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THE ALKALI-CARBONATE REACTION AND ITS REACTION PRODUCTS AN EXPERIENCE WITH ARGENTINEAN DOLOMITE ROCKS

C.A. Milanesi[1], S.A. Marfil[2], O.R. Batic[3] and P.J. Maiza[4]
Laboratorio de Entrenamiento Multidisciplinario para la Investigación Tecnológica
(LEMIT-CIC) Calle 52 entre 121 y 122. La Plata (1900). Argentina

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ABSTRACT

Three dolomitic rocks from Argentina were studied under different test conditions (ASTM C 586, ASTM C 227, CSA A23.2-14A, powdered rock samples immersed in strong alkali solutions). X-ray diffraction (XRD), optical microscopy (OM) and scanning electron microscopy (SEM) analyses of the various reaction products detected under these conditions are presented. Results are compared with the alkali expansivity of the dolomitic rocks and are also used to discuss the scope and applicability of the different reaction mechanisms proposed in the literature. It has been concluded from this research that the mechanism originally proposed by Hadley is adequate to explain the reaction mechanisms that operate in concrete structures under natural service conditions.

Introduction

Many cases of alkali-carbonate reactivity (ACR) of dolomitic rocks have been reported from many parts of the world, mainly in USA, Canada and recently in China (1,2,3,4,5). In spite of numerous research studies carried out since the beginning of the sixties, the deleterious reaction/expansion mechanisms of these rocks are still not well known.

Various hypotheses have been developed to explain the expansive behavior observed on alkali-reactive dolomitic rocks (1,2,3,6). However, despite the existence of many controversial views in this respect (3,7,8,9), most theories are in agreement with one point: wherever expansion occurs, a chemical reaction called dedolomitization does also occur.

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[1] Fellowship holder CIC. Lecturer of La Plata National University.
[2] Researcher CIC. Lecturer of South National University.
[3] Researcher CIC. Lecturer of La Plata National University.
[4] Researcher CONICET. Professor of South National University.

The fact that the mineral dolomite is prone to enter into a chemical reaction with alkali solutions has been recognized for some time. Swenson and Gillott (10) were the first to suggest that expansion of certain carbonate rocks may be the result of a dedolomitization reaction.

X-ray diffraction studies performed by Hadley (11) on expansive rocks which had reacted with alkali solutions showed a decrease in the amount of dolomite, an increase in calcite content and the appearance of brucite. According to this author, in concrete the reaction would proceed in two stages. In the first one the dolomite reacts with alkali solutions forming calcite, brucite and an alkali carbonate in solution. Subsequently, in a second stage, the alkali carbonate would react with the cement hydration products, thus regenerating the alkalis of the pore solution.

Many authors have agreed with Hadley's hypothesis (12,13). Nevertheless, the main doubt in this concern is that volume change associated with dedolomitization reaction is negative. Conversely, Deng et al. (6) have theorized that this volume change may actually give rise to expansion as a result of the many voids enclosed by the reaction products.

Experimental studies carried out by Prince et al. (14) on powdered dolomite showed that the alkali-dolomite reaction does not always follow this generally accepted schematic two-step mechanism. They also showed that the alkali does not simply act as a catalyst but it directly intervenes in the nature of the phases formed. Thus, as a result of the alkali attack, either brucite and calcite or brucite and pirssonite ($CaNa_2(CO_3)_2.2H_2O$) may appear, depending on the relative activities of Ca^{2+} and Na^+ ions present in the alkali solution.

In addition to these phases, some more reaction products have been reported in the literature, such as gaylussite ($CaNa_2(CO_3)_2.5H_2O$), buetschliite ($Ca_2K_6(CO_3)_5.6H_2O$) and portlandite ($Ca(OH)_2$) (2). Gaylussite has also been found at the surface of rock samples which have been soaked for a long time in 1N NaOH solution at room temperature in certain studies (2,15,16).

This paper reports a study conducted on three dolomitic rocks from Argentina examined under different standard test conditions such as ASTM C 586, ASTM C 227 and CSA A23.2-14A. In order to promote the dedolomitization reaction, additional tests were also carried out by immersing powdered rock samples in strong alkali solutions, varying both the concentrations and the time of immersion. XRD, OM and SEM analyses of the various reaction products detected under these conditions are presented. The results are compared with the alkali expansivity of the dolomitic rocks and are also used to discuss the scope and applicability of the different reaction mechanisms proposed in the literature.

Materials and Experimental Methods

Materials

Portland cement. An ordinary portland cement (Type I according to ASTM C 150) with high alkali content (1.14 % Na_2O eq.) was used to make mortar and concrete mixtures.

Aggregates. Three dolomitic rocks from different parts of Argentina were selected for this study. The main petrographic characteristics and the alkali reactivity of these rocks are given in subsequent paragraphs.

Calcitic dolomite (OLA). This is a fresh and compact non-reactive medium-grained (100 to 200 μm) sedimentary rock, consisting of dolomite, some calcite and a small amount of quartz (Figure 1A) (17,18). It has a little amount of insoluble residue of about 3%.

