

Mechanism of Alkali-Carbonate Reaction

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ABSTRACT

In this article, the microstructure of a reactive carbonate rock was studied in detail by use of optical microscope and SEM/EDAX. Experimental results show rhombic dolomite crystallites distributed separately in a matrix composed of fine grained calcite and clay. The clay forms a network between the fine grained calcite. After the reaction of the reactive carbonate rock with alkali solution, brucite crystals are seen parallelly oriented on the surfaces of dolomite crystals. A mechanism of expansion based on the observation of microstructure is illustrated: the M^+ , OH^- ions and water molecules pass through the clayey network channels and then react with the minute dolomite crystals. So the cause of expansion was identified as the entering of active ions and water molecules into a restricted space and inducing the crystals produced from dedolomitization an incessant growth and rearrangement on the surfaces of dolomite crystals.

1. INTRODUCTION

According to Gillott and Swenson(1), the mechanisms of alkali-carbonate reaction might be classified into two categories: a direct mechanism and an indirect mechanism. The direct mechanism(2) attributes the excessive expansion to the dedolomitization taking place from the attack of alkali upon the dolomite crystals. Sherwood(2) considered that the expansion could be caused by the double salts produced by dedolomitization. The experiment carried out by Hadly(3) showed that the single crystals of dolomite in alkali solution could also produce expansion. However, since the sum of the volumes of solid products is less than that of the reactants, and from some other experimental facts, Gillott and Swenson(1) considered that the direct mechanism could hardly be tenable. On the contrary, Gillott and Swenson proposed an indirect mechanism which considered that the adsorption of water by the anhydrous clay and other fine grained materials, in which the surface hydration and formation of hydrous double layers plus the swelling action of clay minerals all lead to intense expansion, was the real cause of the deterioration reaction. The dedolomitization reaction simply developed channels for access of moisture. Nevertheless, the mechanism of the reaction is still argued. In order to clarify the mechanism, we have studied the microstructure of the reactive carbonate rocks before and after the alkali solution treatment in detail by various kinds of microscopes. The possibility of the dedolomitization reaction was calculated by thermodynamical data. Based on these experimental results, a mechanism and a

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model of alkali-carbonate reaction were proposed.

2. MICROSTRUCTURE OF REACTIVE AND NON-REACTIVE CARBONATE ROCKS

Reactive carbonate rock (Kg) was taken from Kingston, Ontario, Canada, it was proved, to be an alkali reactive rock, in the past. The non-reactive rock (An) was taken from Anhui Province, China. By means of observation under microscope, it was proved that the dolomitic rock from Anhui, China contains 95% dolomite and is composed of well developed coarse crystals. The microstructure of reactive carbonate from Canada was investigated and described in detail by Gillot(4). The sizes of dolomite crystals are generally smaller than 50μ , the matrix is composed of fine grained calcite (about 2μ) and clay. We treated the rock sample with dilute HCl solution, the calcite crystals were slightly destroyed, but no effect was found on dolomite crystals and clay. After such treatment, the microstructure of the rock might be clearly shown by Fig. 1, a and b. The mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ of clay (in Fig. 1, b) determined by EDAX varied between 1.86-1.90, and $\text{SiO}_2/\text{K}_2\text{O}$ varied between 7.18-8.86.

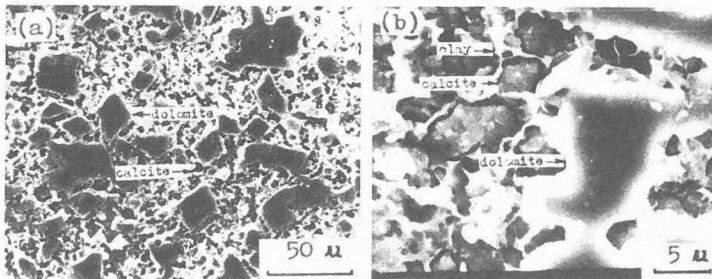


Fig. 1 Microstructure of reactive rock (Kg) treated with dil. HCl sol.

