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▶ To cite this version:

HAL Id: cea-03667888

https://cea.hal.science/cea-03667888

Submitted on 13 May 2022

Study of alkali-silica reaction occurring in cemented waste packages based on simplified model and concrete medium approaches

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KEYWORDS: alkali-silica reaction, extent of reaction, flint aggregate, model medium

Abstract

Nuclear power production generates radioactive waste, the management of which is an important industrial and environmental issue. Low – or intermediate – level radioactive aqueous waste can be concentrated by evaporation, stabilized and solidified with Portland cement before being sent to disposal. Interactions can however occur between the waste and the cement phases or aggregates, and decrease the stability of the final waste forms.

The formation of a gel-like product, which results from an alkali-aggregate reaction, has been recently observed at the surface of cemented drums of evaporator concentrates. Its properties differ however from those usually reported for alkali-silica gels in many aspects: (i) very low calcium concentration, (ii) significant presence of Zn^{2+}, Cl^-, $B(OH)_4^-$ and SO_4^{2-} ions, (iii) high formation rate, (iv) rather limited damage of the cementitious matrix considering the amount of gel produced.

This work investigates the progress of alkali-silica reaction in the cemented drums, by studying the deterioration rate of the aggregates in model systems and in simulated concrete specimens.

A synthetic alkaline solution, which mimics the pore solution including the waste, was used to degrade the siliceous aggregates under controlled conditions. The extent of degradation caused by alkali-silica reaction was determined by weighing the residual flint aggregates and quantified by thermogravimetric analysis (TGA), specific surface area measurements, and gas pycnometry.

A concrete specimen, formulated to be representative of the concrete embedding the radioactive waste, was cast and submitted to a thermal cycle, before being cured at 20°C and 90% relative humidity. Samples were taken from the concrete specimen and were observed at the micrometric scale using a scanning electron microscope coupled with energy dispersive X-ray analysis (SEM-EDX). The aggregates contained in the concrete were then mechanically and chemically retrieved, before being characterized by TGA.

The model medium allows highlighting the advanced dissolution of the flint constitutive of the aggregates, leaving intact the most crystalline fraction of the grains. These results comply with the observations led on aggregates extracted from concrete samples, using SEM-EDX. Using this model medium, high degradation extent of the aggregates can be achieved. Indeed, the degradation progress of aggregates in concrete medium after 18 months could be reached in only a few hours using the model medium.

1   Introduction

Nuclear power production generates radioactive wastes, the management of which is an important industrial and environmental issue. Thus, low - or intermediate - level radioactive aqueous waste streams can be concentrated by evaporation, stabilized and immobilized with a hydraulic binder, usually a Portland cement or a blast furnace slag cement, before being sent to disposal. Interactions can however occur between some waste components and the cement phases or aggregates, and decrease the stability of the final waste forms. Aqueous waste streams, produced by Doel nuclear power plant in Belgium, were concentrated by evaporation, leading to evaporator concentrates with numerous chemical species. The presence of boron and the acidic pH of the waste led to the addition of sodium hydroxide in order to maintain the workability of the fresh concrete and avoid a too long setting time. The concentrate was then stored in tanks at 80°C to avoid borate crystallization, until the cementation step. This latter consisted in an in-drum mixing process, in which the raw materials were introduced in the order detailed hereinafter. Firstly, siliceous aggregates were introduced into the empty drum. Afterwards, the warm concentrate was incorporated. Lastly, the cement was added to the mixture. The warm concentrate incorporation and the exothermic hydration of the cement phases led to a peculiar thermal history of the drums, with a temperature rise up to 90°C, as shown in Figure 1.
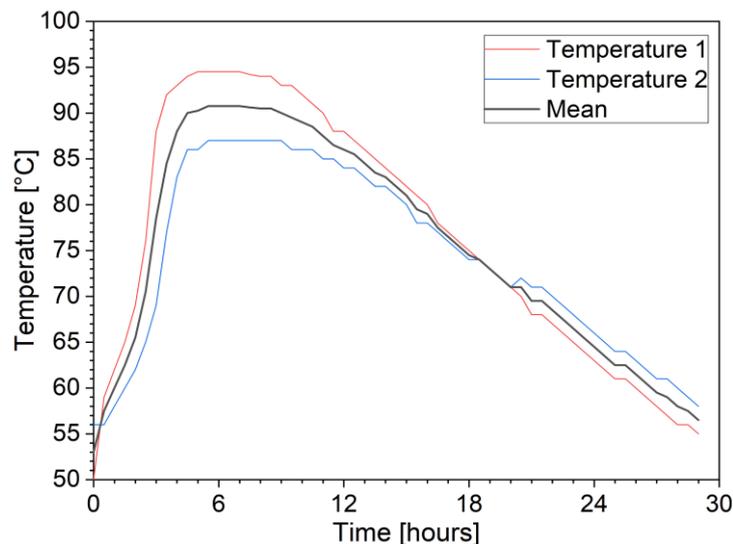