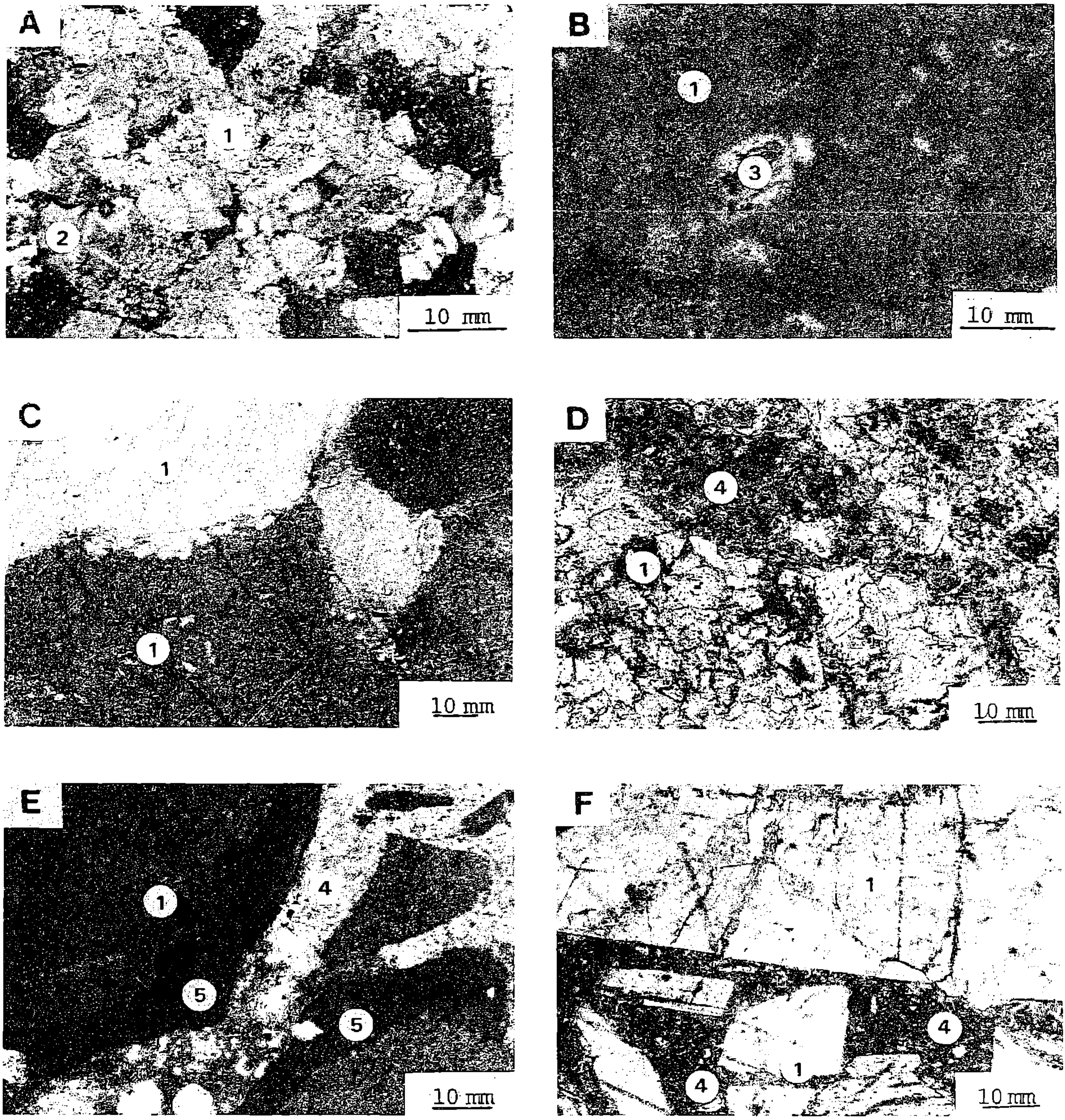

FIG. 1.
Photomicrographs of fresh rock samples: (A) OLA, (B) VAL, (C) CBA. Photomicrographs of thin sections of ASTM C 227-87 mortar bar at 5 year-storage: (D) OLA, (E) VAL, (F) CBA.*(1: Dolomite, 2: Quartz, 3: Feldspar, 4: Matrix, 5: Calcitic reaction rim).*

Dolomite (VAL). This is a fresh and porous fine-grained (10 to 30 μm) hydrothermal rock, consisting of dolomite and a minor amount of quartz, feldspar and clasts of rhyolitic volcanic rocks (Figure 1B). X-ray lines of calcite were not detected in XRD analyses of the fresh rock (Fig. 3A). XRD examination of its insoluble residue, which was found to vary between 10 and

20%, showed the presence of various argillaceous minerals (illite, montmorillonite and sepiolite).

In previous studies, this rock exhibited a high alkali susceptibility (17,18). Nevertheless, despite the presence of minor amounts of smectite and potentially reactive siliceous components in this rock, results obtained both in these and other studies (17,19,20) have denied the existence of expansive phenomena associated either with water uptake by clay minerals or alkali-silica reaction.

Dolomitic limestone (CBA). This is a compact non-reactive medium- to coarse-grained (1500 to 4500 μm) metamorphic rock, consisting of calcite, some dolomite and a minor amount of quartz (Figure 1C). It has a small amount of insoluble residue of about 3 %.

The sand used for making concrete specimens was a known non-reactive siliceous river sand according to ASTM C 1260 and CSA A23.2-14A test methods (21,22). This sand is a material of proved characteristics, widely used in the preparation of control mixtures for laboratory test research (20,23).

Experimental Methods

Several alkali reactivity test methods may be applied for evaluating the ACR, some of which are ultra-accelerated (24,25,26). For this study, however, three mildly accelerated test methods were selected: the rock cylinder and the concrete prism test methods, both of which are specifically intended for evaluating the ACR (27,28), and the mortar bar method (29). The ASTM C 227 test method is known to be inadequate to detect the ACR due to the low degree of expansion obtained (29,30,31,32). The authors, in agreement with the literature, have obtained the best results when a reactive rock is used as coarse aggregate (tests performed on concrete specimens) (9,18). The mortar bar method was then applied for comparative purposes only. The main guidelines of the test methods applied in this study are given below.

