

## Experimental modeling of burnt oil shale impact towards ASR

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### Abstract

The alkali-silica reaction (ASR) is a civil engineering issue that can be inhibited using supplementary cementitious materials such as burnt oil shale. Furthermore, these allow an improvement of the properties of the concrete as increasing density and compressive strength. Currently, the tests to characterize the development of the ASR in concrete are very long and can take more than a year.

This paper proposes to model the impact of mineral addition towards ASR by short time laboratory testing via the model reactor in order to assess the inhibition. The study was conducted on fine flint aggregate, as a reactive aggregate, with burnt oil shale as supplementary cementitious material.

At the end of the tests, a liquid phase and a solid phase are recovered. The liquid phase is analyzed by Inductively Coupled Plasma Emission Spectroscopy (ICP-OES) to follow the evolution of the chemical elements in solution. The solid phase was analyzed by BET/BJH method, thermogravimetric analysis (TGA) and helium pycnometry. Microscopic observations by Scanning Electron Microscope (SEM) were also carried out.

The results show an increase of the absolute density whereas porosity and specific surface decrease by adding burnt oil shale. This addition yields less aggregate alteration. The observation by SEM shows less micro-cracks and a modification of reaction products in the presence of burnt oil shale. ICP-OES analyses are consistent with less dissolved silica in solution.

**Keywords:** ASR; burnt oil shale; model reactor; pozzolanic reaction; reactive aggregate

## 1. INTRODUCTION

The Alkali-Silica Reaction (ASR), defined for many years as one of the most damaging reactions in concrete, initiates the alteration of the SiO<sub>2</sub> crystal lattice and generates expansive reaction products. Mineral additions are a way to reduce expansion due to ASR to valorize reactive aggregates. The additions may be of natural fine aggregates, burnt or raw materials such as finely milled burnt oil shale or industrial by-products such as blast furnace slag or fly ash. In the presence of mineral additions, the pozzolanic reaction could occur [1]. The reactive silica of pozzolans reacts with interstitial alkaline hydroxides [2], then the calcium of CH from clinker hydration combines with the silica and form pozzolanic C-S-H with a low calcium concentration [3] and varying proportions of water [4]. The pozzolanic C-S-H could fix alkalis [5]. Indeed, the use of mineral addition is a way to increase the capacity of alkali-neutralization to not exceed the threshold of alkali neutralization of the granular skeleton and hence decreasing the concrete expansion [6]. Therefore, potentially reactive aggregates can be valorized and a non-degraded concrete is obtained. Supplementary Cementitious Materials (SCMs) such as burnt oil shale have been demonstrated to improve mechanical properties [7, 8]. Finely crushed burnt oil shale allow filling the voids as silica fumes and fly ashes [9]. The employment of burnt oil shale in highly alkali cement has already shown good results to mitigate the ASR development [10, 11]. In this paper, the Dottenhausen shale was used. It's characterization was carried out by Thiéry et al. [12]. The use of burnt oil shale from Dottenhausen has already shown a beneficial effect with respect to the ASR in Bourdot et al. [13]. Nevertheless, the study required more than a year and a half of data recovery, analysis and observations. In order to reduce this time of characterization of ASR development but also of the impact of burnt oil shale on this pathology, this study focuses on the use of the model reactor developed by Bulteel et al. [14] to study the inhibition. As a first step, a reference reactive aggregate, flint aggregate, was tested to assess the feasibility and reproducibility of this process for other aggregates. This model reactor is composed of a liquid and a solid phase, which was studied over

time by different physical and chemical analysis methods. The solid phase was also observed microscopically.

## 2. MATERIALS AND METHODS

### 2.1 Materials

The aggregate used in this study is a potentially alkali-reactive aggregate with a pessimum effect. The bulk whole-rock main element oxide composition is given in Table 2.1. The aggregate is a flint aggregate from Conchil le Temple in France. The flint reactive aggregate used as a reference is named aggregate C in this paper. The aggregate is very reactive and has been studied previously [6]. The reactive 4/14 mm coarse aggregate, employed in this study, was crushed and reduced to a fraction size of 0.16/0.63 mm.

Burnt oil shale (BOS) used in this study is a residue from the combustion of so-called “Black Shale” from Dotternhausen Power Plant (Germany). Residues resulting from the calcination of oil shale are burnt oil shale. The main element oxide composition of BOS is presented in Table 2.1. BOS is considered as pozzolanic material [13] with respect to standards NF EN 450-1 [15] and ASTM C618 [16].