Figure 1. Thermal history of the cemented waste packages

The formation of a gel-like product was observed in 2013, at the surface of some of the waste packages cemented between 1983 and 2012, leading in some cases to cracks in the stabilization matrix and to the leaking of some canisters [1]. This alteration of the immobilization matrix jeopardizing the conformity of the drums regarding current regulations, it is a matter of concern to understand more precisely the root causes of this gel-like product formation and to anticipate if a drum is either going to produce more gel in the future or not.

This work aims at investigating the progress of alkali-silica reaction (ASR) in the cemented waste drums, by studying the deterioration rate of the aggregates in a model medium and in simulated concrete specimens.
The model medium approach was initially developed by Bulteel et al. [2] and was adapted in this work to take into account the chemical complexity of the cemented waste. A synthetic alkaline solution, designed as a non-radioactive surrogate of the waste, was used to degrade a flint aggregate for different durations under controlled conditions. The extent of degradation caused by ASR was quantified by weighing the residual flint aggregate and characterizing it using thermogravimetric analysis (TGA). Its deterioration state was assessed by specific surface area (SSA) measurements and gas pycnometry.
Non-radioactive concrete specimens, formulated to be representative of the concrete embedding the waste, were cast and submitted to a thermal cycle representative of the thermal history endured by the cemented waste packages (Figure 1), before being cured at 20°C and 90% relative humidity. Samples were taken from the concrete specimens and were observed at the micrometric scale using a scanning electron microscope coupled with energy dispersive X-ray analysis (SEM-EDX). The aggregates contained in the concrete were retrieved mechanically and chemically, before being characterized by TGA.

2   Materials and methods

2.1   Analytical techniques

Thermogravimetric analyses (TGA) were performed using a Netzsch STA 409 PC device. 100 mg of degraded flint aggregate were put into an alumina crucible and the analysis was performed under a 50 mL/min nitrogen flow using the following temperature program: dynamic step from 25°C to 105°C with a 2°C/min rate, isothermal step at 105°C for 3 hours, dynamic step from 105°C to 1000°C with a 3°C/min rate, isothermal step at 1000°C for 1 hour.

Specific surface area (SSA) values of degraded flint aggregate were determined using a Micromeritics ASAP 2020 surface area system. Prior to the analysis, samples were frozen in liquid nitrogen and freeze-dried at 30 µbar for at least 4 days. Then, they were degassed at 90°C and 3 µbar for 40 hours. Finally, nitrogen sorption isotherms were obtained within the range $0.05 < P/P^0 < 0.30$ at liquid nitrogen temperature (77 K), which allowed to apply BET theory and to assess SSA values.

Volumetric mass densities of degraded flint aggregate were measured using a Micromeritics AccuPyc II 1330 helium gas pycnometer. The analysis chamber had a nominal volume of 1 cm^3 and was calibrated beforehand. Each volumetric mass density value considered hereinafter is the mean value of 20 stable measurements.

Polished sections of concrete samples were observed by scanning electron microscopy (SEM) using a FEI Inspect S50 SEM device in high vacuum mode, with an acceleration voltage of 15 kV, a current intensity of 50 nA, and a working distance of 9.7 mm. Elemental mappings were performed using energy dispersive X-ray analysis (EDX) with a Bruker X-flash SSD detector (10 mm^2 area) in high vacuum.

2.2   Materials used

Silicate species are named after Engelhardt nomenclature [3] as Q^n, with n between 0 and 4 being the number of silicon atoms the considered silicon atom is linked with, via oxygen bridges.

