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Carbonation in the pore solution of metakaolin-based geopolymer

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ABSTRACT

An experimental approach based on the study of the pore solution of metakaolin-based geopolymer has been established in this study to investigate the phenomenon of carbonation in these materials. The results obtained showed a very fast decrease in the pH, compared to Portland cement, and an almost total carbonation of the pore solution in natural condition after only 14 days. In natural CO_2 conditions, the formation of sodium carbonate did not lead to a decrease of pH below 10.5 at one year, thus limiting the risk of corrosion by depassivation of the reinforcement. Accelerated carbonation performed under 50% of CO_2 highlighted the formation of large amounts of sodium bicarbonate responsible for a lower pH of the pore solution, and a potential risk of corrosion by carbonation. That result also demonstrated that the accelerated carbonation tests made for Portland cement are not representative of the natural reaction in geopolymer cases.

1. Introduction

Carbonation is a reaction occurring between carbon dioxide from the air and the Portland cement paste. It is one of the most harmful degradation processes and can drastically affect the long-term durability of civil infrastructures [1] [2]. The reaction mechanisms and the consequences of this reaction on Portland cement structures are widely known and many standardised tests exist to assess the kinetics and the impact of this reaction. The most damaging consequence of the carbonation of concrete is due to the dissolution of the portlandite. Portlandite constitutes the most significant hydroxide (OH^-) supply of the Portland cement paste, maintaining a high pH of 12.5, so the consumption of this hydrate will lead to a reduction of the pH of the pore solution to a value under 9. This low pH will have a major impact in the case of reinforced concrete because, at this basicity ($pH < 9$), the steel loses its passivation layer [3] regardless of the potential of the solution, and can then corrode. Once the corrosion of the reinforcement has started, localised or generalised bursting may result. The relatively low concentration of CO_2 in the atmosphere (0.03–0.04%) makes carbonation a slow process in dense, chemically stable cementitious materials. This has led to the development of accelerated testing methods exposing the material to high CO_2 concentrations, from 0.1% to 50% to induce faster carbonation. The propagation of the reaction is then observed in using a coloured indicator, phenolphthalein, which is pink under basic conditions ($pH > 9$) and is colourless below this value.

There are a limited number of published studies evaluating carbonation of alkali-activated materials, and far fewer on low calcium content systems as geopolymers. The largest number of published studies on the carbonation of alkali-activated systems concern slags, and they seem to be in general agreement that these materials are more susceptible to carbonation than conventional Portland cements [4]. Regarding the reaction product, in the carbonation of slag activated by sodium hydroxide or silicate, the reaction products obtained are mainly calcium and sodium carbonates [5] [6]. Concerning the sodium carbonates formed, Bernal et al. [7] [8] found that, under atmospheric CO_2 concentrations, the formation of natron ($Na_2CO_3 \cdot 10H_2O$) was favoured while, under accelerated carbonation testing conditions (CO_2 concentrations between 1% and 100%), the formation of nahcolite ($NaHCO_3$) prevailed. These authors also showed that the formation of trona ($Na_3H(CO_3)_2 \cdot 2H_2O$) was favoured over natron when the temperature of exposure increased slightly, whatever the CO_2 concentration. This study concluded that, under artificial CO_2 content, the modifications of the carbonate (natron)/bicarbonate (trona) phase equilibrium promotes the formation of bicarbonates that would lead to a more notable decrease in pH, by as much as 2 pH units [7].

No references were found on the carbonation of pure metakaolin-based geopolymer but two studies focusing on fly ash-based geopolymer having a low calcium content gave information on the carbonation of these systems. Criado et al. [9] assessed the effect of the curing conditions on the carbonation products of class F fly ash geopolymer (calcium content 2.44%). Using XRD, they identified that, when the fly ash was activated with sodium hydroxide, herschelite (form of zeolite having $NaAlSi_2O_6$, $3H_2O$ formulation) was formed, but when a sodium silicate was used, sodium bicarbonate appeared without any herschelite. It should be noted that the presence of sodium bicarbonate and not sodium

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carbonate was in agreement with the study presented by [7] and would be due to the heat treatment (cured at 85 °C). According to the authors, carbonation occurred very rapidly during the early stages of the process when the material was in contact with the atmosphere. This fast carbonation, inducing the formation of sodium bicarbonate, would lead to a decrease of pH and therefore a less efficient activation of the ashes. This initial carbonation process can be avoided by simply controlling the environmental curing regime (high relative humidity). More recently, Badar et al. [10] have studied the corrosion of steel bars induced by accelerated carbonation in low and high calcium fly ash geopolymer concretes. These fly ashes contained 1.97%, 5% and 12.93% of calcium and were activated with a blend of commercial sodium silicate and 14 M of sodium hydroxide. It was found that, for all the concrete formulations, accelerated carbonation led to a remarkable decrease in the pH, a reduction in the mechanical strength properties, and an increase in the total porosity. The drop in pH, in both low-Ca and higher-Ca fly ash geopolymers, was associated with the carbonation of the pore solution, as sodium carbonates were observed as the main reaction products formed in specimens exposed to 5% of CO_2. The authors concluded this study by stating that low-Ca class F fly ashes were more suitable than those containing higher levels of Ca for the production of steel-reinforced geopolymer concrete from a durability point of view, as the chemical and physical properties of these materials seemed to reduce the risk of corrosion in the steel reinforcement.