Table 2.1: Bulk whole-rock main element oxide composition of aggregate C and BOS by XRF and LOI, in wt% [13]

Element	LoD <sup>b</sup>	Aggregate C	BOS
Na <sub>2</sub> O	0.1	0.9	0.4
K <sub>2</sub> O	0.1	<LoD	3.7
MgO	0.1	<LoD	2.2
CaO	0.1	<LoD	24.5
Fe <sub>2</sub> O <sub>3</sub>	0.1	0.7	10.3
Al <sub>2</sub> O <sub>3</sub>	0.1	0.2	17.8
SiO <sub>2</sub>	0.1	97.9	28.3
SO <sub>3</sub>	0.1	0.6	8.6
LOI <sup>a</sup>	0.04	0.7	4.9
Sum total	-	100.8	100.7

a LOI: loss on ignition obtained by TGA analyses.

b LoD: limit of detection.

### 2.2 Model reactor

The SiO<sub>2</sub> present in the aggregate C was previously characterized by reactivity towards ASR [14]. The aim was to determine the proportion of free SiO<sub>2</sub> (potentially reactive). The determination of the free SiO<sub>2</sub> proportion was based on petrography, XRD, and XRF analyses. The reactive part of free SiO<sub>2</sub> was determined by means of the model reactor. The model reactor method is based on a part of the AFNOR P18-594 standard [17] described by Bulteel et al. [14]. The model reactor was used to simulate the ASR and to measure free SiO<sub>2</sub> evolution over time. Then, the reactive free SiO<sub>2</sub> proportion was determined.

The model reactor used for this study is the Aggregate C - Portlandite - NaOH – BOS model. An aggregate mass, which corresponding to 1 g of SiO<sub>2</sub> equivalent (according to XRF analyses), was introduced in a closed stainless steel container with portlandite and sodium hydroxide at 0.79 M. BOS is added from 0 to 1 g. The container was autoclaved at 80°C for 7 days to accelerate the chemical kinetics.

The initial SiO<sub>2</sub> is considered to be only composed of tetrahedrons Q<sub>4</sub> (SiO<sub>2</sub>), as determined by Monnin et al. [18]. During reaction, the initial SiO<sub>2</sub> is altered: Q<sub>4</sub> are consumed and transformed to Q<sub>3</sub> and then converted to Q<sub>0</sub> (H<sub>2</sub>SiO<sub>4</sub><sup>2-</sup>, H<sub>3</sub>SiO<sub>4</sub><sup>-</sup>). At the end of the test, the dissolved SiO<sub>2</sub>, Q<sub>0</sub>, and other element in the liquid phase are analysed by ICP-OES. The siliceous solid residue is composed of unaltered SiO<sub>2</sub>

Q<sub>4</sub> and altered SiO<sub>2</sub> Q<sub>3</sub> (State 1). After acid treatment, the ASR gels, portlandite and carbonated matrix are dissolved (State 2). The residue is composed of Q<sub>4</sub>, protonated Q<sub>3</sub> (SiO<sub>5/2</sub>H), as determined and in very small proportion of insoluble minerals (clays, feldspar, trace minerals). The residues at state 1 and 2 were observed by SEM. The solid phase at state 2 was also analysed by physical methods.

## 2.3 Analytical methods

### 2.3.1 ICP-OES

The liquid residue was analysed by Inductively Coupled Plasma Emission Spectroscopy (ICP-OES) with a VARIAN 720-ES spectrometer in order to follow the evolution of the proportions of elements, especially alkalis, as a function of the proportion of burnt oil shale and as a function of time. The elements monitored are those occurring during the alkali-silica reaction, i.e.: Si, Ca, Na, K, Al and S. Indeed, the increase in Si and the decrease in alkali concentrations (Ca, Na, K) can be indicators of the degradation of silica. Sulphur and aluminium are followed because of their occurrence in BOS. The evolution of each of these elements will make it possible to highlight the development of ASR and the action of BOS.

### 2.3.2 SEM

The observations of the solid residue were carried out with a FEG-HITACHI S-4300SE/N Scanning Electron Microscope equipped with a Thermoscientific Ultradry EDX (Energy Dispersive X-Ray) detector after C-sputter. The specimen surface was assessed using Back-scattered Electron (BSE) imaging mode. Mineral compositions were confirmed by EDX, which was operated at 20 kV and 3.0 nA with a 1 µm probe diameter at the point of incidence. Element spectra were acquired for 60 s with ~20% dead time.

### 2.3.3 Physical methods

The study of the physical parameters was carried out on the solid product resulting from autoclaving after acid attack i.e. at State 2 by thermogravimetric analysis (TGA), helium pycnometry and by BET/BJH method in order to follow the evolution of the density, the porosity and the specific surface.

The density was obtained using an Micromeritics AccuPyc 1330 instrument.

