

KINETICS OF ALKALI-CARBONATE REACTION

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ABSTRACT

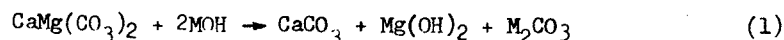
According to the mechanism of alkali-carbonate reaction(ACR), the process of dedolomitization in ACR is most important factor to cause expansion. Therefore, the studies of kinetics of reaction of dedolomitization in more detail is essential for further understanding the mechanism of ACR. By means of DTA, DTG and electronmicroscope, the influences of size of grains and temperature on the rate of reaction were studied. The experimental results were treated by mathematical analysis and showed that the rate of reaction of dedolomitization was controlled by the diffusion process of ions as well as the nucleation and growth process of crystalline products. While the chemical reaction process was not a step to control the process of dedolomitization, because the rate of this process was very fast. Furthermore, from the study of kinetics the mechanism was discussed. It was concluded that the expansion was caused by topochemical reaction and pressure of crystallization.

1. INTRODUCTION

Since 1957 Swenson[1] discovered the deterioration of concrete caused by ACR in Canada, the similar deteriorations were discovered in succession in America[2]. But the topic of ACR was scarcely studied comparing with that of alkali-silica reaction. Several years ago we have studied the mechanism of ACR [3] and rapid test method to determine the alkali reactivity of carbonate rock [4]. This paper reports the results studied on kinetics of ACR. Such basic research may be very helpful for a deep understanding the mechanism of expansion and for obtaining the most suitable conditions to determine the alkali reactivity of carbonate aggregate.

2. PROCESS OF REACTION

Before establishing the mathematical equations of kinetics of reaction, it was needed to understanding the process of reaction. For this purpose, the particles of carbonate rocks were immersed in alkali solution and observed under optic and electron microscope after certain periods to find out the real process of reaction. The chemical reaction of dedolomitization can be described as following:



Where M represents K or Na. The experimental results proved that the reaction was carried out from the surface of outside towards the inside of the parti-

cle and ions of K or Na remained in the solution. In the process of dedolomitization, Mg^{++} diffused out to crystallize to form brucite in the outside of original particles, but the calcite was crystallized in situ.

The observation under electron microscope proved that if the reaction was carried out in solution, Mg^{++} diffused far away from the surface and crystallized in solution. However, if reaction of dedolomitization was taken place in cement paste and the aggregate was reactive carbonate rock come from Kingston, Canada, the brucite was crystallized in the surface of original crystalline particles of dolomite, that was between the matrix composed of fine particles of clay and calcite and crystal of dolomite.

3. MATHEMATICAL EQUATIONS OF KINETICS OF REACTION

Based on the above experimental results and for the purpose of simplifying the calculation, it was assumed: (1) the particles were sphere; (2) reaction of dedolomitization was carried out in situ, the volume of formed calcite layer was equal to the volume of original reacted dolomite; (3) Mg^{++} diffused out and crystallized in solution. According to the above assumptions, the rate of reaction may be controlled by: (1) the diffusion process of ions through calcite layer; (2) process of chemical reaction carried out on the surface of nucleus of unreacted dolomite crystal; (3) process of nucleation and crystal growth of reaction product.

Three processes described above are connected in series and composed the total process of dedolomitization. Each process has its own resistance, total resistance is the sum of the three resistances. If the resistance of one process is much higher than others, the rate will be determined by it, and this process is called the rate-determining step.