TABLE 1

ASTM C 586, ASTM C 227 and CSA A23.2-14A Test Expansions

Sample (Designation)	Expansion (%)					
	ASTM C 586 (16 weeks)	ASTM C 227 (6 months)	ASTM C 227 (12 months)	ASTM C 227 (5 years)	CSA A23.2-14A (12 months)	CSA A23.2-14A (5 years)
OLA	-0.103	0.017	0.023	0.030	0.004	0.013
VAL	1.929	0.060	0.069	0.100	0.032	0.205
CBA	-0.024	0.017	0.025	0.034	0.004	0.015
Suggested limits	0.200 (+)	0.050 (*)	0.100 (*)	-	0.030 (#)	-

(+) Expansion limit according to Rogers (4).
(*) Expansion limits according to Grattan-Bellew (32).
(#) Expansion limit according to CSA (36).

k Cylinder Method. A modified version of ASTM C 586 test method (27) was applied for study. Length changes were measured on rock cylinders (19 mm in diameter and 75 mm ngth) while immersed in 1N NaOH solution at room temperature. The volume of alkali tion to the volume of rock specimen ratio was about 7.

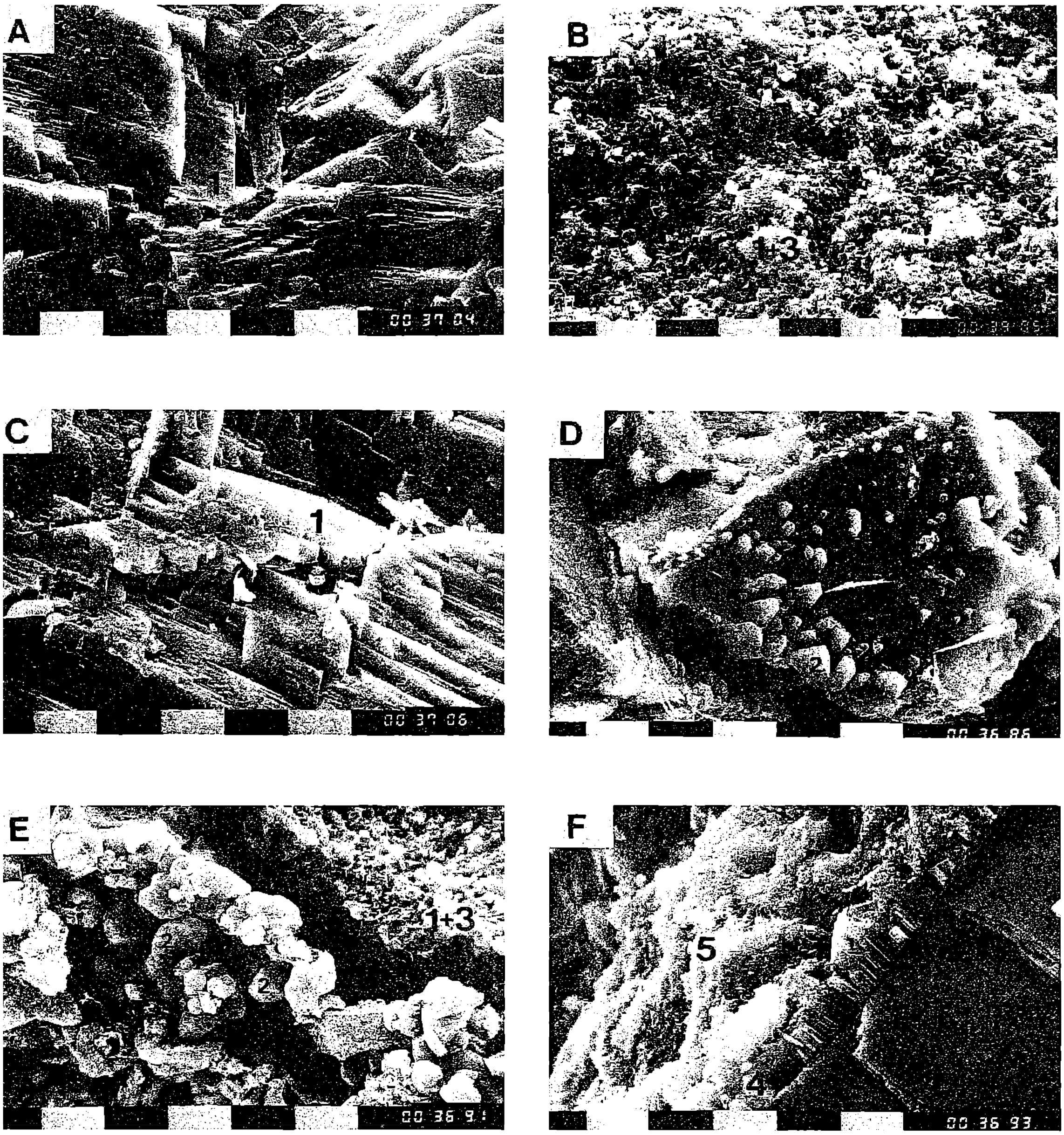

FIG. 2.

