

MECHANISM OF THE ALKALI-DOLOMITE REACTION

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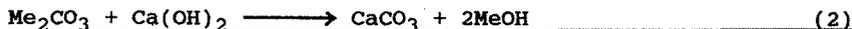
This study shows that the alkali-dolomite-reaction does not follow the schematic two-step mechanism generally adopted. It expresses mainly the displacement of the dolomite dissolution equilibrium, under the action of hydroxide ions. The reaction products depend on the relative activities (concentrations) of Ca^{++} and Na^+ . The high values of the $[\text{Ca}^{++}]/[\text{Na}^+]^2$ ratio encourage the crystallization of brucite and calcite while the lower values give brucite and pirsonite.

INTRODUCTION

The alkali carbonate reaction has been studied by several researchers such as Sewenson and Gillot (1), Hadley (2), Poole (3), Ozol and Newlon (4). In particular, Gillot (5) pointed out that a concrete made from a Kingstone dolomitic limestone was subject to expansion. He attributed this to the dedolomitization of the mixed calcium-magnesium carbonate and the subsequent exfoliation of the associated clay minerals.

Although certain researchers (Tang et al. (6)) give a slightly different interpretation of the expansion process, most authors, Regourd et al. (7) Regourd-Moranville (8) Deloye (9) Poole (10), agree that dedolomitization follows the two-stage mechanism put forward by Hadley (2).

Hadley (2) suggests that the dolomite and the alkali react in a first step to give brucite, calcite and the alkaline carbonate. In a second step, the alkaline carbonate reacts with the lime, giving calcite and regenerating the alkali.



Me = Na^+ , K^+ or Li^+

In this mechanism, the regenerated alkali practically plays the role of a catalyst and the dedolomitization process

appears globally as a reaction between the lime and dolomite. Under these conditions, the nature of the reaction products should not be influenced by the alkali concentration. Moreover, since lime becomes less soluble in the presence of alkalis, the dedolomitization should decrease when the proportion of alkali is increased. Yet it seems, on the contrary, that an increase in the proportion of alkali encourages the reaction. Hadley's proposed mechanism must therefore be an oversimplification.

We intend to study some aspects of the dedolomitization mechanism, paying particular attention to the respective roles of the lime and alkali.

EXPERIMENTAL PROCEDURE

The reaction products were studied on pure paste obtained by mixing fixed proportions of the ingredients. We used dolomite powder containing less than 8% calcite. The other reagents: soda, calcium chloride and lime, were chemical products of "rectapur" quality. The pastes were kept at 40°C for 24 H in a saturated atmosphere and then dried before being analyzed by X Ray diffractometry.

RESULTS

1) Role of the alkali in dolomite removal

In order to examine the role of the alkali, we prepared three mixtures containing the same quantities of dolomite and lime but different proportions of alkali. Mixture n° 1 contained no alkali, whereas mixtures n° 2, 3 and 4 contained 0.5, 1 and 3g respectively of NaOH. Figure (1) shows the diffractograms for the reaction products obtained from these mixtures.

To follow the evolution of the different phases, we chose peaks where no superposition occurred. For brucite $Mg(OH)_2$ we took peak (B) at 4.79 Å; for calcite ($CaCO_3$), peak (C) at 3.04 Å; for dolomite $CaMg(CO_3)_2$, peak (D) at 2.02 Å; and for pirsonite $CaNa_2(CO_3)_2 \cdot 2H_2O$, peak (P) at 5.15 Å.

Diffractogram (1a) was obtained from a mixture of dolomite and lime only. A brucite peak (Br) is already visible and the calcite peak (C) has increased. We thus deduce that dedolomitization is indeed possible in contact with lime in the absence of any alkali.

When a small quantity of soda is introduced into the reacting medium (diagram 1b), a further decrease is observed in the dolomite peak (D) while there is a very marked increase in the intensity of the calcite (C) and brucite (B) peaks. The dedolomitization is thus stronger.

For mixture n° 3, which was richer in alkali (diagram 1c), the dolomite peak has again decreased slightly. The main feature of this diagram is that the calcite peak (C) has

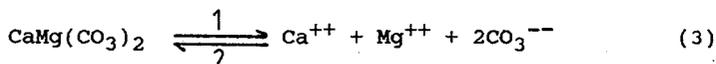
markedly decreased, whereas the pirsonite ($\text{CaMg}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) peak (P) has appeared. Thus, contrary to what was expected, it was neither calcite nor sodium carbonate that formed but pirsonite, which is a double calcium-sodium carbonate.