Let R_d , R_c , R_n and V_d , V_c , V_n respectively to represent the resistances and rates of diffusion process, chemical reaction process and process of nucleation and crystal growth; F , degree of reaction; V , total rate of reaction; $R(=R_d + R_c + R_n)$, total resistance; t , time of reaction; $Q_d(R_d/R)$, $Q_c(R_c/R)$ and $Q_n(R_n/R)$, relative resistances; K_d , K_c and K_n , respective reaction rate constants. By mathematical changes, we obtained:

$$R_d = K_d \left[(1-F)^{1/3} - 1 \right] \quad (2)$$

$$R_c = K_c (1-F)^{-2/3} \quad (3)$$

$$R_n = K_n \left[-\ln(1-F) \right]^{(1-n)/n} / n(1-F) \quad (4)$$

$$\frac{dt}{dF} = R = R_d + R_c + R_n \quad (5)$$

Considering the induction period ended at t_0 , F_0 , then integrating equation (5) from t_0 , F_0 to t , F , thus

$$t - t_0 = -K_d \left[\frac{3}{2} (1-F)^{2/3} + F \right] - 3K_c (1-F)^{1/3} + K_n \left[-\ln(1-F) \right]^{1/n} + K_d \left[\frac{3}{2} (1-F_0)^{2/3} + F_0 \right] + 3K_c (1-F_0)^{1/3} + K_n \left[-\ln(1-F_0) \right]^{1/n} \quad (6)$$

4. EXPERIMENTAL METHODS AND RESULTS

Using two samples, one was coarse crystalline dolomite from Nanjing, China(NM), the other was well known reactive carbonate rock from Kingston, Canada.

500 mg fine particle sample(40-80 μm) was taken and put in 300 ml 0.4N KOH solution. Such samples were separately kept at 20, 40, 60 and 90°C. The degree of reaction was determined by TGA(thermogravimetric analysis) at 420-450°C, that means to determine the amount of product(brucite), then calculating the degree of reaction. Thus, the values of degree of reaction(F) in a number of more than one hundred were obtained. Then, the values of degree of reaction (F) obtained at different periods were put into equation(6) and K_d , K_c and K_n were calculated. The results of calculation showed that K_c was very small comparing with K_d and K_n and could be neglected. It means that the rate of chemical reaction is very fast and is not a rate-determining step. From K_d and K_n , the Q_d and Q_c at different degrees of reaction were calculated. The results were showed in Fig.1 and Fig.2. It can be seen that either diffusion process or process of nucleation and crystal growth is the rate-determining step.

Additionally, the relationship between rate of reaction and size of particles was studied. The samples were put in 0.4N KOH solution and reacted during 14 days. The results were showed in Fig.3. This figer shows that the