- a - Distribution of rhombic dolomite crystals, SEM 300x
- b - Distribution of calcite crystals and network of clay, SEM 2,000x

As the particles of clay are too small to be seen, the distribution of clay in the reactive rock was examined as follows, the Kg sample was first polished into a thin section, then thinned down by the technique of bombardment by argon ions. Finally the sample was examined under STEM in high magnification. At the same time the chemical composition of each mineral was determined by EDAX. The results showed that the clay formed a network in the matrix and the mass ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{K}_2\text{O}$ of clay vary between 1.76-2.03 and 11.08-13.99 respectively.

3. CHARACTERISTICS OF MICROSTRUCTURE OF CARBONATE ROCKS AFTER REACTION WITH ALKALI SOLUTION

When the non-reactive carbonate rock (An) was touched with alkali solution, a slight reaction of dedolomitization took place on the surfaces and the interfacial faces between crystals. By coating a layer of alkali solution on the surfaces of sample (An) and putting it in a sealed container with 100% RH for one month, a small amount of reaction products was seen in the interfacial layer between crystals.

A piece of reactive carbonate rock (Kg) was put in a 0.38 N KOH solution; a large expansion took place after immersion for about 6 months. Afterwards, the rock sample was taken up and cut to a plate, then it was

polished to a thin section and again thinned down by the bombarding technique with argon ions. When such treated sample was observed under STEM/EDAX, it showed clearly that in the interior of the reactive rock sample, there was a ring of crystals, surrounding each rhombic dolomite crystal. The thickness of the ring was about $2\ \mu$, the crystals were parallelly oriented and much empty spaces exist between these crystals. The morphology is shown in Fig. 2 a and b. When the sample was observed under high magnification, it showed that these crystals were composed of $25\ \text{\AA}$ fine particles (Fig. 2 c). According to the chemical composition determined by EDAX (Fig. 2 d) these crystals were almost pure brucite- $\text{Mg}(\text{OH})_2$. These brucite crystals were surrounded by particles of calcite and clay (matrix) which formed exterior rings. From the interior side of the ring of brucite crystals towards the center of dolomite crystal, the ratio Ca/Mg is gradually reduced.

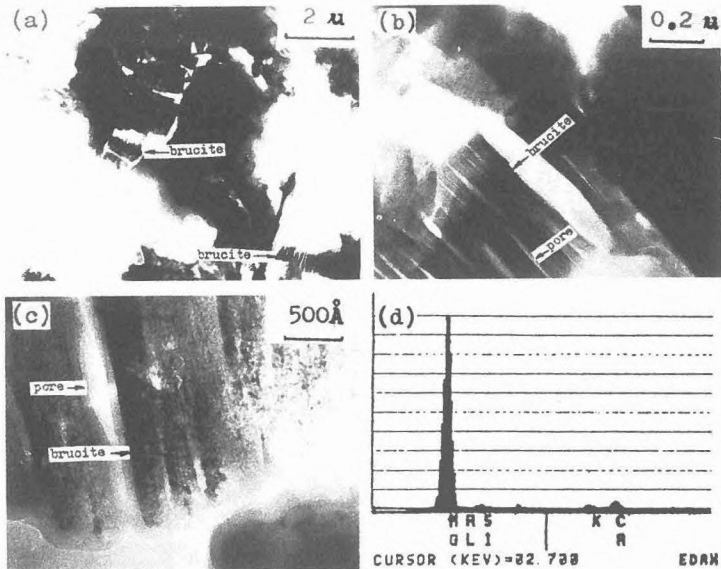


Fig. 2 Scanning transmission electron micrograph of reactive carbonate rock (Kg) after treatment with alkali solution
 a - showing the layer of brucite crystals surrounding the rhombic crystal of dolomite, STEM 6,000x
 b - magnification of a, STEM 50,000x
 c - magnification of a, STEM 200,000x
 d - EDAX of the parallel crystals of brucite.

From the results described above, it shows that in the process of dedolomitization, the crystallization of brucite seems to take place by ions migrated to the outside. The calcite formed seems to remain at its original places. At the same time, the empty spaces between brucite crystals are filled with liquid. Consequently, it leads to the conclusion that growing and rearranging of crystals are possible in the process of dedolomitization.

In addition, a piece of reactive carbonate rock attacked first by alkali solution then polished and treated with dilute HCl, was also examined under SEM, a deep ditch surrounding rhombic dolomite crystal was clearly observed. The ditch may have formed due to the treatment with dilute HCl which made the brucite crystals disappear. At the same time, the chemical composition of the remaining nuclei of dolomite crystals was determined

point by point by EDAX. The results also showed that the ratio Ca/Mg reduced gradually from the edge of the remained dolomite crystal to its interior. This result is consistent with that obtained by STEM/EDAX.

