

CAN METAKAOLIN-BASED GEOPOLYMERS SUFFER FROM ALKALI-SILICA REACTION?

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Abstract

This research assesses the behaviour of metakaolin-based geopolymers in the presence of alkali-reactive aggregates. Geopolymer mortars were made with flash metakaolin and sodium waterglass solution in presence of seven different aggregates, each having different levels of reactivity to alkali-silica reaction (ASR). The behaviour of geopolymer in presence of such reactive aggregates was investigated by monitoring the dimension changes in accelerated conditions at 60°C and 95% RH for up to 250 days. SEM and EDX analyses were also performed at 170 days to visualize the newly formed products. A comparison with an ordinary Portland cement (OPC) was made for all aggregates in order to evaluate how strongly geopolymers were affected by ASR.

Results showed that geopolymers, although they contained high concentrations of alkalis, were more able to resist ASR than OPC was, and no characteristic swelling was observed for the geopolymer specimens. The conclusions were the same with other test conditions, e.g. by varying the temperature of the test or the size of the specimens. Only aggressive conditions, like immersion in a 1M NaOH solution, led to a non-negligible expansion of geopolymer mortars, but with very slow reaction kinetics compared to OPC. The non-accelerated test confirmed that the geopolymer seemed to develop no harmful reaction in presence of reactive aggregates and optimal conditions for ASR.

The non-swelling behaviour of metakaolin-geopolymers could be due to various phenomena: fast decrease in the pH, lack of calcium in the new-formed products, or accommodation of the gels in the porous network. The results of this paper allowed us to conclude that, under the same condition and in spite of their very high concentration of sodium, geopolymers have a higher durability than OPC regarding the alkali-silica reaction.

Keywords: Geopolymer, Alkali-silica reaction, Metakaolin, Mortar, Durability.

1 INTRODUCTION

The evolution of knowledge on geopolymers (GP), and more generally on alkali activated materials (AAM), tends to show that they could potentially offer an efficient alternative to ordinary Portland cement (OPC) in particular applications. Alkali-activated materials began to emerge as a new material for civil engineering more than three decades ago, and recent years have seen an increase in research by the international scientific community and also by industrial firms. However, the question of the durability of AAM, especially the metakaolin-based geopolymer, appears as a major issue.

Geopolymers are composed of a source of aluminosilicate (e.g. metakaolin) activated by a high-pH solution (e.g. sodium silicate). Alkali contents in OPC concretes are typically in the range 2-6 kg/m³. In the case of geopolymers, the activator usually involves very high alkali concentration which reaches 50-150 kg/m³ for the formulation of concrete.

What is the durability for these materials in view of their high alkaline content? Knowing the problems of alkali-silica reaction sometimes found in Portland cement concrete, how this pathology can affect geopolymer concretes?

The current literature on ASR in alkali-activated materials does not allow their behaviour towards this reaction to be predicted, although some tendencies have emerged from these studies [1]. Studies of aluminosilicate systems (based on fly ash or metakaolin) show that they seem to resist ASR better than OPC. But the limited number of existing articles, in which the accelerated tests, the formulation and the aggregates used are different most of the time, show that no conclusion can actually be drawn regarding ASR resistance of geopolymers.

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Two studies partly or totally dedicated to ASR of activated fly ash (AAFA) systems were carried out by Fernández-Jiménez, Palomo and García-Lodeiro [2,3]. The authors used a standardised test (ASTM C1260) to evaluate the ASR of AAFA systems compared to those containing Portland cement. Generally speaking, the alkali-activated fly ash mortars presented much lower expansions than their OPC replicate. However it cannot be said that AAFA systems were completely safe regarding ASR swelling.

The results on metakaolin-based geopolymers are rare. Li et al. [4,5] compared the ASR-behaviour of cement-based binders (Portland cement and slag, fly ash and silica fume) to one geopolymer composed of metakaolin, fly ash, silica fume and alkali-activator. The alkali content in the geopolymer reached 12.1%. The reactive aggregate was a crushed quartz glass with an amorphous silica content of more than 90%. The ASR test was based on ASTM C441, itself based on ASTM C227 (38°C). The results showed that the higher expansions were obtained for mortars containing Portland cement only, followed by mixtures with pozzolans (65 to 82% reduction of expansion). The geopolymer mortar, which contained a much higher alkali content than OPC-based mortars (12.1% vs. less than 1%), led to negligible length variations (0.01% at 14 days and -0.03% at 90 days). According to the authors, "geopolymers do not generate any dangerous alkali-silica reaction", since there would be not enough free alkalis to react with the reactive aggregate and thus produce alkali-silica gel, as Na^+ and K^+ are fixed in the framework cavities of SiO_4 and AlO_4 to balance the negative charge of Al^{3+} .

