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CORRELATION BETWEEN REACTION AND EXPANSION OF ALKALI-CARBONATE REACTION

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ABSTRACT

Compacted cylinders made of reactive minerals (dolomite and magnesite) and Portland cement in the ratio of 4:1 were prepared to observe the expandability of the two solid-volume-reducing reactions—alkali-dolomite and alkali-magnesite reaction. After measuring the reaction degrees determined by quantitative XRD analysis, it was found that expansion correlated well with the degree of the reaction occurred in the compacts. This result provided a positive evidence towards the previously proposed expansion mechanism, which suggested that the expansion of alkali-carbonate reaction is due to the formation and growth of the reaction products in confined space.

Introduction

Since alkali-carbonate reaction (ACR) was first recognized in 1957(1), many cases of concrete deterioration due to such an expandable reaction were reported. However, the expansion mechanism of ACR are not clearly understood. Up to now several theories (2-6) have been proposed to explain the expansive force underlined the deleterious process. The two noticeable explanations came from Gillott (2) who suggested that the absorption of water by clays of newly exposed clay containing in reactive carbonate rocks are the main reason of the expansion, and Tang (3) who proposed that the formation and growth of brucite due to dedolomitization was expandable. Obviously the main point of these arguments was focused on whether dedolomitization, a solid-volume-reducing reaction, is expandable.

In the previous investigations (7,8), it was observed that the two solid-reducing reactions—alkali-dolomite and alkali-magnesite reaction can cause expansion of rock prisms, concrete bars and specially prepared compacts. Microstructural study showed that the expansion was due to the formation and growth of the reaction products in confined space.

The two reactions and their solid-volume changes can be formulated as follows:

Alkali-dolomite reaction (ADR, i.e., dedolomitization):

$$CaMg(CO_3)_2 + 2MOH = Mg(OH)_2 + CaCO_3 + M_2CO_3$$

$64.341 cm^3/mol$ $24.63 cm^3/mol$ $36.93 cm^3/mol$ $\Delta V = -4.3\%$

Alkali-magnesite reaction (AMR):

$$MgCO_3 + 2MOH = Mg(OH)_2 + M_2CO_3$$

$28.28 cm^3/mol$ $24.63 cm^3/mol$ $\Delta V = -12.9\%$

Where M represents Na, K and Li.

The purpose of compacts was mainly to simulate the interface of reactive minerals and surrounding matrix in carbonate rock. Because of high porosity and high alkali content, reactions occurring in compacts, which allow easily to monitor the degree of reaction, are much more severe than those in rocks or aggregates when they are immersed in alkali solution or in concrete with high alkali cement. Although it is not suggested that all reaction products will definitely attribute to the expansion, it is reasonable to assume that the acting part is proportion to the amount of reaction products formed. Therefore, the reaction as a whole will be correlated with the expansion. This paper purports to confirm such a prediction and provide more further evidence of the expansion mechanism.

Experimental

Materials

High purity of coarse-grained magnesite and dolomite and fine-grained limestone were available. XRD analysis revealed only a trace of impurities containing in the samples. The chemical compositions of the rocks and ordinary Portland cement with alkali content 0.51% Na_2O equivalent used in the test are listed in Table 1. Pure α-Al_2O_3 powder less than 0.08mm in size was adopted as a control sample in the study.

Table 1 The Chemical compositions of the materials (wt %)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Loss	Σ
Magnesite (LM)	0.54	0.15	0.24	0.20	47.07	—	51.66	99.86
Dolomite (NM-0)	0.36	0.16	0.16	31.38	20.98	—	46.64	99.68
Limestone (HN0)	0.32	0.31	0.16	54.95	0.56		43.49	99.79
Portland Cement	20.72	4.91	4.23	61.39	1.23	2.30	4.08	99.48

Material Preparation

To simulate the compacted interface of dolomite crystals and surrounding matrix in reactive carbonate rocks, artificial compacted cylinders were prepared. Dolomite and Magnesite samples were crushed to the size of less than 0.04mm and 0.088-0.15mm respectively and mixed with Portland cement at the ratio 4:1. Alkali content in solid was 1.5% Na_2O equivalent adjusted by KOH. With water/solid ratio 0.1, the mixture was compacted under 300 MPa sustaining for about one minute. Compacts was usually controlled at the size of ϕ 9x30 mm. Stainless steel pins were then cemented on their both ends. At least five parallel cylinders are needed for each sample series. After 7 days curing in the moist container, the cylinders were measured for their original length and then autoclaved at 150°C in 10% KOH solution for a series of ages. Length change at each pointed age can be calculated.