The measurements of the porosity and the specific surface were performed by a Micromeritics 2010 ASAP analyser and are based on the physical methods of gas adsorption and desorption on solids. Measurements were made with nitrogen as adsorbable gas (P<sub>0</sub> = 720 Torr) and the working temperature is that of liquid nitrogen (77 K). From the nitrogen desorption isotherm, the B.J.H. (Barrett, Joyner and Halenda) calculation method allows the determination of the volume distribution of pores between 0.001 and 0.300 µm and the specific pore volume of the material in this pore range [19]. The specific surface is determined by B.E.T (Brunauer, Emmett and Teller) calculation method [20].

The mass loss was determined by TGA using a Netzsch STA409C instrument, rising at a rate of 3°C·min<sup>-1</sup>. The mass lost due to CO<sub>2</sub> correspond in major part to the LOI (loss on ignition).

## 3. RESULTS AND DISCUSSION

### 3.1 Chemical characterization of the liquid phase

The liquid residue, extracted from the model reactor at 7 days, was analysed by ICP-OES. The element concentrations are presented in Figure 3.1.

The proportions of silicon in solution decrease with the increasing rate of burnt oil shale in the model reactor. The amount of Si in solution evolves from about 15,000 to 6,000 ppm, a decrease of about two-thirds. The decrease in Si concentrations is essentially due to the decrease in Q<sub>0</sub> formed. Moreover, this decrease could also be related to the contribution of Si to the formation of pozzolanic C-S-H of lower C/S than C-S-H.

Sodium concentrations tend to decrease with the proportion of BOS. Sodium is the control element for alkali fixation on the pozzolanic C-S-H formed and on the burnt oil shale.