Literature on fly ash and metakaolin based systems are not conclusive regarding the susceptibility of these materials to ASR. Those studies generally provide results on only a few different aggregates, and use a single accelerated test to assess the impact of the ASR on the geopolymer. The purpose of this study is therefore to evaluate as thoroughly as possible the behaviour of metakaolin-based geopolymer against ASR, by using seven sand aggregates having variable reactivity but also by comparing the influence of the different conditions of accelerated and natural testing. A comparison with an ordinary Portland cement (OPC) for all aggregates is made to ensure their alkali-silica reactivity and compare how the ASR affects these two matrices.

2 MATERIALS AND METHODS

2.1 Materials

All the geopolymers were made using "flash" metakaolin [6]. 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. This process is faster and consumes less energy than traditional methods (e.g. rotary kiln). Due to the lower purity of the deposit, this metakaolin contained about 50 % of impurities, mainly quartz (44 %).

The activating solution was an industrial waterglass solution (Betol 49T, Woellner) containing 8% Na_2O by mass and having a $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of 3.3. Pure NaOH was added to this commercial solution 24 hours before mixing to obtain the desired amount of alkalis in the final formulation. The comparison was made with a CEM I 52.5 mortar in which were added pure KOH to boost the alkali amount of the OPC mortars. The cement was a CEM I 52.5 N CE CP2 NF (0.48% Na_2O equivalent), according to NF EN 197-1.

Seven sands were selected in order to cover a wide range of types and geological origins, from low to high kinetics of silica dissolution. Their type and mineralogy are listed in Table 1. For each aggregate, particle size was controlled by sieving between 0.16 mm and 2 mm.

- Sand **a** was a marble sand composed entirely of calcite, and thus having no silica to be dissolved. This sand was chosen as a reference for non-reactive aggregate as it usually presents no trace of ASR [7].
- Sand **b** was a siliceous sand used in standard mortars in accordance with EN 196-1 [8]. This quartz sand is usually considered as non-reactive regarding ASR, although it can expand slightly in accelerated test conditions [9].
- Sand **c** was a quartzite sand of metamorphic origin and it was selected for its low kinetics of silica dissolution [10]. It contained mainly quartz, phyllosilicate minerals (mica-type such as muscovite) and amorphous silica (around 7.6% by mass) [9].
- Sand **d** was a sedimentary siliceous limestone composed of calcite and dolomite, with significant amounts of impurities including quartz, plagioclase feldspars, micas, kaolinite and pyrite. It contained around 7% by mass of amorphous SiO_2 [9] and was considered to have a low kinetics of silica dissolution in ASR tests [10].

- Sand **e** was an alluvial sand containing opal (around 10% by mass), well crystallised quartz and plagioclase feldspars [11]. This sand was chosen for its high alkali-silica reactivity and its high kinetics of silica dissolution due to the presence of opal [11].
- Sand **f** was a glass resulting from the crushing of glass bottles. It was chosen for its amorphous structure and thus the large amount of silica available to be dissolved (around 68% by mass), leading to high ASR-expansion [10,12]. This kind of aggregate is often used as the modelled aggregate in ASR studies (e.g. [10]).
- Sand **g** was an opal corresponding to igneous rock having a predominant glassy phase. It is very deleterious and is commonly reported in laboratory experiments as a reference mineral for the study of ASR [7].

