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Questions and answers about alkali-carbonate reaction seen through the lens of osmotic mechanism

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Abstract

Previous studies on a fine-grained dolostone from Valcheta (Río Negro, Argentina) proved that this rock reacts deleteriously with concrete alkalis following a mechanism similar to ACR (ASR gel formation inside mortar or concrete microstructure is not observed; the greater the dedolomitization, the higher the expansion; the expansion is not controlled by SCM or lithium admixtures, and so on). Considering that none of the key mechanisms currently under discussion is able to fully describe the behavior of the Valcheta dolostone, the authors have recently proposed an alternative model of expansion for this rock, based on the osmotic phenomenon. The model explains the effect of the main factors of the concrete expansion process (pH of the pore solution and nature of the associated alkaline cation, temperature of the concrete, etc.) and answers the classic questions of the ACR: Why dedolomitization does not always produces expansion? Why is it so difficult to inhibit ACR?, Why the expansion of concrete increases with the maximum size of coarse aggregate?, among others. It is concluded that the model can explain the expansion of the most well-known alkali-carbonate reactive rocks, although it needs to be tested by the scientific community.

Keywords: alkali-carbonate reaction; dedolomitization; osmotic mechanism; dolomitic aggregates

1. INTRODUCTION

Fortunately, the alkali-carbonate reaction (ACR) is not a frequent durability problem for concrete. Unlike the alkali-silica reaction (ASR), ACR reaction has only been reported in Canada, USA, and China [1-6] and therefore, it is a research topic that has not been widely explored.

However, from the academic point of view, this subject is very interesting because of the controversies about the expansion mechanisms of this reaction [7-11].

Since its discovery in 1957 [12] different theories for ACR have been proposed, some of which have been disregarded over time [13-15].

Nowadays, there are two schools of thought: One headed by Tang and collaborators [16-20] and the other, by Katayama [21-24] and Grattan-Bellew and Katayama [25]. According to Tang's et. al theory

[16, 18, 20], aggregate expansion occurs when the elements that participate in the reaction (H_2O, OH^-, K^+, Na^+) penetrate into the limited spaces of the rock microstructure. These reactants use the clayey network of the rock as an access route, and their migration takes place because of the free energy change of the reaction ($\Delta G°_{To} < 0$). Simultaneously, the growth and rearrangement of calcite and brucite crystals around the dolomite crystals constitute a second component of the expansion.

Katayama [21-24] and Grattan-Bellew and Katayama [25] consider that the reaction of the expansive dolomitic aggregates is a combination of deleterious ASR and innocuous dedolomitization reaction: ASR originates from the presence of micro- (<60 µm) and cryptocrystalline quartz (<2 µm) in the aggregate, while the ACR generates brucite + calcite and a carbonatic halo around the aggregate.

Although in Argentina there are no records of concrete structures in service affected by the ACR, laboratory researches initiated in the early 1990s [26, 27] identified a variety of dolostone (Valcheta dolostone) in the area of Valcheta (province of Río Negro, Argentina) that presents expansive characteristics very similar to those of the typically reactive American carbonates [28-31].

The most relevant conclusions of these studies [26-31] are the following:

- In alkaline environment, dolostone has expansive behavior accompanied by a clear mineralogical transformation, which results in calcite and brucite formation, at the expense of dolomite (dedolomitization). Despite the deleterious phenomena observed in rock prisms, or in mortar or concrete bars (expansion, cracks, etc.), the formation of other reaction products (ASR gels) is not observed.

- When dolostone is used as fine or coarse aggregate, the higher the alkali content of the mixture or the test temperature the greater the mortar or concrete expansion,

- In coincidence with other researchers, the rock expansion in LiOH solution is less than that obtained in NaOH or KOH (for solutions of similar concentration).

- The influence of the aggregate grain size on the expansion responds to the classic pattern of ACR: the larger the aggregate particle size, the greater the mortar expansion.

- Reducing the alkali loading of concrete to 1 kg of Na_2O_{eq}/m^3 is not enough to inhibit the expansion of the dolostone used as coarse aggregate.

- Despite having used several supplementary cementing materials (SCMs), with tested effectiveness for ASR inhibition (40% fly ash, 60% ground blast furnace slag, 10% silica fume, 30% natural pozzolans), none was able to control the expansive effect of the reaction. On the contrary, some of them even promoted it.