For mixture n°4, even richer in alkali (diagram 1d), the peaks of pirsonite and brucite have increased and the peak of calcite has practically disappeared.

What finally becomes clear from this is that the dedolomitization activity is directly linked to the alkali concentration. The more alkali there is in the reacting medium, the stronger the dedolomitization. The alkali does not simply act as a catalyst; it intervenes directly in the nature of the phases formed. To better account for this result, we suggest a different reaction mechanism from that proposed by Hadley (2), which justifies the nature of the crystallized phases better.

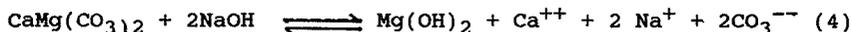
2) Mechanism of the alkali-dolomite reaction

The dedolomitization reaction should be seen as the result of a displacement of the equilibrium of dissolution of the $\text{CaMg}(\text{CO}_3)_2$ mineral.



From the above equilibrium equation for the dissolution of the dolomite, we can see that any addition of OH^- ions leads to precipitation of the magnesium in the form of brucite and a displacement of the equilibrium towards 1. The higher the hydroxide ion content, the more complete the reaction.

In the case where the OH^- ions are provided by soda, the alkali dolomite reaction can be written:



If the magnesium and hydroxide ions in equilibrium with the $\text{Mg}(\text{OH})_2$ precipitate are considered negligible, the other ions present are Ca^{++} , Na^+ and CO_3^{--} . These ions essentially give rise to three types of compounds:

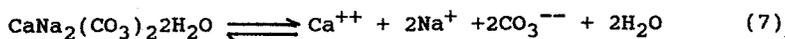
- carbonates of calcium (calcite, aragonite, vaterite),
- carbonates of sodium ($\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$, NaHCO_3 , $\text{Na}_2\text{CO}_3 \cdot \text{HCO}_3 \cdot 2\text{H}_2\text{O}$, etc.)
- double carbonates of calcium and sodium (pirsonite, gaylussite, etc.).

Under our experimental conditions (high pH and long drying of the samples) the three most probable phases were: $\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ (pirsonite), CaCO_3 (calcite), and Na_2CO_3 .

The equilibria of dissolution of these three compounds can be written as follows:



$$K = [\text{Ca}^{++}] [\text{CO}_3^{--}] = 10^{-8.37} \quad (6)$$

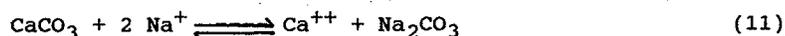


$$K = [\text{Ca}^{++}] [\text{Na}^+]^2 [\text{CO}_3^{--}]^2 [\text{H}_2\text{O}]^2 = 10^{-9.54} \quad (8)$$

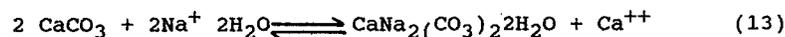


$$K = [\text{Na}^+]^2 [\text{CO}_3^{--}] = 10^{+0.732} \quad (10)$$

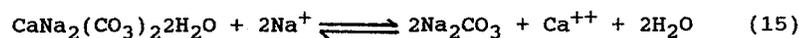
By combining these equations two by two, we obtain a system of three equations which predict the domain of stability of the three compounds according to the activities (concentrations) of Ca^{++} and Na^+ . A schematic representation is given in figure (2) for two values of $[\text{H}_2\text{O}]$ (0,9 and 1)



$$K = [\text{Ca}^{++}]/[\text{Na}^+]^2 = 10^{-9.102} \quad (12)$$



$$K = [\text{Ca}^{++}]/[\text{Na}^+]^2 [\text{H}_2\text{O}]^2 = 10^{-7.2} \quad (14)$$



$$K = [\text{Ca}^{++}][\text{H}_2\text{O}]^2/[\text{Na}^+]^2 = 10^{-11,004} \quad (16)$$

We note that:

1) the sodium carbonate is stable for very low calcium content and high sodium concentrations:

$$[\text{Ca}^{++}]/[\text{Na}^+]^2 < 10^{-11,004} / [\text{H}_2\text{O}]^2$$

2) calcite forms preferentially when the relative concentration of calcium is high $[\text{Ca}^{++}]/[\text{Na}^+]^2 > 10^{-7.2} [\text{H}_2\text{O}]^2$,

3) pirsonite is the stable form as soon as the reacting medium contains a little more sodium than calcium:

$$10^{-11,004}/[\text{H}_2\text{O}]^2 < [\text{Ca}^{++}]/[\text{Na}^+]^2 < 10^{-7.2} [\text{H}_2\text{O}]^2$$

It is thus to be expected that the products obtained by dedolomitization should change with the sodium content. We checked the conclusions of this analysis by studying the reaction products for two series of mixtures. In the first series we kept the dolomite/alkali ratio constant and varied the amount of calcium. In the second series we kept the dolomite/calcium ratio constant and varied the alkali content.

3. Alkali-dolomite reaction in presence of increasing quantities of calcium

In this test we kept the dolomite/soda ratio constant and added increasing amounts of CaCl_2 . Figure (3) shows the diffractograms that were recorded.

Diffraction (3a) corresponds to the case of a mixture composed of dolomite and soda only, with no external supply of calcium. We can see that practically complete dedolomitization has occurred, giving pirsonite (peak P) and brucite (peak B). The reaction can be written:

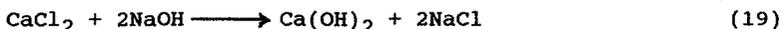


When a small proportion of CaCl_2 is added to the mixture (diffraction 3b), the pirsonite peaks are smaller and calcite peaks appear (peak C).

When the CaCl_2 content is increased slightly (diagram 3c), the pirsonite peaks become very weak and calcite is the main phase formed. The reaction can be written:



All these phases can be clearly identified on diagram (3c), where we can also note small peaks for lime, which are due to the following reaction:



If the CaCl_2 content is further increased (diagram 3d), the latter reaction is the one that occurs preferentially and the concentration of hydroxide ions is fixed by the solubility of the lime. This brings us back to the case of a reaction between dolomite and lime; weak dedolomitization takes place, giving calcite and brucite.



Thus, for a given dolomite/alkali ratio, increasing the calcium content encourages the formation of calcite to the detriment of pirsonite. The dedolomitization is less and less intense because the amount of hydroxide ions decreases.

4) Alkali-dolomite reaction in presence of increasing quantities of soda

For this test, we fixed the dolomite/ CaCl_2 ratio and progressively increased the soda content. The results are shown in figure (4).

Diffraction (4a) was obtained for low soda content. Little dedolomitization occurs but it yields calcite (peak C) and brucite (peak B).

When the proportion of soda is increased (diagram 4b), more dolomite is transformed, as demonstrated by a reduction of the dolomite peaks and an increase in the calcite peaks.

For a further increase in the soda content (diagram 4c), almost complete dedolomitization is observed. It gives calcite

(peak C) and brucite (peak B). A small pirsonite peak can already be seen (peak P).

Beyond this soda content (diagram 4d), the formation of pirsonite rather than calcite is clearly observed.

So it is indeed the alkali content that determines the intensity of the dedolomitization reaction; only the reaction products change. Calcite crystallizes out for high $[Ca^{++}]/[Na^+]^2$ ratios, whereas pirsonite crystallizes out for low $[Ca^{++}]/[Na^+]^2$ ratios. Brucite forms in all cases and the equilibrium displacement is caused by its crystallization.

These results explain why, in Portland cement mortar, the main products of the dedolomitization are calcite and brucite and not pirsonite and brucite. Indeed, in this type of cement, the $[Ca^{++}]/[Na^+]$ ratio is generally high because the sources of calcium are numerous (lime, gypsum, anhydrite, etc).

Moreover as dedolomitization occurs whenever a sufficient local concentration of OH^- is reached, two main consequences can be drawn:

a) tests intended to detect reactive dolomitic granulates will not be very discriminating, since dedolomitization occurs in any dolomite when it is in contact with a solution rich in alkalis;

b) it is possible to guard against the risks of alkali-dolomite reaction by depleting the interstitial solution of hydroxide ions. This can be done by, for example, adding reactive substances to the mortar.

