MICROSTRUCTURAL EVOLUTION AND MECHANICAL BEHAVIOUR OF ALKALI ACTIVATED FLY ASH BINDER TREATED CLAY

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Abstract

This work focuses on the use of alkali activated fly ash-based binder to enhance engineering characteristics of soft clay-rich soils and as a substitute to standard stabilisers (e.g., lime or cement). Especially, it examines the microstructural evolution of a calcium-rich fly ash from coal combustion-based binder activated by a sodium-based alkaline solution. To this end, the processes generating the microstructure and the evolution of the pore network over time are investigated. A second point addressed by this study is how the presence of kaolin particles affects the microstructural features of the binder. The microstructure has therefore been investigated by considering the binder alone and the binder mixed with kaolin. The effects of microstructural evolution have been observed at macroscopic level by means of one-dimensional compression tests.

The combination of completing techniques has been used including Optical microscopy, Scanning Electron Microscopy and Mercury Intrusion Porosimetry in order to gain an overview of the complex pore structure.

Microstructural changes occur around calcium-containing phases derived from fly ash which are the reactive phases of the system. Namely, the dissolution of calcium-rich grains leads to the formation of new compounds that first cover the grain surfaces and then further grow into the available space. Furthermore, the evolution of the pore network over time is characterized by a progressive filling of capillary pores by new compounds while small nanometric pores are being formed and associated with the newly formed silicate-calcium chains. Similar tendencies are observed when the binder is mixed with the soil although the general porosity is lesser due to the filling of pores by small-sized kaolinite platelets. Experimental evidences at microscale level have been linked to the macroscopic behaviour of treated soil.

Keywords: Kaolin, Fly ash, Soil treatment, Alkali activated material, Microstructure, Mechanical Behaviour

1. Introduction

Soft clay-rich soils are frequently encountered in construction sites. Their poor mechanical performances represent a critical issue in engineering projects and are

commonly improved by using either Ordinary Portland Cement or lime as a soil stabiliser. Nevertheless, those conventional stabilisers are associated with high carbon dioxide emissions and energy intensive processes, significantly increasing the worldwide carbon footprint (Scrivener and Kirkpatrick, 2008, Xi et al. 2016). The anthropogenic carbon emissions have been increasingly recognized to be one of the main responsible of climate changes and environmental degradation (United Nations, 2004). In the low carbon agenda, it is then of outmost relevance the development of cost- and carbon-efficient technologies. In the construction sector, for which cement production contributes to at least 5–8% of global carbon dioxide emissions (Scrivener and Kirkpatrick, 2008), alternative industrial by-products (e.g. high-calcium fly ash, rice husk ash, silica fume) have been successfully used as cementing agents in soil improvement resulting in environmental and economic benefits (Basha et al. 2003, Nalbantoğlu 2004, Sargent 2015, James & Pandian 2016).

As an alternative, the use of Alkali Activated Material (AAM) as a soil stabiliser is gaining more and more attention over the past ten years. Alkali Activated Materials are defined as any binder system derived by the reaction of an alkali metal source (usually alkali hydroxide and alkali silicate solutions) with a solid aluminosilicate powder (commonly metakaolin, fly ash, blast furnace slag or natural pozzolan) (Buchwald et al., 2003; Shi et al., 2006). It gives a hardened material at room temperature with mechanical properties potentially suitable for Portland cement replacement. Alkali Activated Materials could constitute a viable sustainable soil binder because of their lower CO_2 emission process compared to traditional Portland cement (Duxson et al. 2007; McLellan et al. 2011, Zhang et al. 2014). Furthermore, recent studies have shown a positive potential and feasibility results of using alkali activated binders for soil improvement, and

this not only for different types of soil i.e. clayey soil (Wilkinson et al., 2010; Singhi et al., 2016; Vitale et al. 2017, Vitale et al. 2019; Vitale et al. 2020a, 2020b), sandy clay (Cristelo et al., 2011), marl, marlstone (Cristelo et al., 2012), silty sand (Rios et al., 2016) or else road aggregates (Tenn et al., 2015); but also for different applications i.e. in deep soft soil (Cristelo et al., 2011), at shallow depth (Zhang et al., 2013) or in rammed earth construction (Silva et al., 2013).

Works on alkali activated binder treated soils are relatively recent and constitute a novel domain of application. Our study particularly focuses on the use of a calcium-rich fly ash from coal combustion activated by sodium-based alkaline solution as a binder for clay kaolin stabilisation. Kaolin was selected as a model soil that represent a wide class of clays encountered in engineering projects and for maintaining the system simple. Kaolinite being not reactive to alkaline activation at ambient temperature, a more reactive aluminosilicate source is required for chemical reactions to occur. For that purpose, a calcium-rich fly ash was selected in the context of resource-saving being an industrial waste. The main aim is to assess the feasibility of using this novel binder for soil treatment.

When addressing the feasibility of using a class of material for a novel application, there are several important parameters to consider such as the composition, microstructure and processing which all ultimately affect the performance-to-cost ratio of a material (Askeland et al., 2011). A detailed understanding of both the composition but also the structure of the binder across length scales is therefore required in order to control materials properties through its processing.

Two main length scales of investigation can be distinguished with relevant importance. A first one is the particle scale and corresponds to the identification of the different phases

constituting particles in terms of chemical composition and crystal structure. Important properties of particles depend on the arrangements of atoms and types of bonding within each phase (Clemens et al., 2008). A second scale of observation is at the level of group of particles, or microstructure. Microstructural investigations for alkali activated materials are of prime importance as their physical properties depend largely on their pore network characteristics and microstructure (Nath et al., 2016; Lawrence and Jiang, 2017). This is associated with the fact that the microstructure controls the transport properties of the binder and the stability of the matrix when exposed to aggressive agents (van Deventer et al., 2015).

In our previous study the physicochemical evolution of similar systems than those herein studied was carried out i.e. identification and evolution of the constitutive phases until 28 days of curing time at an atomic level. It showed that the soil i.e. kaolin was not reactive. Whereas, fly ash was partly reactive. Some of its phases such as the vitreous phase and quartz were mainly unreactive, while calcium-containing phases represented the reactive phases. The new compounds formed were an amorphous silicate consisting of chains combined with calcium probably incorporating three-dimensional four-fold aluminium environments and thenardite Na_2SO_4 (Coudert et al., 2019).

The present work focusses on the microstructural description, taking into account the knowledge gained about the physicochemical evolution of the system. The study was designed in three stages. An initial stage consisted in the identification of the phases present in the reactive aluminosilicate source i.e. the original calcium-rich fly ash and description of their structure, shape and size distribution. The different constituents of fly ash being inhomogeneously reactive (Provis and Deventer, 2009), it was important to identify the reactive phases around which microstructural changes were predominant. A

second stage focussed on the investigation of the microstructural evolution of the alkali activated fly ash binder during the first 28 days of curing, including (i) a description of the dispersion and arrangement of phases, (ii) an understanding of which processes generate the microstructure over time and (iii) a pore network characterisation. Fly ash being a highly inhomogeneous material (Provis and Deventer, 2009), a key point was to determine the homogeneity of processes across the sample at a microscopic level. Besides, a particular emphasis was put at understanding microstructural changes and processes around calcium particles which are the main reactive phases. A third stage focussed on the interaction of the fly ash-based binder with the kaolin clay to understand how the presence of kaolin modifies the microstructural features of the system. As previously stated, kaolinite is unreactive during the alkaline activation. However, because of its small size kaolinite acts as a filler of the porosity (Coudert et al., 2019) and undoubtedly plays a role on the microstructural evolution. The effects at macroscopic level have been highlighted with reference to one dimensional compression results, showing the improvement of the mechanical performances of the treated soil as function of binder percentage and curing time. A final comparison between the performance of cement treated soil with alkali activated binder treated soil has shown for highlighting the effectiveness of the improvement.

2. Material and methods

2.1 Materials

A Polish fly ash derived from hard coal and coal slime combustion in fluidised bed boiler was used. Its chemical analysis is given in Table 1, and consists primarily of SiO_2, Al_2O_3

and CaO. The fly ash contains, approximately, 52% of particles sized lower than 45 µm and 41% lower than 10 µm.

Speswhite kaolin provided by Imerys Minerals UK, and whose chemical composition is given in Table 1 was used. It is mainly constituted of kaolinite (95%) and secondarily of muscovite (4%) (Chemeda, 2015). The kaolin contains, approximately, 100 % of particles sized lower than 10 µm and 80 % lower than 2 µm.

A unique alkaline solution was used: a sodium silicate with a mass ratio SiO_2/Na_2O of 1.7 and a dry mass percentage of 44%; supplied by Woellner Group and named GEOSIL 34417.

Table 1 - Chemical composition (wt. %) of raw fly ash and kaolin.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	CaO_{free}[a]	MgO	SO_3	Na_2O	K_2O	H_2O	L.o.I.
Fly ash	39.4	19.8	7.4	18.6	5.2	1.8	4.1	2.0	1.8	0.0	1.7[b]
Kaolin	49.2	34.5	1.2	0.0	0.0	0.2	0.0	0.1	1.7	13.1	12.0[c]

[a] Free calcium oxide content
[b] L.o.I = Loss on ignition 900 °C
[c] L.o.I = Loss on ignition 1000 °C

2.2 Sample preparation

Sample preparation consisted in (i) mix of liquid sources i.e. silicate and water (ii) mix of aluminosilicate powders i.e. fly ash and kaolin in the case of soil-source sample (iii) mix of (i) and (ii) previously prepared.

For microstructural analyses, two types of mixes were studied and named F100 and KF50. F100 is the fly ash-based alkali activated binder. It corresponds to a solid phase made of fly ash only, whereas KF50 is the alkali activated binder treated soils and corresponds to a solid phase made of 50% of fly ash and 50% of kaolin in mass.

To ensure a good workability, the amount of added water with respect to the solid mass (e.g. mass of kaolin and fly ash) was fixed to 50% for all the samples. Additionally, the mass ratio of alkaline solution to fly ash was fixed to 50% for all the samples, giving the initial molar ratios (considering that kaolin is unreactive): Si/Al = 2.0, Si/Na = 3.5 and Al/Na = 1.8. The Al/Na ratio was not fixed to one because of the presence of calcium ions in high quantity in our system playing a role of charge compensation as well as sodium.

The paste obtained was poured in closed plastic molds and cured at room temperature (20 °C). Samples were finally demoulded and freeze-dried at curing times of 24 hours, 3, 7 or 28 days.

