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Similarity between alkali–aggregate reaction and the natural alteration of rocks

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Abstract

This article aims to demonstrate that the mechanisms governing the natural alteration of rock also lead to the development of alkali–aggregate reaction. We have used the alteration of granite to pinpoint two processes that are often involved. In the first, existing minerals are transformed into minerals with expansive properties (such as the transformation of biotite into chlorite and expansive smectite). In this case, the expansion occurs in the structural layers of the mineral and may cause relatively localized deterioration in the original material. In the second process, the mineral constituents are initially hydrolyzed in the surrounding water, which gradually becomes saturated with silica, alumina, and various cations. New phases evolve from this water, yielding gels or well-crystallized products. In the case of the granite investigated, the product is laumontite ($Al_2O_3 \cdot 4SiO_2 \cdot CaO \cdot 4H_2O$), which is formed from the water in the cracks. The crystallization of this zeolite generated significant cracking in the samples examined. We have demonstrated experimentally that similar type of zeolite ($Al_2O_3 \cdot 2SiO_2 \cdot CaO \cdot 5H_2O$) forms readily when a mixture of lime and metakaolin is reacted with water in the presence of sodium hydroxide. This mixture contributes the silica, alumina, and cations required to initiate the reactions.

Keywords: Alkali–aggregate reaction; Alteration; Zeolite; Granite; Metakaolin

1. Introduction

The natural materials used as concrete aggregate nearly always react with water. Most aggregates more or less slowly hydrolyze, releasing various components into the reaction environment. The hydrolysis kinetics depends on the nature of the aggregate constituents, their size, their crystallinity, and rock texture as well as experimental conditions (temperature, pH, moisture, and so on).

Although mainly siliceous materials such as opal and chalcedony have often been implicated in alkali–aggregate reaction, we now know that a large range of silicate rocks can also produce this type of alteration: granite and quartzite [1]; phyllite, quartzite, and gneiss [2]; granodiorite [3]; sedimentary aggregates [4]; chert, jasper, and siltstone [5].

To simplify the approach, one can assume that most silicate rocks used as concrete aggregates are composed of a few main types of mineral: quartz, feldspars, and micas. They are produced by the combination of four essential components in varying proportions and geometry: silica, alumina, water, and compensating cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}). In concrete, these components react with lime, which contributes basicity and calcium ions. Consequently, studying the potential of reaction between the concrete aggregates and interstitial liquid can be reduced to a simple reaction system containing the essential constituents in suitable proportions. Since this kind of study is monotonous to implement exhaustively, we have limited our experiment to several simple cases that enable us to demonstrate the similarity between alkali–aggregate reaction and the processes by which rock is naturally altered.

2. Methodology

We opted for a simple mixture composed of lime, metakaolin, and demineralized water.

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Table 1
Chemical composition of kaolin

SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	SO_3	LOI	Total
57.5	27.0	2.2	–	1.0	–	0.5	1.9	1.0	1.3	8.0	100.4

- The metakaolin was obtained by heating commercial kaolin to 750°C; the chemical composition is provided in Table 1. The heating process is designed to destroy the material's crystallinity and enhance reactivity. Metakaolin contributes silica, alumina, and slight amounts of Na^+, K^+, to the reaction environment.
- Hydrated lime was used, which contributes calcium ions as well as basicity.
- Demineralized water was used to reduce the possibility of introducing unwanted ions into the system.

Mixing the metakaolin and lime with water results in a specific type of aluminosilicate cement paste–aggregate interface. This mixture serves as the basis for investigating the potential for alkali–aggregate reaction.

The reaction products were demonstrated by using different methods of investigations:

- X-ray diffraction (XRD) analysis with CuKα radiation,
- differential thermal analysis applied in air atmosphere at heating rate of 10°C/min with 40 mg of sample,
- ICP emission for major and minor elements and ICP-MS for trace elements.:

From our perspective, two figures are essential in order to properly interpret the development of the different reactions. Fig. 1 provides the variations in silica and alumina solubility in response to pH. It shows that alumina is highly soluble in acid (pH <4) and highly alkaline (pH >11) environments, but very slightly soluble in the pH range of natural water (4<pH<10). Silica is weakly soluble under a pH of 10 but is radically soluble beyond this threshold. Both silica and alumina are therefore highly soluble in the typical pH range of interstitial liquid in concrete (pH of about 13). Fig. 2 gives lime solubility in the presence of alkali. It shows that lime solubility decreases inversely to alkali content and temperature.