2.2 Mix designs and Methods

Mix designs

All mortars were prepared with one part of metakaolin or cement for three parts of sand (by mass). The solid/liquid ratio for geopolymer mortars and the w/c ratio for OPC was set to 0.5 and KOH tablets were added to the OPC water to reach 8 kg/m³ of Na₂O_{eq} (including alkalis of the cement) in order to provide a sufficient amount of alkali for the reaction. The geopolymer mortar was prepared in two steps. First, the pure NaOH and water were added to the industrial waterglass solution to reach a final H₂O/Na₂O molar ratio of 17 (mass composition: 50% metakaolin, 41% waterglass, 4.2% NaOH, 5.3% water). After the total dissolution of the sodium hydroxide, the solution was cooled to 20°C for 24 h and then introduced into the metakaolin-sand mix until a homogeneous mixture was obtained. Thus the geopolymer paste had the following molar ratios: SiO₂/Al₂O₃=3.6; Na₂O/Al₂O₃=0.9 and H₂O/Na₂O=17.

Sample preparation

Mortars were prepared according to European standard EN 196-1 [8]. This standard describes the procedure (mixing and casting) used for the preparation of mortars, and has been validated for the preparation of geopolymer mortars [13]. They were cast in 4x4x16 cm and 2x2x16 cm prisms (expansion measurements) and 2x2x2 cm cubes (other tests). The samples were demoulded after a cure of 24h at 20°C and 95% RH.

Immediately after demoulding, all the prisms were measured using the scale micrometre method (specimens had stainless steel shrinkage bolts at both ends). Each measurement was the mean of three values from three replicate specimens. After these measurements, some prisms were covered with waterproof paper to protect the specimens from exterior exchanges, particularly for the carbonation. It was decided to allow 28 days for the cement hydration and geopolymerisation reactions before starting the accelerated tests. The specimens were therefore stored at 20°C in sealed plastic bags during this period. Only specimens made with the mixture of opal-marble (10%-90% by mass) sand were placed directly in non-accelerated test conditions at 20°C and 95% R.H.

Test methods

After 28 days without external exchange, the prisms were stored at 20°C, 38°C or 60°C, after being placed either on grids in watertight containers containing 20 mm of water (mortar bars were not in contact with the water) or immersed in solutions (water, saturated CaO or 1M NaOH) depending on the test. Expansion and mass measurements were performed every seven days after the containers and the prisms had been cooled for 24h at 20°C. This test was based on the standard NF P 18-454 [14] and was designed for concrete, but it has also been validated on mortars and 2x2x16 cm specimens [12].

Observations using a scanning electron microscope (JEOL JSM-6700F and JEOL JSM-6380 equipped with a RONTEC EDX system and JEOL JSM-6700F) were carried out on some mortar cubes (after platinum or carbon metallisation) at 170 days to observe the presence or absence of gel and to obtain information on their morphology and composition.

3 RESULTS AND DISCUSSION

3.1 Expansion based on accelerated tests at 60°C

Expansion measurements were performed every seven days, up to 250 days, on each 2x2x16 cm OPC and GP specimen, all kept under the same accelerated conditions (in watertight containers containing 20 mm of water at 60°C). The evolution of these expansions over time is presented in Figure 1. As expected, swelling trends were observed for OPC. The curves involving geopolymer

binder (Figure 1) showed similar behaviour regardless of the sand used, since no change in dimensions was measured over time for any mortar, even in the presence of very reactive aggregates.

Since expansion was measured for OPC in presence of the sands b, c, d, e and f, confirming a certain reactivity of these materials, while no expansion seemed to occur for the geopolymer mortars with the same sand, geopolymer appears to be more efficient than the cement in this field of durability.

3.2 No expansion = no ASR?

No expansions were measured on the geopolymer prisms but this did not mean that no ASR occurred. A scanning electron microscopy study was carried out at 170 days on the 2x2x2 cm specimens cured under the same conditions as the prisms to verify the presence or absence of alkali-silica gel in these matrices when the two most reactive sands (e: sand with opal, and f: soda glass) were used.

Observations were made on the geopolymer mortars in presence of the alluvial sand (Figure 2a) and the soda-glass sand (Figure 2b). Despite the absence of expansion of these two specimens, reaction products were seen in both cases. For the alluvial sand (GP-e), cracked gel morphology, similar to ASR gels observed for OPC-e, was found within cavities (Figure 2a: P2). However, very little gel was observed on the entire sample. On the other hand, many spots of reaction products were observed inside cavities or interfaces between geopolymer and sand on GP-f mortar, which was made of crushed glass (Figure 2b).