M micrographs (x 1500) of fresh rock samples: (A) OLA, (B) VAL, (C) CBA. SEM crographs (x 1500) of the transition zone of dolomite aggregates in CSA concrete prism er a 5-year storage: (D) OLA, (E) VAL, (F) CBA. *(1: Dolomite, 2: Calcite, 3: Clay fibers, Calcium (hydroxide?) crystals, 5: Matrix).*

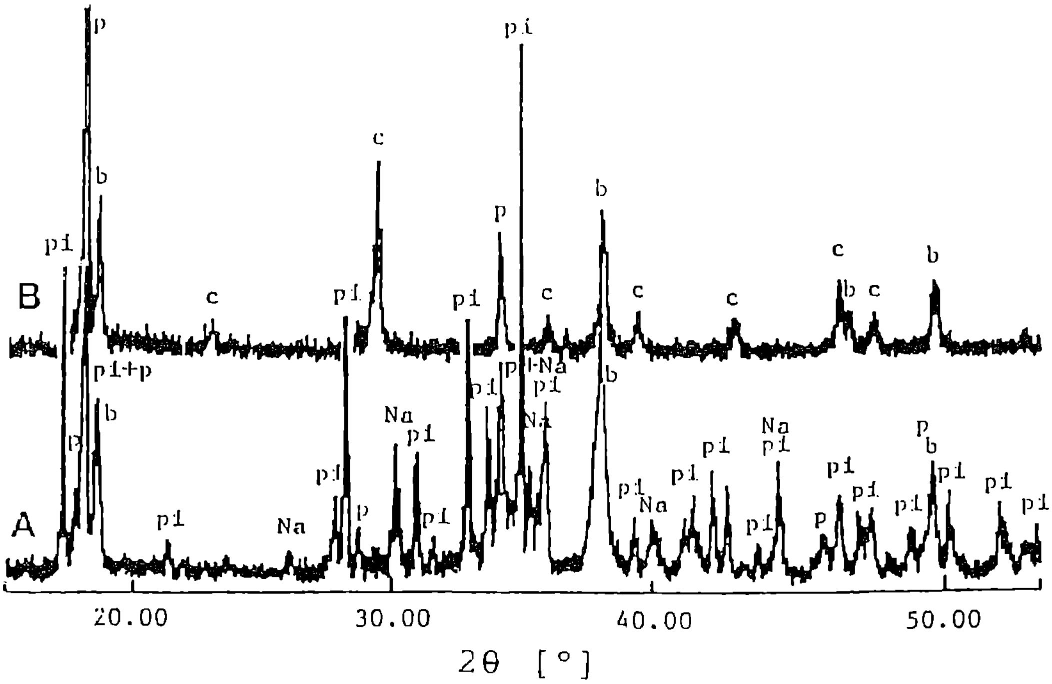

FIG. 3.
XRD patterns of VAL rock samples. (A) untreated rock, (B) rock cylinder after a 4-month immersion in 1N NaOH, (C) piece of aggregate extracted from a CSA concrete prism at 5 years. (d: dolomite, b: brucite, c: calcite, q: quartz, f: feldspar).

Mortar Bar Method. 25x25x285 mm mortar bars were made according to ASTM C 227-87 (i.e. maintaining a constant flow and storing the bars in wicked containers) (29) and the resulting expansions were measured up to 5 years.

Concrete Prism Method. 75x100x460 mm concrete prisms were made according to CSA A23.2-14A-M77 (i.e. a cement content of 310 kg/m^3)(28) and their expansions were monitored up to 5 years. In order to avoid an excessive alkali leaching, the prisms were put into tightly sealed plastic bags containing 100 mL of water according to the advice given by Rogers and Hooton (33). Expansion results obtained with the current Canadian standard (34) were published in a previous paper (17). Presently, however, a higher cement content for this test method is suggested (i.e. 420 kg/m^3) (22,35).

X-Ray Diffractometry. The various reaction products resulting from the dedolomitization reaction were identified by means of XRD analyses. Ni-filtered Cu-Kα radiation at 35 Kv-15 mA was used in a Rigaku Dmax. IIIC diffractometer.

Results

Alkali-Expansivity Tests. Expansion results for rock cylinders, mortar bars and concrete prisms are given in Table 1. These results, bearing in mind the maximum expansion limits suggested by the literature, clearly show that VAL is the only one sample that has an abnormal expansion behavior resulting from the alkali attack.

OM and SEM observations of the microstructure of rock cylinders (as discussed in the following item) did not reveal remarkable mineralogical changes, except for those from the VAL sample. These studies were published in a previous paper (17).

OM observations of thin sections of ASTM C 227 mortar bars at 5 years clearly showed, once again, how differently these three types of rocks behave. In fact, in the case of OLA and CBA samples (coarse grains and low porosity) the contacts between aggregates and paste were not altered (Fig. 1D and 1F). In the case of VAL sample (fine grains and high porosity), on the contrary, a remarkable change took place at the interface zone showing the presence of cracks and reaction rim development as a result of the dedolomitization reaction (Fig. 1E).

