

Microscopical and mechanical evaluation of the durability of SiO₂ aggregates[★]

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Received: 15 August 2015 / Received in final form: 27 November 2015 / Accepted: 11 December 2015
Published online: 3 May 2016 – © EDP Sciences 2016

Abstract. The durability of SiO₂ compounds is closely related to its structural properties. In this work three natural siliceous aggregates (called G1, G2 and G3) are studied. Improvement of the durability of the starting material leads to a significant energy savings by extending the lifetime of structures. The chemical composition of the three natural aggregates shows that G1 and G2 have almost the same chemical composition (SiO₂) and G3 is different and contains SiO₂ quartz type and calcite as major components (SiO₂, calcite and dolomite). X-ray diffraction (XRD) shows that natural aggregates G1 is more crystallized than G2 and G3. After alkali silica reaction (ASR) process, the reactivity of G3 aggregate seems to be higher than the G1 and G2 aggregates. The mechanical results show the slight difference between mortar containing G1 (M.G1) and that containing G2 (M.G2). Their compressive strength is 10% less than that of reference (M.SS). As it is more reactive, G3 seems improving the compressive strength of M.G3, compared to M.G1 and M.G2.

1 Introduction

SiO₂ compounds are involved in a large number of applications in various fields: constructions, geosciences, chemistry, semiconductor and glasses industries... [1,2]. Based on the SiO₂ aggregates, the large walls of the concrete may be used to store energy during the day and release it during night time and consequently reducing the need for auxiliary heating and cooling [3]. Improvement of the durability of the starting material leads to a significant energy savings by extending the lifetime of structures. One application of paramount importance is civil construction, as concrete is mostly constituted of silica-based materials. The durability of concrete is severely affected by the so-called alkali-silica reaction (ASR). Many studies were performed in order to explain the mechanisms involved in the ASR based on chemical aspects [4-6]. In addition, the efficiency of the ASR is strongly

dependent on the micro-structural state of the starting material [7-10]. As an illustration, perfectly ordered quartz is almost insensitive to ASR. Recently, we have undertaken a study of ASR on a flint aggregate. The reaction begins with the rupture of the siloxanes bonds Si-O-Si and our results support the formation of amorphous and nano-crystalline phases, which precipitate in the aggregate. However, the presence in flint [11-13] of different domains such as crystalline, disordered and amorphous [14,15] inside the starting material leads to an overlap of different mechanisms and to complex reaction kinetics, which prevent clear understanding of the mechanisms. New solutions have been proposed to slow down the reactivity of the starting aggregate [16,17].

The aim of this paper is to study the relationship between the reactivity of natural SiO₂ aggregate and its nano-crystalline structure. For that, different characterization techniques were used (X-ray diffraction [XRD] and transmission electron microscopy). To test their valorization potential in cementitious material, different aggregates (G1, G2 and G3) are incorporated in standardized mortars, which are characterized mechanically and compared to reference mortar, containing standardized sand.

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[★] Contribution to the topical issue "Materials for Energy Harvesting, Conversion and Storage (ICOME 2015) – Elected submissions", edited by Jean-Michel Nunzi, Rachid Bennacer and Mohammed El Ganaoui

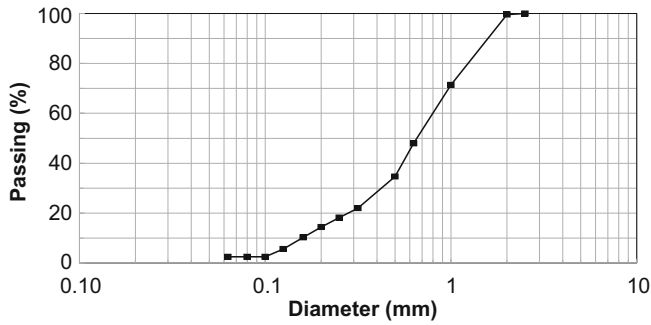


Fig. 1. Size distribution of used sands.

Table 1. Physical properties of tested sands.

	Type	ρ (g/cm ³)	w (%)
SS	Standardized sand	2.65	0.9
G1	Natural aggregate	2.57	1.76
G2	Natural aggregate	2.56	1.61
G3	Natural aggregate	2.75	2.28

2 Experiments

2.1 Materials

The materials used in this research are siliceous natural aggregates (called G1, G2 and G3). The G1 and G2 aggregates are of the rock type and the G3 is of alluvial type. These aggregates are heterogeneous appearance crystalline structure is based on quartz for G1 and G2, and quartz, calcite for G3 as major components.