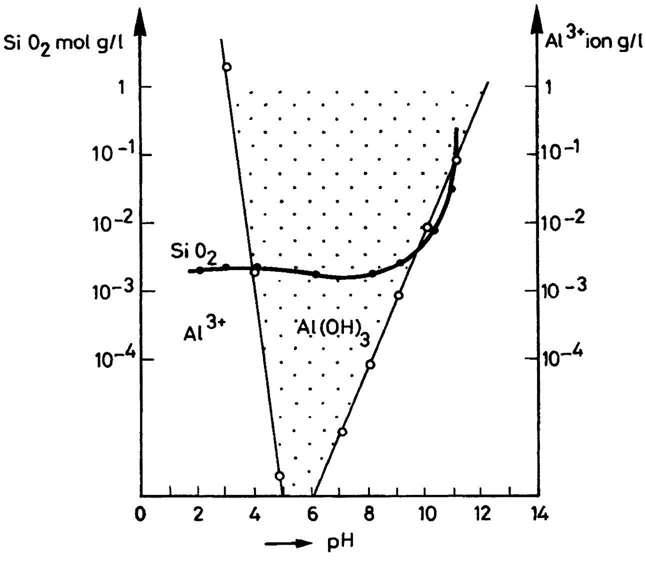

Fig. 1. Silica and alumina solubility versus pH; [6,7].

3. Results and discussion

When metakaolin, lime, and water are combined, different phases may crystallize, depending on the conditions. The following describes three experimental results illustrating the reactions that can occur in solution between reactive aggregates and cement paste. We will point out the similarity between the mechanism underlying these reactions and the natural process by which rocks are altered.

3.1. Alkali–aggregate reaction with a simplified reaction model

We begin with a base mixture comprising 60% metakaolin and 40% lime. Mixing these ingredients with demineralized water yields a paste that can be cast in sealed tubes and maintained under controlled conditions. Three cases were considered.

3.1.1. Case 1: high-calcium concentration in the interstitial liquid

When the basic mixture is mixed and maintained at ambient temperature, lime solubility is high. There is an

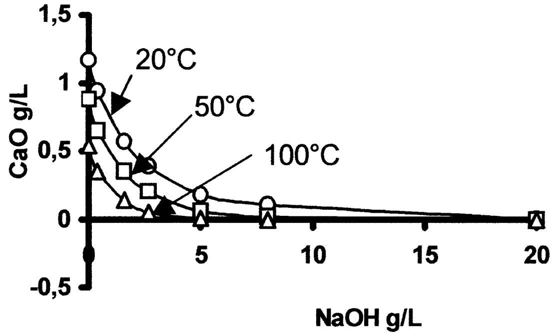

Fig. 2. Lime solubility in presence of alkali [8].

abundance of calcium ions in the interstitial liquid and the pH is greater than 12.5 because of the presence of some alkali brought by the metakaolin. Under these conditions, silica and alumina go into solution more or less rapidly, reacting to yield two distinct hydration products: tetracalcium aluminate hydrate ($Al_2O_3{\cdot}4CaO{\cdot}19H_2O$) and a calcium silicate of the CSH type ($CaO{\cdot}SiO_2{\cdot}H_2O$). Both are precipitated as soon as saturation levels are reached. The aluminate is clearly crystallized, while the silicate is much less so. This is represented by Eq. (1):

$$\begin{aligned}&\mathrm{Al_2O_3\cdot 2SiO_2 + 5Ca(OH)_2 + 19H_2O}\\ &\text{Metakaolin}\qquad\text{Lime}\qquad\text{Water}\\ &\quad\rightarrow \mathrm{Al_2O_3\cdot 4CaO\cdot 19H_2O}\\ &\qquad\text{Tetracalcium aluminate hydrate}\\ &\qquad + \mathrm{CaO\cdot SiO_2\cdot H_2O}\\ &\qquad\quad\text{Calcium silicate hydrate}\end{aligned}\tag{1}$$

3.1.2. Case 2: low-calcium concentration in the interstitial liquid

When the basic mixture is maintained at 40°C after mixing, lime solubility decreases due to heat (Fig. 2). Under these conditions, the silica and alumina in solution precipitate using the available calcium, yielding gehlenite hydrate ($Al_2O_3{\cdot}SiO_2{\cdot}2CaO{\cdot}8H_2O$) and calcium silicate hydrate (CSH) ($CaO{\cdot}SiO_2{\cdot}H_2O$). Eq. (2) illustrates this evolution.