Figure 2b gives a good illustration of the morphology of the sample analysed, where it was possible to clearly distinguish the presence of a newly formed product that looked like a gel layer (P4) around 10 μm thick at the interface between the glass grain (P3) and the geopolymer paste (P5). EDX analysis showed the presence not only of elements typically found in ASR-gels (Si, Na, Ca) but also of a significant quantity of Mg, an element that was initially in the glass aggregates. The question arises as to whether this new compound was an ASR-gel, or just a product due to the reaction of the external glass layer with the surrounding environment rich in hydroxide and alkalis. It should be noted that the presence of gel layers around glass aggregates had already been seen by Idir et al. [15,16]. These authors found that glass particles attacked by alkaline solutions in model systems formed reaction rings around the grains, which were regarded as alkali-silica gels containing small amounts of calcium.

3.3 No expansion: why?

Dissolution of the reactive silica - pH of the pore solution

Alkalinity and pH of the pore solution are known to have a major impact on the attack of silica in reactive aggregates, since they control the breakdown of the amorphous phase, according to the mechanisms described by Dent Glasser and Kataoka [17,18]. The pH is partly driven by the alkali concentration in the pore solution, which itself depends on the soluble alkali of the cement in OPC systems. Alkali contents in OPC concretes are typically in the range 2-6 kg/m³. In the case of geopolymers, the activator usually involves very high alkali concentration which reaches around 150 kg/m³ for the formulation used in this study. The solubility of amorphous or not well crystallised silica is strongly dependent on the pH values, especially in high-pH ranges. A variation of one pH unit can modify the solubility of silica by several orders of magnitude [19].

In order to evaluate the medium surrounding the aggregates in a geopolymer-based matrix, a study of the pore solution pH was made on a geopolymer paste having the same formulation as the mortars of this study. For this, a high-pressure device for extracting fluid from porous materials [20] was used on the geopolymer at various times. Figure 3 reports the evolution of the pH inside the geopolymer pores up to 180 days, for a sample kept at 20°C and 95% R.H., i.e. in contact with the atmosphere, and for a sample kept in a sealed bag without any external exchanges.

It can be seen that, although there was a strong initial pH of 14 which was imposed by the activating solution, the pH dropped rapidly in the following days, at a rate proportional to the logarithm of time. After 14 days in a moist atmosphere (same conditions as ASR accelerated testing), the pH was lower than 12 and reached 10.5 at 6 months, while it stabilised at around 12.5 in endogenous conditions. This rapid decrease of the pH was probably due to the carbonation of the pore solution, which led to the consumption of alkalis to form alkali-carbonate compounds [21]. According to this study and assuming a similar evolution of the pH for the specimens used for the ASR study in view of their relatively small size (2x2x16 cm), at least two main hypotheses can be put forward to explain the absence of ASR in geopolymers:

- The first one is related to the very high initial pH in the mixture, which can lead to a very rapid reaction of the amorphous silica within the aggregates and the hydroxides present in the solution. This phenomenon, already described by Gifford and Gillott [22] in their work on alkali-activated slag, would occur during the early period of hardening.
- The second hypothesis is that the fairly rapid drop in the pH would not leave enough time for hydroxides to break the silica network within the aggregates, thus reducing the formation of alkali-silica gels and so limiting the harmful effect of ASR. Since the amount of reaction products is an important parameter, less ASR gel (for a given gel composition) implies less probability of expansion. Results from the literature [23,24] tend to show that this hypothesis is plausible, as a pH decrease of 0.3 (e.g. 13.7 to 13.4) could lead to 50-75% less silica being dissolved. At pH below 13, the reduction is even more significant, which means that the attack on the reactive aggregates can perhaps be strongly reduced.

Expansion of the gel formed - Role of calcium

It is generally assumed that calcium plays an important role regarding ASR expansion in Portland-cement-based materials. On the one hand, silica-based reaction products with high calcium contents are usually associated with C-S-H formed by cement and pozzolan hydration, with Ca/Si ratios of approximately 1.7-1.0 for typical and pozzolanic C-S-H, respectively. These products are responsible for the strength increase and do not involve any abnormal swelling behaviour. But, on the other hand, many authors have stated that a calcium deficiency in alkali-silica reaction products would lead to an absence of swelling [18]. In diluted modelled systems, the portlandite content would be one of the main factors determining the amount of dissolved silica: in the presence of calcium, more silica would be dissolved [25]. Without added Portlandite, the reaction initially produces alkali-silica compounds, but the reaction would stop as soon as the solution became saturated with respect to silica. In OPC alkali-reactive systems, it is expected that the potential of the reaction products for an expansion may be highest at a Ca/Si ratio between 0.20 and 0.30 [25].