2.2 Experimentals

The sample preparation and the ASR procedure used have been described previously [9,10]. The flint aggregate was powdered and the distribution of the average particle size showed two maxima, at 160 μm and 630 μm , before the reaction. 1 g of crushed flint was subject to accelerated ASR at 80 °C with a mixture of 0.5 g of portlandite $\text{Ca}(\text{OH})_2$ and 10 mL of potash solution KOH at 0.79 mol/L. The soluble reaction products containing calcium and potassium were removed by selective acid treatment [9,10].

XRD measurements were performed in the reflection mode using a Shimadzu Bruker D8 Advance diffractometer (Cu-K λ radiation = 1.5418 Å), which operates at 40 kV and 40 mA. Data were collected in the range of 5°–75° in the 2θ scale with a step size of 0.02° and a counting time of 0.5 s/step.

The TEM investigations were performed with a FEI Tecnai G2-20 instrument operating at 200 kV accelerating potential. It is equipped with a filament of lanthanum hexaboride LaB₆, a double-tilt holder and Gatan digital camera.

For their valorization in a cementitious material, coarse aggregates were firstly crushed using jaw crusher and

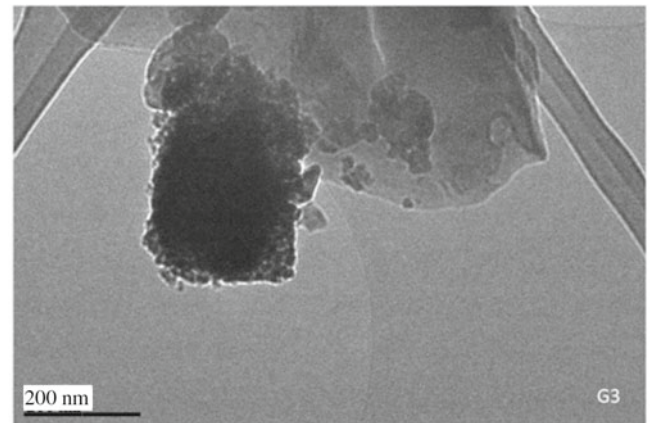
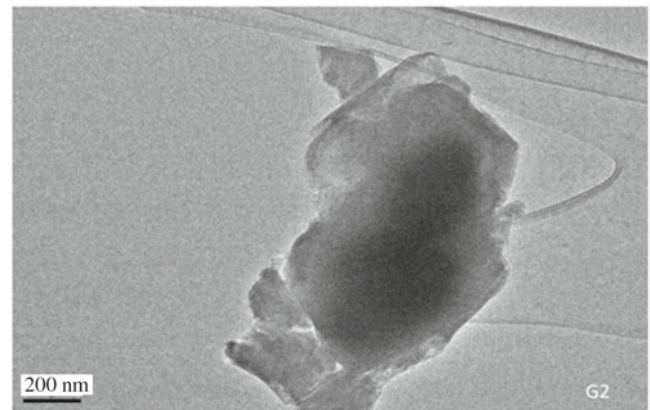
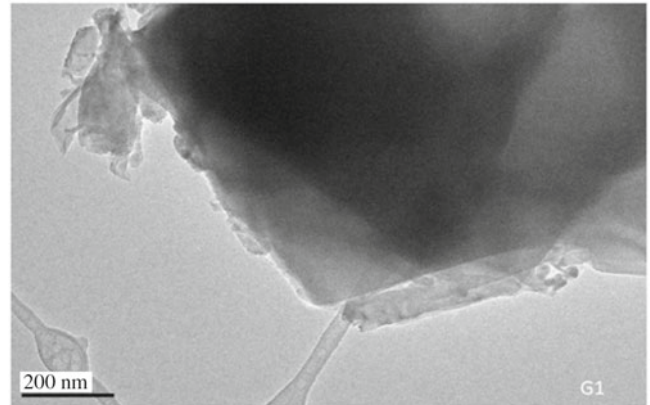


Fig. 2. TEM Micrographs of natural aggregates G1, G2 and G3.

sieved, before constituting the granular skeleton of standardized sand (SS). Our research aims at comparing the mechanical properties of standardized mortars [18], containing different sands (SS, G1, G2 and G3) with the same size distribution (Fig. 1). The physical properties of four used sands are summarized in Table 1. The used procedures are described in reference [19].