Samples for one dimensional compression tests were prepared with the described technique. Three mixes have been considered in the study, namely KF10, KF20 and KF40 corresponding to a solid phase made of 10%, 20% and 40% of fly ash with reference to dry mass of solids (fly ash+ kaolin). Remoulded samples were prepared by hand mixing solids, alkaline solution and water at their liquid limits (i.e. w_L=67% for KF10, w_L=60% for KF20, w_L=55% for KF40). Samples were poured in the mould and placed in oedometer cell without compaction. Treated samples were cured for 24 hours, 7, 14, 28 and 60 days before mechanical testing.

2.3 Methods

Samples were studied by Optical and Scanning Electron Microscope from polished section. Freeze-dried samples were impregnated under a vacuum with an acrylic resin (LR White). The polymerisation of the resin was performed in an oven at 60 °C over 48 h. The samples were then polished with diamond powder. The observations from Optical

Microscopy were done with a Nikon LV100 polarizing optical microscope combined with a ccd Nikon DS-2Mv camera and the NIS Element BS software. Whereas the observations from Scanning Electron Microscope were done with a HITACHI SU5000 scanning electron microscope equipped with an energy-dispersive X-ray analyser (Quantax microanalyser system composed of X-Flash® SDD detector and the Esprit software). The polished samples were coated with carbon before the observation. The microscope was operated at an accelerating voltage of 20 kV and working distances of 10 mm.

MIP tests were performed by a double chamber Micromeritics Autopore III apparatus. In the filling apparatus (dilatometer) samples were outgassed under vacuum and then filled by mercury allowing increase of absolute pressure up to ambient one. Using the same unit the intrusion pressure was than raised up to approximately 200 kPa by means of compressed air. The detected entrance pore diameters ranges between 134 μm and 7.3 μm (approximately 0.01 MPa - 0.2 MPa for a mercury contact angle of 139°). After depressurisation to ambient pressure, samples were transferred to high-pressure unit, where mercury pressure was increased up to 205 MPa following a previously set intrusion program. The smallest detected entrance pore diameter was about 7 nm. Corrections to pore-size distribution due to compressibility of intrusion system were applied performing a blank test.

One dimensional compression tests have been performed in standard oedometer cells, where vertical stress was conventionally applied in successive steps ($\Delta\sigma v/\sigma v = 1$) within the stress interval 10 ÷ 2400 kPa. Micrometer dial gauges with an accuracy of 0.001 mm have been used to measure vertical displacements.

3. Results and discussion

The first section of results presents the general characteristics of the raw fly ash which constitutes the reactive aluminosilicate source of the mixes. The second part examines the microstructural evolution of the binder. The third part focusses on the description of system made by kaolin and the alkali activated binder and its mechanical performance.

3.1 Raw fly ash

The fly ash used here contains various components. Its composition consisting of (i) a vitreous phase and (ii) various crystalline phases i.e. calcium-containing minerals: anhydrite $CaSO_4$, calcite $CaCO_3$ and portlandite $Ca(OH)_2$, and other minerals: quartz SiO_2, feldspar $(K,Na,Ca)(Si,Al)_4O_8$, hematite Fe_2O_3 and muscovite $(Si_3Al)O_{10}(Al_2)(OH)_2K$ (Coudert et al., 2019).

Its particle size distribution reflects this diversity with 52 % of particles lower than 45 µm, 41 % of particles lower than 10 µm and 12 % of particles lower than 2 µm.

Figure 1 confirms this great variety also detectable by Scanning Electron Microscopy. In fact, the fly ash presents an extremely heterogeneous microstructure with particles of different shapes and ranging from 1 µm to more than 200 µm. The vitreous phase is itself heterogeneous and made of (i) some spherical particles (see G Figure 1B), (ii) bigger unshaped particles (see G Figure 1C) and (iii) aggregates of small particles primarily (see G Figure 1D).

Some crystallised angular shaped minerals can also be distinguished and correspond to quartz (see Q Figure 1A&D) or feldspar (see F Figure 1B).

Finally, regarding calcium-rich phases, our previous study showed that calcium-containing minerals i.e. anhydrite $CaSO_4$, calcite $CaCO_3$ and portlandite $Ca(OH)_2$ are

interlaced together (Coudert et al., 2019). Especially, they are interlinked within a nodule shape structure generally of 50 to 200 µm size as seen on Figure 1B (particle labelled C).

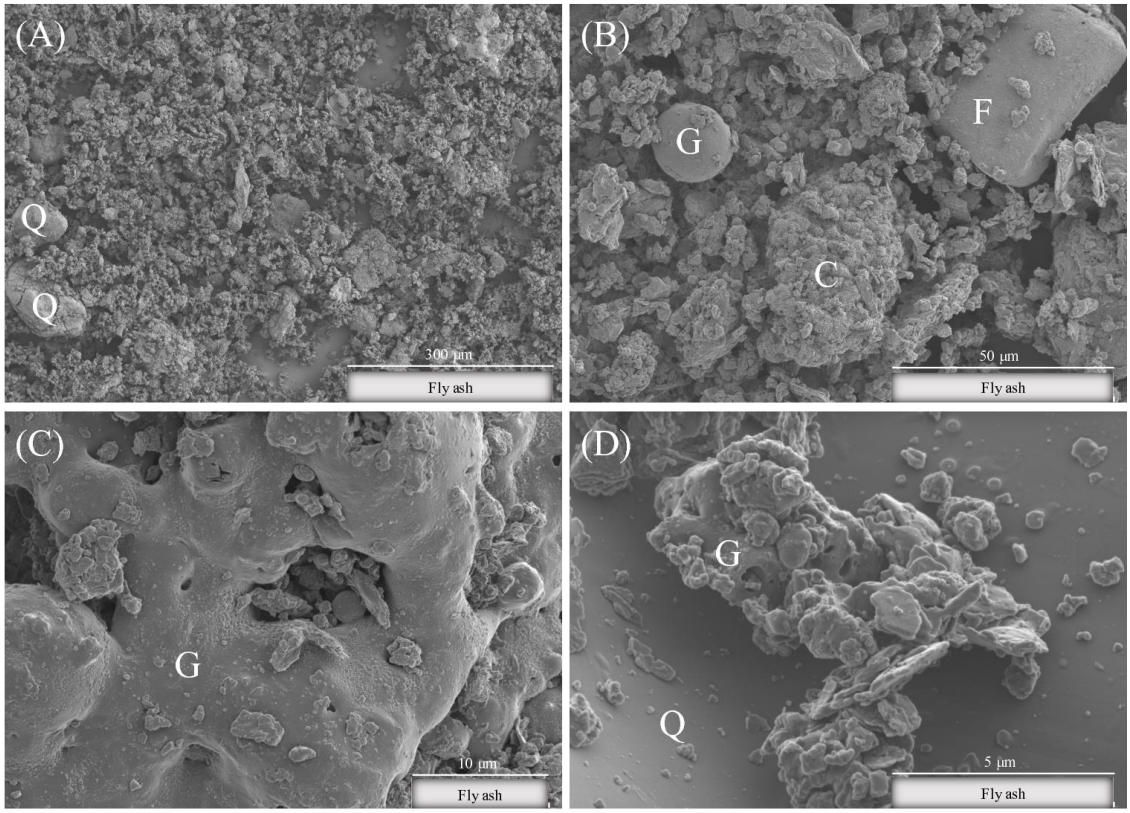

Fig. 1 SEM micrographs of the raw fly ash; C=calcium-rich particle; F=feldspar; G=glass; Q=quartz.

3.2 Alkali activated fly ash binder

3.2.1 Optical Microscopy

Figure 2 shows the microstructural evolution of the alkali activated fly ash binder over time by optical microscopy. Observations were carried out until 28 days as chemical reactions are fully developed at that curing time (Coudert et al., 2019).

After 24 hours of curing, dispersed dark spots of around 50 µm to 200 µm size are seen across the overall sample (see particles labelled C on Figure 2A&B), and correspond to reactive calcium-rich nodules by analogy with the previous observations of the raw fly

ash constituents (section 3.1). They represent approximatively 15 % of the mixture. Whereas the brown matrix includes the vitreous phase and calcium-free minerals from fly ash.

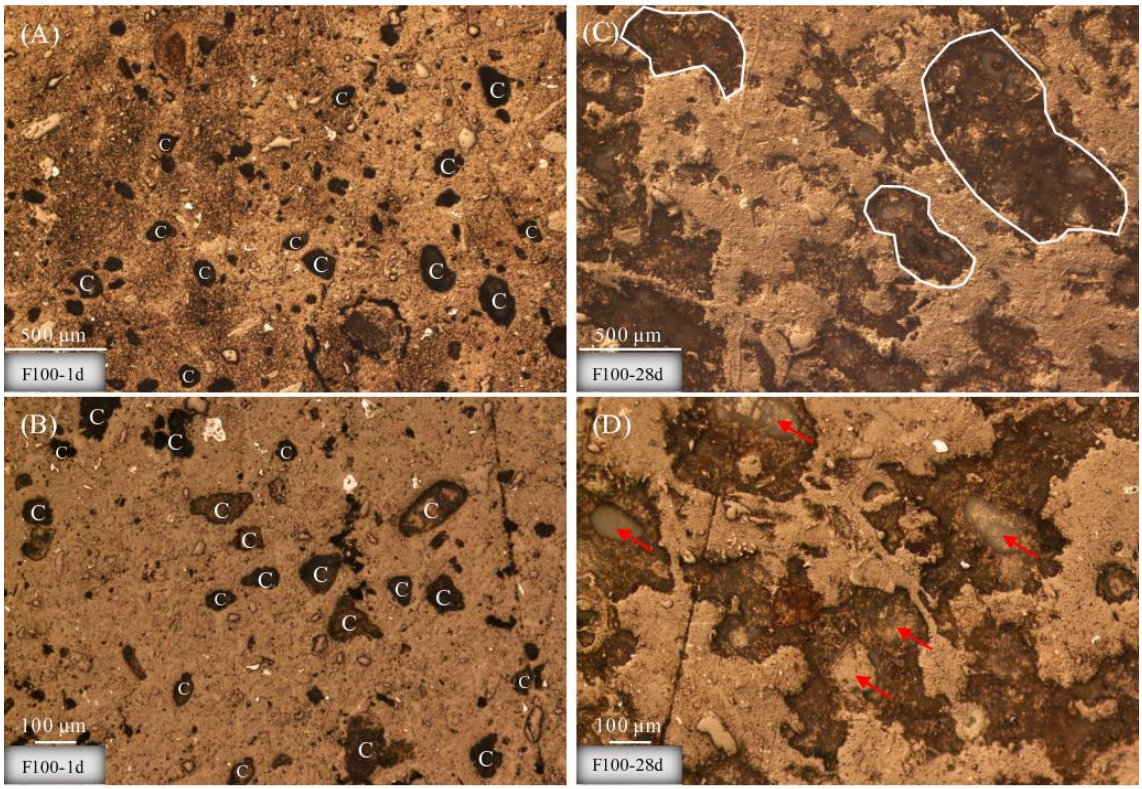

Fig. 2 Optical microscopy images of the alkali activated fly ash binder F100 (A) and (B) after 24 hours, (C) and (D) at 28 days*;* C=calcium-rich particle.