4. MECHANISM AND MODEL OF THE REACTION

On the basis of above described experimental results, it is proved that in the reactive carbonate rock, clay is not embedded in the rhombic dolomite crystals, nor is cracking produced in dolomite crystals by the reaction of dedolomitization, the dolomite crystals are distributed in isolation in the reactive rock, so it is not possible for the reaction of dedolomitization to make channels for the imbibition of water by clay. On the contrary, clay forms a network between the fine calcite grains, thus a matrix surrounding the dolomite crystals is formed. Consequently, the network of clay furnishes channels, through which the H_2O , $M^+(K_0 \text{ or } Na^+)$, OH^- can migrate into the interior of the reactive rock. Since the ΔG_{298} of dedolomitization reaction, according to the calculation carried out by us, is -5.38 Kcal/mol), this reaction is thermodynamically possible, which means that the ions M^+ , OH^- and water molecules do react with the dolomite crystals. So when these ions and water molecules migrate into the restricted space originally occupied by dolomite crystals, expansion results. Moreover the growing and rearranging of brucite crystals might also lead to expansion. Though empty space is present between the brucite crystals and the sum of the volumes of solid products of reaction is less than that of the reactants. In view of these considerations, a model of expansion is suggested as shown in Fig. 3.

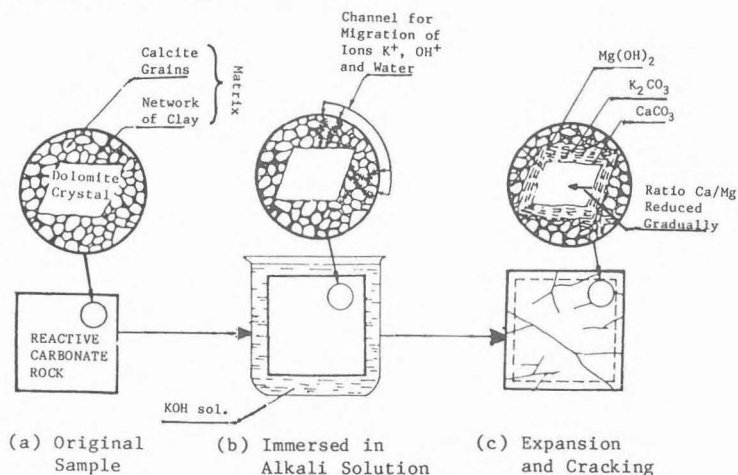


Fig. 3 Schematic diagram of the mechanism and model of alkali-carbonate reaction

The above mentioned mechanism explains reasonably the effects of each component of the reactive carbonate rock in the process of expansion. The network of clay furnishes channels for ionic migration, the skeleton of fine grained calcite plays the role to restrict the expansion until the expansion force extends a certain value. The expansion is eventually generated by the dedolomitization of the isolated rhombic dolomite crystals. Of course, the water imbibition by dry clay also causes expansion. The osmotic pressure generated by the difference of ionic concentrations between the reaction liquid and the pore solution of the cement paste might also contribute to some extent to the increased expansion.

5. CONCLUSIONS

(1) The microstructure of the reactive carbonate rock is characterized by a distribution of rhombic crystals of dolomite in a matrix composed of clay and fine grained calcite, the clayey part exists as a network.

(2) The ΔG_{298} of the reaction of dedolomitization is negative so this reaction is thermodynamically possible.

(3) Under the attack of alkali solution, the M^+ , OH^- ions and water penetrate through the channels of the clay network and react with the dolomite crystals. The expansion is caused by these ions and water molecules migrating into the restricted spaces and by the growing and rearranging of the products from dedolomitization.

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REFERENCES

1. Gillott, J.E. and Swenson, E.G., Q.J. Eng. Geol. Vol. 2, 7-23 (1969)
2. Sherwood, W.C., Newlon, H.H., Washington Symp. Highway Res. Board, No. 45, 41-56 (1964)
3. Hadley, D.W., Proc. Highway Res. Board, Vol. 40, 462-474 (1961)
4. Gillott, D.W., Geological Society of America Bulletin, Vol. 74, 759-778 (1963)