In the case of fly ash-based geopolymers, Fernandez-Jiménez et al. [2] and García-Lodeiro et al. [3] suggested that the deficiency of calcium in their systems could partly explain the lower expansion observed, although there was some evidence of an attack of the reactive aggregates. In the current work, the only calcium in metakaolin-based geopolymer is provided by the metakaolin, which contains less than 2% by mass of CaO. The calcium deficiency could thus be a factor influencing the difference in behaviour of ASR gels, most likely in their expansion phase. The only mixture that led to higher calcium gels was the one made of crushed glass in the geopolymer matrix, but the newly formed product might not have been ASR gel in the strictest meaning of the term.

Propagation of the gel into the porous network - accommodation of the gel

The SEM observations made on the different samples did not find as much gel as in OPC systems (except maybe for glass aggregate mixtures, but some doubts can be voiced as to whether the reaction rims were ASR gels or not). However, the presence of gel is not necessarily associated with swelling, whatever its nature. The accommodation of the gel by the porosity of the paste is the basis of several numerical models. It has been shown [26] that, depending on the size of reactive grains, the gels might not induce ASR-swelling. The porosity of the paste is sufficient to give the gel enough space to diffuse into the paste without exerting excessive stress on the solid skeleton and so without causing swelling.

Gifford and Gillott [22] already supposed that the viscous alkali silica gel produced in alkali-activated slag (AAS) systems could be more easily accommodated in the porosity of AAS systems than in OPC concrete. Geopolymers are known to have a porous network different from that of OPC mixtures [27,28]. The result of a previous study on the geopolymer porous networks and its differences with OPC system [13] could explain the differences in gel accommodation between those two materials. The total pore volume (accessible by water) was much higher for the geopolymer (53%) than for OPC (43%), at $w/c = 0.5$. It was also found that the geopolymer had a monomodal porous network centred around 25 nm when the cement presented a bi- or tri-modal network and the differences between the median pore access diameters of these two matrices show the regularity of the geopolymer networks compared to OPC. Moreover it has been shown [13] that the porosity of geopolymer was probably strongly connected. Thus the volume accessible to the gels was larger and more accessible than in OPC, so it could be imagined that this would greatly reduce the appearance of internal tension, and thus the damage caused by ASR.

3.4 Can geopolymers swell in other accelerated or natural conditions?

Accelerated tests

Expansion values were measured for each cement and geopolymer mortars in several accelerated condition at 14 and 100 days (Table 2). According to the accelerated tests considered the acceptable limit for expansion value varies. If one sets the limit at 1 mm/m (16 days according to ASTM standard C1260-94) it was observed that the test conditions of immersion in a CaO saturated solution or in water do not lead to significant expansion for both OPC and geopolymers. The negligible expansion of OPC is consistent because the test conditions are not known to promote the alkali-aggregate reaction. However it is interesting to note that even in presence of calcium, the GP dimensions of the specimens remain unchanged. Indeed, some theories about swelling of AAR gels in cement system indicate that the presence of calcium plays an important role [29] so some studies explain the absence of expansion in the aluminosilicate system (fly ash or metakaolin systems) activated by alkali by the absence of calcium [3].

All other conditions of tests conducted have led to an expansion greater than 1 mm/m in cement mortar. The expansion curves for these tests (OPC and GP) are presented on Figure 4. Comparison of expansions obtained for Portland cements and geopolymers presented on Figure 4 shows that after 28 days of accelerated test, all OPC mortars have exceeded the limit of 1 mm/m compared to geopolymer which showed no significant swelling even after 100 days of test.

