Study of the thermal treatment of SiO₂ aggregate

N Tahiri¹,², L Khouchaf¹,*, M Elaatmani², G Louarn³, A Zegzouti² and M Daoud²

¹ Univ-Lille Nord de France, Research Center of Ecole des Mines de Douai, Rue Charles Bourseul BP10838 59808, Douai, France.
² Cadi Ayyad University, Chemical Department, Faculty of Sciences Semlalia, Bd Prince My Abdellah, 40000, Marrakech, Morocco.
³ Institut des Matériaux Jean Rouxel, UMR 6502, Université de Nantes-CNRS, 2, 14 Rue de la Houssinière 44322, Nantes Cedex, France.

*Corresponding author : lahcen.khouchaf@mines-douai.fr

Abstract: Crystalline quality and the silanoles defects (Si–OH) present within the structure of natural SiO₂ play an important role in its reactivity. In this work, the relationship between the loss of silanoles and the crystallinity improvement upon heating between 450 °C and 650 °C was shown using X-Ray Diffraction (XRD) and Fourier Transform mid Infrared Spectroscopy in Attenuated Total Reflection (ATR). A shift of the principal band Si-O-Si from 1078 cm⁻¹ to 1082 cm⁻¹ and the decrease of the intensity of the Si–OH bands at 555 cm⁻¹ and at 950 cm⁻¹ upon heating between 450 °C and 650 °C were shown. The reduction of the band is correlated to the loss of silanoles. In agreement with FT-IR results, the decrease of the FWHM of the XRD peaks shows that the crystalline quality is improved upon heating. This result leads to a decrease of the reactivity of SiO₂ aggregate under chemical attacks.

Keywords: SiO₂; Reactivity; Thermal treatment; Crystallinity

1. Introduction
To improve the properties, such as strength and durability, of some materials, SiO₂ compounds may be used [1,2]. The reactivity of SiO₂ compounds depends on the chemical process that occurs in amorphous or poorly crystallized SiO₂ present in the mineral aggregates [3, 4, 5]. SiO₂ compound is a natural SiO₂ used as an aggregate in composite materials such as concrete. The degradation of concrete depends on the crystalline quality of the aggregate [6].

The presence of defects in the structure of the silica increases its reactivity [7, 8, 9] with respect to alkali-silica reaction (ASR) which causes the dissolution of the silica network, the formation of expansive gels and hence the damage of the concrete [10,11,12,13]. Previous studies have confirmed the presence of silanoles groups in natural silica used directly in the initiation step of the ASR [14, 15, 16].

P. Schmidt et al. [17, 18] showed that this type of defects can be reduced by heat treatment. According to them, a heat treatment of natural silica results in the formation of siloxane bridges Si-O-Si according to reaction below,

\[
\text{Si-OH + HO-Si} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}
\]
According to the equation above, consumption of silanoles Si-OH leads to siloxane Si-O-Si bonds formation, which improves the recrystallization of the material due to an increase of crystallite size [18, 19]. However, the choice of temperature, speed and duration of the heat treatment are important parameters for the maximum silanoles evaporation and at the same time to avoid the fracturing aggregate phenomenon [17, 18, 19].

The loss of silanoles begins at 250 °C, resulting in the formation of siloxane and water molecules trapped in small pores isolated within the grains. Most silanoles are removed between 550-600 °C [17]. Increasing the temperature above 500 °C leads to a rise in the pressure level, which causes the isolated fracture appearance, allowing water molecules to drain [17] from pores.

Another factor that affects the temperature of fracturing is the speed of the heat treatment; if this speed is high enough, it leads to the occurrence of a temperature gradient between the interior and exterior of the grain in heat treatment, resulting in a heterogeneous thermal expansion and thus fracturing [18].

The duration of heat treatment plays an important role in the process of dehydration of flint [20]. P. Schmidt et al. [17] found that there is no difference between samples heat treated for 3 h and 6 h regarding the loss of silanoles, and a heating time of 50 minutes is largely sufficient [20].