- The incorporation of Li_2CO_3 into concrete (2.8% by weight of cement) could reduce the expansion by only approximately 25%.

Although the above statements correspond to the classic pattern of ACR, from a petrographic point of view, Valcheta dolostone does not have the distinctive textural characteristics of dolomitic rocks typically reactive due to ACR [32, 33]: small crystals of dolomite immersed in a fine-grained matrix of microcrystalline calcite and clay minerals (with other minor accessory minerals). However, this dolostone has both essential characteristics to develop ACR [34]: fine-grained dolomite crystals (<50 μm) and permeability to allow alkalis to get into the rock. Therefore, because none of the theories proposed in the literature could satisfactorily explain the behavior observed in Valcheta dolostone, the authors proposed an alternative theory based on the osmotic phenomenon [31]. This model explains the effect of the main factors involved in the rock expansion process: pH of the solution contained in concrete pores, curing temperature, alkaline cation associated with OH- ion, aggregate particle size, etc.

In this work, the most important features of the osmotic model are described, and its prediction capacity is analyzed to answer the classic questions of ACR and the experimental evidence available.

2.   THE ACR THROUGH THE LENS OF OSMOTIC MECHANISM

2.1   Is the osmosis phenomenon possible in dolomitic rocks?

Osmosis is the passage of solvent molecules (usually H_2O) between two solutions of different concentration, separated by a porous membrane, called semipermeable membrane (the membrane lets H_2O molecules pass, but offers resistance to the passage of the solute molecules). The movement of H_2O molecules occurs from the zone of lowest to highest concentration [35]. According to van't Hoff's expression (eq. 1), osmotic pressure can be expressed as follows:

$$\Pi = i.R.T.\Delta_c \tag{1}$$

Where Π is the osmotic pressure, i the van't Hoff correction factor, R the universal gas constant, T the absolute temperature, and Δ_c the concentration difference of the solutions [35].

Figure 2.1a shows the results obtained with the osmotic cell method (Figure 2.1b) [36, 37], applied to two dolomitic aggregates: one expansive (Valcheta dolostone, VD) and the other non-expansive (Olavarría dolostone, OD) [26].
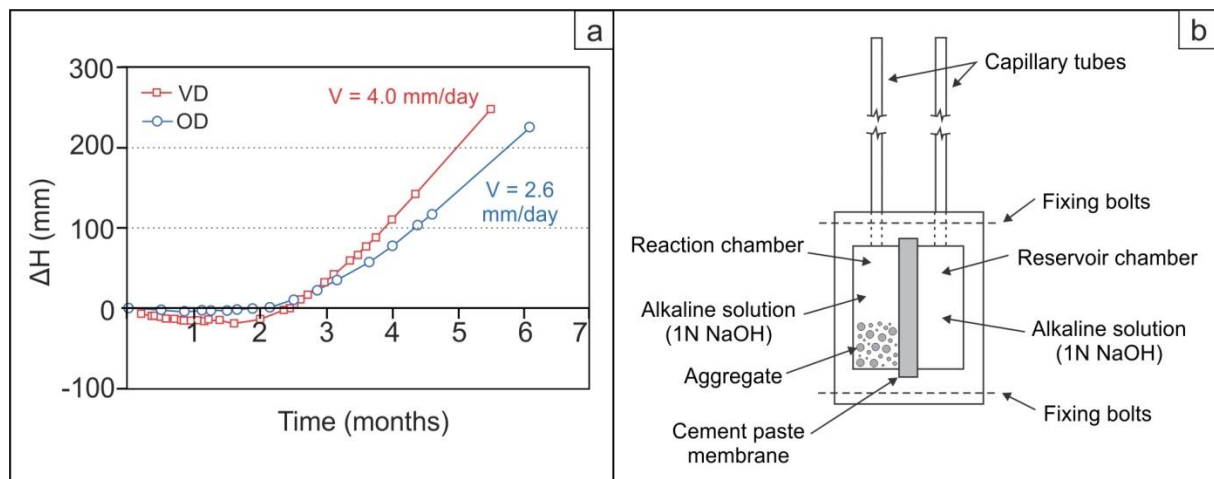
Figure 2.1: a) Results of the osmotic cell method: expansive dolostone (VD), non-expansive dolostone (OD); b) osmotic cell scheme.