By comparison, at 28 days, no dark spots are visible but instead large dark zones whose edges are less well defined (see encircled areas on Figure 2C), and correspond to new products formed. Figure 2D shows a closer observation of those large dark reactive areas. The initial nodule shapes can still be distinguished at 28 days but instead of a dark spot as observed at 24 hours it is a hollowed greyish structure that is seen as shown by the red arrow (Figure 2D). This structure is associated with dissolution features over time of the calcium-rich phase, and in accordance with the previous results about the physicochemical evolution which indicate that calcium-containing phases are the main

reactive phases. New compounds corresponding to dark areas are therefore formed around the hollowed dissolved calcium nodules. Those new compounds have been identified in a previous study as thenardite Na_2SO_4, and an amorphous silicate consisting of chains combined with calcium probably incorporating three-dimensional four-fold aluminium environments (Coudert et al., 2019).

As a consequence of those observations, the spreading of the darker areas at 28 days gives an idea of the extent of the reaction and widening of the new compounds formation across samples. In this system, half of the sample encompasses the new compounds and is hence reactive whereas the initial calcium nodules represented only 15 % of the sample. Besides, those new compounds seem homogeneously spread across the sample which likely could give a homogeneously reinforced material at the macroscopic scale.

Results from optical microscopy therefore match with the observed physicochemical evolution i.e. principal changes occur around calcium-rich reactive particles. That is why the next session focusses on the in-situ microstructural transformation of calcium-rich phases induced by the alkaline solution.

3.2.2 Scanning Electron Microscopy (SEM)

Figure 3 shows microstructural observations from a polished section and combined chemical mappings of the alkali activated fly ash binder after 24 hours of curing. Chemical mappings on Figure 3B&C indicate the presence of a calcium-rich nodule labelled 1 on Figure 3A and predominantly made of calcium and sulphur. Additionally, those calcium-rich particles display a granular aspect on their surface.

Surrounding this calcium-rich particle, the area labelled 2 on Figure 3A corresponds to a porous zone distinguishable by the presence of dense black areas characteristic of the

filling resin of low atomic mass. Chemical mappings of that porous zone show an enrichment in silicon and sodium (Figure 3D&E) indicating the presence of the sodium-silicate Na_2SiO_3 alkaline solution at that short curing time. Additionally, filament like structures are observed within that area (see red arrow on Figure 3A), and considered as the beginning of the secondary phases formation i.e. the amorphous silicate consisting of chains combined with calcium and potentially aluminium. In fact, a former study about cementitious microstructures has shown the formation of similar arrangements associated with Calcium Silicate Hydrates whose structure strongly resembles the one of our newly formed chains (Scrivener, 2004). Moreover, it appears that those filament structures are stacked around particles corresponding to the initiation of the reaction process after 24 hours of curing.

Figure 4 also shows microstructural observations of the alkali activated fly ash binder after 24 hours of curing, and particularly illustrates the microstructural difference between a calcium-rich particle and a particle from the vitreous phase both originally present in the fly ash. They can both be distinguished by SEM by their chemical composition and microstructural features. Regarding calcium-rich particles, they present a nodule shape with a granular surface (see 3 on Figure 4A) as previously observed (Figure 3A). Whereas particles from the vitreous phase display a vesicular structure (see 1 on Figure 4A) and can be distinguished using chemical mappings by their enrichment in silicon and aluminium (Figure 4D&E).

In between those two particles, a porous area labelled 2 on Figure 4A and with filament like structures can once again be observed and evidences the initiation of the reaction processes. Consequently, from Figure 3 as from Figure 4 it is noticeable that the alkali activated binder after 24 hours of curing presents a high porosity created by the fly ash

grains of various sizes and that is filled by water, alkaline solution, and the new product starting to be formed.

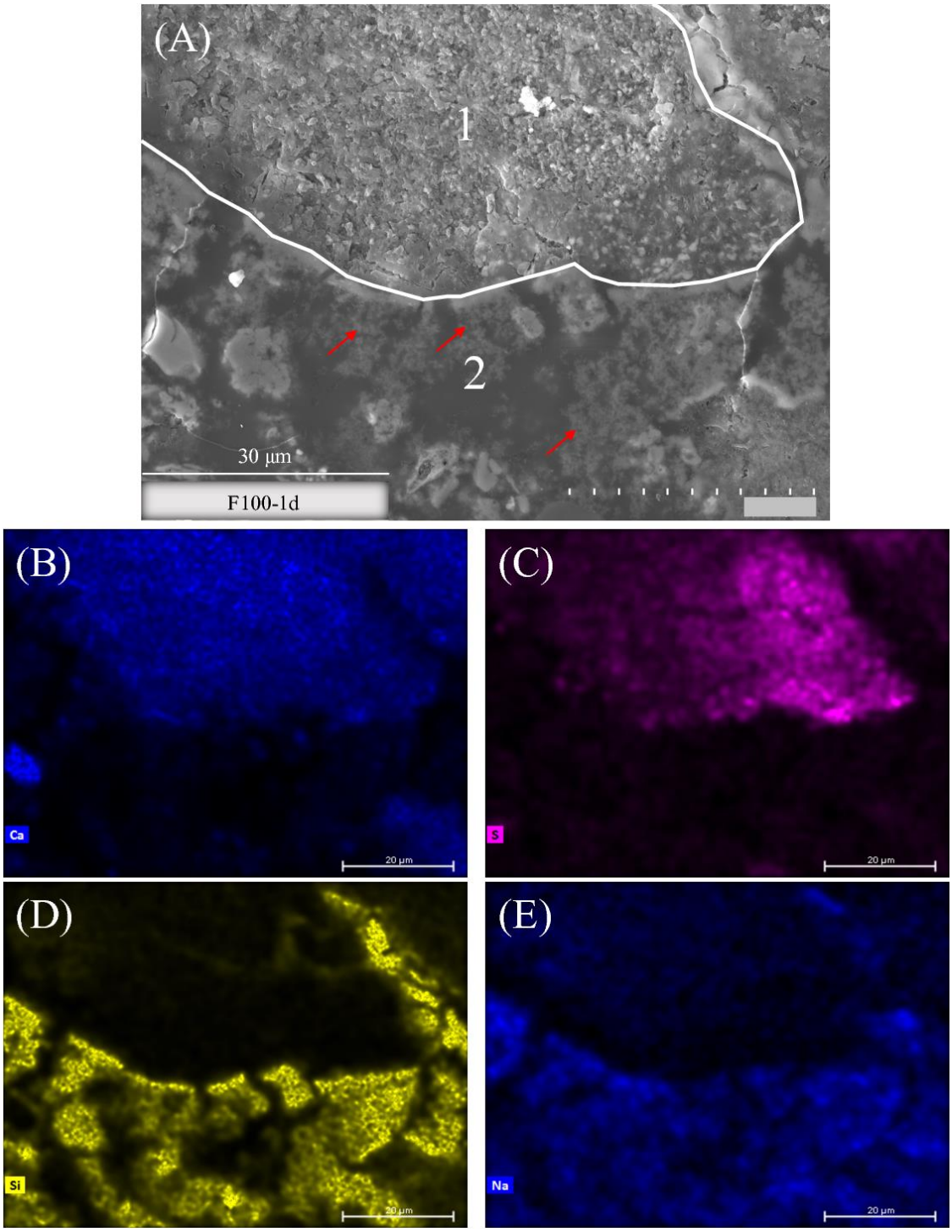

Fig. 3 SEM observations of the alkali activated fly ash binder F100 after 24 hours of curing: (A) SEM micrograph, and chemical mappings of: (B) calcium, (C) sulphur, (D) silicon and (E) sodium.