The aim of this work was to follow the structural changes of a natural flint aggregate subjected to different temperatures. The objective was to minimize defects (silanoles type) and improve the crystallinity of the aggregate to optimize its use as a concrete skeleton. The study was conducted using the X-ray diffraction, infrared spectroscopy, and the transmission electron microscope.

2. Materials and methods

The aggregate used in this study is a natural flint with 99.1% of SiO$_2$; it has a disordered crystallographic structure compared to alpha quartz. The sample underwent experimental heat treatment at two temperatures (table 1) and was analyzed by means of different techniques.

The procedure of heat treatment is summarized in figure 1.

Table 1. Annealing temperatures

| Sample Annealing temperature | T$_3$ | T$_3$t$_1$ | T$_3$t$_2$ |
|-----------------------------|-------|------------|------------|
| 25°C                        | 450°C | 650°C      |

Figure 1. Procedure of heat treatment

XRD measurements were performed in the reflection mode using a Shimadzu Bruker D8 Advance diffractometer (Cu-K$_\lambda$ radiation = 1.5418 Å"), which operates at 40 kV and 40 mA. Data were
collected in the range of 25°–75° in the 2θ scale with a step size of 0.02° and a counting time of 0.5 s/step.

Spectra were acquired with a Brucker VERTEX 70 FTIR spectrometer in reflection mode. They were recorded by collecting 100 scans at 4 cm\(^{-1}\) resolution in the range of 400–5000 cm\(^{-1}\).

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 LaB\(_6\), a double-tilt holder and Gatan digital camera.

3. Results and discussion

3.1. Transmission Electron Microscope

Figure 2 shows an image of sample T\(_3\). Zones of different sizes ranging from ten nanometers to a few hundred micrometers, with angular sides characterizing angles of quartz can be seen. Moreover, other areas of a rather disordered or amorphous appearance are observed.

![Figure 2. TEM micrograph of T\(_3\)](image)

3.2. X-ray diffraction

Figure 5 shows the XRD patterns of sample T\(_3\) and quartz, which were analyzed in the same conditions indicating the crystallized structure of both compounds. By comparing the two diagrams of samples, it can be seen that they have the same peak positions, while T\(_3\) has broader and less intense ones compared to the quartz peak. It can be deduced that sample T\(_3\) is mainly composed of a crystalline-phase quartz, with the presence of structural defects and disordered fraction.
To evaluate changes in the crystallinity of the samples as a function of temperature, the width at half height of the diffraction peaks of the raw flint and after heat treatment was studied.

According to figures 4 and 5, the intensity of the peak (101) increases and the Full Width at Half Maximum (FWHM) decreases with temperature. This result indicates an improvement in the crystallinity of heat treated T₃. It can also be seen that the FWHM is lower at the temperature of 650 °C.
3.3. Infrared spectroscopy

Figure 6 shows the infrared IR spectra between 400 cm\(^{-1}\) and 1400 cm\(^{-1}\) of the unheated (T\(_3\)) and heated (T\(_{3t1}\), T\(_{3t2}\)) flints.

The infrared spectrum of unheated flint T\(_3\) has a broad band between 1000 and 1300 cm\(^{-1}\). This band consists of two strong peaks located at 1078 cm\(^{-1}\) and 1163 cm\(^{-1}\). These peaks are associated with the stretching vibration of Si-O-Si [21, 22, 23, 24, 25]. In addition, bending vibrations attributed to Si-O-Si [18, 20, 21, 23, 25, 26] located at 455 cm\(^{-1}\), 509 cm\(^{-1}\), 778 cm\(^{-1}\) and 800 cm\(^{-1}\) are observed in the spectrum.