Although this method was developed to study the expansion mechanisms of ASR [38], its application to dolomitic aggregates allows verifying that the osmosis process is also possible in ACR.

The dedolomitization reaction (eq. 2) developed by the dolomitic aggregate produces the accumulation of carbonate ion (CO_3^{2-}) in the reaction chamber.

$$CaMg(CO_3)_2 + 2\,OH^- \rightarrow Mg(OH)_2 + CaCO_3 + CO_3^{2-} \tag{2}$$
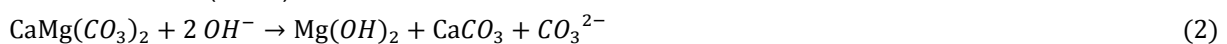
This causes the movement of H_2O molecules through the hydrated cement paste (semipermeable membrane) to match the concentration of carbonate ion in both chambers. This positive flow (from the reservoir to the reaction chamber) is due to the osmotic phenomenon and is generated by the dedolomitization of the aggregate. Note that Schmitt and Stark [37], based on the observation of the behavior of several aggregates in service, propose a rate of flow limit between 1.5 mm/day and 2.0 mm/day.

2.2 The osmotic model applied to ASTM C586 test method

When a rock prism is immersed in the test solution (1M NaOH), the ions (Na^+, OH^-) begin to diffuse into the rock pores, [OH^-] goes up and the dedolomitization reaction begins (Figure 2.2). By promoting the dissolution of CO_3^{2-}, this reaction triggers two simultaneous processes:

a) Flow of H_2O into the rock (osmosis). The difference in concentration (Δ_c) of CO_3^{2-}, between the rock pore solution and the test solution, is responsible for the osmotic pressure (eq. 1) that produces the rock expansion. However, for the osmotic phenomenon to take place, the distance between the pore and the prism surface must be large enough for the rock to behave as a semipermeable membrane (that is, the pore diameter and the tortuosity of the access channels to that point must be sufficiently intricate to hinder ion mobility as to generate an impermeable effect) [39].

b) Diffusion of CO_3^{2-} out of the rock. The same concentration gradient (Δ_c) that generates the osmotic process drives the diffusion of CO_3^{2-} out of the rock (named inverse diffusion, to distinguish it from ionic diffusion generated inside the rock).

When the reaction is incipient, the concentration of CO_3^{2-} within the rock pores is low, and the influence of the two phenomena described above (osmosis and inverse diffusion) is limited: the osmotic pressure inside the pore is low and is absorbed by the granular rock skeleton (rock expansion ≈ 0; [CO_3^{2-}] solution ≈ 0).

With the reaction progress, CO_3^{2-} concentration in the rock pores increases, the osmotic pressure rises, and rock prisms expansion begin to be recorded. At the same time, the inverse diffusion (displacement of CO_3^{2-} out of the rock) is greater, and the presence of this ion in the test solution begins to become evident.
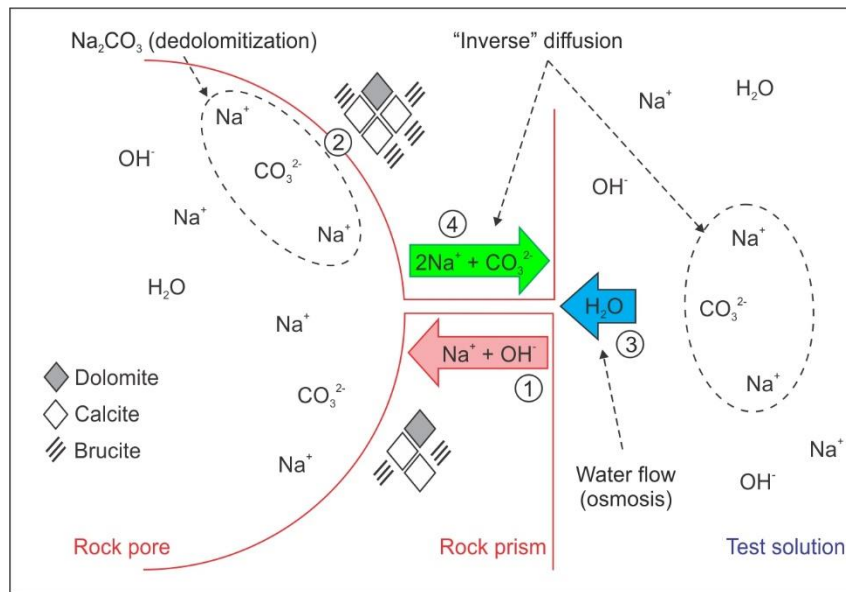
Figure 2.2: Stages of the expansion mechanism through osmosis. 1. Diffusion of Na^+ and OH^- ions into the rock pore. 2. CO_3^{2-} presence indicates that dedolomitization is in progress. 3. Osmosis (water flow due to Δ_c). 4. Inverse diffusion (diffusion of Na^+ and CO_3^{2-} ions outside the rock).