More detailed comparative studies by SEM analysis on fresh rocks and Canadian test concrete aggregates revealed that the OLA sample dedolomitized as well, though only superficially and locally (Fig. 2A and 2D). Similary, SEM observations at the interface zone of the VAL aggregate revealed significant mineralogical changes caused by the ACR (Fig. 2B and 2E). The results were also corroborated by XRD (Fig. 3C). No mineralogical alteration

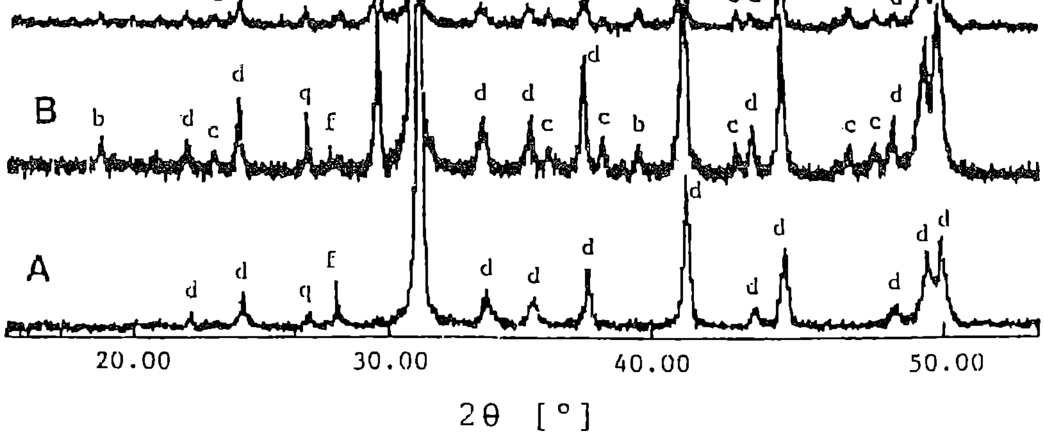

FIG. 4.

XRD patterns of VAL powdered rock samples. (A) After a 7-day treatment with 2N NaOH solution, (B) After a 4-day treatment with 10N NaOH solution. *(pi: pirssonite, c: calcite, b: brucite, p: portlandite, Na: sodium carbonate).*

could, however, be detected by SEM observations in the transition zone of the CBA aggregate (Fig. 2 C and 2F).

XRD Analyses

Studies performed on ASTM C 586 rock cylinders. In order to study mineralogical changes that took place over the course of this test, some XRD examinations were performed. XRD analyses of the surfaces of dolomite rock cylinders after a 4-month alkali immersion (1N NaOH) were compared with similar analyses of the original fresh rock. As shown by figures 3A and 3B, the results obtained from VAL sample proved that a strong dedolomitization does occur. Nevertheless, except for calcite and brucite, no other reaction products were observed. On the contrary, identical studies carried out either on OLA or CBA samples did not show any difference between fresh and tested rock samples. These facts were also corroborated by examination of thin sections of the alkali-treated rock cylinders using the alizarine staining method (37). In this method, the rock sample is immersed in alizarine-containing HCl solution for a few minutes, after which calcite is stained deep red while dolomite is not.

Studies performed on powdered rock samples. Powdered rock samples (< 75 μm) from each of the studied rocks were immersed in 1N NaOH solution at 40°C for 4 days. In all cases, calcite and brucite were detected while dolomite was not. The same results were obtained using 1N KOH solution. Some additional experiments were also carried out using 2N and 10N NaOH solutions. Pirssonite, brucite and a minor amount of calcite were detected at 4 days when the concentration of the solution was 2N. At 7 days, some X-ray lines of portlandite, brucite, pirssonite and sodium carbonate were identified but calcite could not be detected (Fig. 4A).

As shown in Fig. 4B, portlandite, brucite and calcite were formed at 4 days when the concentration of the NaOH solution was raised to 10N. It must be noted that all the calcite disappeared when immersion time was extended to 7 days.

Discussion

As Prince et al. (14) stated, the reaction products of dedolomitization depend on the relative concentrations of Ca^{2+} and Na^+ ions. Thus, the high values of the $[Ca^{2+}]/[Na^+]^2$ ratio encourage the crystallization of brucite and calcite while the lower ones give brucite and pirssonite. They also considered that this observation could account for the fact that the reaction products observed either in laboratory mortar or concrete specimens or in altered concrete structures are only calcite and brucite. In fact, in portland cement mixtures there are many sources of calcium ions (such as portlandite, gypsum) to give a high $[Ca^{2+}]/[Na^+]^2$ ratio. Then, it is unlikely that pirssonite will appear as a reaction product. However, in spite of being very interesting, this new approach cannot explain some of the experimental results presented in this paper.

As shown in Fig. 3B, the dedolomitization of the VAL rock sample (under ASTM C 586 test conditions) occurred in the presence of alkalis without any additional calcium ions being supplied. However, except for calcite and brucite, no other reaction products were observed. So, why was pirssonite not detected in these tests if, a priori, there is no external supply of calcium ions?

Firstly, since these rock prisms throughout the test were only in contact with a 1N NaOH solution, it would appear quite feasible to admit the existence of some internal (rather than external) source of Ca^{2+} ions. According to the literature (38,39), Ca^{2+} ions may be derived from the clay minerals by cation exchange with sodium from the test solution. Nevertheless, this hypothesis was not tested by the authors and it is not known whether the amount of leachable calcium would be sufficient to account for the displacement of the dolomite dissolution equilibrium.

As mentioned above in the introduction, according to the mechanism proposed by Hadley (11), in concrete, the alkali carbonate produced by the dedolomitization reaction would react with the cement hydration products, say with $Ca(OH)_2$, thus regenerating the alkalis of the pore solution. If we asume that the alkali in cement is predominately NaOH, this reaction could be written as follows:

$$Na_2CO_3 + Ca(OH)_2 ===> 2\ NaOH + CaCO_3 \qquad (1)$$

which, at least, would partly explain the formation of large amounts of secondary calcite crystals in the transition zone of carbonate aggregates, which is sometimes observed at considerable distance from the reaction sites (8,12,13,44).