$$\begin{aligned}&\mathrm{Al_2O_3\cdot 2SiO_2 + 3Ca(OH)_2 + 6H_2O}\\ &\text{Metakaolin}\qquad\text{Lime}\qquad\text{Water}\\ &\quad\rightarrow \mathrm{Al_2O_3\cdot SiO_2\cdot 2CaO\cdot 8H_2O}\\ &\qquad\text{Gehlenite hydrate}\\ &\qquad + \mathrm{CaO\cdot SiO_2\cdot H_2O}\\ &\qquad\quad\text{Calcium silicate hydrate}\end{aligned}\tag{2}$$

3.1.3. Case 3: calcium concentration drastically lowered due to the addition of alkali (NaOH)

In this instance, the composition of the mix used in the preceding case was modified by replacing 10% of the lime with sodium hydroxide; the cement paste was maintained at 40°C. The introduction of alkali results in a reversion of lime dissolution as shown in Eq. (3) (contribution of hydroxyl ions).

$$\mathrm{Ca(OH)_2 \leftrightarrows Ca^{2+} + 2OH^-}\tag{3}$$

The calcium concentration in the interstitial liquid decreases, but the pH increases. Under these conditions, the highly soluble silica and alumina precipitate with little calcium in solution to yield a calcic zeolite with the formula $Al_2O_3{\cdot}2SiO_2{\cdot}CaO{\cdot}5H_2O$ (ICDD-PDF11-589). For clarity, this zeolite will be referred to as zeolite X throughout this paper. Eq. (4) and Fig. 3 illustrate this evolution.

$$\begin{aligned}&\mathrm{Al_2O_3\cdot 2SiO_2 + Ca(OH)_2 + 5H_2O}\\ &\text{Metakaolin}\qquad\text{Lime}\qquad\text{Water}\\ &\quad\rightarrow \mathrm{Al_2O_3\cdot 2SiO_2\cdot CaO\cdot 5H_2O}\\ &\qquad\text{Zeolite X}\\ &\qquad + \mathrm{CaO\cdot SiO_2\cdot H_2O}\\ &\qquad\quad\text{Calcium silicate hydrate}\end{aligned}\tag{4}$$

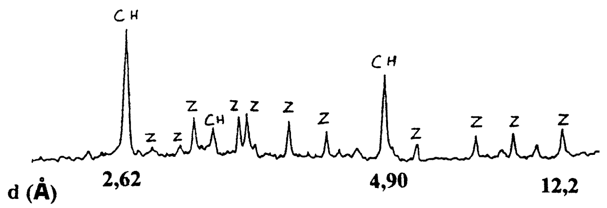

Fig. 3. X-ray diagram of zeolite X.

Succinctly put, the results reveal that reaction products clearly vary depending on operating conditions. They may either be gels or well-crystallized products. They may be aluminates, silicates, or aluminosilicates. All these products crystallize in a low volume of liquid containing few leachates in which silica, alumina, and cations gradually dissolve. The introduction of alkalis in the system results in newly formed components that are calcium poorer.

If one assumes that the reaction mixes under study (metakaolin+lime+water) simulate the cement paste–aggregate interface, than one would expect that alkali–aggregate reaction would also yield similar products. In particular, as Ca^{2+} is always low in concrete pore solution, products similar to Case 3 would be expected. The following example shows that zeolites can be formed in this condition through the natural alteration of granitic aggregate.

3.2. Real case of the natural alteration of granitic aggregate

This study involves cores measuring 70 mm in diameter taken from a granite mass along the shores of the Rizzanèse in Corsica. Macroscopic observation, along with permeability and porosity testing, were used to classify the specimens into two groups: those apparently sound with low-helium permeability (10^{-17} m^2) and low porosity (lower than 1%); and those that are leached in appearance and with a helium permeability of the order of 10^{-15} m^2 and a porosity of about 2%.

All specimens were stored immediately after coring in a covered core bank to protect them from the weather. After 6 months of storage, many sound cores clearly evidenced cracking and produced a fine, pink-colored powder (Fig. 4). Moreover, the coarse fragmentation of the leached cores revealed thin layers of a greenish powder, which tends to generate cracks locally in the samples. Representative cohesive fragments of both groups were examined under optical microscope using polarized light; scrapings of the powdered products were subjected to XRD.

3.2.1. Leached specimens

Thin slides produced from cohesive fragments were used to reveal the main minerals in the granite: quartz, feldspar,

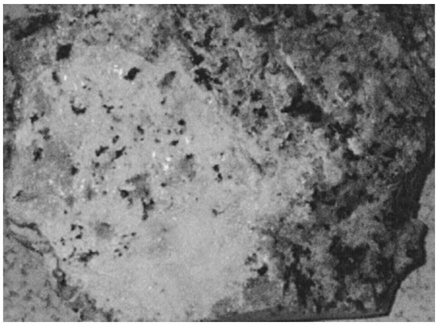

Fig. 4. Pink–colored powder of laumontite.

and mica, as well as many minor minerals such as chlorite, amphibole, and alanite. The feldspars were altered and the biotites highly chloritized.