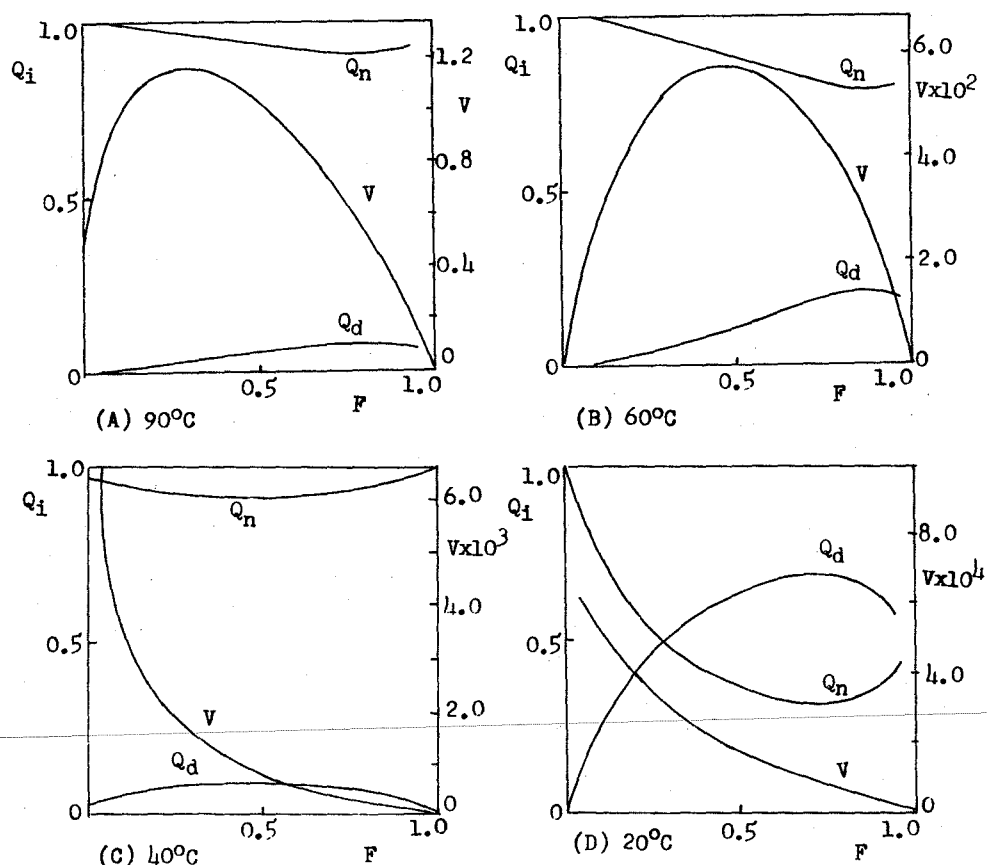


Fig.1 NM in 0.4N KOH sol., $V(dF/dt)$ —calculated by degree of reaction per day(1/D); F—degree of reaction; Q_i —relative resistances

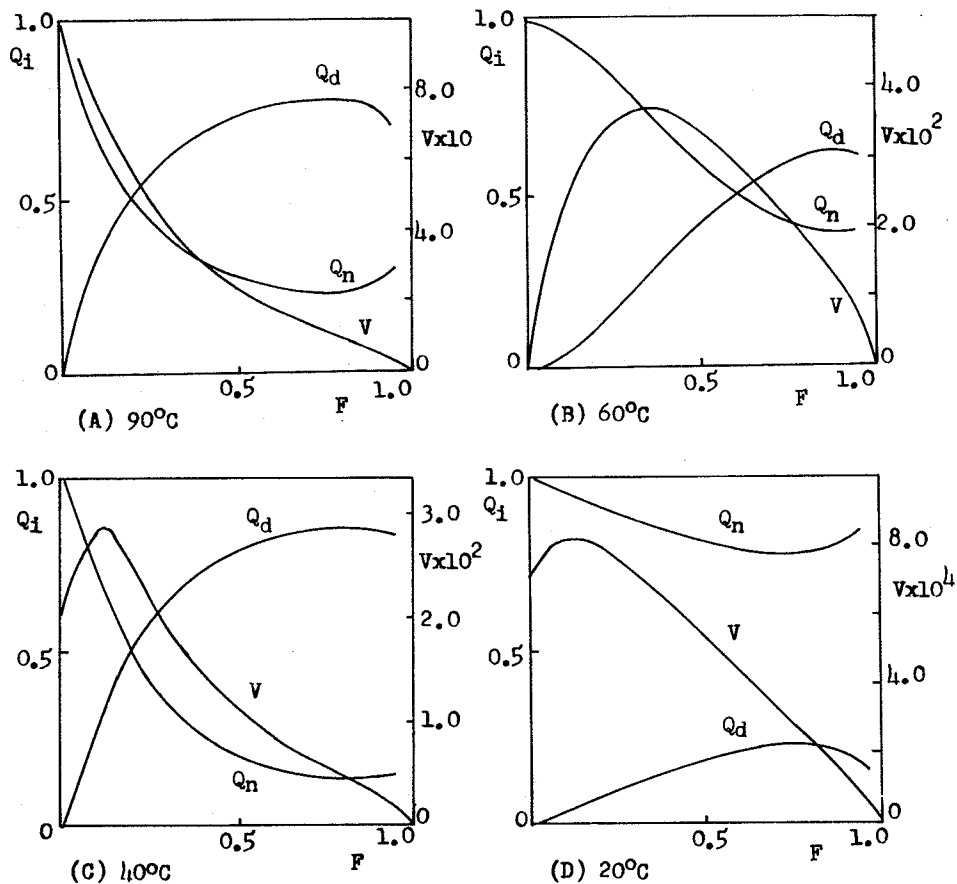


Fig.2 CK in 0.4N KOH sol., $V(dF/dt)$ —calculated by degree of reaction per day(1/D); F—degree of reaction; Q_i —relative resistances.