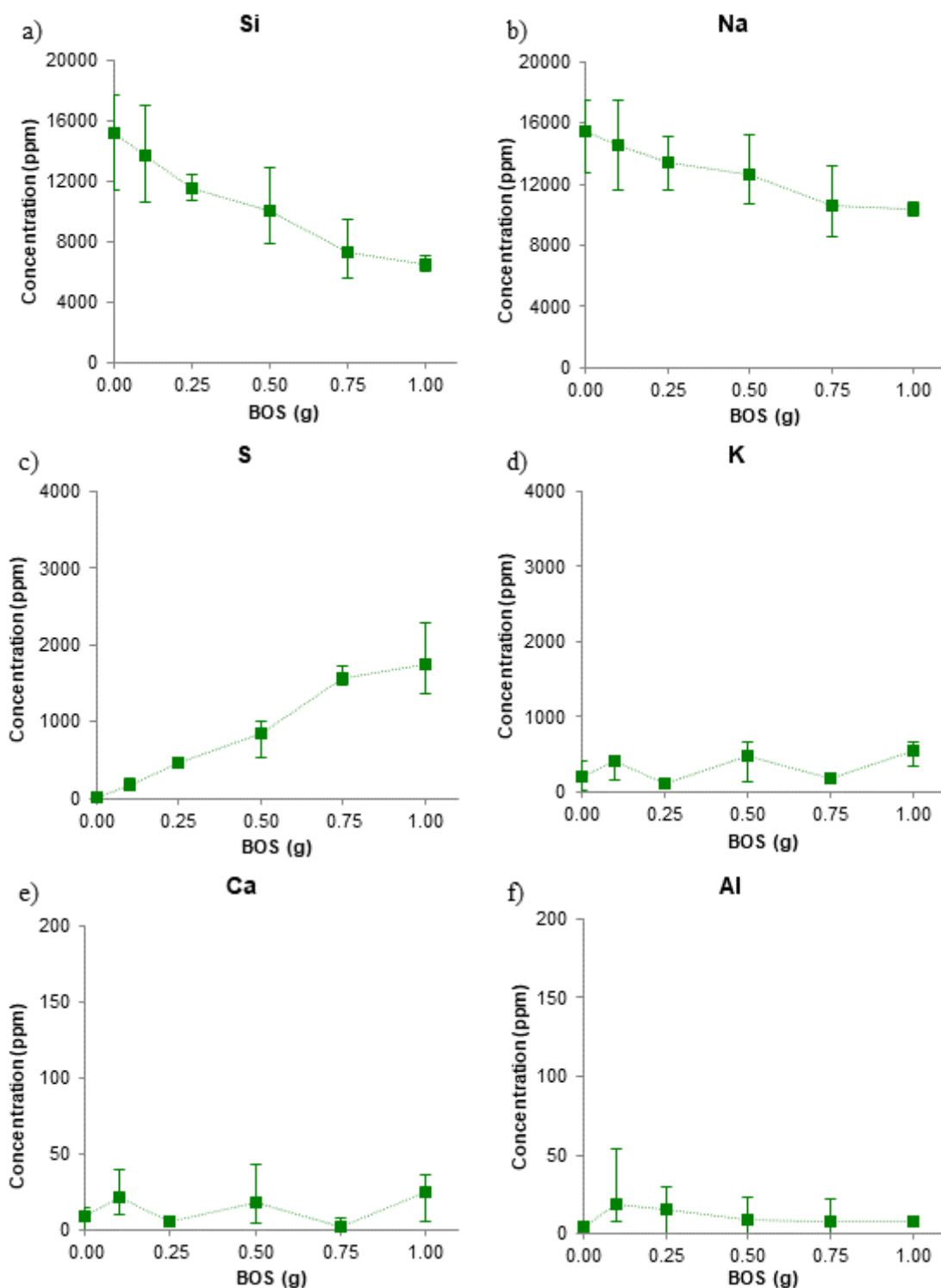


Figure 3.1: Element concentrations by ICP-OES of liquid residue from the model reactor at 7 days with increasing proportion of BOS.

On the contrary, the proportion of sulphur tends to increase with the amount of BOS in the model reactor. The values reached at 1 g of BOS are similar to those of environments with BOS and without aggregates. Sulphur in solution thus comes from burnt oil shale, it is a control element of the presence of burnt oil shale. In the same way, the potassium is brought by the mineral addition, hence the increase of the concentration with the proportion of BOS. Aluminium tends to increase for small proportions in BOS (up to 0.10 g) and then to decrease when the proportion in BOS is higher (more than 0.25 g). Aluminium is therefore consumed by the production of pozzolanic C-S-H known to promote the fixation of this element.

The calcium element does not appear to be significantly affected because it is buffered by the excess presence of portlandite.

### 3.2 Microscopic observations

SEM observations were made on the solid residue at State 1 (recovery without acid etching with ethanol, acetone and ether rinsing - recovery of all reagents and solid reaction products) and at State 2 (recovery with acid etching and acetone and ether rinsing - recovery of healthy and degraded silica).

In State 1 and State 2 the SEM images show degradation of the silica grains after autoclaving for 7 days at 80°C without burnt oil shale. The SEM images show a degraded silica with very cracked areas at State 1 (Figure 3.2 a and b). Silica appears in different forms in State 2: rather smooth and cracked or lumpy with micro porosities (Figure 3-4). At State 1, EDS analyses detect the presence of alkali (Na) and calcium in the silica (Figure 3-3a).

The degraded silica, which is lumpy in form, has formed reaction products. These reactions products have a low C/S ratio (less than 1, Figure 3.3b), and are in needle, sheet or filled form. Figure 3.2c and d, show a cracked gel with needles characteristic of their development.

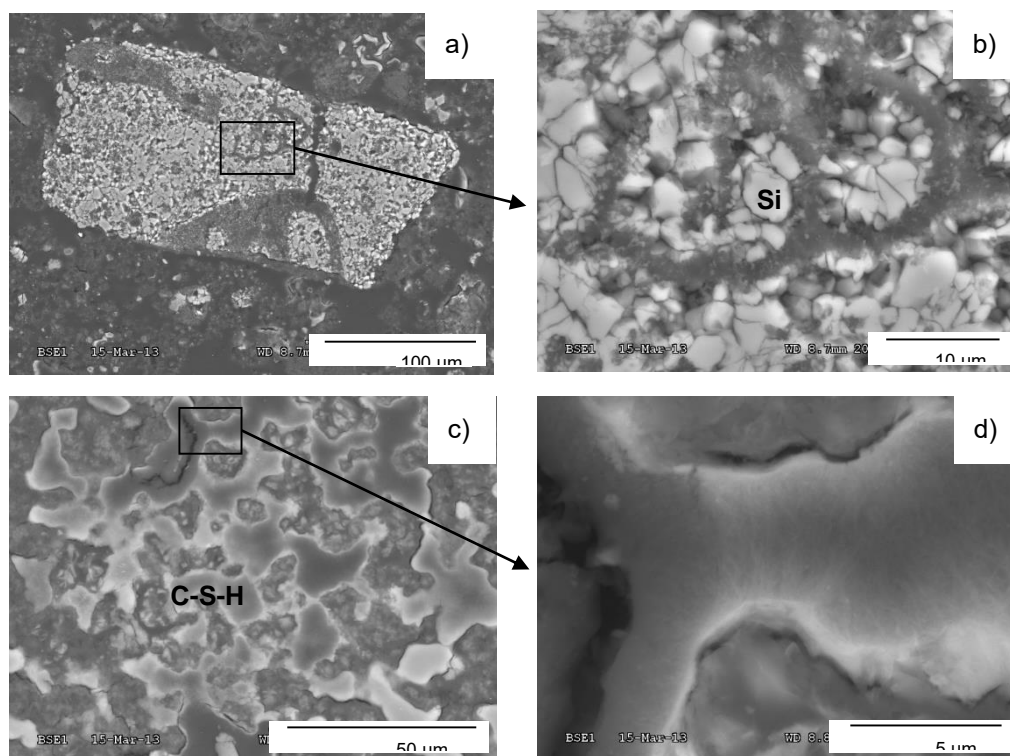


Figure 3.2: SEM images for solid residues at State 1 without BOS. Altered silica (a), zoom on altered silica with alkalis (b), reaction product C-N-S-H (c) composed with needles and with cracks (d).