To keep constant the water-to-cement ratio ($w/c = 0.5$), and then the maniability of manufactured mortars, the absorbed water (w (%)) was added in the mixer.

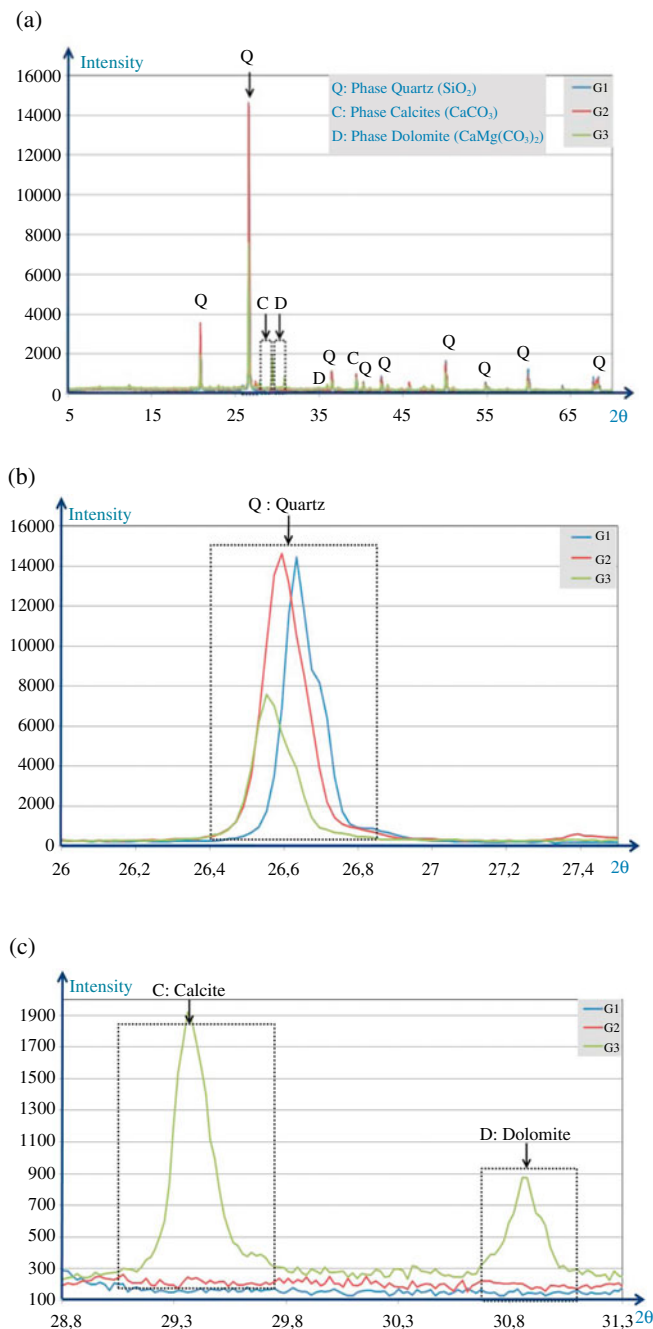


Fig. 3. (a) XRD patterns of G1, G2 and G3 before ASR, (b) XRD patterns of G1, G2 and G3 before ASR showing the peak (101) of quartz, (c) XRD patterns of G1, G2 and G3 before ASR showing the peak of calcite and dolomite in G3 only.

The tested $4 \times 4 \times 16$ cm³ samples are manufactured with Portland Cement CEM I 52.5 R and tap water. The w/c is kept at 0.5. 24 h after manufacturing, specimens were demoulded and water-cured for 28 days. The result of compressive and flexural strengths of mortars is the average of three tests.

As shown in Table 1, G1 and G2 have approximately the same density that SS, which confirm their siliceous nature. G3 has the highest water absorption.

3 Results and discussion

3.1 Physical and chemical study

3.1.1 Transmission electron microscope (TEM)

The Figure 2 shows three images for aggregates G1, G2 and G3. Zones of different sizes ranging from 100 nm to a few hundred nanometers, with angular sides characterizing angles of quartz can be seen for G1 and G2. Moreover, other areas of a rather disordered or amorphous structural can be seen. For G3 a more heterogeneous aspect is observed.