At least two compacts were necessary for determining the reaction degree at each time point. The curing processes were just the same as that of expansion measurement. At the pointed curing age, the compacts were washed by water for several minutes to remove the surface alkali solution and heated at 100°C for 8 hours and pulverized to the size less than 5 μm. Before sealed in glass bottles for further analysis, the samples were dried at 105 °C for 4 hours.

Quantitative X-Ray Diffraction Analysis

Matrix-flushing method (9,10) was chosen to determine the reaction degree in compacts for its convenience and accuracy. The intensity of a reflection line refers to the integrated intensity above the background which is required for quantitative analysis. Modern high performance X-Ray diffractometer and the development of analysis techniques allow more accurate calculation of the intensity. Profile fitting technique (a computer program called PRO-FIT (11)) was performed to determine reflection intensities in the present investigation. After profile fitting, the observed data were well smoothed avoiding occasional fluctuation in counts and eliminating the influences by other peaks through decomposing the over-lapping peaks.

Table 2 Operation conditions of X-Ray powder diffractometer analysis

Diffractometer	Dmax-rB X-Ray Diffractometer
Target	Cu
Scan mode	Step-scan mode with 0.02° intervals in 2θ
Fix time	5 second
Volt and current	40.0 KV, 100 mA
Divergence and receiving slit	1.00°, 0.15°

High purity and well crystallized corundum (d=3.980 g/cm^3 about 2 μm in size) was chosen as the flushing agent. It was mixed with equal amount of the dolomite (NM-0), the magnesite (LM) as well as pure limestone (HN-0) and $Mg(OH)_2$ of analytical grade and all the samples plan to test. Because the homogeneity of the component in the mixture and particle size may greatly influence the diffraction intensities, extremely care should be made to assure the mixture of completely mixing and of similar particle size among the testing samples. In the experiment, the components were mixed by hand using an agate mortar for one hour for each sample. It should be noted that mixing should be as slight as possible to prevent greatly reducing the particle size. The test conducted three times for each sample.

Readings of the intensity are fitted by Pearson VII function using the computer program PRO-FIT. The average values of the calculated intensities which were tested three times for each sample were used to determine the reference intensities (K values) of dolomite, magnesite, calcite and brucite. Then, they were used to evaluate the weight percentages of these components in compacts.

In fact, the weight percentage changes of dolomite or magnesite did not directly mean the reacting amount in compacts because the reference weight of the overall amount of a compact in dry state was changing with the reaction course. In spite of no considerable influence on the testing results, correction were made in this study to minimizing the influences of the combined water due to cement hydration on the overall solid weight of a compact. The weight losses were measured between 105 - 950°C of α-Al_2O_3 compacts after certain hours autoclaving at 150°C in 10% KOH solution. The results are illustrated in Figure 1.

Therefore, the reaction degrees of dolomite and magnesite in compacts can be calculated after correcting the combined water in compacts, i.e., considering the changes of the reference-weight level. Although the calculation was somewhat approximate, it was considered accurate enough for quantitative X-Ray diffraction analysis.

Using corundum (α-Al_2O_3) as flushing agent, the reference intensities (K values) of dolomite (NM-0), calcite (pure limestone HN-0), magnesite (LM) and brucite ($Mg(OH)_2$ chemical agent of analytical grade purity) are listed in Table 3.

The relative deviations of integrated intensities were usually about 1% for the three runs. Applying the matrix-flushing method to test several mixtures of known mineral composition, the results showed that the relative deviations of all tested composition were within 5%. Therefore, the matrix-flushing method and the integrated intensity calculation by the PRO-FIT program were considered suitable for determining the mineralogical changes in compacts.