2.2.1   Flint aggregate

The flint aggregate studied in this work was extracted from a littoral formation of flint pebbles in the North of France. It was used to simulate the reactive siliceous aggregates used during the 1980's to immobilize the waste at Doel Nuclear Power Plant. It contained 96% SiO_2, minor amounts of $CaCO_3$, Al_2O_3, Fe_2O_3 and traces of MgO, Na_2O and K_2O (elemental composition expressed as oxides) as determined by ICP-AES after borate fusion at 950°C and hydrochloric dissolution. Its initial particle-size distribution was between 0.063 mm and 16 mm. At its natural state, this flint aggregate is predominantly constituted by Q^4 silicon atoms and around 7% Q^3 silicon atoms, which are natural crystalline flaws in its network [2].

2.2.2   Alkaline suspension (waste surrogate)

The alkaline suspension was a non-radioactive surrogate containing the main species of the waste. Its composition is detailed in Table 1.

Table 1. Theoretical composition of the alkaline solution used as a surrogate of the waste (mmol/kg)

Species	Concentration	Species	Concentration
Na_2SO_4	127	$NaNO_3$	13
H_3BO_3	1136	NaCl	132
Na_2SiO_3	225	NaOH	2476
$Na_3PO_4 \cdot 12\,H_2O$	136	$Ca(OH)_2$	279

Powders were added to ultrapure water to reach the desired composition. The heterogeneous solution was then heated at 90°C and stirred at 350 rpm during 46 hours. Some undissolved salts remained after this step. The total theoretical sodium content of this suspension was 3734 mmol/kg.

2.3   Model medium approach

In the model medium approach presented in this work, the flint aggregate was submitted to an alkaline solution in presence of a calcium reservoir. The medium was prepared in an autoclave, which was sealed and submitted to a temperature rise in order to accelerate the degradation process.

2.3.1   Alkaline degradation

Two grams of flint aggregate were poured in stainless steel autoclaves, pre-heated at 90°C. Beforehand, its granular distribution adjusted between 0.16 mm and 0.63 mm by grinding and sieving, in order to increase its reactive surface and thus to accelerate the degradation process. Ultra-fine particles were discarded in order to keep exclusively the deleterious fraction regarding ASR. The airtightness of these
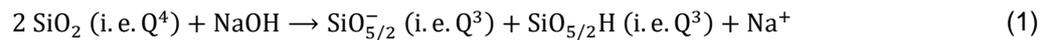
autoclaves was checked with water beforehand, and only those exhibiting less than 2% leakage after 8 days at 90°C were used thereafter.

One gram of calcium hydroxide was added in the autoclave to simulate the influence of the Portland cementitious matrix by providing a calcium reservoir.

20 mL of the alkaline solution were then added in the autoclave in order to cover the solids. Beforehand, the remaining undissolved salts were removed by filtration under vacuum at 0.2 µm, in order to avoid silica dissolution coming from both flint aggregate and residual undissolved sodium metasilicate during the degradation. The composition of the filtrated solution was measured by ICP-AES to be $[Na] = 3.1\pm0.2$ mol/kg, $[Si] = 112\pm6$ mmol/kg, and $[Ca] = 0.027\pm0.001$ mmol/kg. The smaller experimental concentrations regarding these elements mainly resulted from the reach of an equilibrium between undissolved salts and the solution. In particular, the low experimental dissolved calcium content could result from the low and retrograde solubility of calcium hydroxide in alkaline media [4].

After sealing, autoclaves were heated at 90°C for a desired duration. This temperature is representative of the highest temperature reached by the cemented waste drums (Figure 1), after the cementation step. Degradation durations of 4 hours, 15 hours, 1 day, 3 days and 8 days were chosen in order to monitor the evolution of the system along with the degradation duration and to reach the final balance. Autoclaves were then quenched in an ice-water bath for one hour, in order to stop the degradation reactions, and were opened to recover both liquid and solid phases.

During this alkaline degradation, hydroxide ions provided by the solution break the siloxane bonds of the flint aggregate to form silanol sites: some Q^4 silicon atoms are thus converted to Q^3 silicon atoms, as shown in reaction (1).
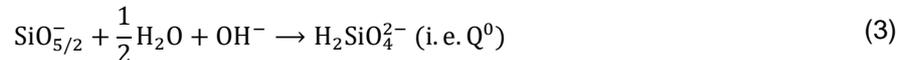
$$2\,SiO_2\ (i.e.\,Q^4) + NaOH \longrightarrow SiO_{5/2}^-\ (i.e.\,Q^3) + SiO_{5/2}H\ (i.e.\,Q^3) + Na^+ \tag{1}$$

Given the alkalinity of the degradation medium, the silanol sites are in a deprotonated state, as shown in reaction (2).

$$SiO_{5/2}H + OH^- \rightleftarrows SiO_{5/2}^- + H_2O \tag{2}$$

Electroneutrality is then ensured by cations present in the solution (Na^+, Ca^{2+}…). Some silicon atoms can be converted to Q^2 or Q^1 silicon atoms, however their proportion is deemed negligible compared to the proportion of Q^3 formed.