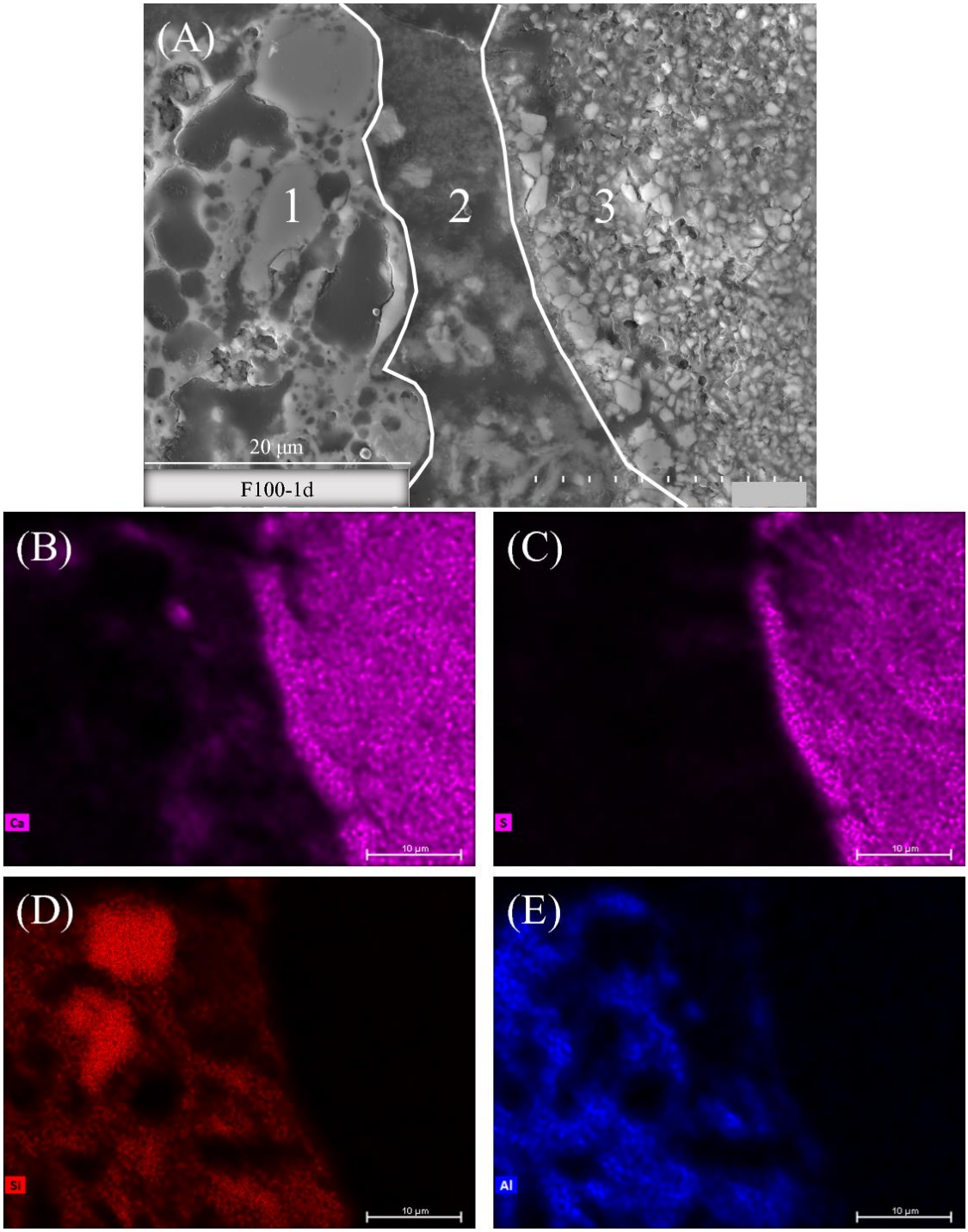

Fig. 4 SEM observations of the alkali activated fly ash binder F100 after 24 hours of curing: (A) SEM micrograph, and chemical mappings of: (B) calcium, (C) sulphur, (D) silicon and (E) aluminium

Figure 5 shows SEM observations and combined chemical mappings of the alkali activated fly ash binder after 28 days of curing. It especially focuses on the interface between a calcium-rich nodule labelled 1 and the surrounding matrix labelled 2.

Regarding the calcium-rich nodule, it displays a hollowed structure, especially in its centre, and as similarly observed previously by optical microscopy in section 3.2.1. In addition, those hollowed structures show dense black zones indicating the presence of filling resin and therefore porosity. Those structural characteristics strongly contrast with calcium nodules after 24 hours presenting a granular surface, and are attributed to the dissolution of calcium-rich phases over time leaving behind a porous body. It is supported by chemical mappings on Figure 5B&C showing a strong impoverishment in calcium and sulphur in the hollowed area with respect to nodules after 24 hours.

An enrichment in calcium and sulphur is seen in the outer part of the nodule suggesting a mechanism of dissolution of calcium and sulphur moving from the calcium nodules to the matrix. Moreover, few silicon supplied in that system by the alkaline solution is detected above the edges of the calcium nodule and inside implying that the alkaline solution penetrates through the calcium-nodule accelerating its dissolution. The coloration due to the silicon presence inside the nodule is few marked as unreactive quartz which corresponds to intensely coloured and well defined edges spots on the silicon chemical mapping (Figure 5D) are present in the matrix and induces a rescaling of the silicon coloration.

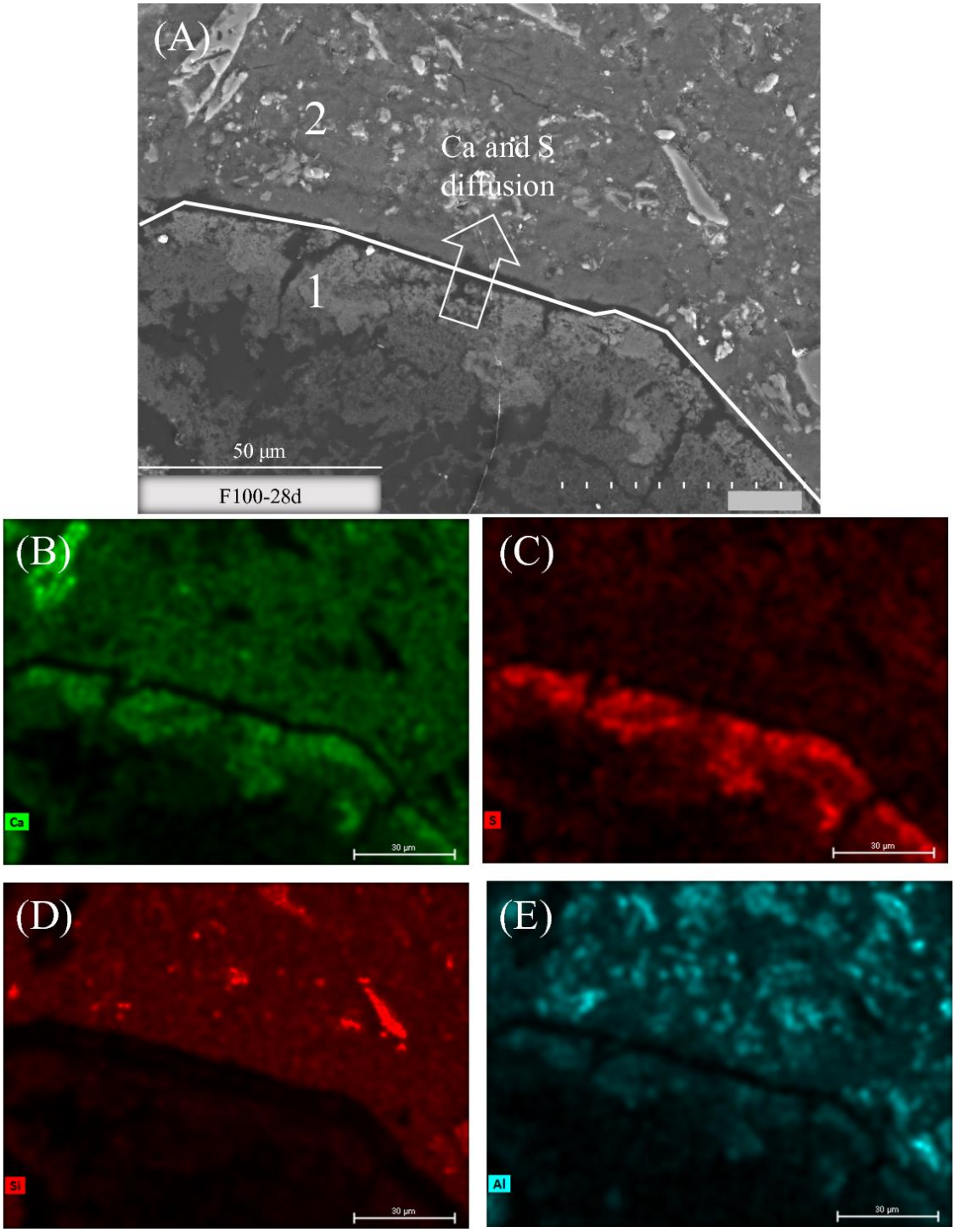

Fig. 5 SEM observations of the alkali activated fly ash binder F100 at 28 days: (A) SEM micrograph, and chemical mappings of: (B) calcium, (C) sulphur, (D) silicon and (E) aluminium.

Regarding the area surrounding the calcium nodule labelled 1, it is massive and presents a low porosity compared to the binder after 24 hours. It corresponds to the area where

new products are formed. Its chemical mappings show a high content of calcium and silicon which is in accordance with the physicochemical investigation that showed the formation of silicate chains combined with calcium over time. The wide diffusion of calcium into the matrix is clearly seen from Figure 5 when compared to the binder after 24 hours of curing for which calcium is contained and restrained to the nodule surface (see Figure 3 and Figure 4). Concerning sulphur elements, as well initially present in the nodule in the form of anhydrite $CaSO_4$, its dissolution occurs in a lesser extent and seems stopped to the outer part of the nodule at 28 days (Figure 5C). The physicochemical evolution of this system showed that dissolved sulphur combine with sodium to form thenardite Na_2SO_4 at 28 days (Coudert et al., 2019). Consequently, the presence of thenardite is restrained to small areas around the calcium-rich particles, whereas silicate two-dimensional chains combined with calcium are widely spread all around the calcium nodules. The formation of this thenardite crust limited around calcium nodules can be explained by the low amount of sulphur elements compared to calcium (see chemical composition of the raw fly ash in Table 1), that already all precipitated in this small area. The conjoint chemical mapping of sodium to localise thenardite is not shown here as sodium is a volatile element for which it is difficult to get a chemical mapping showing a reliable representativeness of sodium dispersion.

Finally, important crackings are observed around calcium-rich particle as seen on Figure 5 and are associated with shrinkage processes frequently observed for alkali activated materials (Fang et al., 2018).