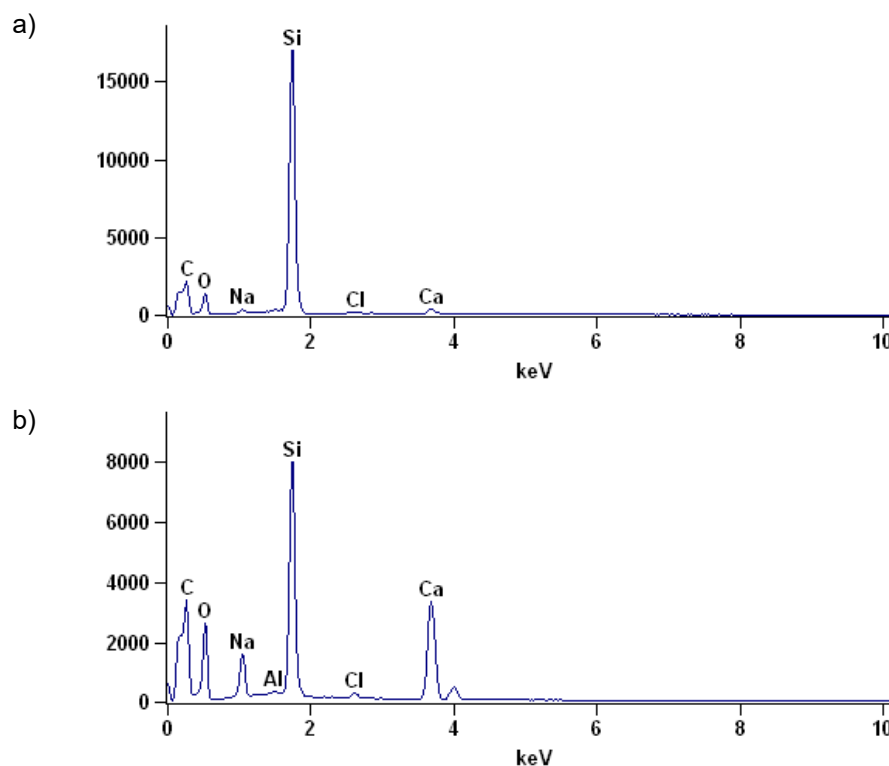


Figure 3.3: EDS analyses of altered silica (a) and reaction product C-N-S-H of Figure 3-2d (b).

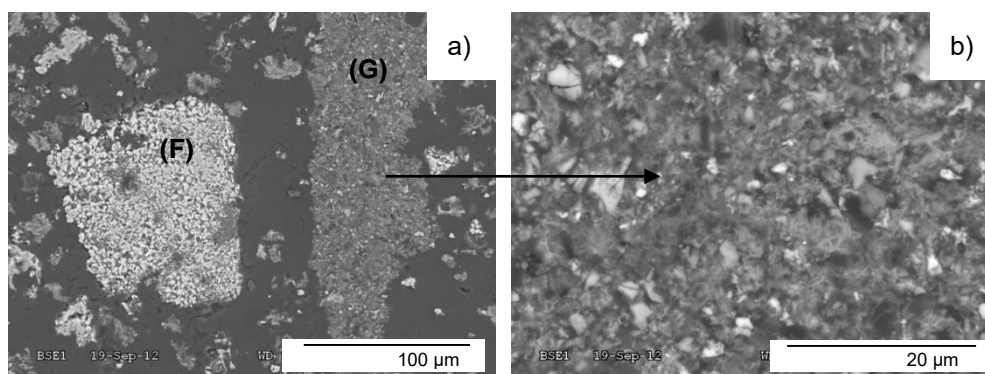


Figure 3.4: SEM images MEB for solid residues at State 2 without BOS: altered silica (F) and lumpy aggregate residue (G) (a) with micro-cracks (b).

In the presence of 0.5 g of burnt oil shale, the SEM images at State 1 and State 2 show a degraded silica but with healthy areas (Figure 3.5, Figure 3.7). At State 2, with 0.5 g of burnt oil shale, the SEM images show a silica which appears less altered and without apparent porosity (Figure 3.5a and b).