Figure 2.3 shows, in a prism cross section, the position of the reaction front (up to the zone where dedolomitization has occurred), the concentration profiles of CO_3^{2-} (soluble) and the solid reaction products (calcite + brucite). Point 1 represents the location of a pore, close to the prism surface, in which all the dolomite has been consumed (there is no more contribution of CO_3^{2-} to the rock pore solution). In addition, in this pore, carbonate ion concentration has decreased due to the inverse diffusion process. Point 2 is located near the border of the reaction front. In this area, the dedolomitization is incipient (there is still enough unreacted dolomite) and there is contribution of CO_3^{2-} from the surrounding sectors, so its concentration is greater than that of point 1. Point 3 is within the rock prism, away from the reaction front, so there has been no dedolomitization ($[CO_3^{2-}] = 0$).
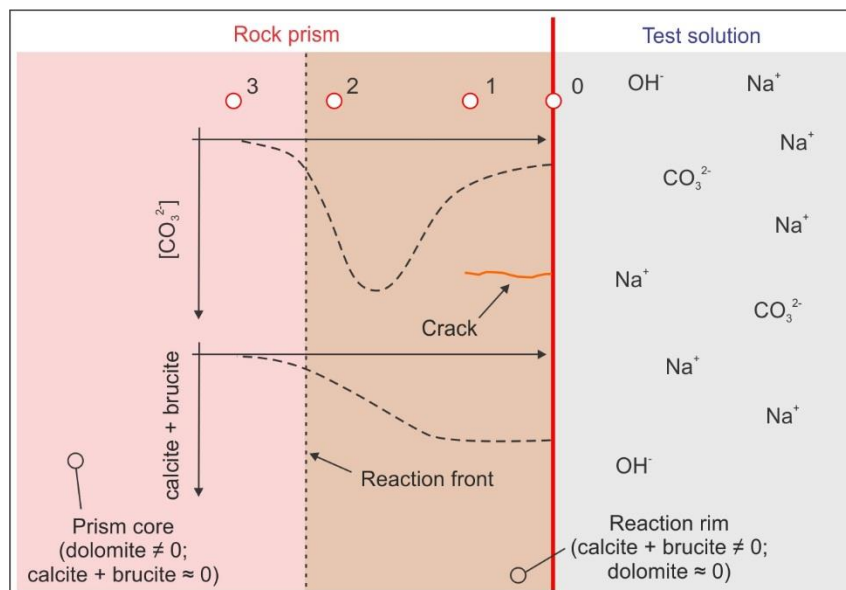

Figure 2.3: Concentration profiles of CO_3^{2-} (soluble) and solid reaction products (calcite and brucite) across the transversal section of the rock prism.

In this scheme, although the concentration of point 0 is close to that of the test solution (since it is a pore near the prism surface), its osmotic pressure is null (the distance between the pore and the surface is small, whereby the rock is unable to behave as a semipermeable membrane).

The extension of stages 1 and 2 (Figure 2.2) mark the induction period, which is governed, among other factors, by the rock permeability and the type of alkaline cation associated with OH^- (Na^+, K^+ or Li^+) [31].

For the osmotic mechanism to take place, the carbonate generated by dedolomitization must be soluble (Na_2CO_3, K_2CO_3, etc.). When dedolomitization is caused by $Ca(OH)_2$ (eq. 3), the carbonate precipitates as calcite ($[CO_3^{2-}] = 0$), and the osmotic pressure is zero ($\Delta_c = 0$). From this it follows that the expansion produced by the $Ca(OH)_2$ attack [31] must be attributed to the volume increase of the solid reaction products (eq. 3 predicts a volume increase of approximately 50%) and not to an osmotic phenomenon.

$$CaMg(CO_3)_2 + 2\,OH^- + Ca^{2+} \rightarrow Mg(OH)_2 + 2\,CaCO_3 \tag{3}$$
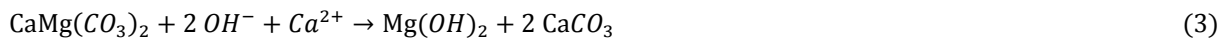
2.3 The osmotic model applied to concrete

Once CO_3^{2-} leaves the dolomitic aggregate (inverse diffusion) and gets into the matrix-aggregate transition zone (TZ), it is combined with $Ca(OH)_2$ produced by cement hydration to generate calcite ($CaCO_3$) (Figure 2.4).