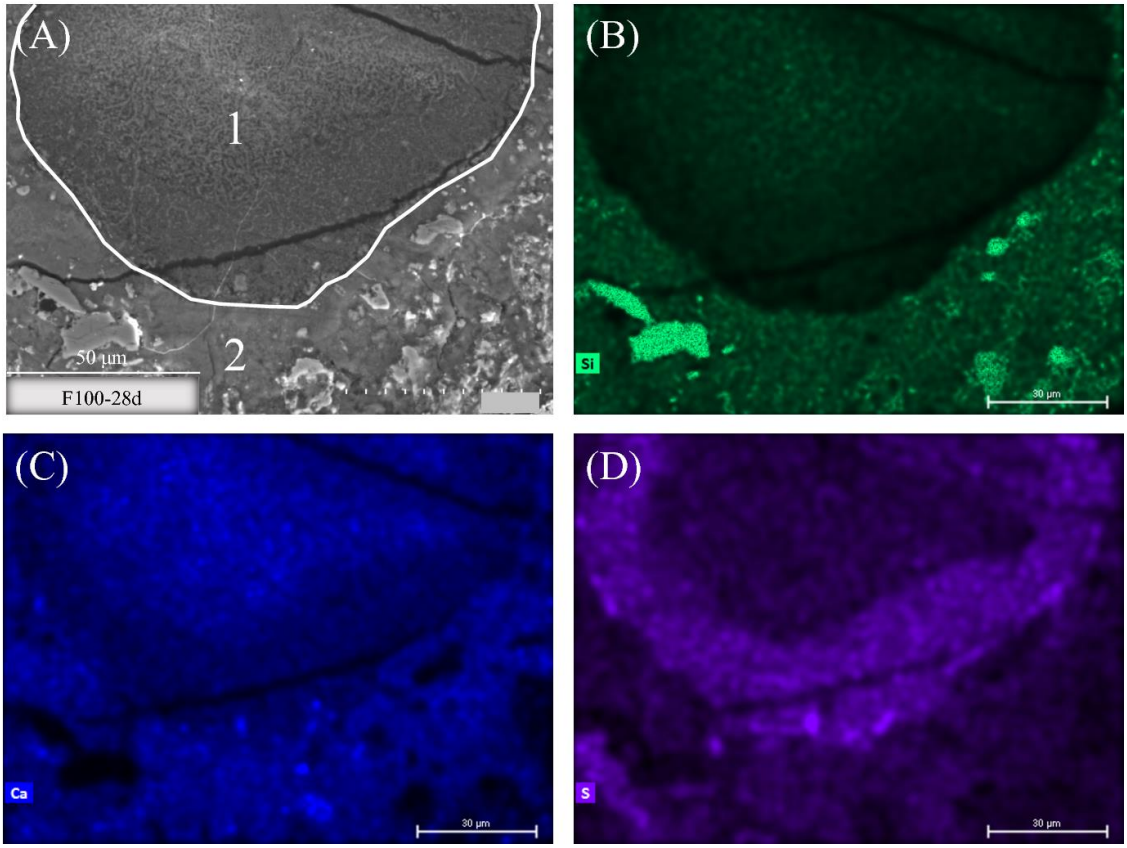

Fig. 6 SEM observations of the alkali activated fly ash binder F100 at 28 days: (A) SEM micrograph, and chemical mappings of: (B) silicon, (C) calcium and (D) sulphur.

Figure 6 shows the alkali activated fly ash binder at 28 days, and more particularly a calcium-rich reactive nodule labelled 1 surrounded by a dense matrix comprising both new products and non-reactive phases such as quartz or aluminium containing minerals. However, in that case the extent of dissolution of the calcium nodule appears lower as the hollowed structure is not seen but rather a granular microstructure similar of those observed after 24 hours. Chemical mappings show that the dissolution of that nodule did start as calcium is widely diffused into the matrix, and an enrichment in sulphur is once again seen in the outer part of the nodule. Nevertheless, the dissolution is at a different stage as calcium is still strongly detected in the centre of the nodule and no hollowed structure is noticed. Consequently, the extent of reaction of a calcium-rich nodule varies

locally. A lesser porosity of the calcium nodule could for instance moderates its dissolution. Its size, its content in calcium and sulphur or else the amount of water locally available are also all parameters that may locally affect the extent of reaction.

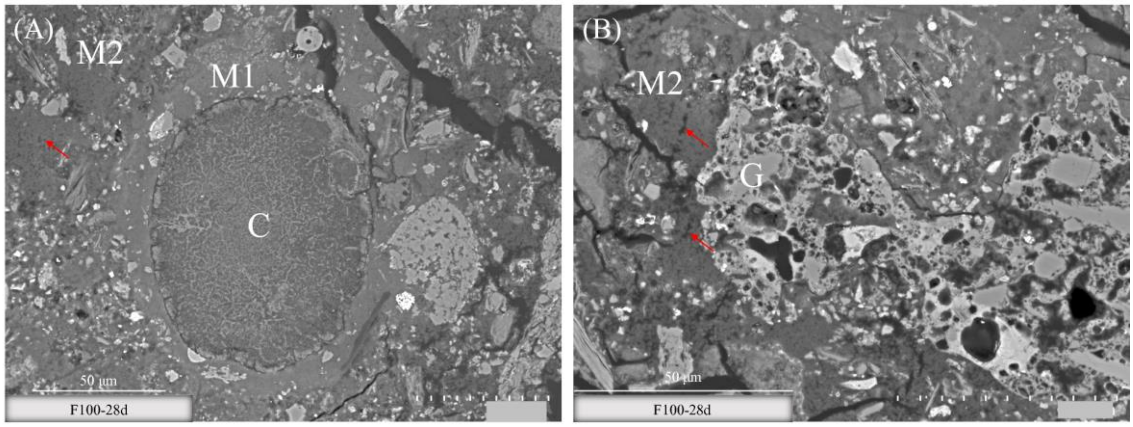

Fig. 7 Comparing SEM microstructural changes of the alkali activated fly ash binder F100 at 28 days around: (A) a calcium-rich nodule labelled C, and (B) a particle from the vitreous phase labelled G; M1 = dense matrix; M2 = porous matrix

Figure 7 shows micrographs of the alkali activated binder after 28 days, and more particularly the difference between microstructural changes occurring (A) around a calcium rich particle identified as the dark reactive zones in optical microscopy, and around a glassy particle identified as the brown matrix in optical microscopy.

It is worth noting that although amorphous and extremely porous the vesicular glassy phases reaction is negligible as its vesicular structure remains similar to the one after 24 hours (see Figure 4A, particle labelled 1). This observation is in accordance with our previous study about the physicochemical evolution of that system which shows that the vitreous phase mainly remains unreactive (Coudert et al., 2019). It is well known that the rate of reaction of the aluminosilicate vitreous phases of fly ash at ambient temperature following alkaline activation is slow and takes several days (Provis and Deventer, 2009; Wardhono et al., 2015). Whereas the calcium-rich particles in our mixes are extremely

and quickly reactive as the formation of new products containing calcium already starts after 24 hours as seen previously in Figure 3. Hence, the faster reaction of calcium-rich particles leads to the formation of dense products (as seen in Figure 7A) freezing the system and preventing the later reaction of the aluminosilicate glassy phases.

Massive and dense areas are observed around calcium-rich nodules (see Figure 7A), while a more porous matrix is seen around vesicular glassy phases (see Figure 7B). The comparison in Figure 7 hence evidences that there are different matrices forming the alkali activated treated soil: (i) a first circularly-shaped matrix identified around calcium-rich particles and presenting a high density labelled M1 on Figure 7A, and (ii) a more porous matrix less bonded labelled M2 on Figure 7A&B whose pores are shown by red arrows, and located around glassy phases of lower reactivity. A previous investigation of that system by Nuclear Magnetic Resonance showed the signature of only one type of silicate chains combined with calcium and spreaded into the matrix as a new compound (Coudert et al., 2019). Therefore, Scanning Electron Microscopy provides an additional information: although the atomic structure of the silicate chain remains similar, the arrangement of those phases in the matrix varies following the local environment. Similarly to the great heterogeneity of fly ash, the matrix formed is also highly heterogeneous.

3.2.3 Mercury Intrusion Porosimetry (MIP)

Figure 8A shows cumulative curves of mercury intrusion porosimetry tests of the alkali activated fly ash binder over time. The longer the curing time, the lower is the cumulative intrusion volume ratio implying a progressive decrease of the overall porosity over time, and in accordance with the general tendencies observed by SEM in section 3.2.2. It is

owed to the progressive filling of pores by the new compounds formed i.e. calcium-silicate two-dimensional chains and thenardite.

Figure 8B shows the frequency distributions of pore entrance diameters belonging to the alkali activated fly ash binder over time. Samples at 24 hours, 3 and 7 days all show one broad modal pore sizes between 0.05 µm and 3 µm. However, from 24 hours to 7 days the frequency of those pores progressively decreases due to their filling by newly formed compounds. Whereas, at 28 days a narrower modal pore size at about 2 µm is observed. By analogy with SEM pictures, those remaining pores at 2 µm could correspond to either the size of the cracks seen around calcium particles and associated with shrinkage as previously observed on Figure 5, the porosity formed within calcium nodules after their dissolution also seen on Figure 5, or else pores that have not been filled by new compounds within the more porous matrix previously identified and labelled M2 on Figure 7.

Finally, in the area of lower pore size i.e. below 20 nm the increase of frequency over time corresponds to the formation of a new class of pores inside the matrix. It is associated with the formation of the silicate two-dimensional chains combined with calcium, whose structure resembles those of Calcium-Silicate Hydrates (i.e. C–S–H phases commonly found in Portland cement) known for possessing an intrinsic porosity of a nanometer size (Muller, 2014). However, this small new class of pores cannot be fully probed by MIP technique whose detection limit in the small entrance pore size is of 7 nm.