In fact, from a thermodynamic point of view, calcite is usually more stable than portlandite. In other words, if the NaOH concentration is kept within "certain limits" the reaction takes placeas per Eq. (1), i.e. from the left to the right. If the NaOH concentration, however, exceeded such limits the reaction could be rather different.

Let us consider, for instance, the case of a carbonate rock immersed in 1 N NaOH at 23 °C (i.e. under similar conditions to those of the ASTM C 586 Test Method), and let us evaluate, at least in an approximate way (as the value for the constants is calculated for zero ionic strengh and at 25 °C), the possibility of $Ca(OH)_2$ precipitation, under this test conditions, based on the solubility products given by Reardon (43). The equilibrium of dissolution of $CaCO_3$ can be written as follows:

$$CaCO_3 <=====> Ca^{2+} + CO_3^{2-} \quad (K_{sp} = 3.9 \times 10^{-9}) \qquad (2)$$

so, calcium ion concentration would be equal to:

$$[Ca^{2+}] = 6.2 \times 10^{-5}\ mol/L$$

Now, let us consider the equilibrium of dissolution of calcium hydroxide:

$$Ca(OH)_2 <=======> Ca^{2+} + 2OH^- \quad (K_{sp} = 6.5 \times 10^{-6}) \qquad (3)$$

In this case, an increase in the quantity of OH^- ions in the solution would cause, by the so-called "common ion effect", a decrease in the solubility of Ca^{2+} ion. In fact, solubility measurements of portlandite in high alkali solutions, carried out by Duchesne and Reardon (45), have recently showed that $Ca(OH)_2$ solubility markedly decreases near two order of magnitude for a 4 molal alkali concentration.

As it is known, precipitation of a given substance from a solution containing its ions can only takes place when its ionic product is greater than its solubility product (K_{sp}). In the system under study ($CaCO_3$ + 1N NaOH solution), meanwhile Ca^{2+} ions are supplied by the dissolution of $CaCO_3$ ($[Ca^{2+}] = 6.2 \times 10^{-5}$ mol/L), OH^- ions are supplied by NaOH ($[OH^-] = 1$ mol/L). So, for this system, the ionic product of $Ca(OH)_2$ would be greater than its solubility product:

$$[Ca^{2+}] \times [OH^-]^2 = 6.2 \times 10^{-5} > K_{sp}\,(Ca(OH)_2) = 6.5 \times 10^{-6}$$

This fact, would make $Ca(OH)_2$ precipitate, increasing the amount of soluble carbonate (CO_3^{2-}) in order to satisfy the equilibrium conditions of equations (2) and (3).

In support of the above, there are many references in the literature (2 ,3, 40, 41, 42). SEM examinations carried out by Sims and Sotiropoulos (42) on dolomite rock cylinders from Libya detected the formation of abundant calcium hydroxide plates after a 13-month alkali immersion in 1N NaOH solution at 23 °C.

Sherwood and Newlon (2) showed that powdered samples of reactive rocks react with strong alkali solutions at room temperature forming either brucite and gaylussite ($CaNa_2(CO_3)_2.5H_2O$), or brucite, buetschliite ($Ca_2K_6(CO_3)_5.6H_2O$) and portlandite ($Ca(OH)_2$), depending on the nature of the alkali cation of the solution (i.e., Na^+ or K^+). XRD studies carried out by Swenson and Gillott (3) similarly showed that when a mixture of calcite and dolomite was covered with a 2M NaOH solution and left to evaporate slowly for several weeks, portlandite and pirssonite appeared as the dominant phases, together with brucite and calcite.

XRD analyses carried out by Buck and Dolch (40) showed that the so-called negative reaction rims observed on limestone rocks, is due to an alkali (hydroxyl) reaction between the rock and concrete pore solution, whereby some of the calcite at the rock surface is transformed into calcium hydroxide. Chen and Wang (41) similarly observed by SEM that the surface of a crystaline limestone dissolved to precipitate tabular portlandite on it.

In summary, as may be inferred from the above literature review, the precipitation of portlandite (in strong alkali solutions), thanks to the dissolution of calcite (appearing as a result of dedolomitization, for example), might be written as follows:

$$CaCO_3\downarrow + 2\,NaOH \Longrightarrow Ca(OH)_2\downarrow + CO_3Na_2 \qquad (4)$$

The above analysis could account for the coexistence of portlandite and sodium carbonate in the reaction products which were observed by XRD under strong alkali conditions (2N and 10N NaOH). From the above, as both the reactants and the reaction products for the reacting systems studied are known, the following global chemical equations could be written:

$$\underset{\text{Dolomite}}{CaMg(CO_3)_2} + 2NaOH \Longrightarrow \underset{\text{Brucite}}{Mg(OH)_2} + \underset{\text{Calcite}}{CaCO_3} + Na_2CO_3 \qquad (5)$$

$$\underset{\text{Dolomite}}{2CaMg(CO_3)_2}+4NaOH+2H_2O \Longrightarrow \underset{\text{Brucite}}{2Mg(OH)_2} + \underset{\text{Pirssonite}}{CaNa_2(CO_3)_2.2H_2O} + \underset{\text{Calcite}}{CaCO_3}+Na_2CO_3 \qquad (6)$$

