at 38°C for 28d