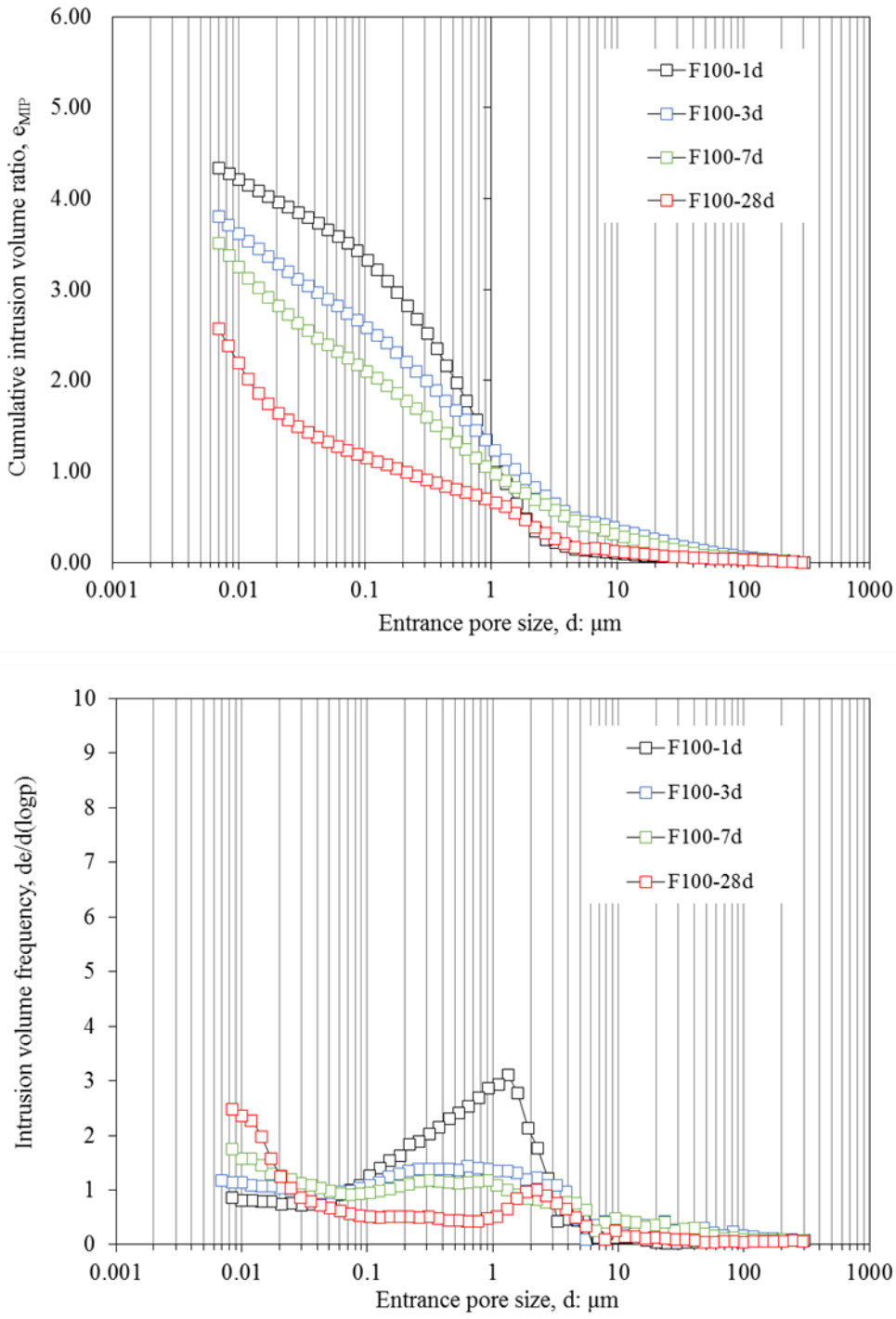

Fig. 8 Comparing mercury intrusion porosimeter tests of the alkali activated fly ash binder F100 over time and in terms of (A) cumulative intrusion volume ratios, (B) intrusion volume frequency ratios as a function of entrance pore size.

3.3 Interaction between the alkali activated fly ash binder and kaolin

The following section aims at understanding the interaction between kaolin and the alkali activated fly ash binder previously described. Our former study focussing on the physicochemical evolution of the same mixes herein studied showed that kaolin was not reactive during alkaline activation and did not modify the reaction sequence when compared to the one of the alkali activated fly ash binder alone (Coudert et al., 2019). Accordingly, similar mechanisms of ions dissolution precipitation from the calcium-rich particles into the matrix leading to the formation of new products also occur in the alkali activated fly ash binder treated soil as previously described for the binder in section 3.2.2, and hence will not be detailed here.

Regarding the pore network structure, our previous study also showed that kaolinite platelets were homogeneously spread across the matrix. This section consequently aims at giving a deeper insight of the influence of kaolin on the microstructure with respect to the binder alone.

Figure 9 shows microstructural observations of the alkali activated fly ash binder treated soil over time by optical microscopy. Similarly, to the alkali activated fly ash binder, after 24 hours of curing, dispersed dark spots corresponding to calcium-rich nodules are seen across the overall sample, whereas at 28 days larger dark zones encompassing the newly formed compounds have grown around those nodules. Hollowed greyish nodule structures at 28 days can also be distinguished as for the binder and associated with the dissolution of calcium-rich particles.

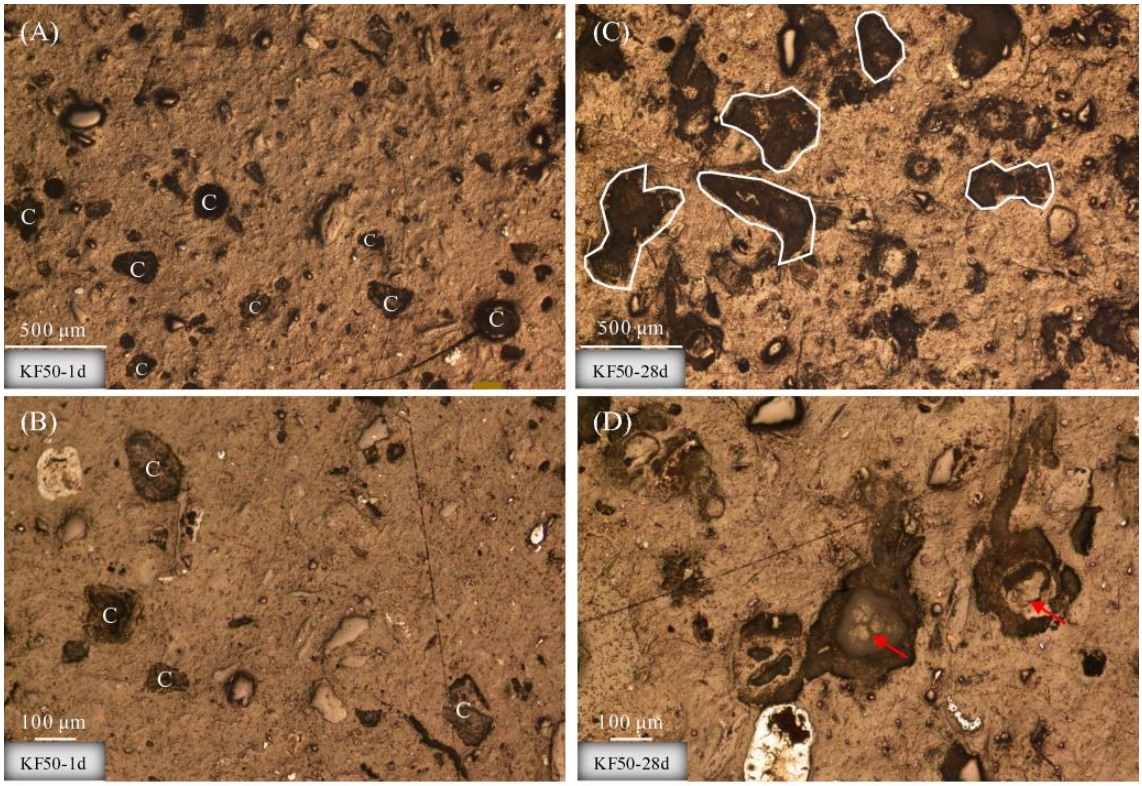

Fig. 9 Optical microscopy images of the alkali activated fly ash binder treated soil KF50 (A) and (B) after 24 hours, (C) and (D) at 28 days, C=calcium-rich particle.

The widening of darker zones which indicates the extent of reaction is lesser than the binder and represents around ¼ of the sample. This is consistent with the proportions of aluminosilicate solid considering that half of fly ash containing the reactive calcium nodules has been replaced by non-reactive kaolin in this soil-binder mixture. Consequently, the growth and development of new products into the available spaces does not seem influenced by the presence of kaolin.

Figure 10 shows micrographs of the alkali activated binder treated soil. After 24 hours crackings around and inside calcium nodules are seen (see particle C on Figure 10A), and associated to shrinkage similarly to the alkali activated fly ash binder at 28 days. The treated soil at 28 days however shows less marked crackings as shown on Figure 10B which focusses on the interface between a calcium-rich nodule labelled 1 and the

surrounding dense matrix labelled 2. It is attributed to the presence of kaolinite acting as a filler at the periphery of the calcium-rich nodules (see red arrows on Figure 10B showing kaolinite platelets).

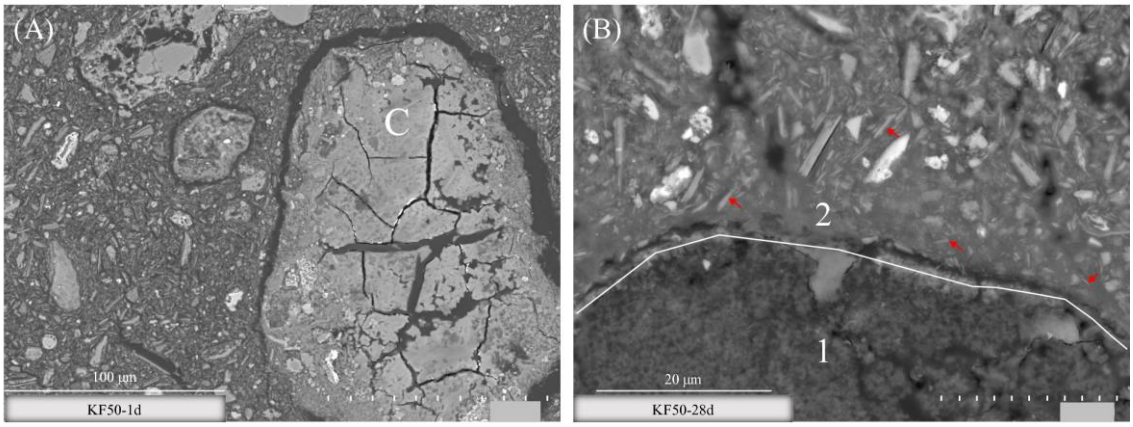

Fig. 10 SEM micrographs of the alkali activated fly ash binder treated soil KF50 at (A) 24 hours and (B) 28 days.

Figure 11A shows cumulative curves of mercury intrusion porosimetry tests of the alkali activated fly ash binder treated kaolin over time. Similarly to what was observed for the alkali activated binder, a decrease of the total porosity is detected over time.

Figure 11B shows the frequency distributions of pore entrance diameters belonging to the treated soil over curing time. Similarly to the alkali activated fly ash binder, the treated soil at 24 hours shows one modal pore sizes. Nevertheless, compared to the binder it is associated with a lower entrance pore size value around 0.4 µm and a much thinner peak. The non-presence of a wide class of pores between 0.05 µm and 3 µm at 24 hours as seen for the alkali activated fly ash binder is associated with the filling of the spaces between the coarse grains of fly ash by the small sized kalinite platelets. At 24 hours, kaolin therefore leads the organisation of the system microstructure as the typical pattern of kaolin (i.e. a monomodal curve with a peak around 0.4 µm) is shaping the curve.