This process reduces $Ca(OH)_2$ availability in the TZ and so the new CO_3^{2-} contribution, which reaches this zone with the advance of dedolomitization, cannot be consumed and remains dissolved in the cement paste pore solution.

Since the cement paste can act as a semipermeable membrane [38], the carbonate ion accumulation in the TZ causes the osmotic phenomenon to extend beyond the border of the aggregate and generate expansion in the paste.
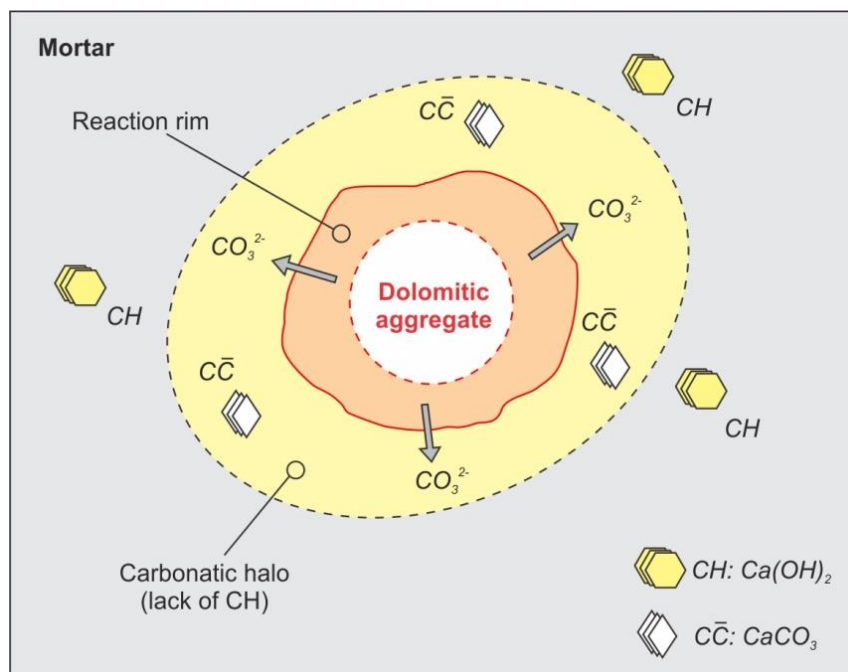

Figure 2.4: Scheme of the osmotic mechanism that operates in concrete [31]

3. THE OSMOTIC MODEL REGARDING ACR CLASSIC QUESTIONS

Ten questions concerning the ACR are presented, formulating their respective answers through the lens of osmotic theory.

3.1 Is dedolomitization necessary for expansion?

Yes, dedolomitization is a necessary condition to produce concrete expansion.

If ACR is caused by an alkaline solution of Na, K or Li, and the rock is able to work as a semipermeable membrane, the aggregate dedolomitization, in a first stage, generates the appearance of carbonate ions (CO_3^{2-}) that dissolve in the solution contained in the rock pores. These ions generate hydraulic pressure of osmotic nature, which is caused by the ingress of H_2O molecules into the rock and is responsible for the aggregate expansion.

In a second stage, CO_3^{2-} diffuses towards the TZ to form the carbonatic halo. During this phase, the remaining CO_3^{2-}, which has not been consumed to form the carbonatic halo, forces the paste to work as a semipermeable membrane, extending the expansive hydraulic pressure to the mortar surrounding the aggregate.

If ACR is activated by a $Ca(OH)_2$ solution, the osmotic phenomenon is restricted because of the low solubility of calcite. However, if the temperature and the contact time between the rock and the solution are high and long enough, the volume of the solid reaction products (calcite + brucite) is considerably greater ($\approx 50\%$) than the volume of reacting dolomite, and expansion is possible. However, the interest of this last aspect is merely academic, since the reaction rate of $Ca(OH)_2$ attack is very slow at room temperature.