3.1.2 The X-ray diffraction (XRD)

The XRD patterns of three aggregates are shown in Figures 3a–3c. Figure 3a shows that G1 and G2 aggregates contain SiO₂ quartz type as major component compared to G3 as observed in Figure 3b. In contrast, G3 contains SiO₂ quartz type and calcite (CaCO₃) as major component and the dolomite phase (CaMg(CO₃)₂) as minor phase (Fig. 3c) confirming that G3 is more heterogeneous than G1 and G2.

X-ray powder patterns for G1A, G2A and G3A after ASR reaction are shown in Figure 4a. Except some phases with long- and medium-range disorder, making it amorphous to X-ray diffraction, the patterns exhibit the presence of SiO₂ quartz type Figure 4b and Ca(OH)₂ for G1A, G2A and G3A. In addition, G3A contains calcite. Note the absence of the dolomite phase after reaction in G3A is observed in Figure 4c.

Figure 4c shows the peak corresponding to portlandite phase where the intensity decreases from G1A to G3A (IG1A > IG2A > IG3A).

It seems that even if the presence of calcite in G3 may improve its resistance, the complete transformation of dolomite after ASR increases its reactivity. This result is confirmed by the portlandite behavior. Note that after ASR, the intensity of the Portlandite peak decreases from G1A to G3A showing that G3 consumes more portlandite than G1 and G2 as seen in Figure 4d.

3.2 Mechanical study

The compressive strength of reference mortar (M.SS) is of ≈ 67 MPa. This high strength characterize materials with CEM I 52.5 R, considered as high quality cement, with high reactivity. The incorporation of G1 and G2 aggregates decreases by $\approx 10\%$ the compressive strength of mortars (Fig. 6). As the granular skeleton is the same for all tested aggregates, this difference could be attributed to