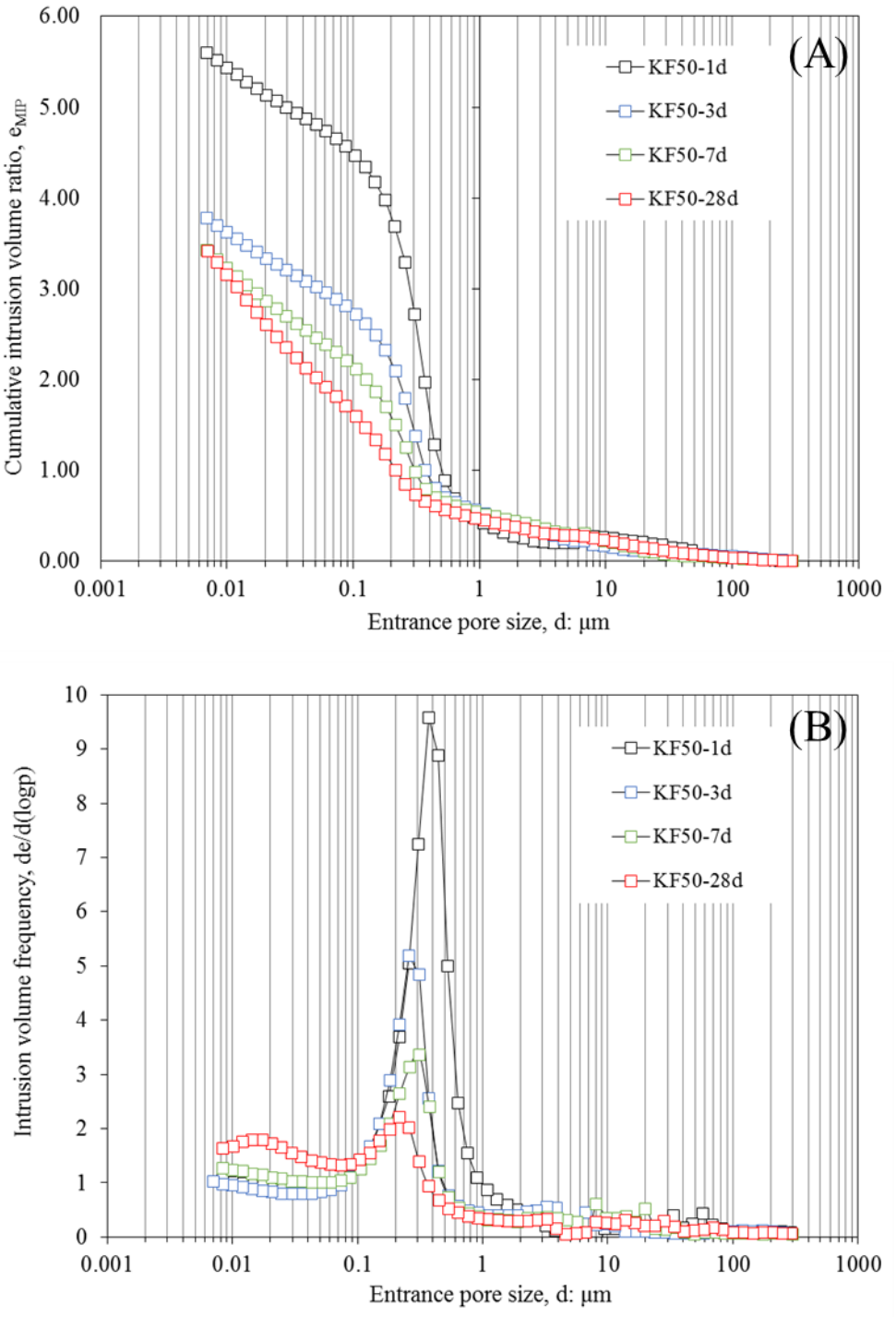

Fig. 11 Comparing mercury intrusion porosimeter tests of the alkali activated fly ash binder treated soil KF50 over time and in terms of (A) cumulative intrusion volume ratios, (B) intrusion volume frequency ratios as a function of entrance pore size.

Increasing the curing time, the filling of largest pores around the peak is seen as for the binder and due to the progressive filling of those pores by the newly products formed. A little shift of the residual peak towards smaller entrance diameters is also observed.

Finally, the formation of a new class of pores in the area of lower pore size i.e. below 30 nm is observed between 7 and 28 days of curing. Similarly to the binder, it is associated with the intrinsic porosity of the newly formed silicate-calcium chains. The delay in detection compared to the binder is due to the lower amount of phases formed for that system.

Figure 12 shows the results of one dimensional compression tests on KF20 and KF40 treated samples at increasing curing times, namely 24h, 7, 14 and 28 days. Addition of alkali activated binder induces an overall reduction of compressibility of the treated samples, with reduced volume strains for reference vertical stresses. The reduction is more relevant for increasing curing times, showing the stiffer behaviour of the treated sample. Coupled with the reduction of compressibility, an increase of yield stress of the samples is observed. The transition from a reversible behaviour to an irreversible one is shifted (yield stress) to higher vertical stresses. The shift is more relevant for higher amount of binder and at increasing curing time, revealing the reactivity of the binder to promote an improvement of the mechanical response of the treated soil. For stress levels higher than yield stress, treated samples show a higher compressibility coefficient (i.e. slope of the compressibility curve), depending on the destructuration stage induced by load increase, more evident for longer curing times and higher binder content. As a confirmation, in Figure 13 the compressive behaviour of treated samples is reported as function of binder contents. Sample prepared at 10%, 20% and 40% of alkali activated fly ash and cured for 24 hours before testing show a progressive improvement mainly

related to the amount of new compounds forming over time. Compressibility curves show a reduction of compressibility evidenced by the relevant decrease of volume strains and an increase yield stresses of the treated samples, whose extent depends on binder content.

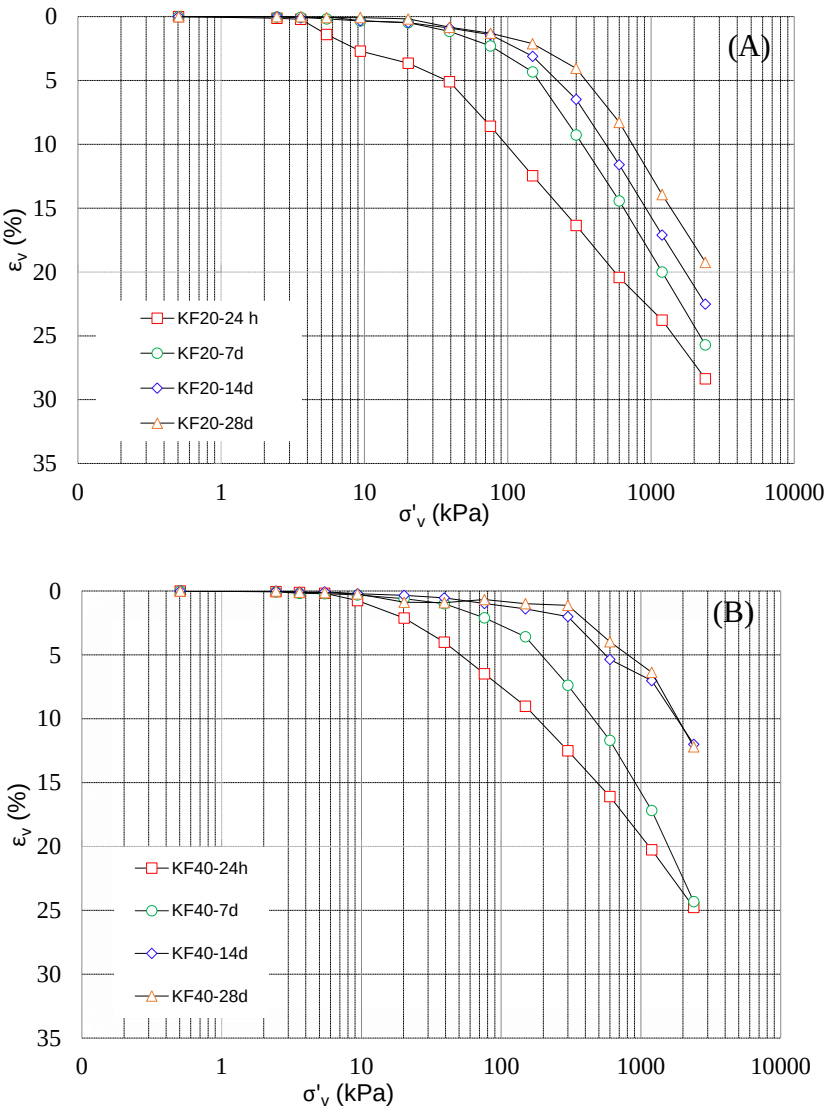

Fig. 12 One dimensional compression curves of alkali activated binder treated samples at 24 h, 7, 14 and 28 days of curing: (A) KF20; (B) KF40.

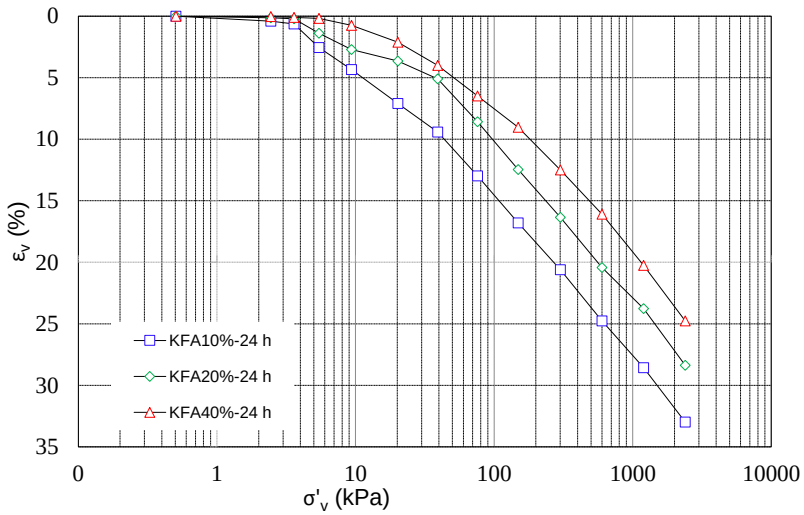

Fig. 13 One dimensional compression curves of treated samples as function of binder contents (i.e. KF10, KF20, KF40) at 24 hours of curing.

3.4 Comparison with Portland cement

This last section focusses on a comparison with microstructural development in Portland cement for which the mechanisms involved appear alike. This comparison particularly helps at providing a better understanding of (i) how microstructures are formed and (ii) interpreting the short and long-term performances of the treated soil regarding the evolution of the binder over time. At macroscopic level, the effectiveness of alkali activated binder soil treatment has been highlighted by comparison with mechanical performance induced by Portland cement.