3.2 Why does dedolomitization not always produce expansion?

To have expansion, the rock must be permeable enough and, in turn, behave as a semipermeable membrane. Dolomite crystals must be surrounded by a clayey interconnected network that allows the ingress of reactive ions (OH^-, Na^+, K^+, etc.) and hinders the diffusion of carbonate ions (CO_3^{2-}).

If the rock has high compactness and, therefore, low permeability, the ingress of the alkaline solution, and also the attack velocity, will be very slow. In other words, dedolomitization could generate deleterious effects, but in a period of time that would exceed the service life of most structures; that is, in practical terms, the rock could be considered innocuous.

In summary, dedolomitization is a necessary but not enough condition.

3.3 Is it necessary for the dolomitic aggregate to have the typical characteristic texture to be potentially expansive?

For the rock to have expansive behavior, two simultaneous conditions must occur:

• The dolomite crystals must be small enough (<50 μm) for the reaction to proceed quickly and can be verified within a period of time comparable to the expected service life of the structure.

• The rock must have a minimum insoluble residue content (> 5% approximately), mainly clayey and interstitial. This structure must form a network of channels that, on the one hand, allows the access of aggressive ions (OH^-, Na^+, K^+) to the rock and, on the other, can behave as a semipermeable membrane.

The main condition for the rock to be expansive is that it is composed of dolomite. In other words, in light of the osmotic theory, it is not essential that the rock has calcite or the characteristic texture of Canadian carbonates, which are typically reactive (dolomite crystals embedded in a microcrystalline calcite matrix). It is also not essential that the rock is particularly compact (Valcheta dolomite is highly porous and permeable, and still shows a deleterious expansive behavior).

3.4 Why does the expansion increase with the aggregate size?

In order for the rock to work as a semipermeable membrane, the diameter of the aggregate particle must be large enough to hamper the transport of the CO_3^{2-} out of the rock through the intricate clayey rock network. The smaller the particle size, the closer to the surface its pores will be, which will facilitate the transport of CO_3^{2-} outside the rock, thus, limiting its work as a semipermeable membrane.

This could explain why it is possible to see aggregate particles of small size (less than 1 mm), completely dedolomitized, without any visible cracks around [30].

3.5 Why does the rock in LiOH expand less than in NaOH or KOH?

Experiences carried out by Milanesi [31] show that the beginning of rock expansion, when using several alkaline solutions of similar concentration, is related to the atomic radius of the alkaline cation associated with the OH^- ion. Indeed, the time of the incubation phase is shorter with LiOH (≈ 2 weeks), than with NaOH (≈ 6 weeks) or KOH (≈ 12 weeks). In other words, the smaller the size of the cation, the faster

the expansion begins, which indicates that the process is diffusive and the rock permeability is very important for the attack mechanism.

On the other hand, several studies [31, 39, 48] agree that the expansion of reactive dolomitic rocks (ACR) in LiOH is always smaller than in NaOH or in KOH (for solutions of similar concentration). According to the osmotic theory, since Li_2CO_3 solubility ($\approx$ 1.3%) is much lower than Na_2CO_3 (23.5%) or K_2CO_3 (52.7%) solubility [49], it is clear that the concentration difference (Δ_c) that can be achieved with LiOH, on which the osmotic pressure depends (eq. 1), will always be lower than that obtained with NaOH or KOH.

3.6   Why are SCMs not effective in inhibiting ACR?

In general, it is accepted that supplementary cementitious materials (SCMs) allow controlling the deleterious effects of ASR through the following mechanisms [40]:

- Reduction of concrete alkalinity
- $Ca(OH)_2$ consumption
- Refinement of concrete pores

The reduction of alkali content limits the pH of the concrete pore solution and thus, the solubility of the reactive silica. $Ca(OH)_2$ is necessary for gel formation: without $Ca(OH)_2$, silica remains dissolved in the pore solution, without generating expansion. Finally, the refinement of the concrete pore structure limits the mobility of the ions involved in the reaction (Na^+, OH^-, etc.) and slows ASR.

In ACR, unlike ASR, the reduction of alkali content, in practical terms, has less beneficial effect and only postpones the expansion of concrete [28, 41].