An XRD diagram of the greenish powder shows the base-peak located at 14 Å on a standard slide. When the specimen is heated to 500°C, the peak at 14 Å divides into two peaks at 14 and 10 Å. When the specimen is treated with ethylene glycol, however, the peak at 14 Å divides into two peaks at 14 and 17 Å. This demonstrates the presence of chlorite–smectite interstratified mineral.

Alteration of the granite has therefore led to the formation of an expansive mineral. This expansion, which results from the adsorption of a water molecule between layers, causes localized cracking in the rock.

3.2.2. Sound specimens

These specimens comprised mainly quartz, feldspars, and mica, as well as many minor minerals such as epidote, sphene, sericite, ilménite.

XRD and chemical analysis were used to identify the pink powder as a calcic zeolite with the chemical formula $Al_2O_3 \cdot 4SiO_2 \cdot CaO \cdot 4H_2O$. This zeolite was formed through the natural alteration of granite in the absence of cement. Its crystallization caused significant cracking in the rock (Fig. 5).

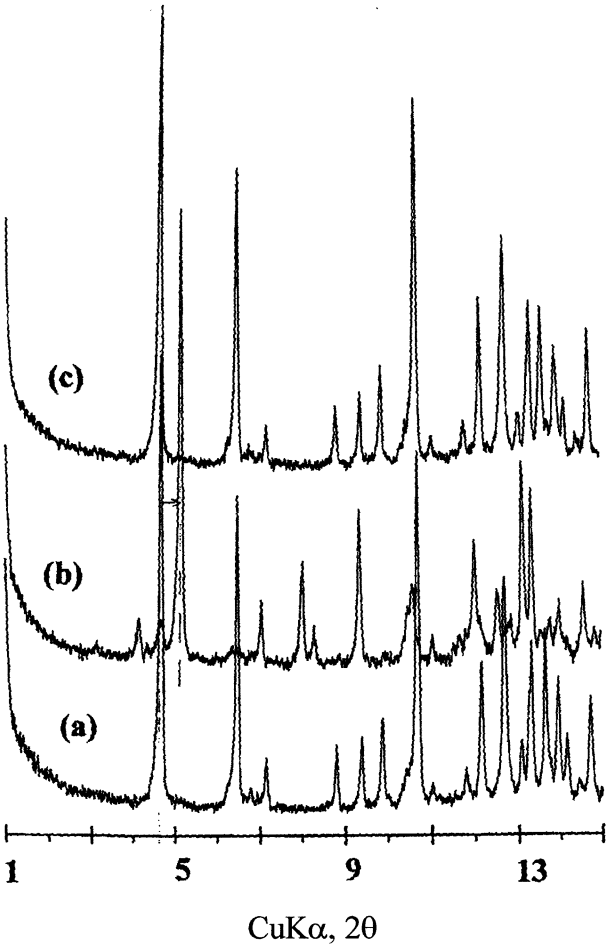

Fig. 6. XRD of laumontite (a) normal slide; (b) heated slide; (c) ethylene-glycol treated slide.

XRD (Fig. 6a compare to Fig. 6c) shows that ethylene glycol adsorption does not cause expansion of this zeolite. The mineral structure is clearly modified, however, when the powder is heated. As illustrated in Fig. 6b, heating does not simply displace the X-ray peaks; it replaces the initial product with one or more new products.

Fig. 5. Cracks due to laumontite crystallization.

The thermal analysis curves (Fig. 7) reveals mass loss during heating in four successive steps, which correspond to evaporation of water from the mineral at 120°C, 155°C, 390°C, and 450°C.

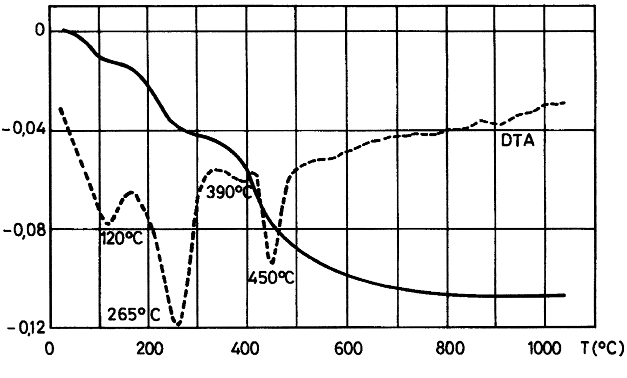

Fig. 7. Thermal analysis curves of laumontite.