It was found that immersion in a 1M NaOH solution at 60°C resulted in the highest expansions for both OPC and geopolymer. At 100 days of test, GP mortars almost reach the limit value (0.9 mm/m), while in all other cases it does not exceed 0.4 mm/m. This result supports the argument of some authors who criticize the aggressiveness of this test (usually performed at 85°C) and his reliability to reflect the reality of the reaction. The second most important expansion is observed for 4 x 4 x 16cm dimension OPC specimens who showed that when the volume is multiplied by 4, the expansion of OPC increases by 25% while it remains unchanged in the case of geopolymer. It was also shown herein that the reduction of the test temperature (60°C to 38°C) decreases also the reaction kinetics because under those conditions the OPC reach the limit value of 1 mm/m only at 28 days instead of within 7 days at 60°C. Once again no effect was observed on specimens of geopolymer.

Finally the study of prisms having undergone no external exchanges highlights that the intrinsic properties of geopolymer does not entail any swelling in the presence of reactive aggregates, unlike OPC mortars kept in the same conditions and leading to significant expansions.

Non-accelerated tests

In order to observe the phenomenon without altering the chemical reaction taking place in these matrices, a non-accelerated test was launched on OPC and GP mortars with a mixture of opal-marble sand, near "pessimum" proportion. The expansions measured are presented on Figure 5. This figure shows that even at room temperature, if favourable conditions for development of AAR-gels are met, significant expansions are obtained in systems made of Portland cement. On the other hand, no change in dimensions was obtained in the geopolymer system, even after 100 days, despite the high alkali content of this system.

Since that the absence of swelling does not mean the absence of gel formation, a study using scanning electron microscope was carried out on GP mortar in the presence of opal-marble sand mix after 7 days at 20°C and 95RH. It was shown (Figure 6) that gel was present at the interface between the geopolymer paste and the opal aggregates. These gels (of a thickness around 10µm) found in large quantities in the analysed sample have a similar morphology than AAR gels commonly observed in Portland cement -reactive aggregates mixtures. A complex siliceous structure was also observed on these specimens, structure which looks like AAR-gel with "rosette" morphology (Figure 7). Thus the geopolymer's system led also to a formation of a product of reaction at the interface paste-reactive aggregates with similar morphologies to the AAR-gels found in OPC.

The formation of this gel probably indicates that there has been dissolution of the reactive silica of the aggregates, as in OPC. However the non-expansive character of these products let us think that they might not be considered as equivalent reaction product like those found in OPC systems.

4 CONCLUSIONS

The experimental studies performed in this paper were intended to assess the ASR-behaviour of Metakaolin-geopolymer mortars in the presence of reactive sands. The work was carried out on geopolymer and OPC mortars incorporating seven different alkali-reactive sands, each having a different level of reactivity, and used different test conditions, accelerated or not. The morphology and compositions of the products of reaction formed were analysed using SEM and EDX after 170 days of cure. Regarding the experimental results obtained in this study, the following conclusions can be drawn:

- The incorporation of reactive sands in metakaolin-based geopolymer mortars activated by sodium silicate does not lead to the ASR swelling characteristic of OPC mortars. This could be due to various phenomena: fast decrease of the pH, lack of calcium in the new-formed products, or accommodation of the gels in the porous network.
- Some gels with morphologies similar to those of ASR gels were observed at paste-aggregate interfaces or in cavities in mortars made with the reactive sands containing opal.
- The formation of a reaction product, covering the entire surface of the glass grains in the sand and resulting in a significant decrease in adhesion between the sand and the geopolymer, was observed. The question arises as to whether this new compound was an ASR gel or just a product due to the reaction of the external glass layer with the surrounding environment rich in alkalis.
- The results of the different accelerated test conditions used in this study allow it to be stated that, whatever the parameters studied and whether they were favourable or unfavourable to the development of ASR swelling gel, no characteristic swelling was observed in geopolymer mortars in presence of reactive sand, except for the immersion in 1M NaOH solution.
- The results provided by the non-accelerated test also showed the absence of expansion of GP mortars when all favourable conditions (for OPC expansion) were combined, and highlighted the formation of reaction products in the GP with morphologies close to the ASR products found in OPC. However, the results of this study tend to show that these reaction products do not lead to expansion, whatever the conditions.

Due to their very high alkali content compared to OPC, geopolymers give rise to many questions, especially regarding their durability. The results of this study provide some answers concerning the alkali-aggregate reaction, by showing that the durability of the geopolymer against ASR could be higher than that of OPC under the same test conditions.