The role of $Ca(OH)_2$ in ACR is also different. $Ca(OH)_2$, when combined with CO_3^{2-} dissolved in the pore solution of the cement paste, causes it to precipitate (calcite), leading to the formation of the carbonatic halo. During this process, $Ca(OH)_2$ consumption has a beneficial effect for concrete, since it delays the activation of the osmotic phenomenon in the paste. In the long term, once the carbonation halo ($Ca(OH)_2$ $\approx$ 0) is formed, this zone becomes the reservoir of CO_3^{2-}, which comes from the aggregate (product of dedolomitization) and promotes osmotic pressure inside the paste. In this sense, by creating areas without $Ca(OH)_2$ in the paste, the SCMs produce a similar effect to carbonatic halos: they allow carbonate ions to remain dissolved in the concrete pore solution and keep the osmotic process active inside the paste. Finally, the refinement of pores contributes to the work of the paste as a semipermeable membrane, favoring the osmotic process.

In summary, for ACR, the only beneficial effect that SCMs have (although transitory) is to defer the expansion of concrete, by reducing its alkalinity. Then, the consumption of $Ca(OH)_2$ by the SCMs would only move the osmotic process to the paste.

Several experiences [28, 29, 42] show that the effect of incorporating a SCM (fly ash, natural pozzolan, silica fume, etc.) into the mortar or concrete is always the same: the initial expansion decreases but, in the long term, it accelerates, reaching or overcoming the reference mixture (without addition). This peculiar behavior can be explained by the preceding reasoning.

3.7   Which is the role of calcium hydroxide in ACR?

For Tang et al. [19], the presence of $Ca(OH)_2$ in hydrated cement paste contributes to ACR development by different routes. First, the CO_3^{2-}, present in the concrete pore solution, when reacting with $Ca(OH)_2$, moves the equilibrium of the dedolomitization reaction to the right (acceleration) and results in alkali recycling (eq. 4):

$$CO_3^{2-} + Ca(OH)_2 \rightarrow CaCO_3 + 2\,OH^- \tag{4}$$

On the other hand, according to these researchers, calcium hydroxide (similar than Na, K or Li) can react with dolomite and generate expansion. In summary, for these researchers, the role of $Ca(OH)_2$ in the ACR is greater than in ASR.

Without $Ca(OH)_2$, there is no expansion by ASR [43, 44]: silica dissolves, but gel does not form (there is no expansion). Otherwise in the ACR the presence of $Ca(OH)_2$ is not necessary for the expansion. The clearest example is the ASTM C586 test: the rock can expand in 1M NaOH solution, without external calcium contribution. In addition, as discussed in Section 3.6, in the long term the use of SCMs, far from inhibiting expansion (as occurs in ASR), increases it.

3.8 Why do magnesite and calcite expand?

Tang and Deng [20] reported expansion results obtained in cylindrical mortar specimens (ϕ 10 mm x 40 mm), made from pure samples of magnesite ($MgCO_3$) and calcite ($CaCO_3$), immersed in 10% KOH solution at 150° C. These researchers support that the expansive behavior recorded in these mortars is due to the crystallization pressure generated by the solid products of the reaction ($Mg(OH)_2$ and $Ca(OH)_2$) (eqs. 5 and 6):

$$MgCO_3 + 2\ \text{KOH} \rightarrow Mg(OH)_2 + K_2CO_3 \tag{5}$$

$$CaCO_3 + 2\ \text{KOH} \rightarrow Ca(OH)_2 + K_2CO_3 \tag{6}$$

Alternatively, these expansive processes can be explained by the osmotic theory: when using KOH as the attack solution, both chemical reactions produce soluble potassium carbonate (K_2CO_3), which generates the osmotic pressure inside the mortar, at the level of the cement paste-aggregate interface, with the consequent expansion.

3.9 Why does the dolomitic rock of Kingston (Canada) expand?

Katayama [21-24] established that the expansion associated with ACR is caused by ASR, due to the presence of cryptocrystalline quartz in the aggregate.

Although several studies have demonstrated the existence of clear signs of ASR [11, 23, 24], the concretes evaluated are in general of advanced age (> 25 years) or exposed to very rigorous test conditions (1 N NaOH solution at 80 °C for 28 days). In the presence of metastable siliceous phases (cryptocrystalline quartz) in the aggregate, this makes the formation of ASR gels inevitable.