However, the information provided by the literature on the subject does not allow conclusions to be drawn on the resistance of pure metakaolin-based geopolymer to carbonation. Thus, the main purposes of this study are:

- ➔ to highlight the type and kinetics of reaction between the metakaolin-based geopolymer and the atmospheric CO_2,
- ➔ to determine the impact of this reaction on the geopolymer paste, especially on the pH of the pore solution,
- ➔ to assess the relevance for geopolymers of the existing tests standardised for Portland cement,
- ➔ to identify the potential durability risks of this reaction.

To the author's knowledge, no standards or existing procedures make it possible to achieve these objectives. Thus, an experimental approach focused on the analysis of pore solution was developed for this study.

2. Experimental program

2.1. Geopolymer synthesis

The source of aluminosilicate used in all the geopolymer formulations presented here was a metakaolin obtained by flash calcination, produced in the south west of France by ARGECO Développement. The term "Flash calcination" refers to the combustion process (temperature around 700 °C) where the particles of kaolinite are transformed into metakaolin by passing near a flame for a few tenths of a second [11]. The specific surface area of the flash metakaolin was 13 m^2/g (BET). The mineralogical analysis (Fig. 1) shows an amorphous phase corresponding to metakaolin, in addition to quartz (SiO_2, Powder Diffraction File (PDF) # 46-1045), and small amounts of anatase (TiO_2, (PDF) # 21-1272), mullite ($Al_6Si_2O_{13}$, (PDF) # 84-1205), calcite (CaO, (PDF) # 47-1743) and kaolinite ($Al_2Si_2O_5(OH)_4$, (PDF) # 83-0971). The proportion of each phase presented in the legend of Fig. 1 was calculated by Rietveld refinement, using the free license software Maud [12]. The chemical composition obtained by ICP-OES, using an Optima™ 7000 DV ICP-OES (PerkinElmer) equipped with a CCD sensor, presents the mass content of oxides in the metakaolin (Table 1). These results showed a very large silica content, mainly due to the significant presence of quartz (around 40% by weight, Fig. 1).

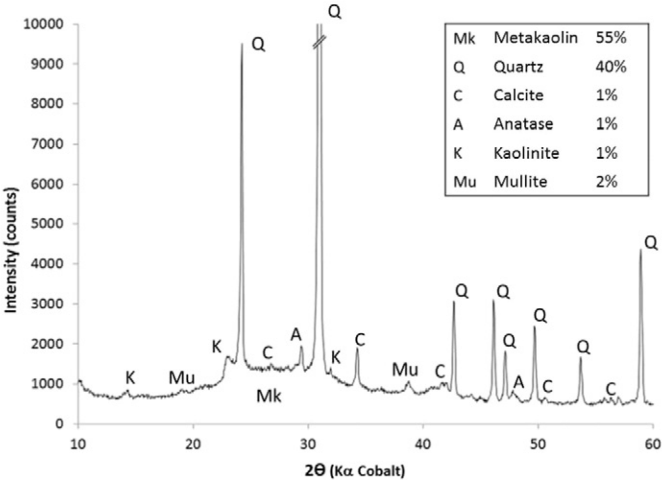

Fig. 1. XRD pattern of flash-calcined metakaolin with Rietveld quantification of phases.

The activating solution was an industrial waterglass solution (Bétol 47T, Woellner) containing 16.9% Na_2O by mass and having an SiO_2/Na_2O ratio of 1.7. The geopolymer were prepared by mixing the components in the following mass percentages: 52% MK, 41.5% Bétol 47T, and 6.5% water (corresponding to the following molar ratios: $SiO_2/Al_2O_3 = 3.6$; $Na_2O/Al_2O_3 = 0.9$; $H_2O/Na_2O = 14.5$; quartz in metakaolin was not counted in SiO_2 of the geopolymer), until a homogeneous mixture was obtained. Then, the pastes were cast in 91 × 62 × 40 mm plastic moulds, hermetically sealed, and stored at 20 °C. After 24 h, the three different curing conditions presented in Table 2 were applied. For cure condition 1, the prisms were not removed from the plastic moulds, in order to prevent any external exchanges. The second condition of cure was achieved by placing the prism in a conditioned room at 20 °C and 95% R.H. Finally, a part of the sample was placed in a chamber connected to an inlet for carbon dioxide in order to maintain an atmosphere containing 50% of CO_2 (according to the French standard XP P18–458, where the relative humidity was lowered to 50% RH instead of 65% RH for logistical issue).

2.2. Experimental approach

Because of the insolubility of calcium carbonate, the methods developed to assess the carbonation of Portland cement all focus on the measurement of the carbonation front, mainly with the phenolphthalein indicator. In the case of the geopolymer, although the pH variation induced by carbonation could be visible via a colour indicator, a distinct carbonation front is difficult to determine given the high solubility and mobility of the sodium carbonate [9] [13]. Moreover, the red colour of the geopolymers (due to the colour of the initial metakaolin containing red iron oxides) makes difficult the observation of the pink colour transition when phenolphthalein is used.

It was thus decided to develop a method for the study of carbonation through the pore solution. This method could provide precise pH values, which are, to the author's knowledge, not yet referenced in the literature for metakaolin-based geopolymer. In order to simplify the study, it was chosen to evaluate the impact of the carbonation reaction on pure geopolymer pastes, to assess the reaction at the binder level, and avoid possible reaction alterations due to the contribution of other chemical elements provided by aggregates. Moreover, studying the formation of carbonates in solution requires working at a repeatable volume of water to have comparable concentrations and the volume of water extracted from the geopolymer must be high enough to allow the measurements to be achieved. Thus, the impact of relative humidity during the test, linked to the water saturation of the geopolymer, is of major importance. This R.H. value was chosen by studying the results of Boher et al. [14] obtained on metakaolin-based geopolymer having