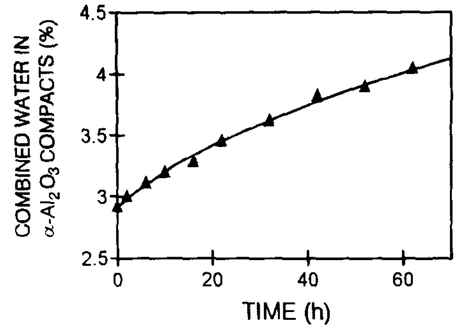

Figure 1 Percentages of the combined water in α-Al_2O_3 compacts after certain hours autoclaving at 150°C in 10% KOH solution

Table 3 K values of the minerals tested

Minerals	Test No.	I_i (Counts)	I_c (Counts)	$K=I_c/I_i$	Average of K
Dolomite (NM-0)	1	19890	7631	0.3837	0.3848
	2	19515	7523	0.3855	
	3	19155	7381	0.3853	
Calcite (HN-0)	1	17502	5529	0.3159	0.3174
	2	17228	5501	0.3192	
	3	17334	5494	0.3169	
Magnesite (LM)	1	28030	10840	0.3867	0.3866
	2	27797	10781	0.3878	
	3	28482	10971	0.3852	
Brucite $Mg(OH)_2$	1	17027	9542	0.5604	0.5650
	2	16777	9569	0.5704	
	3	16944	9560	0.5642	

Results and Discussions

The amount of dolomite and calcite in dolomite (NM-0) compacts, and magnesite and brucite in magnesite (LM) compacts were analyzed by the matrix-flushing method with the help of the computer program PRO-FIT. The weight percentages X(t) of the tested phases at different autoclave ages are shown in Figure 2 and 3.

After reference weight correction, the percentages of dolomite and magnesite reacted, calcite and brucite produced (weight fraction) and the expansions of compacts at different autoclave ages are illustrated in Figure 4 and 5. The results showed that the reaction degree and the expansion of compacts changed in a similar pattern. The close correlation of the two factors are obvious when the reaction degrees are plotted against expansion percentages, as shown in Figure 6 and 7.

The result showed that reaction degrees can be monitored by both the amount of dolomite consumed and by calcite produced in dolomite compacts, and by the amount of magnesite reacted and brucite formed in magnesite compacts. The very good linear correlation of the figure 6 and 7 provided a powerful confirmation that the expansion of compacts was directly caused by the reaction occurring at the surface of dolomite or magnesite just as previously suggested. Therefore, it was logical to observe that the expansion of compacts at a certain autoclave age decreased with the increment of dolomite or magnesite particle sizes because of the reduction of the reacting surface area in compacts (7).

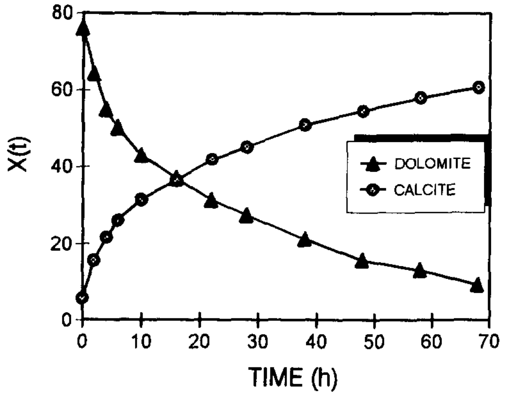

Figure 2 Weight percentage X(t) changes of dolomite and calcite in dolomite compacts at different autoclave times analyzed by the matrix-flushing method

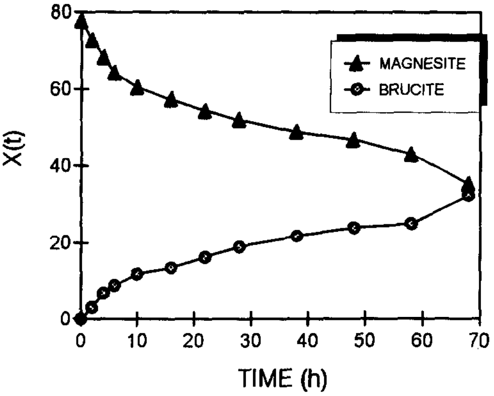

Figure 3 Weight percentage X(t) changes of magnesite and brucite in magnesite compacts at different autoclave times analyzed by the matrix-flushing method