In the opinion of the authors, Kingston's dolomitic rocks are affected by both reactions (ASR + ACR) and this explains the existing confusion. Experiences carried out with the Kingston aggregate [45] show that, when 40 % of fly ash is incorporated into the mortar (amount enough to control ASR [32, 33]) its expansion decreases slightly. This behavior can be interpreted as part of the effect of the SCM on ASR.

3.10 Is there a way to inhibit ACR?

In a first instance, it seems a difficult objective. First, the osmotic pressure, which originates the concrete expansion, begins with the carbonate ion (CO_3^{2-}) dissolution inside the rock, as part of the dedolomitization reaction. Since this reaction is spontaneous, it is not possible to inhibit it, even by drastically reducing the alkali content of the concrete, as has been demonstrated experimentally [6, 41, 46].

An alternative that has been examined by some researchers [47], and could be deepened, is to use chemical additives to balance the CO_3^{2-} concentration between the rock and the hydrated cement paste. These experiences show that the use of Li_2CO_3 reduces the expansion to ~50%. However, the life time of this additive in concrete is low, since CO_3^{2-} reacts very easily with $Ca(OH)_2$ to form calcite, neutralizing it.

4. CONCLUSIONS

The osmotic model is simple and explains the effect of the main factors of the concrete expansion process:

- Effect of alkaline cation: The expansive mechanism basically depends on the alkaline cation associated with the hydroxyl ion.
  - ✓ If the attack is caused by an alkaline solution of Na, K or Li, and the rock is able to act as a semipermeable membrane, the expansion is of osmotic nature (the pressure is caused by the entrance of H_2O molecules into the rock, due to CO_3^{2-} dissolution, generated by dedolomitization). In a second stage, the CO_3^{2-} diffuses towards the TZ to form the carbonatic halo: the remaining carbonate ions, which have not been consumed by calcium hydroxide in the halo formation, force the paste to work as a semipermeable membrane, extending the expansive hydraulic pressure to the mortar surrounding the aggregate.

The cation influences the process of rock expansion, indirectly, modifying:

      - Solubility of the alkali carbonate resulting from dedolomitization (the higher the carbonate solubility, the greater the osmotic pressure). This explains why the rock expansion in LiOH is less than that recorded in NaOH or KOH.

      - Diffusion velocity of the ions that participate in the process (Na^+, K^+, Li^+, CO_3^{2-}): the smaller the cation size (Li < Na < K), the faster the expansion begin and the more limited the extension of the main expansion phase is (this makes the inverse diffusion process faster, which relaxes the osmotic pressure and limits the rock expansion). This last phenomenon would explain why the expansion of the prism in KOH is greater than that obtained in NaOH.

✓ If the attack is motivated by a calcium hydroxide solution, the osmotic phenomenon is restricted by the low solubility of calcite. However, if the temperature and the contact time between the rock and the solution are high and long enough, the volume of the solid products of the reaction (calcite + brucite) is considerably greater ($\approx$ 50%) than the volume of reacting dolomite, and expansion is possible.

- The pH effect of the contact solution. According to Tang et al. [17], the higher the pH, the more aggressive the reaction. The increase in pH accelerates the dedolomitization reaction due to the difference in CO_3^{2-} concentration (Δ_c). According to van't Hoff's expression (eq. 1), the osmotic pressure (Π) is directly proportional to Δ_c.

- Temperature effect. In ACR, the higher the temperature (T), the greater the expansion. According to van't Hoff's expression (eq. 1), the osmotic pressure (Π) is directly proportional to T.

- Role of water in the expansive mechanism. The movement of the water molecules into the aggregate is driven by the osmotic phenomenon itself, to balance the difference in concentration of the carbonate ion between the solution contained in the rock pores and the adjacent mortar.

- Need for a semipermeable membrane. To expand, the rock must behave as a semipermeable membrane. For this, dolomite crystals must be surrounded by an interconnected clayey network, which allows the entrance of reactive ions (OH^-, Na^+, K^+, etc.) and hinders the diffusion of CO_3^{2-} outside the rock. This would explain the existence of numerous cases reported in the literature [31, 50, 51] of high compact rocks (low water absorption and low permeability), with insoluble non-clayey residue, in which, even when the progress of dedolomitization is evident, the rock expansion is negligible or zero.

In view of the above, the authors consider that the model is ready to be tested by the scientific community.

5. ACKNOWLEDGEMENTS

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