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Characterization of heterogeneous SiO_2 materials by scanning electron microscope and micro fluorescence XAS techniques

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Abstract

Micro X-ray absorption near edge structure XANES and micro fluorescence experiments have been carried out using X-ray microbeam from synchrotron radiation source with high brightness to investigate the local structural evolutions of heterogeneous and natural SiO_2 submitted to alkali-silica reaction ASR process. Compared to elemental maps obtained by Environmental Scanning Electron Microscope ESEM, micro fluorescence X maps showed the diffusion of potassium cations inside the grains with higher accuracy. Si K-edge spectra show the disorder induced by the dissolution of the grain from the outside to the inside. Potassium K-edge spectra do not show significant changes around K cations. The breaking of Si–O–Si bonds and the disorder of the $(SiO_4)_n$ network may be affected to potassium cations.

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1. Introduction

The study of the structural evolution of SiO_2 is of great importance in the field of materials science [1]. Synthetic SiO_2 compounds are used for several applications depending on the scale and the related field (semiconductors industry, optics species,...). Natural SiO_2 compounds are also very much used in geosciences, chemistry,... Properties of either synthetic or natural SiO_2 compounds interest both Physicists and Chemists [2]. In particular, heterogeneous and natural SiO_2 is a major component of concrete. The presence of some defects and the local structure are the substantial parameters, which influence the durability of such a composite material like concrete [3]. Compared to homogeneous and synthetic SiO_2 compounds, the study of the structural properties of heterogeneous and natural SiO_2 within the concrete is more difficult [4]. To study heterogeneous materials, the high brightness of synchrotron radiation enables to obtain data with good quality from micro zones containing elements with low energy absorption edges. X-ray absorption spectroscopies such as EXAFS and XANES at the Si K-edge are very sensitive to local structure changes in SiO_2 references compounds [5–8]. Other studies have been performed in heterogeneous materials such as SiO_2 aggregate [9,10]. In a recent study [11] we have developed a multi-technique and multi-scale approach in order to follow the structural properties of a natural heterogeneous material such as SiO_2 flint. The physicochemical analysis and characterization of the SiO_2 flint by using XRD, ESEM, EXAFS, XANES and NMR techniques have performed. Substantial and accurate information have been obtained which help us to progress in the

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knowledge of the nano-mechanisms involved during the SiO_2 degradation. One phenomenon that takes part in the degradation of the concrete is called alkali-silica reaction (ASR) [12–15]. Several works have been carried out in order to study the effects of the ASR process in the degradation of concrete containing SiO_2 as an aggregate type [12–15]. The structural behavior of SiO_2 aggregate during its degradation is a good parameter in the evaluation of the durability of the concrete [10]. The formation and the evolution of amorphous and poorly crystallized phases could induce a variation of the volume of the aggregate and consequently participate in its swelling, at the origin of the rise of internal stresses in the concrete [4].

However, local order simultaneously around different atoms such as silicon, calcium and potassium atoms in the phases resulting from ASR process has not yet been studied. In previous EXAFS, XANES and NMR studies [10,11], we showed the structural changes in the aggregate and introduced a new explanation of the mechanism of the degradation of the SiO_2 aggregate by ASR.

The aim of this study is to use micro-beam probe for micro zones in order to follow the evolution of the local structure of heterogeneous and natural flint aggregate SiO_2 during the ASR process. The results will be compared to those obtained by environmental scanning electron microscope by microanalysis probe.

2. Experimental and material

The aggregate studied is a natural flint with 99.1% of SiO_2 as indicated by X-ray fluorescence analysis and has a disordered crystallographic structure compared to alpha quartz. The aggregate has been submitted to a procedure attack by ASR process, which has been previously described [4] but is briefly summarized here. The aggregate (1 g of crushed flint) was subjected to accelerated ASR at 80 °C with a mixture of 0.5 g of portlandite $Ca(OH)_2$ and 10 ml of potash solution KOH at 0.79 mol/l.

Environmental scanning electron microscope (ESEM) ''ElectroScan 2020'' equipped with EDS Microanalysis system ''Oxford Link Isis'' was used to perform imaging and elemental maps and some profiles. The electron source is a tungsten filament. The accelerating voltage is fixed at 20 kV with a probe current of 130 pA. A long electron secondary detector (ESD) at a working distance of 19 mm is used in order to reduce the skirt beam phenomena which can be produced after interaction between electron beam and the gas present in the sample chamber [16]. Elemental maps and the profiles of the different elements were collected using a 10 mm^2 surface of a Si(Li) detector with a takeoff angle of 30° and a 0° sample tilt. Such system has an energy resolution of 133 eV at 4900 eV. The starting aggregate (before reaction) was powdered at liquid nitrogen temperature. The average particle size of the grains is in the range 160–630 μm. After ASR attack, the grains are embedded in a resin and polished. No water was used neither during the preparation process nor during ESEM and XAS experiments. The specimen was observed directly without any coating process. The removing of charges on the surface of the sample is done by the ionisation of helium gas introduced in the chamber by primary electron beam [16].

Micro XRF and micro XAS experiments were carried out on the LUCIA beamline at the swiss light source (SLS) [17]. The high brightness of synchrotron radiation leads to obtain data with good quality from micro zones of heterogeneous materials. Micro fluorescence elemental maps have been obtained with an incident photon energy $E = 4200$ eV in order to improve emission yield of different elements (Ca, K, Si and O). Micro XANES spectra at Si K-edge, K K-edge were recorded using InSb(1 1 1) and Si(1 1 1) monochromators respectively. Three scans were averaged with a step of 0.3 eV and 3 seconds by steps were chosen. Spectra were recorded, at room temperature, under high vacuum (10^{-5} Torr) in fluorescence mode on a grain embedded in epoxy resin. Micro zones of the grain have been studied with 6×12 μm^2 beam sizes obtained by a Kirkpatrick–Baez (KB) reflecting mirror system. This operation needs a particular attention in order to be sure that the localized zone is the one to characterize. Elemental maps have been registered in order to localize the diffusion of different cations. Data analysis was performed using ATHENA software [18].

3. Results

Fig. 1 shows the image of the studied grain obtained from environmental scanning electron microscope (ESEM). The image obtained with backscattered electrons (BSE) mode shows a chemical contrast and indicates the heterogeneous characteristic of the aggregate.

The elemental maps obtained by microanalysis probe in the ESEM (Fig. 2) show the distribution of different

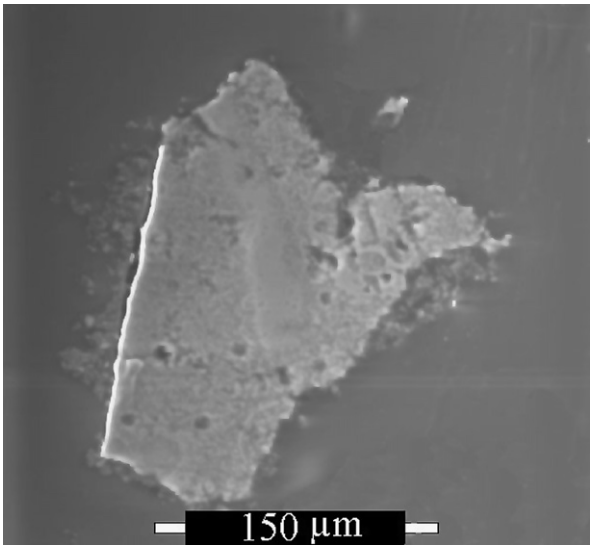

Fig. 1. Environmental scanning electron microscope BSE micrograph of the studied grain.