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TABLE 1: Types and mineralogy of the reactive used.

I.D.	Name	Type	Mineralogy	Theoretical ASR reactivity
a	Marble sand	-	Calcite	none
b	Quartz	-	Quartz	very low
c	Quartzite	Metamorphic	Quartz, micas (tr), amorphous material (tr)	medium
d	Siliceous limestone	Sedimentary sand	Calcite, quartz, micas (tr), feldspars (tr)	medium
e	Sand with opal	Alluvial sand	Quartz, feldspars, opal	high
f	Soda-glass	Crushed glass	Amorphous material	high
g	Opal	Igneous	Amorphous material, tridymite, quartz (tr)	high

TABLE 2: Values of expansion (mm/m) measured at 14 and 100 days on GP and OPC mortars according to the accelerated test conditions.

Binder	Cure condition	T (°C)	Specimens dimensions (cm)	Expansion (mm/m)	
				14d	100d
OPC	100% RH	60	2 x 2 x 16	2.5	2.9
GP				0.1	0.1
OPC	100% RH	38	2 x 2 x 16	0.6	1.7
GP				0.3	0.3
OPC	100% RH	60	4 x 4 x 16	3.3	3.9
GP				0.0	0.0
OPC	Without exchanges	60	2 x 2 x 16	1.3	2.2
GP				-0.3	-0.3
OPC	1M NaOH	60	2 x 2 x 16	3.5	5.5
GP				0.4	0.9
OPC	Saturated CaO	60	2 x 2 x 16	0.7	0.8
GP				0.3	0.3
OPC	Water	60	2 x 2 x 16	0.7	0.8
GP				0.3	0.4

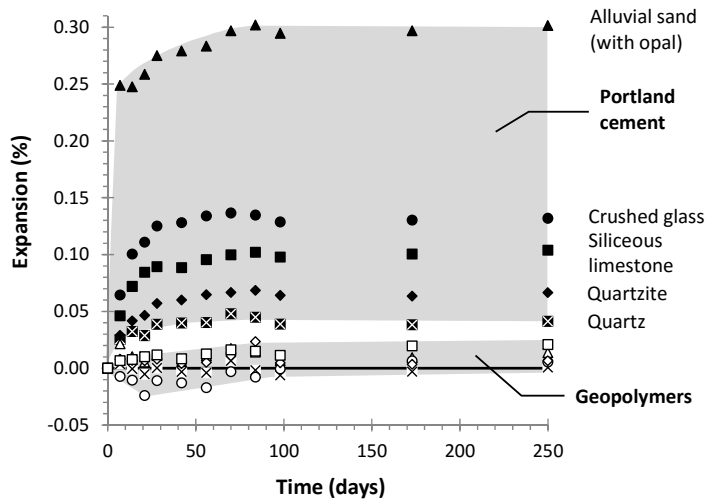


FIGURE 1: Expansion curves with time for OPC and GP mortar conserved at 60°C and made with six different sands : quartz, quartzite, siliceous limestone, alluvial sand with opal and crushed soda-glass (error bars less than 0.03% for OPC and 0.01% for GP).