The BOS found in the residue at State 1 has retained their initial morphology. The silica of burnt oil shale may present alkalis from the interstitial solution. The silica of the burnt oil shale appears slowly degraded and reacted (Figure 3.5d). The observation of residual BOS in the SEM is consistent with the residual mass data from the blank tests at state 2. Indeed, BOS is still observable after acid attack, nevertheless the proportion of burnt oil shale remains low compared to the mass of the residue from the model reactor consisting of 0.5 g of burnt oil shale.

C-N, K-S-H type C-S-H with a low C/S (less than 1) have been identified (Figure 3.6c and d) and characterized not far from burnt oil shale.



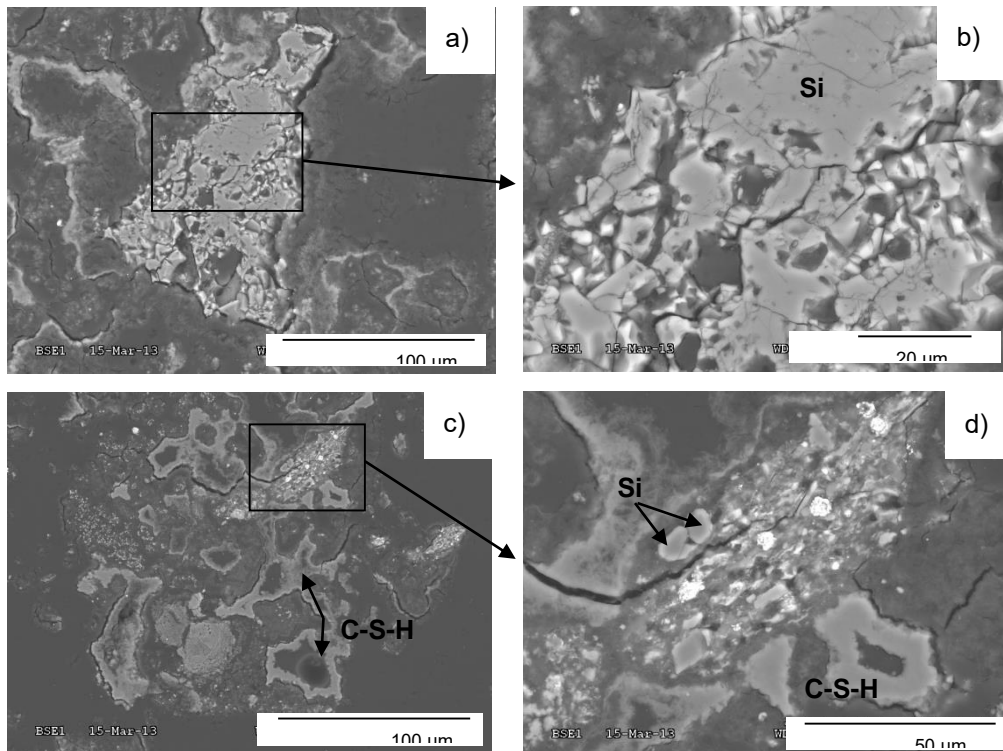


Figure 3.5: SEM images for solid residues at State 1 with 0.5 g BOS: altered silica (a) with cracks and unaltered zones (b), zone with BOS and reaction products (c), C-N, K-S-H (d).

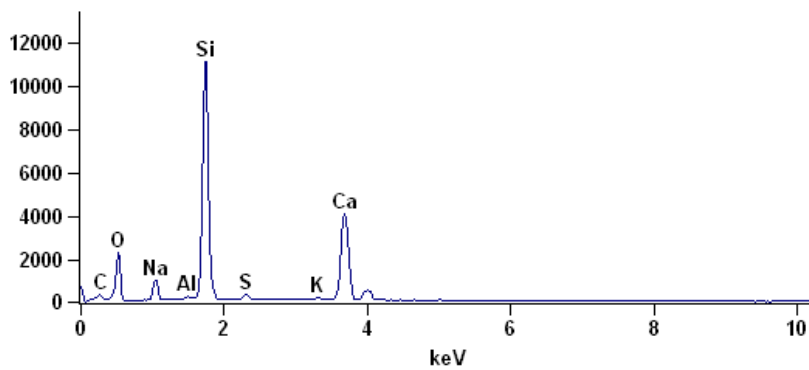


Figure 3.6: EDS analyses of reaction product C-N, K-S-H of Figure 3-5d.