Table 2
Chemical composition of laumontite

SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	SO_3	LOI	Total
57.12	19.13	1.71	0.02	0.64	8.74	1.15	1.17	0.21	0.16	9.74	99.79

These two examples definitely indicate two possible routes by which concrete aggregates are altered.

- In the first case, aggregates are altered by direct conversion of the initial minerals into other minerals (e.g., conversion of biotite and plagioclase to expansive smectite-type chlorite). The expansion occurs in the structural layer of the mineral and may result in more or less localized cracking.
- In the second case, the initial minerals are hydrolyzed in fissure solution in the rock, then recrystallized into new products that are quite distinct from the initial minerals. Precipitation occurs in the saturated liquid; crystal growth can cause the rock to burst.

3.3. Comparison of AAR and natural alteration

The above findings definitively demonstrate that the evolution of silicate rock does not always yield the conventional phyllites commonly encountered as a result of hydrothermal or meteoric alterations (e.g., kaolinite, illite, smectite). This evolution may also lead to the crystallization of loose 3D zeolitic lattices.

Among the newly formed products by the natural alteration of granite, we identified laumontite, a zeolite with the formula $Al_2O_3 \cdot 4SiO_2 \cdot CaO \cdot 6H_2O$. Its mechanism of formation is the same as the one which enabled us to obtain a calcic zeolite from a mixture of lime, metakaolin, and NaOH. Two successive phases are involved: the hydrolysis of major constituents (silica, alumina, and cations) in the interstitial liquid, followed by precipitation of the hydrate phases.

In the case relating to zeolite X crystallization ($Al_2O_3 \cdot 2SiO_2 \cdot CaO \cdot 5H_2O$), silica, alumina, and some alkali (Na^+, K^+) are contributed by the metakaolin, while lime and NaOH contribute most compensating ions (Na^+ and Ca^{2+}). Since silica and alumina are both highly soluble at this high pH, the zeolite formed evidences the same SiO_2/Al_2O_3 ratio as in the initial metakaolin.

In the case relating to laumontite crystallization ($Al_2O_3 \cdot 4SiO_2 \cdot CaO \cdot 6H_2O$), the pH level (8 to 10) results from the hydrolysis of aluminosilicates in the granite. At these pH values, silica is more soluble than alumina (Fig. 1) and the reaction environment is therefore relatively higher in silica. This accounts for the SiO_2/Al_2O_3 ratio being higher in the laumontite than in the zeolite X.

These zeolites are 3D arrangements of SiO_2 tetrahedrons in which a certain number of Si^{4+} ions have been replaced with Al^{3+} ions. The resultant charge lacking is compensated by the Na^+, K^+, and Ca^{2+} cations. Although the alkali ions do not explicitly appear in the structural formula of laumontite, they are present in the cage structure as indicated in the chemical analysis provided in Table 2. The same holds for iron, which gives the powder its pink color.

In the deterioration caused by AAR, the newly formed products can crystallize from the solution at the cement paste–aggregate interface. They can also be obtained by direct transformation of the minerals initially involved and lead to the formation of expansive smectites. A few essential items need to be pointed out at this time.

- The aggregates generally contain all the components required for the development of AAR; the alkalis and calcium often occur in the initial rock.
- AAR can develop without cement, although it is a very slow process which occurs at the geological scale. The cement contributes the alkalinity needed to cause the silica and alumina in the aggregate to go into solution relatively quickly.
- The newly formed products are not always gels; they may also be zeolitic structures. In these zeolites, alkalis need not to be present in significant quantities since the electrical balance of the 3D zeolite network can be provided by substitutions of the type 2 (Na^+, K^+) — Ca^{2+} within the cage structure. As is commonly known, zeolites freely exchange cations and water molecules with the surrounding environment.
- The actual example cited in this study demonstrates that the clearly crystallized components formed in a confined environment can also generate forces strong enough to crack rock and concrete.

4. Conclusion

Basically, most aluminosilicates present in concrete aggregates have the potential for developing AAR on the long term. The actual development of such reactions depends, however, on kinetic considerations and the local environment. AAR development within concrete requires that a liquid film be confined around the aggregate and give rise to hydrolysis. The newly formed products precipitate from this liquid. While the nature of these products varies depending on pH and temperature, the reaction mechanism is the same as that which governs the natural alteration of rock.

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