Some silicon atoms can be further degraded and lead to the formation of monomeric Q^0 silicon atoms, i.e. the solubilization of the silica that constitutes the flint aggregate, as shown in reaction (3).

$$SiO_{5/2}^- + \frac{1}{2}H_2O + OH^- \longrightarrow H_2SiO_4^{2-}\ (i.e.\,Q^0) \tag{3}$$

The dissolved silica can then diffuse within the solution and react with present cations to form new compounds such as calcium silicate hydrates (C–S–H) or calcium sodium silicate hydrates (C–N–S–H). At this state, the medium is designated as "State 1".

2.3.2   Acidic treatment

The solid fraction remaining in the autoclave (state 1) consisted of degraded flint aggregate, residual calcium hydroxide and ions present in the alkaline solution. The following acidic treatment was applied to recover exclusively degraded flint aggregate [5]: acidic washing (250 mL of 1 mol/L HCl at 700 rpm stirring, 4°C during 1 hour), decantation (2 hours at 4°C) and filtration under vacuum (0.45 µm). The solid was then dried at 40°C for 24 hours before being weighed and characterized by helium gas pycnometry and SSA measurement system.

This acidic washing allows destroying the residual reactive medium (remaining calcium hydroxide and newly formed phases) and protonating the silanol sites in the flint aggregate. At this state, the medium is designated as "State 2".

2.3.3   Thermal treatment

Finally, a thermal treatment at 1000°C was applied to the aggregate (state 2) using TGA, to condensate the protonated silanol sites back to siloxane bonds.

The thermal energy allows to condensate two silanol sites (Q^3) into a siloxane bond (Q^4) while a water molecule is released, as shown in reaction (4).

$$2SiO_{5/2}H \xrightarrow{\Delta} 2SiO_2 + H_2O \tag{4}$$

At this state, the medium is designated as "State 3".

2.3.4 Summarizing diagram

A summarizing diagram of the model medium approach is given in Figure 2. One should note that in this diagram, silanol sites naturally present in the flint aggregate are not represented.
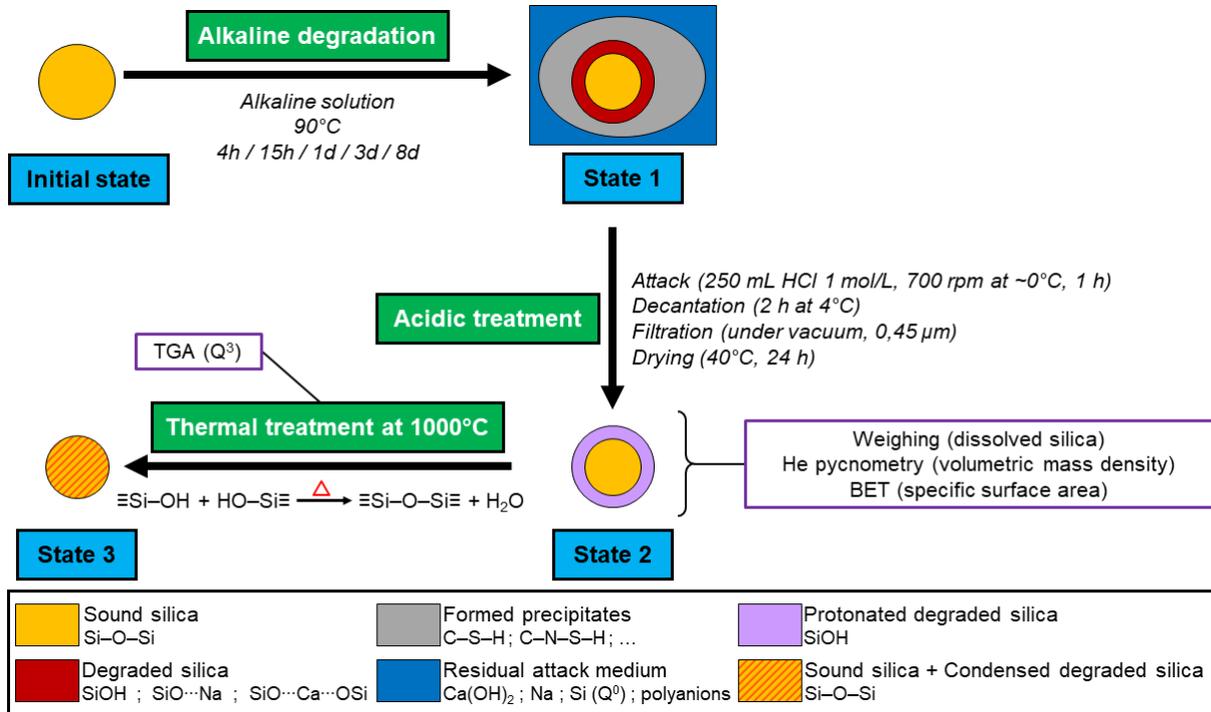