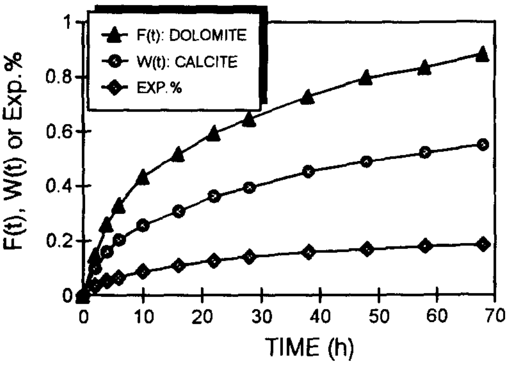

Figure 4 The reaction degrees of dolomite F(t), weight fraction W(t) of calcite formed in dolomite compacts and their expansion percentages at different autoclave ages

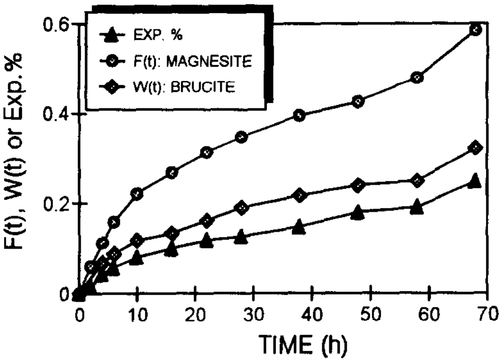

Figure 5 The reaction degree F(t) of magnesite, weight fraction W(t) of brucite in magnesite compacts and their expansion percentages at different autoclave ages

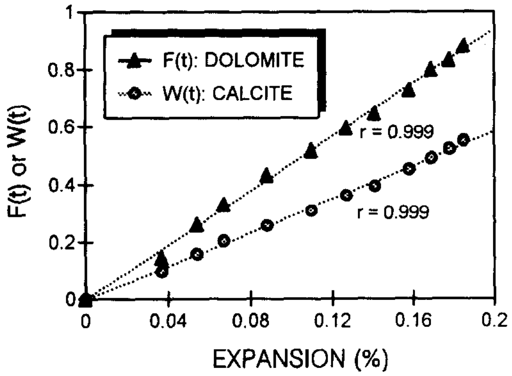

Figure 6 Correlation between the expansion of dolomite compacts and the reaction degrees F(t) of dolomite and weight fractions W(t) of calcite produced in the compacts

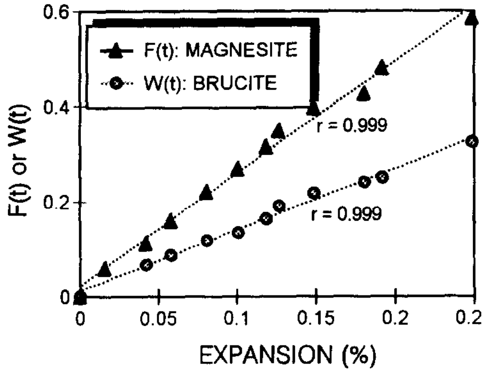

Figure 7 Correlation between the expansion of magnesite compacts and the reaction degrees F(t) of magnesite and weight fractions W(t) of brucite produced in the compacts

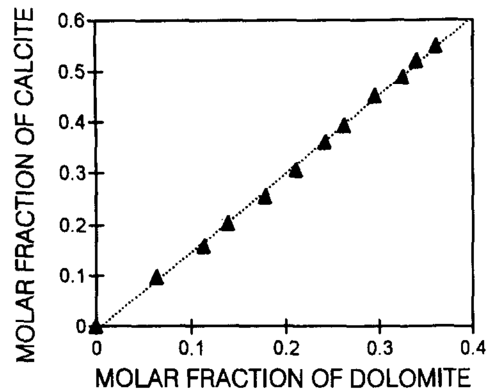

Figure 8 Correlation between the amount of molar fraction of dolomite reacted and molar fraction of calcite produced in dolomite compacts

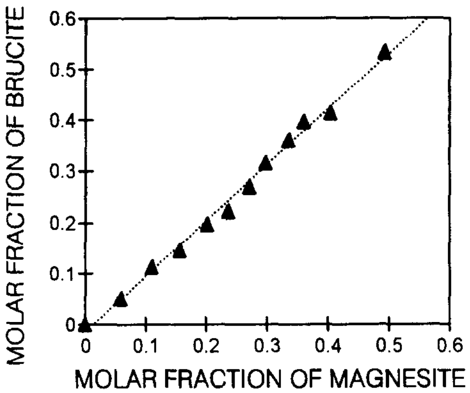

Figure 9 Correlation between the amount of molar fraction of magnesite reacted and molar fraction of brucite produced in magnesite compacts