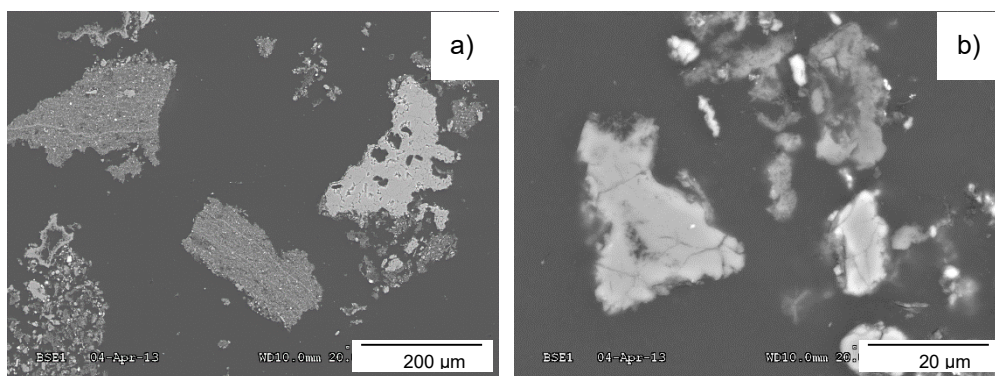


Figure 3.7: SEM images for solid residues at State 2 with 0.5 g BOS (a) and silica residue moderately altered (b).

### 3.3 Physical characterization of the solid phase

The experiments were carried out for the raw flint aggregate C, for model reactor solid residue without burnt oil shale and with different proportions of BOS added, after 7 days of autoclaving at 80°C. The data are averages on at least 3 points. The results are presented in Figure 3.8.

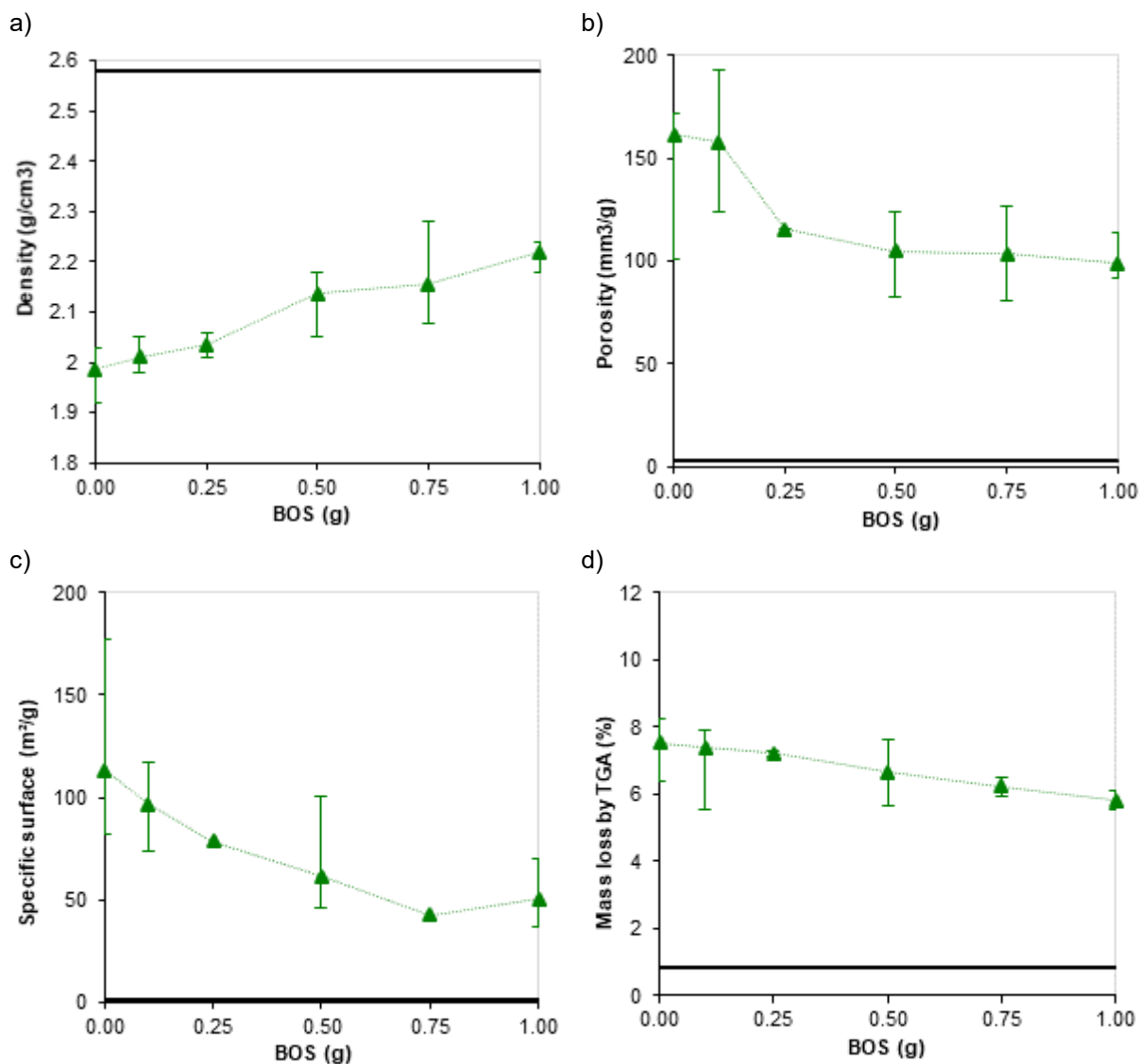


Figure 3.8: Evolution curves of the physico-chemical parameters of the solid residue from model reactor as a function of the proportion of BOS added at 7 days: (a) density, (b) porosity, (c) specific surface, (d) TGA mass loss. Bold line: raw aggregate C values.