Figure 2. Summarizing diagram of the model medium approach

2.4 Concrete medium approach

The flint aggregate used for the concrete mix had a particle-size distribution adjusted between 0.15 mm and 16 mm. It was put into a blender, then the cement – a CEM I 52.5 R SR3-NA, with a C_3A content below 3% and a Na_2O_{eq} content of 0.59% – was added at an aggregate/cement ratio of 4.29. Water was brought by the waste surrogate, the composition of which is detailed in Table 1, leading to a water/cement ratio of 0.51. One should note that for the concrete medium approach, undissolved salts were incorporated in the mix, as the waste surrogate was not filtrated.

A cylindrical specimen (h x d = 11 x 22 cm) was cast and immediately submitted to a thermal cycle representative of the thermal history of the cemented waste drums (temperature rise to 90°C during 4.5 h, isothermal step at 90°C for 4.5 hours, and temperature decrease to 25°C, total duration of 7 days). This step was done at high hygrometry to avoid cement desiccation. The specimen was unmolded after the thermal cycle and cured at 20°C and 90%RH during 18 months Samples around one centimeter in size were then taken and polished before being observed using SEM-EDX.

Some samples taken from the specimen were as well ground under 250 µm and were treated using hydrochloric acid and an EDTA solution, in order to solubilize the cement paste and recover the flint aggregate solely. The solid was dried using acetone then characterized by TGA in order to assess the Q^3 proportion in the flint aggregate after 18 months in a concrete medium.

3 Results and discussion

The model approach allows defining three reaction progress variables noted MFQ^n that represent the molar fraction of each Q^n species after the alkaline degradation (n being 0, 3 or 4), compared to those *initially present* in the flint aggregate, according to equation (5).

$$MFQ^n = \frac{mol_{Q^n}(t)}{mol_{Q^3}(t_0) + mol_{Q^4}(t_0)} \tag{5}$$

MFQ^3 and MFQ^4 are related to the amount of Q^3 formed (i.e. the silanol sites formed) and the amount of residual Q^4 (i.e. the silica that was not altered during the alkaline degradation), respectively. These amounts are respectively determined by TGA and weighing. MFQ^0 is related to the amount of Q^0 formed (i.e. the dissolved silica) that is determined according to the principle of mass conservation.

A fourth reaction progress variable, noted MFQ^{3*}, is defined similarly to equation (5) and represents the molar fraction of Q^3 present in the *residual aggregate* after the alkaline degradation, according to equation (6).