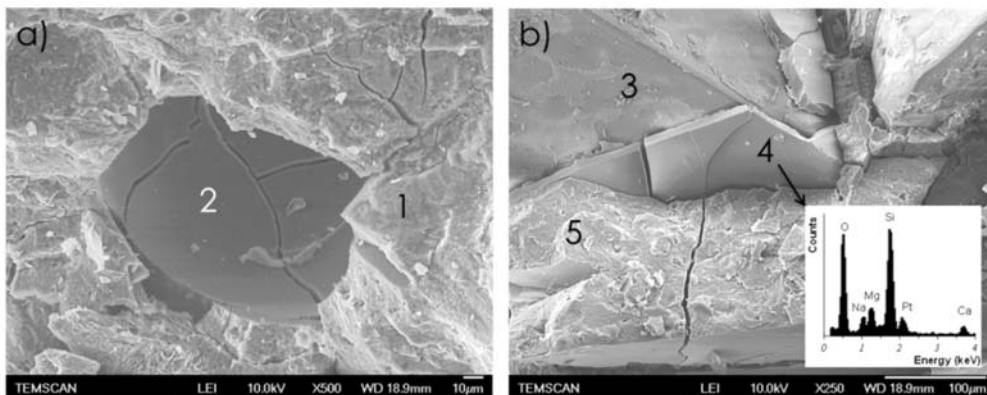


FIGURE 2: (a) Photomicrograph of GP-e mortar at 170 days at 60°C (P1: geopolymer; P2: gel-like ASR product) and (b) Photomicrograph of GP-f mortar at 170 days at 60°C (P3: glass aggregate; P4: gel-like ASR product with EDX analyses and P5: geopolymer).

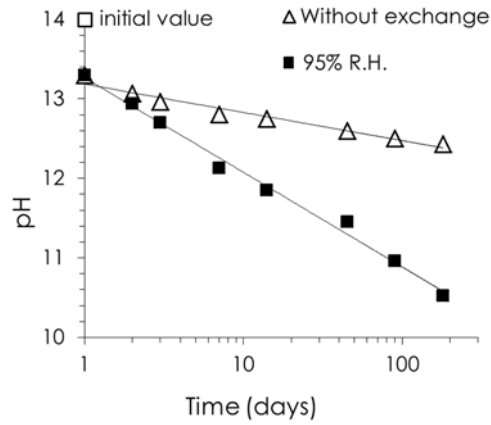


FIGURE 3: pH evolution of the geopolymer pore solution for a paste kept in a moist room (95% R.H.) and in a sealed bag.

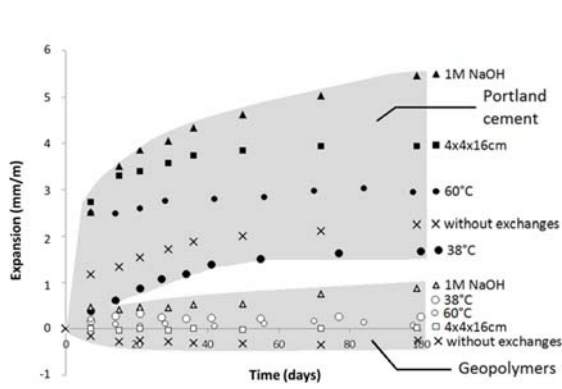


FIGURE 4: Expansion curve with time for specimens (OPC and GP) stored under several accelerated conditions.

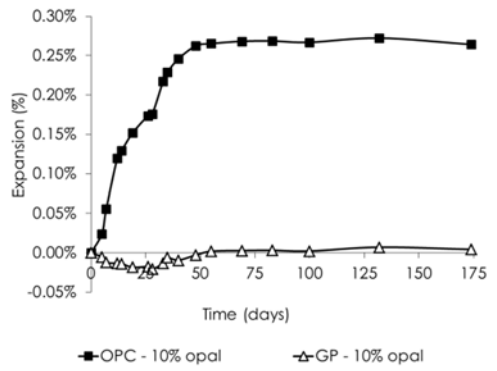


FIGURE 5: Expansion curves of OPC and GP mortars made with 10% of opal and 90% of marble, cured at 20°C and 95% R.H. (error bars less 0.01% for GP and 0.02% for OPC).

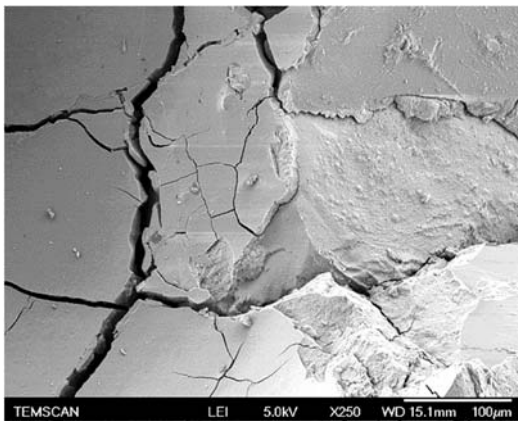


FIGURE 6: Photomicrograph of GP mortar at 170 days showing ASR product with cracking morphology of gel.



FIGURE 7: Photomicrographs of GP mortar at 170 days. ASR product with a "rosette-type" morphology.