Although it is preferred to adopt the changes of dolomite or magnesite as monitoring the reaction degrees in compacts, the reaction products calcite and brucite were proved to be valid as well. Figure 8 showed linear correlation between molar fraction of dolomite reacted and calcite formed in dolomite compacts. The fact that the amount of calcite was larger than that predicted by dedolomitization suggested that cement hydration products (portlandite for example) had been carbonized by CO_3^{2-} produced by dedolomitization. However, the linear relation was still observed. The amount of magnesite reacted and brucite produced in magnesite compacts were approximately equal as shown in Figure 9. This meant that the reaction between brucite and cement or its hydration products was negligible. These results agreed with the observation of the reaction on the interface, between dolomite or magnesite and cement by SEM-EDAX (6).

Reactions occurring inside carbonate rocks are very complicated. Results obtained here have confirmed the expandability of dedolomitization. However, this does not mean that other factors may not take an effect on the expansion of reactive carbonate rocks. It should be noted that the reaction and the morphology of products in compacts are somewhat different from that in the rocks. In addition, the texture and mechanical characters may be different from those of rocks as well. Perhaps due to products formed in high confinement, very little amount of reaction in a rock can cause considerable expansion. Anyway, the formation and growth of crystalline products in the interface of dolomite rhombus and surrounding matrix are suggested at least an important reason for the expansion of the reactive carbonate rocks based on the present investigation.

Conclusions

Based on the investigation of the expansion and reaction of compacts, it is suggested that dedolomitization is expandable though it is a solid-volume-reducing process. These results provide further evidences of the proposed expansion mechanism of alkali-carbonate reaction, which is suggested mainly due to the formation and growth of crystalline products in confined space. Similar to the case of compacts, it is reasonable to understand that the reaction in the interface between dolomite crystals and the surrounding matrix in reactive carbonate aggregates will attribute to the expansion of concrete.

Acknowledgments

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Reference

[1] Swenson, E. G., "A Reactive Aggregate Undetected by ASTM Tests," Bulletin No. 226, American Society for Testing and Materials, pp. 48-51, (1957).

[2] Gillott, J. E., 'Mechanism and Kinetics of Expansion in The Alkali-Carbonate Rock Reaction", *Canadian Journal of Earth Science*, Vol. 1, pp. 121-145, (1964).

[3] Tang Mingshu, Liu Zheng and Han Sufen, "Mechanism of Alkali-Carbonate Reaction," Concrete Alkali-Aggregate Reactions, Proceedings of the 7th International Conference, Ottawa, Canada, pp.275-279, (1986)

[4] Hadley, D. W., "Alkali Reactivity of Dolomitic Carbonate Rocks," *Symposium on Alkali-Carbonate Rock Reactions, Record No. 45*, Highway research board, pp. 1-20, (1964).

[5] Swenson, E. G. and Gillott, J. E., "Alkali-carbonate rock reaction" *Symposium on Alkali-Carbonate Rock Reactions," Record No. 45*, Highway research board, pp. 21-40, (1964).

[6] Tong Liang, "Alkali-Carbonate Rock Reaction", Ph.D. Thesis, Nanjing Institute of chemical technology, China, (1994).

[7] Tong Liang and Tang Mingshu, 'Expandability of solid-volume-reduced reactions" (Submitted to ACI Materials Journal) (1995)

[8] Tong Liang and Tang Mingshu, 'Mechanism of Expansion in Alkali-Dolomite and Alkali-Magnesite Reaction," (Submitted to ACI materials journal) (1995)

[9] Chung, F. H., "Quantitative Interpretation of X-Ray Diffraction Patterns of Mixtures. I. Matrix-Flushing Method for Quantitative Multicomponent Analysis," *Journal of Applied Crystallography*, Vol. 7, pp. 519-525, (1974).

[10] Chung, F. H., "Quantitative Interpretation of X-Ray Diffraction Patterns of Mixtures. II Adiabatic Principle of X-Ray Diffraction Analysis of Mixtures," Journal of Applied Crystallography, Vol. 7, pp. 526-531, (1974).

[11] Toraya, H., 'Whole-Powder-Pattern Fitting Without Reference to a Structural Model: Application to X-Ray Powder Diffractometer Data," *Journal of Applied Crystallography*, Vol. 19, pp. 440-447, (1986)