$$MFQ^{3*} = \frac{mol_{Q^3}(t)}{mol_{Q^3}(t) + mol_{Q^4}(t)} \qquad (6)$$

During the first three days of alkaline degradation, a slight increase then decrease of MFQ^3 and a great increase of MFQ^0 are observed (Figure 3). This suggests a competition between the dissolution of the aggregate and the formation of silanol sites within it, while the dissolution process is predominating due to the high alkalinity of the medium. SSA increases (Figure 4) as siloxane bonds are broken by hydroxide ions to create silanol sites, which opens the siliceous network, and as dissolution wells are formed in the aggregate grains. These phenomena lead to an increase of FMQ^{3*} (Figure 5), i.e. an increase of the Q^3 proportion in the part of the grains that was not dissolved. This results in a volumetric mass density decrease for the residual part of the grains (Figure 6) caused by swelling, following the formation of Q^3 species that occupy a greater volume than Q^4 species.
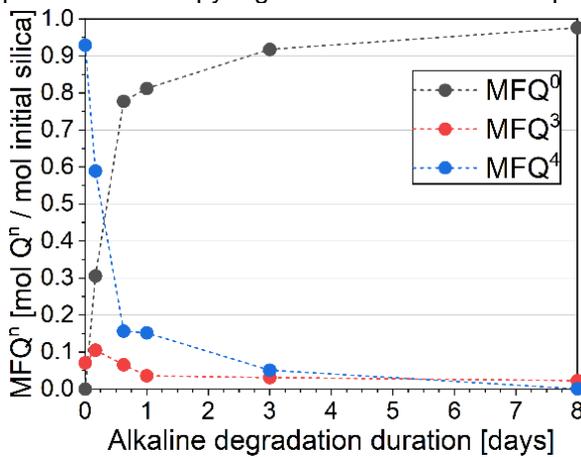

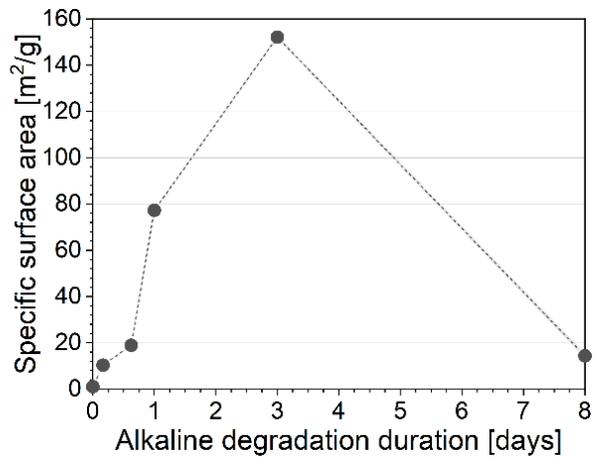Figure 3. Evolution of MFQ^n over time
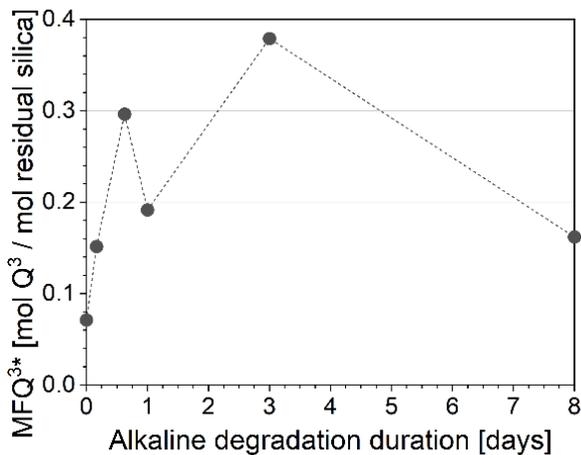

Figure 4. Evolution of SSA over time

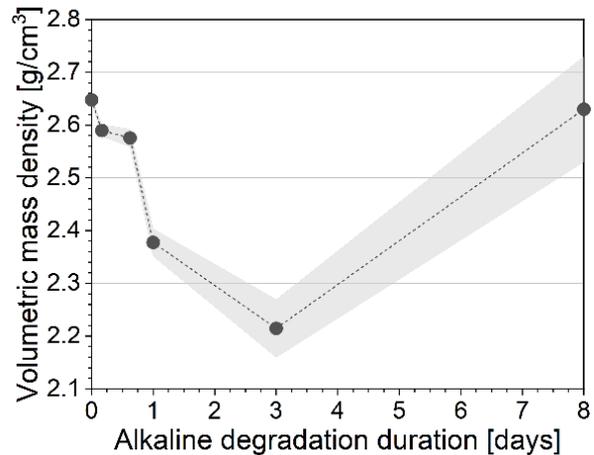Figure 5. Evolution of MFQ^{3*} over time

Figure 6. Evolution of volumetric mass density over time

Beyond three days of alkaline degradation, almost all of the silica is dissolved and converted to Q^0 species (Figure 3) and a few silanol sites remains in the parts of the grains that were not dissolved, as suggested by the decrease of MFQ^{3*} (Figure 5). The extended dissolution of the grains leads to the coalescence of the dissolution wells formed during the first three days of degradation, which results in a SSA decrease (Figure 4). The volumetric mass density of the remaining solid (Figure 6) is close to that of crystalline forms of silica such as quartz (2.65 g/cm^3), suggesting that only the most crystalline part of the grains remains, and that this part was only slightly altered during the alkaline degradation.