$$\underset{\text{Dolomite}}{2CaMg(CO_3)_2}+6NaOH+2H_2O \Rightarrow \underset{\text{Brucite}}{2Mg(OH)_2} + \underset{\text{Pirssonite}}{CaNa_2(CO_3)_2.2H_2O} + \underset{\substack{\text{Calcium}\\\text{Hydroxide}}}{Ca(OH)_2} + \underset{\substack{\text{Sodium}\\\text{Carbonate}}}{2Na_2CO_3} \qquad (7)$$

$$\underset{\text{Dolomite}}{2CaMg(CO_3)_2} + 6NaOH \Longrightarrow \underset{\text{Brucite}}{2Mg(OH)_2} + \underset{\text{Calcite}}{CaCO_3} + \underset{\substack{\text{Calcium}\\\text{Hydroxide}}}{Ca(OH)_2} + \underset{\substack{\text{Sodium}\\\text{Carbonate}}}{3Na_2CO_3} \qquad (8)$$

$$\underset{\text{Dolomite}}{CaMg(CO_3)_2} + 4NaOH \Longrightarrow \underset{\text{Brucite}}{Mg(OH)_2} + \underset{\substack{\text{Calcium}\\ \text{Hydroxide}}}{Ca(OH)_2} + \underset{\substack{\text{Sodium}\\ \text{Carbonate}}}{2Na_2CO_3} \qquad (9)$$

Notes:

(a) Eq. (5) was originally proposed by Hadley (11)
(b) Eqs. (6) and (7) were developed to explain the reaction products observed in 2N NaOH solution at 4 and 7 days, respectively
(c) Eqs. (8) and (9) were developed to explain the reaction products observed in 10N NaOH solution at 4 and 7 days, respectively

Finally, throughout this analysis it is also necessary to keep in mind the basic aspects related to the kinetics of a chemical reaction. It is known that an excessive increase either in the specific surface of the reactants (powdered rocks) or in the concentration of the solution (2N, 10N and so on), or both, as the case may be, may not only alter the rate but also the type of the chemical reactions involved. In this regard, for example, as mentioned above, Swenson and Gillott (3) showed that powdered reactive rocks react with strong concentrations of NaOH forming not only brucite and calcite but also pirssonite, quite an odd reaction product for concrete. On the contrary, when test conditions are not so severe (as those resulting from testing of rock aggregates instead of powdered rock, for instance), the dedolomitization of the rock may not take place appreciably, in spite of being in contact with an alkali solution rich in OH^- ions (Fig. 2).

Conclusions

Based on these results the following conclusions can be drawn:

1. XRD studies on rock cylinders showed that dedolomitization occurs at different degrees of intensity, depending on the petrographic characteristics of the rock. In fact, while no mineralogical changes could be found in the OLA and CBA samples, remarkable dedolomitization took place on the VAL sample. Despite the dolomitic nature of the three aggregates involved (i.e., aggregates likely to be dedolomitized) different mineralogical and microstructural characteristics (porosity, texture, grain size, percentage of insoluble residue) should account for this difference in behavior.
2. The comparative analyses of powdered samples ($< 75\ \mu m$) immersed in 1N NaOH solution revealed no differences in behavior. In fact, in the three cases studied (OLA, VAL and CBA) there was a complete dedolomitization, i.e., dolomite disappeared completely forming calcite and brucite.
3. On analyzing the samples of powdered rocks under more severe laboratory conditions (2N or 10N) uncommon compounds such as pirssonite and $Ca(OH)_2$ are formed by the dedolomitization reaction. Such compounds do not occur under real site conditions or more moderate laboratory tests. Thus, it would be reasonable to think that these products should not be considered when explaining the expansion mechanisms of this reaction (ACR).
4. The observed expansions in the alkali reactivity tests on the Valcheta (VAL) sample are due to the ACR. No ASR gels were found in the OM and SEM examinations. The dedolomitization reaction is the only remarkable mineralogical change which took place in the matrix-

aggregate transition zone (calcite and brucite are the only reaction products which were found).

5. The interface studies carried out by SEM examination on 5-year-old concrete samples made with the OLA aggregate showed evident signs of dedolomitization, though localized and only at a surface level. This dedolomitization, however, had no deleterious effects on the concrete. No expansions or deleterious changes were observed at the microstructural level.
6. The mechanisms put forward by Prince et al. seems to describe more accurately the reaction mechanisms that occur during the dissolution of the dolomite. It is deemed necessary, however, to take into account the existence of another parallel reaction mechanism (such as the phenomena of calcite dissolution and the related precipitation of portlandite) to be able to explain by application of this theory the results found in this investigation.
7. Although the expansion mechanism recommended by Deng and Tang (based on the principle of the "tightest pile of particles") is highly interesting (6), its application to the particular case of the Valcheta (VAL) sample is still controversial owing to the reduced compactness of this rock (a key factor for this mechanism).
8. From the above, the mechanism proposed by Hadley is adequate to explain the reaction mechanisms that operate in concrete structures under natural service conditions (room temperature, rock aggregates instead of powdered rock, pH in the order of 13).