The bands located at 555 cm\(^{-1}\) and 950 cm\(^{-1}\) are associated with Si-O bending vibrations of no bridging Si-OH bonds and stretching vibration respectively [20, 21, 22, 23, 26, 27]. Heated flint T\(_{3t1}\) did not show significant changes in the infrared IR spectrum.
The spectrum of the sample heated at 650 °C (T<sub>t2</sub>) shows a reduction of bands located at 555 cm<sup>-1</sup> and 950 cm<sup>-1</sup>, an increased intensity of the bands located at 455 cm<sup>-1</sup> and 800 cm<sup>-1</sup> and a shift of the main band from 1078 cm<sup>-1</sup> to 1082 cm<sup>-1</sup>. The position of this band is connected to the structure in the order of SiO<sub>2</sub>. The shift of the observed position of the band from 1078 cm<sup>-1</sup> to 1082 cm<sup>-1</sup> may be attributed to an improvement in structural order with the increase in temperature in accordance with previous studies [21]. The more the structure is ordered, the more this band is located at the large wave numbers. Similarly, the reduction bands at 555 cm<sup>-1</sup> and 950 cm<sup>-1</sup> at 650 °C can be attributed to the departure of some silanoles groups. These results are in agreement with the XRD changes with temperature.

4. Conclusion

Using XRD in combination with FT, the structural change of SiO<sub>2</sub> natural flint with temperature was successfully investigated. A shift of the principal Si-O-Si band from 1078 cm<sup>-1</sup> towards 1082 cm<sup>-1</sup> and decrease of Si–OH band intensity at 555 cm<sup>-1</sup> and at 950 cm<sup>-1</sup> upon heating between 450 °C and 650 °C were observed. XRD patterns showed a decrease of the FWHM of the peaks (101) upon heating between 450 °C and 650 °C.

According to existing studies, the observation implies the crystalline quality improvement and the decrease of the silanoles Si-OH defects, which lead to a decrease of the reactivity of SiO<sub>2</sub> aggregate under chemical attacks typically by ASR.

References

[1] Najigivi A, Khaloo A, Iraji zad A and Abdul Rashid S 2013 Investigating the effects of using different types of SiO<sub>2</sub> nanoparticles on the mechanical properties of binary blended concrete J. Composites B 54 52-
[2] Hanus M J and Harris A T 2013 Nanotechnology innovations for the construction industry J. Progress in Materials Science 58 1056-1102

[3] Verstraete J, Khouchaf L and Tuilier M H 2004 Contributions of the environmental scanning electron microscope and X-ray diffraction in investigating the structural evolution of a SiO$_2$ aggregate attacked by alkali–silica reaction J. Materials Science 39 6221-6226

[4] Khouchaf L and Boinski F 2007 Environmental scanning electron microscope study of SiO$_2$-heterogeneous material with helium and water vapor J. Vacuum 81 599

[5] Khouchaf L, Hamoudi A and Cordier P 2009 Evidence of depolymerisation of amorphous silica at medium- and short-range order: XANES, NMR and CP-SEM contributions J. Hazardous Materials 168 1188–1191

[6] Yurttas I, Chen D, Hu D W and Shao J F 2013 Influence of alkali silica reaction (ASR) on mechanical properties of mortar J. Construction and Building Materials 47 165–174

[7] Boinski F, Khouchaf L and Tuilier M H 2010 Study of the mechanisms involved in reactive silica J. Materials Chemistry and Physics 122 311–315

[8] Ichikawa T 2009 Alkali–silica reaction, pessimum effects and pozzolanic effect J. Cement and Concrete Research 39 716–726

[9] Khouchaf L, Boinski F, Tuilier M H and Flank A M 2006 Characterization of heterogeneous SiO$_2$ materials by scanning electron microscope and micro fluorescence XAS techniques J. Nuclear Instruments and Methods in Physics Research B 252 333–338