rate of reaction increases considerably as reducing the size(\bar{d}) of the particles to smaller than 80 μm . This conclusion may be used to explain the reason why the size of dolomitic crystals in reactive carbonate rocks is generally smaller than 50 μm . From Fig.3, it also can be seen that as \bar{d} increasing, the rate of reaction of CK is bigger than that of NM, because the dolomitic crystals of former are smaller than 50 μm , that means the size of dolomitic crystals does not be influenced by the size of rock particles. However, for the later, pure coarse dolomitic crystals, the rate of reaction decreases considerably with the increasing of size of rock particles.

The experimental results also proved that the temperature dependence of ACR was in agreement with Arrhenius equation. The rate of reaction of dedolomitization increased sharply with the increasing of temperature.

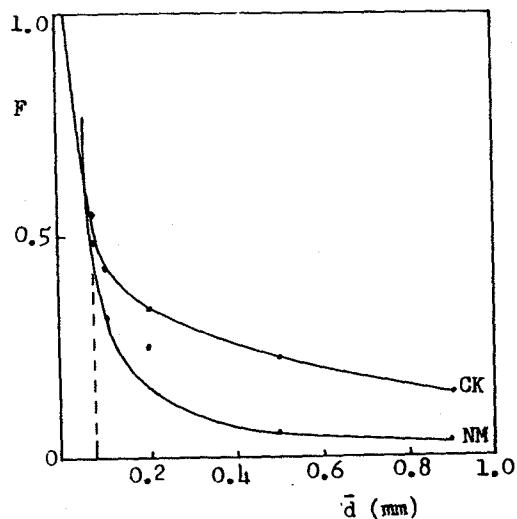


Fig.3 Influence of particle size on degree of reaction (60°C, 0.4N KOH sol., 14 days), \bar{d} —mean size of particles, F— degree of reaction.

5. DISCUSSION

Fig.1 and Fig.2 show that for coarse crystal of dolomite(NM), the rate of reaction is basically controlled by the process of nucleation and crystal growth, except in the middle and late periods at 20°C(Fig.1, D). However, for the reactive carbonate rock from Kingston, Canada, in the middle and late periods, the resistance of diffusion is very important, because in this reactive carbonate rock, the fine crystals of dolomite are surrounded by matrix composed by microcrystalline calcite and clay, thus the formed brucite layer may cover on the surface of original dolomitic crystal[3] and increasing the diffusion resistance.

Using the rapid method for determining the alkali reactivity of carbonate rock suggested by us[4], it was proved that the value of expansion of reactive carbonate rock at 40°C might be higher than that of 60°C. According to the results of studies on kinetics described above, this is due to the rate of nucleation and crystal growth being slower at 60°C than that of 40°C, thus reducing the pressure of crystallization. In the past, we tried using autoclave treatment to determine the alkali reactivity of carbonate rock, but it was not succeeded. The reason may be assumed as following. The expansion of ACK was caused by topochemical reaction and pressure of crystallization[3], in high temperature, Mg^{++} may diffuse out and does not crystallize on the surface of fine crystals of dolomite, thus reducing the pressure of crystallization. Of course, such assumption should be proved by further study.

Based on the above experimental results, we suggest to determine the alkali reactivity of carbonate rock at 40°C, either in alkali solution or by mortar bar test.

6. CONCLUSIONS

1. The results of experiments and mathematical analysis proved that the rate-determining steps of reaction of dedolomitization were diffusion process and process of nucleation and crystal growth. Where the chemical reaction was very fast and was not a controlled factor.

2. By the analysis of kinetics, the expansion test for determining the alkali reactivity of carbonate rock was suggested to be carried out at 40°C.

ACKNOWLEDGEMENT

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