The results show an effect of the BOS on different physical parameters of the insoluble residue, i.e. on the residual silica. Indeed, the increase in the quantity of burnt oil shale in the model reactor seems to reduce the alteration of the silica present in the flint aggregate C.

Initially, the raw aggregate reduced to the 0.16/0.63 mm grain size has a density of 2.58 g/cm<sup>3</sup>. In the test without burnt oil shale after 7 days of autoclaving at 80°C, the siliceous residue has a density of about 2 g/cm<sup>3</sup>, much lower than the value of the raw aggregate, indicating the development of ASR. The addition of BOS increases the density of the residue (to tend towards the initial value), particularly with a high proportion of BOS. Indeed, this parameter increases progressively from 0.1 g of BOS up to 1 g of BOS to reach 2.2 g/cm<sup>3</sup>. This parameter makes it possible to highlight the reduction of the alteration of the aggregate linked to the development of ASR when using burnt oil shale in the model reactor.



The raw aggregate has a porosity and specific surface of 2.75 m<sup>2</sup>/g and 0.97 mm<sup>3</sup>/g, respectively. After 7 days of autoclaving without burnt oil shale, the residue has a specific surface of 113 m<sup>2</sup>/g and a porosity of 161 mm<sup>3</sup>/g. The addition of burnt oil shale reduces these parameters to 50 m<sup>2</sup>/g and 99 mm<sup>3</sup>/g, respectively with 1 g of BOS. These two parameters also indicate a reduction in the damage of the aggregate.

Measurements of mass loss in TGA show a slight influence of burnt oil shale. The raw aggregate has a mass loss of 0.83%. After 7 days of autoclaving without burnt oil shale the loss of mass of the residue by TGA is 7.5 %. The addition of 1 g of BOS slowly reduces the loss of mass. Indeed, the loss of mass in TGA is indicative of the presence of silanols. Therefore, the addition of burnt oil shale shows only a slight reduction in the quantity of Q<sub>3</sub> in the extracted solid residue.

The improvement of the various parameters in the presence of burnt oil shale would tend to show that a pozzolanic reaction would occur. The development of this reaction would decrease the alkalis available to mitigate ASR. However, as the impact of burnt oil shale is not optimal, other environmental conditions can be modified such as temperature or granulometry in order to favour the development of the pozzolanic reaction in competition with the ASR by modifying the kinetics of the reaction and a more marked filler effect.

## 4. CONCLUSION

The model reactor based on a reactive aggregate allow to show a degradation of the silica lattice by the development of the ASR with a simplified medium and physico-chemical analyses of the liquid and solid residue. The same model reactor was used with the addition of burnt oil shale. The model reactor based on flint aggregate and burnt oil shale (BOS) show a beneficial influence of the latter. Indeed, the physical parameters tend towards the values of the raw aggregate. In the same way, the ICP-OES data of the liquid residue show a reduction of the silica dissolution and coincide with the evolutions of the physical parameters of the solid residue. Thus, the addition of BOS could allow the reduction of the dissolution of silica from Q<sub>3</sub> to Q<sub>0</sub>. SEM observations show the formation of C-S-H reaction products and a less marked degradation of the silica in the presence of burnt oil shale. The silica seems to be mainly converted from Q<sub>4</sub> to Q<sub>3</sub>. Consequently, the impact of BOS does not allow an inhibition of ASR with the model reactor used, overdosed in alkaline. But, the study of this model reactor in the presence of burnt oil shale has shown that this mineral addition has a beneficial effect by limiting the development of ASR. Thus, there is agreement with observations previously made on concretes with the reactive aggregate used and observations on model reactor. Nevertheless, even if the environment used allows an important time saving, it is not optimal. While the proportions used of burnt oil shale are very high compared to the proportions used in concrete, the reductions in aggregate alteration are not as great as could have been hoped for. Finally, the results show that a model system could allow the characterization of ASR and the impact of mineral additions to limit the development of ASR. However parameters would need to be re-evaluated to optimize the effect of mineral addition on the development of ASR field concrete.

## 5. ACKNOWLEDGEMENT

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