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References

1. D.W. Hadley, Hwy. Res. Rec. 45, 1 (1964).
2. W.C. Sherwood and H. . Newlon Jr., Hwy. Res. Rec. 45, 41 (1964).
3. E.G. Swenson and J.E. Gillott, Hwy. Res. Rec. 45, 21 (1964).
4. C.A. Rogers, Cem., Concr. and Aggr. 8, 13 (1986).
5. M. Deng, S.F. Han, Y.N. Lu, X.H. Lan, Y.L. Hu and M.S. Tang, Cem. and Concr. Res. 23, 1040 (1993).
6. M. Deng and M.S. Tang, Cem. and Concr. Res. 23, 1397 (1993).
7. P.E. Grattan-Bellew and P.J. Lefebvre, Proc. 7th. Int. Conf. on AAR in Concrete, Ottawa (Canada), Noyes Publications, P.E. Grattan-Bellew Ed., 280 (1986).
8. T. Katayama, Proc. 9th. Int. Conf. on AAR in Concrete, London (U.K.), Concrete Society Publication, 508 (1992).
9. C.A. Milanesi and O.R. Batic, ACI Materials Journal 91, 633 (1994).
10. E.G. Swenson and J.E. Gillott, Hwy. Res. Board Bull. 275, 18 (1960).
11. D.W. Hadley, Proc. Hwy. Res. Board 40, 462 (1961).
12. A.B. Poole, Proc. 5th. Int. Conf. on AAR in Concrete, Cape Town, S252/34, 9 pp. (1981).
13. A. Carles-Gilbergues, J.P. Ollivier, B. Fournier and M.A. Bérubé, Proc. 8th. Int. Conf. on AAR in Concrete, Kyoto (Japan), Okada et al. Editors, 161 (1989).
14. W. Prince, R. Perami and M. Espagne, Cem. and Concr. Res. 24, 62 (1994).
15. H.N. Walker, Cement-Aggregate Reactions, Transp. Res. Bull. 525, 28 (1974).
16. J. Lemish and J.M. Moore, Hwy. Res. Rec. 45, 57 (1964).

17. C.A. Milanesi and O.R. Batic, Cem. and Concr. Res. 24, 1073 (1994).
18. O.R. Batic, C. Cortelezzi, P.J. Maiza, S. Marfil, C.A. Milanesi and R. Pavlicevic, Proc. 10a. Reunión Técnica "Ing. J.F. García Balado" 2, Buenos Aires (Argentina), AATH Editors, 95 (1991) (In Spanish).
19. C.A. Milanesi and O.R. Batic, Proc. Congreso Internacional de Ingeniería Estructural y Tecnología del Hormigón 1, Córdoba (Argentina), AATH & AIE Editors, 79 (1993) (In Spanish).
20. C.A. Milanesi, CIC-LEMIT Annual Reports, March/1993-March/1995 (In Spanish).
21. ASTM C 1260-94, Annual Book of ASTM Standards 04.02 (1994).
22. Cement-Aggregate Reactivity Sub-Committee CSA-A5 Task Group. Proposed Changes to CSA A23.1 and A23.2 as Regards Alkali-Aggregate Reactivity and Associated Test Methods. Draft Document (1992).
23. O.R. Batic and C.A. Milanesi, Document RILEM/TC-106/95/08, 11 pp. (1995).
24. A. Shayan, R.G. Diggins, I. Ivanusec and P.L. Westgate, Cem. and Concr. Res. 18, 843 (1988).
25. P.P. Hudec and J.A. Larbi, Cem. and Concr. Res. 19, 905 (1989).
26. Tang Mingshu, Deng Min, Lan Xianghui and Han Sufen, ACI Materials Journal 91, 26 (1994).
27. ASTM C 586-69 (1986), Annual Book of ASTM Standards 04.02 (1991).
28. CSA A23.2-14A, Methods of Test for Concrete, Canadian Standards Association, Rexdale, Ontario, Canada (1977).
29. ASTM C 227-87, Annual Book of ASTM Standards 04.02 (1987).
30. E.G. Swenson, ASTM Bull. 226, 48 (1957).
31. H.N. Walker, ASTM STP 169-B, 722 (1978).
32. P.E. Grattan-Bellew, Proc. 6th. Int. Conf. on the Effects of Alkalies in Concrete, Copenhagen (Denmark), Danish Concrete Association, G. M. Idorn and S. Rostam Editors, 303 (1983).
33. C.A. Rogers and R.D. Hooton, Proc. 8th. Int. Conf. on AAR in Concrete, Kyoto (Japan), Okada et al. Editors, 327 (1989).
34. CSA-A23.2-14A, Methods of Test for Concrete, Canadian Standards Association, Rexdale, Ontario, Canada (1990).
35. M.A. Bérubé and B. Fournier, Cement and Concrete Composites 15, 27 (1993).
36. CSA CAN3-A23.1-M77, Concrete Materials and Methods of Concrete Construction, Appendix B3, Tests for Alkali-Aggregate Reactivity, Canadian Standards Association, Rexdale, Ontario, Canada (1977).
37. G.M. Friedman, Journal of Sedimentary Petrology 29, 87 (1959).
38. K. Mather, A.D. Buck and W.I. Luke, Hwy. Res. Rec. 45, 72 (1964).
39. W.A. Deer, R.A. Howie and J. Zussman, Rock-forming minerals, Vol. 3, Sheet Silicates, Longmans, Green and Co., Ltd., Editors, 1962.
40. A.D. Buck and W.L. Dolch, ACI Materials Journal 63, 755 (1966).
41. Z. Chen and J. Wang, Cem. and Concr. Res. 17, 544 (1987).
42. I. Sims and P. Sotiropoulos, Proc. 6th. Int. Conf. on the Effects of Alkalies in Concrete, Copenhagen (Denmark), Danish Concrete Association, G.M. Idorn and S. Rostam Editors, 337 (1983).
43. E.J. Reardon, Cem. and Concr. Res. 20, 175 (1990).
44. P.J. Maiza and S. Marfil, Personal Communication (1993).
45. J. Duchesne and E.J. Reardon, Cem. and Concr. Res. 25, 1043 (1995).