Within the concrete medium approach, the concrete specimen mimicking the cement-encapsulated waste was submitted to a thermal cycle and cured for 18 months. Concrete samples were taken after this duration and polished sections were prepared. SEM-EDX observations (Figures 7 & 8) allows highlighting the presence of an alkaline siliceous product, located in veins formed in the cementitious matrix (purple arrow) in the periphery of some flint aggregates.
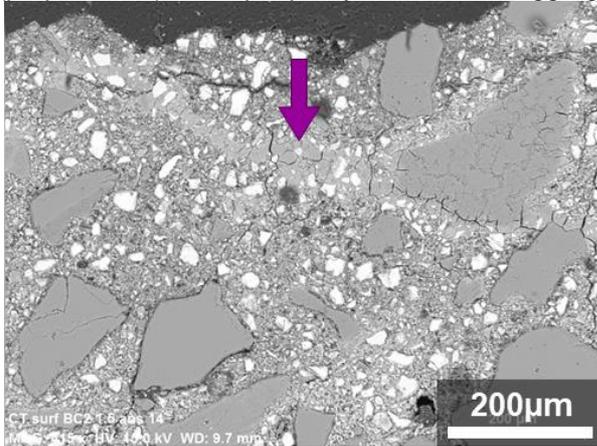

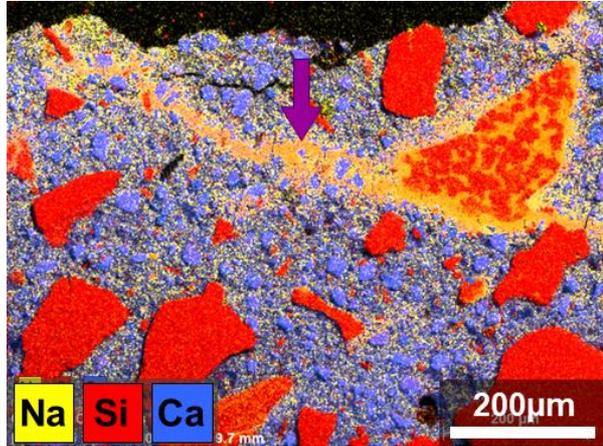Figure 7. SEM picture of a polished section from a concrete sample (back-scattered electrons)

Figure 8. EDX mapping of a polished section from a concrete sample

The said aggregates, that initially contain only traces amounts of sodium, show preferential areas that exhibit a significant sodium content with a Na/Si molar ratio reaching 0.38, highlighting their degradation. The absence of sodium in the remaining areas indicates that some parts of the flint aggregate are less likely to be attacked by the alkaline hydroxide ions. This observation is consistent with the conclusions led with the model medium approach, where only the most crystalline part of the flint aggregate was remaining.

Aggregate samples extracted from the concrete were characterized by TGA in order to assess the proportion of Q^3 that was formed in the grains in the concrete medium. The corresponding MFQ^{3*} proportion of 11.3% is equivalent to 2 hours of degradation in the model alkaline medium. Thereby, the model medium allows reaching a much higher degradation extent than in concrete.

4   Conclusions

The model medium allows highlighting the advanced dissolution of the siliceous network that constitutes the flint aggregate, leaving the most crystalline fraction of the grains as a leftover. These results comply with the observations led by SEM-EDX on concrete samples formulated to be representative of the cemented waste, where preferential degradation areas within the flint aggregate were observed. A chemical extraction of the aggregate initially embedded in the cementitious matrix allowed showing that high degradation extent of the aggregates can be achieved with the model medium. Indeed, the degradation progress of aggregates in concrete medium after 18 months could be reached in only a few hours using the model medium.

The model medium thus appears as an interesting tool to investigate the degradation pathway of aggregates depending on their cementitious environment: the composition of the degradation solution can be changed to mimic various cement systems, the solid and liquid phases can be easily separated for characterization, and high degrees of degradation can be reached within a short period of time. This approach will be used in future works to investigate the influence of the waste composition on the degradation process of the aggregates.

5   Acknowledgements

6   References

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