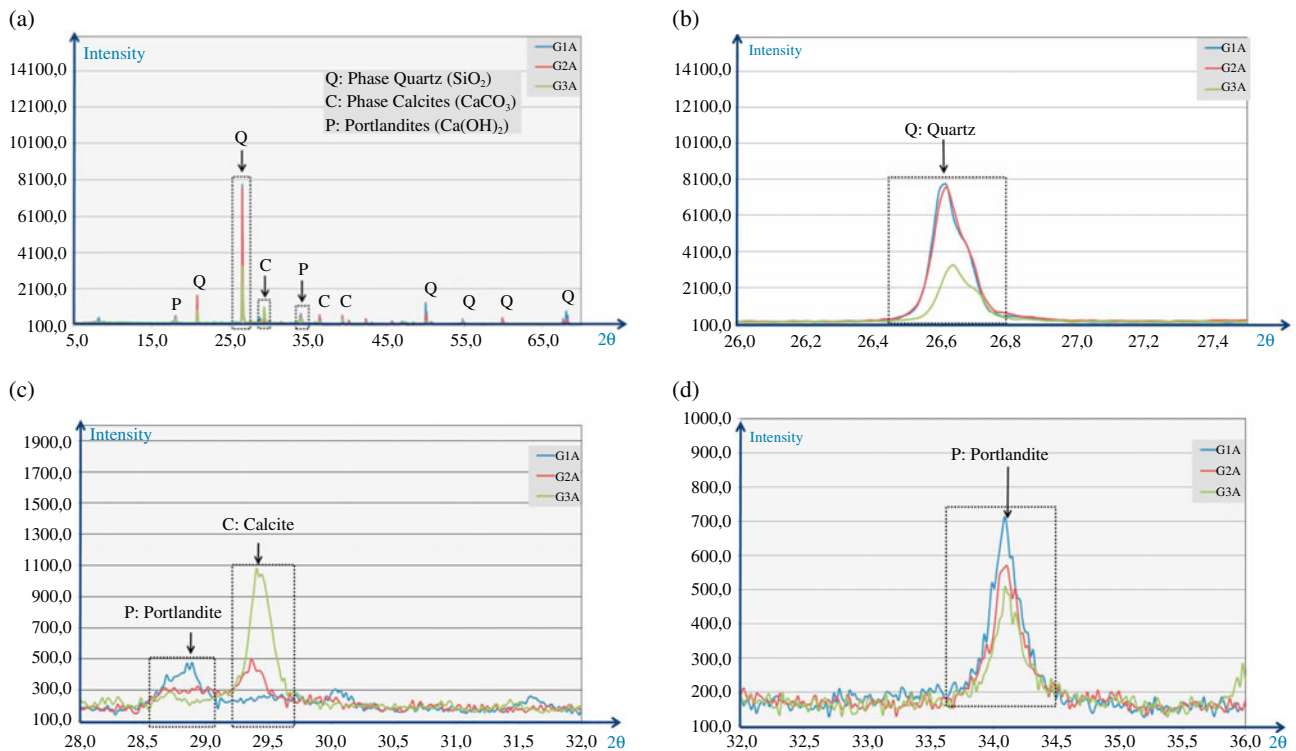


Fig. 4. (a) XRD patterns of G1A, G2A and G3A after ASR, (b) XRD patterns of G1, G2 and G3 after ASR showing the peak of quartz, (c) XRD patterns of G1A, G2A and G3A after ASR showing calcite and portlandite, (d) XRD patterns of G1A, G2A and G3A after ASR showing portlandite.

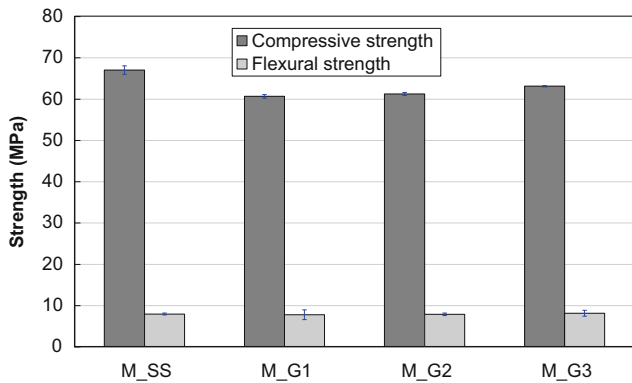


Fig. 5. Compressive and flexural strength of tested mortars.

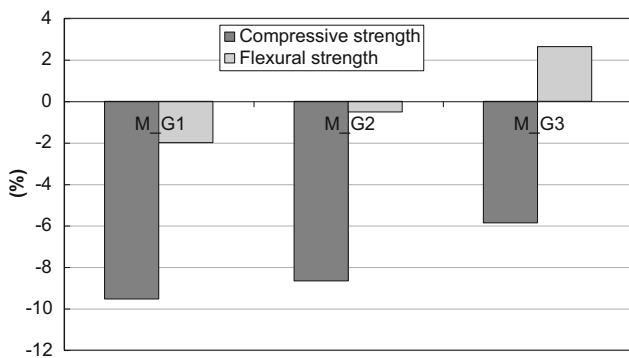


Fig. 6. Relative decrease/increase of compressive and flexural strength of M-G1, M-G2 and M-G3.

the quality/property of natural sands. These sands contain some impurities (organic, clay...), which affect the mechanical strength of mortars (Fig. 5).

Compared to G1 and G2, G3 improves the compressive strength of mortar without exceeding that of reference (-6%). This result confirms previous observations (§1). Indeed, chemical reactions could occur between tricalcium aluminate and calcite from calcareous aggregates [20,21], which improves aggregate/cement paste bound and then decreases the interfacial transition zone (ITZ) porosity.

4 Conclusions

In this research, the behavior and microstructural constituents of three natural siliceous aggregates (called G1, G2 and G3) under ASR process were investigated. The following conclusions can be drawn:

- the structural composition of the three natural aggregates shows that G1 and G2 have almost the same chemical composition (SiO_2) and G3 is different and contains SiO_2 quartz type and calcite as major components (SiO_2 , calcite and dolomite);
- the presence of dolomite phase increases the reactivity of G3;
- after alkali silica reaction (ASR) process, the reactivity of G3 aggregate is higher than the G1 and G2 aggregates;

- even if the measured compressive strengths of manufactured mortars with G1, G2 and G3 are less than that of reference mortar, the difference is minor and the valorization of these aggregates in cementitious materials could be very interesting;
- the reactivity of G3 improves aggregates/cement paste bound and thus the compressive strength of mortar, in comparison to G1 and G2.

This research was supported by European FEDER and region Nord-Pas-de-Calais.

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