[10] Ben Haha M, Gallucci E, Guidoum A and Scrivener K L 2007 Relation of expansion due to alkali silica reaction to the degree of reaction measured by SEM image analysis J. Cement and Concrete Research 37 1206–1214

[11] Prezzi M, Monteiro P J M and Sposito G 1997 The alkali-silica reaction, part I: use of the double layer theory to explain the behavior of reaction-product gels J. ACI Materials 94 10-17

[12] Gao X X, Stéphane Multon S, Cyr M and Sellier A 2013 Alkali–silica reaction (ASR) expansion: pessimum effect versus scale effect J. Cement and Concrete Research 44 25–33

[13] Rivard P, Ollivier J P and Ballivy G 2002 Characterization of the ASR rim application to the potsdam sandstone J. Cement and Concrete Research 32 1259–1267

[14] Verstraete J, Khouchaf L, Bultheel D, Garcia-Diaz E, Flank A M and Tuilier M H 2004 Amorphisation mechanism of a flint aggregate during the alkali–silica reaction: X-ray diffraction and X-ray absorption XANES contributions J. Cement and Concrete Research 34 581–586

[15] Khouchaf L and Verstraete J 2007 Multi-technique and multi-scale approach applied to study the structural behavior of heterogeneous materials: natural SiO$_2$ case J. Materials Science 42 2455–2462

[16] Hamoudi A, Khouchaf L, Depecker C, Revel B, Montagne L and Cordier P 2008 Microstructural evolution of amorphous silica following alkali–silica reaction J. Non-Crystalline Solids 354 5074–5078

[17] Schmidt P, Badou A and Fröhlich F 2011 Detailed FT near-infrared study of the behaviour of water and hydroxyl in sedimentary length-fast chaledony, SiO$_2$, upon heat treatment J. Spectrochimica Acta A 81 552-559

[18] Schmidt P, Masse S, Laurent G, Slodczyk A, Le Bourhis E, Perrenoud C, Livage J and Fröhlich F 2012 Crystallographic and structural transformations of sedimentary chaledony in flint upon heat treatment J.Archaeological Science 39 135-144

[19] Domanski M and Webb J A 1992 Heat treatment of Polish flints J.Archaeological Science 19 601-614

[20] Schmidt P and Fröhlich F 2011 Temperature dependent crystallographic transformations in chaledony, SiO$_2$, assessed in mid infrared spectroscopy J. Spectrochimica Acta A 78 1476-1481

[21] Garnica-Romo M G, Yanez-Limon J M, Villicana M, Perez-Robles J F, Zamorano-Ulloa R and Gonzalez-Hernandez J 2004 Structural evolution of sol–gel SiO$_2$ heated glasses containing silver particles J. Phys. Chem. Solids 65 1045-1052

[22] Barbosa G N and Oliveira H P 2006 Synthesis and characterization of VO$_2$–SiO$_2$ xerogel composites prepared by base catalysed sol–gel method J. Non-Cryst Solids 352 3009-3014

[23] Kim H U and Rhee S W 2000 Electrical properties of bulk silicon dioxide and SiO$_2$/Si interface formed by
tetraethylorthosilicate-ozone chemical vapor deposition *J. Electrochemical Society* **147** 1473-1476

[24] Chen Z L and Shen P 2012 Thermally activated sintering–coarsening–coalescence-polymerization of amorphous silica nanoparticles *J. Ceramics International* **39** 2365-2373

[25] Jung K T, Chu Y H Chu, Haam S and Shul Y G 2002 Synthesis of mesoporous silica fiber using spinning method *J. Non-Cryst Solids* **298** 193–201

[26] El Rassy H and Pierre A C 2005 NMR and IR spectroscopy of silica aerogels with different hydrophobic characteristics *J. Non-Cryst Solids* **351** 1603-1610

[27] Domanski M and Webb J A 1992 Effect of heat treatment on siliceous rocks used in prehistoric lithic technology *J. Archaeological Science* **19** 601-614