CONCLUSION

In this study we have shown that the alkali-dolomite reaction does not always follow the schematic mechanism generally accepted. It mainly expresses the displacement of the equilibrium of dissolution of the dolomite under the action of hydroxide ions.

Dedolomitization can take place on contact with lime in the absence of any alkali. In this case it is not usually very strong as the solubility of lime is relatively limited. It can, however, continue over long periods if the interstitial liquid is constantly renewed.

Dedolomitization can also occur in the presence of alkalis without any additional calcium ions being supplied. Pirsonite is then the stable phase.

When alkali and calcium ions are present at the same time, the phases formed depend on the relative activities of Ca^{++} and Na^+ . High values of the $[Ca^{++}] / [Na^+]^2$ ratio encourage the crystallization of calcite and brucite. Lower values give brucite and pirsonite.

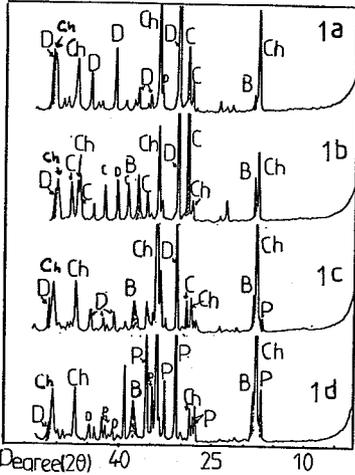
All dolomitic aggregates are necessarily chemically reactive if they are placed in an environment sufficiently rich in OH^- ions. Thus, if the dolomitic mineral is only considered, it seems pointless to distinguish by tests, non reactive and reactive dolomitic aggregates.

ACKNOWLEDGEMENT

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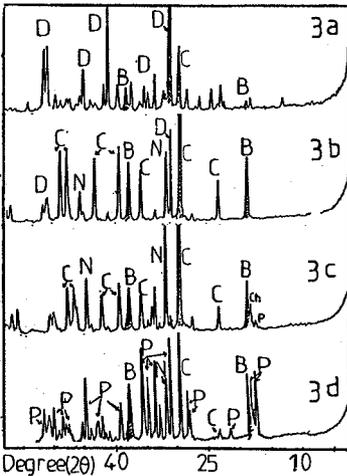
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X.R.D. of the products formed by reaction between dolomite, $\text{Ca}(\text{OH})_2$ and NaOH D = dolomite, Ch = lime, Br = brucite, P = Pirsonite

Figure 1: Role of OH^- ions on the alkali-dolomite reaction



X R.D. of the products formed by reaction between dolomite, NaOH and CaCl_2 D = dolomite, Ch = lime, Br = brucite, P = Pirsonite, N = NaCl

Figure3:Influence of increasing quantities of calcium(CaCl_2)

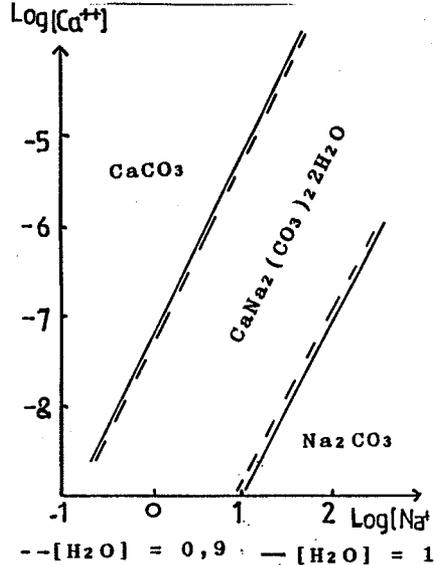
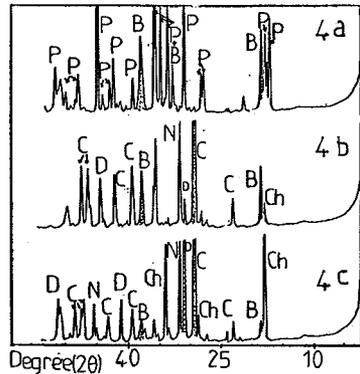


Figure 2: Domain of stability of calcite/pirsonite/ Na_2CO_3



X.R.D. of the products formed by reaction between dolomite, NaOH , and CaCl_2 . D = dolomite, Ch = lime, Br = brucite, P = Pirsonite, N = NaCl

Figure4:Influence of increasing quantities of alkali(NaOH)