3.4.1 Processes generating the microstructure

In cement systems, the dissolution of cement particles releases ions into the pore solution which then combine with water to form mainly Calcium Silicate Hydrates C–S–H (Muller, 2014). In a similar way, in our alkali activated binder, the dissolution of calcium-rich particles from fly ash releases calcium cations into the pore solution which then combine with water and silicon anions from the alkaline solution to form silicate two-

dimensional chains combined with calcium. A former investigation by Nuclear Magnetic Resonance nevertheless showed that the chains structure is slightly different from C–S–H, namely they are not well organized, of high length and may incorporate aluminum in a three dimensional environment which has not been described in literature yet (Coudert et al., 2019).

Secondly, it was reported for cement systems that the first Calcium Silicate Hydrates C–S–H cover cement grains and further grow into the available space. All cement grains are therefore surrounded by a shell of C–S–H (Scrivener, 2004). Again similarly in this study, optical microscopy images clearly show the development and growth of new products around calcium-rich reactive particles suggesting a similar mechanism.

Furthermore, Scrivener (2004) shows that as the cement grains dissolve, this might leave a hollow shell (Scrivener, 2004). The various extent of reaction of individual cement grains depends on their sizes: small cement grains hydrate completely in the first stages and remain as hollow shells of hydration product; whereas big grains further hydrate which forms denser hydration products and which fill in the gap between shell and grain (Muller, 2014). In this study it is also noticeable that calcium-rich reactive phases react at different rates: some completely dissolve after 28 days leaving a hollow shell while other remain with their initial structure and still contain calcium. Consequently, and similarly to what is described in the literature, depending on the calcium nodule size, the local products formed slightly differ which could lead to local variation of the inherent material properties.

3.4.2 Pore network characteristics

Regarding the pore network characteristics of cement systems, two populations of pores are generally distinguished: (i) capillary pores which correspond to space not being filled by solid products of hydration, and (ii) small pores called gel pores associated to the intrinsic porosity of Calcium Silicate Hydrates C–S–H. Over time, while chemical reactions proceed the population of capillary pores decreases whereas the population of gel pores increases, which may lead to the formation of disconnected spaces (Jennings et al., 2008). Our alkali activated binder shows similar tendencies that is a progressive decrease of intermediate pores or capillary pores while a new class of pores associated with silicate-calcium chain products is detected using Mercury Intrusion Porosimetry.

3.4.3 Macroscopic behaviour according to the microstructure evolution

Since both the processes generating the microstructure and the evolution of the pore network over time of our alkali activated binder are similar to cement systems, a similar influence of the microstructure on the short and long-term performances can be expected. Changes in the pore network strongly influence transport properties that govern the rate of all major deterioration processes and the service life of building materials (Wong et al., 2006). Namely the formation of gel pores inside the capillary spaces tends to decrease the connectivity of the pore network inhibiting the transport of aggressive substances such as acids, carbonate or chloride through concrete and therefore enhancing the material durability (van Deventer et al., 2010; Muller, 2014).

Finally, despite the great inhomogeneity of the reactive fly ash the growth and widening of new products appear to occur homogeneously across the sample at a millimetric scale in our alkali activated materials which would benefit the formation of a homogeneously reinforced material.

At volume scale of the sample, a comparison between the mechanical performance induced by alkali activated binder (KF40) and by ordinary Portland cement (KC40) is shown in Figure 14 for samples prepared with the same binder content and cured for 7, 14 and 60 days. No relevant changes in the compressibility curves are observed for KF40 and KC40 samples cured for 7 days before testing (Figure 14A). For longer curing times, results show a higher compressibility reduction and yield stress increase for KF40 treated samples compared to cement treated samples (Figures 14B and 14C). The post-yield behaviour induced by ordinary Portland cement shows the highest slope of the compressibility curve, highlighting a more evident destructuration stage for cement treated samples at increasing vertical stresses.

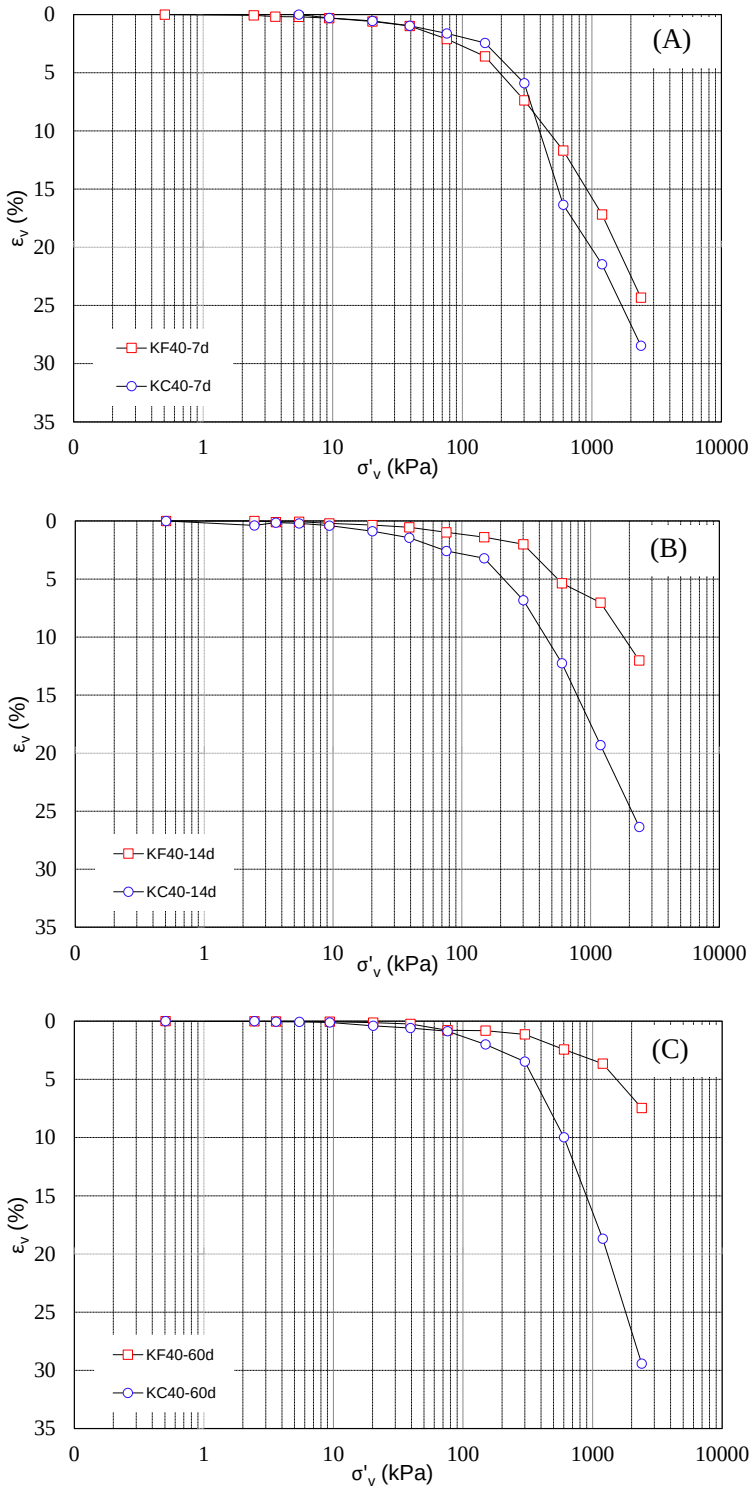

Fig. 14 One dimensional compression curves of treated samples as function of binder type (i.e. KF40 vs. KC40): (A) 7 days of curing; (B) 14 days of curing; (C) 60 days of curing

3 Conclusions

The development of a novel binder that is an alkali activated calcium-rich fly ash for clay soil stabilisation was investigated. The study of its microstructural evolution showed that structural changes occur around calcium-bearing minerals from fly ash which constitute the reactive phases, and whose dissolution leads to the formation of new compounds on its surface first and then growing into the available space. Capillary pore spaces are progressively filled by new compounds (i.e thernadite and silicate-calcium chains) over time. Whereas the newly formed silicate-calcium chains possess an intrinsic porosity of nanometric size conducting to the formation of a new class of small pores over time. Different heterogenous matrices of various porosity and arrangement are however observed across the material and owed to the high heterogeneity of fly ash whose particles locally react differently.

The interaction between the binder and kaolin showed that small sized kaolinite platelets fill the spaces between coarser grains from fly ash. Kaolin is therefore leading the microstructural organisation, that is, the pore network is characterised by pores ranging in lower size compared to the binder. Nevertheless, the microstructural changes remain similar over time i.e. filing of capillary pores and appearance of nanometric pores from silicate-calcium chains.

One-dimensional compression tests performed on treated sample highlighted the effectiveness of alkali activated binders to promote an improvement of the mechanical behaviour of treated soil. A reduction of compressibility and increase of the yield stress soil was observed since the very short term.

The observed microstructural evolution is similar to the one of cement system and should therefore conducts to akin performances that is an increase in strength and ability to resist

to aggressive substances due to changes in transport properties. It has been confirmed by observing the similarities of the mechanical performance of alkali activated binder treated samples with cement treated ones for short curing time. A marked improvement of the mechanical behaviour of soil is induced by alkali activated binder starting from 14 days of curing, representing a viable sustainable alternative to the use of ordinary stabilizing agent for soil improvement.

However, regarding the complexity of both cement and alkali activated systems which are multi-components systems, a coupling of those microstructural observations with mechanical performances and transport properties is of further interest. Namely, a complementary three-dimensional characterisation of the pore network using for instance microtomography would greatly help to assess the connectivity and tortuosity of the pore network which are primordial parameters to understand properly transport properties and therefore durability. Using micro-indentation coupled with Scanning Electron Imaging would also allow to measure local hardness variations following the extent of reaction of calcium particles and therefore help to apprehend how significant are the local microstructural variations for the mechanical performances at a macroscopic scale.

Acknowledgements

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Table 1

Chemical composition (wt. %) of raw fly ash and kaolin.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	CaO_{free}[a]	MgO	SO_3	Na_2O	K_2O	H_2O	L.o.I.
Fly ash	39.4	19.8	7.4	18.6	5.2	1.8	4.1	2.0	1.8	0.0	1.7[b]
Kaolin	49.2	34.5	1.2	0.0	0.0	0.2	0.0	0.1	1.7	13.1	12.0[c]

[a] Free calcium oxide content

[b] L.o.I = Loss on ignition 900 °C

[c] L.o.I = Loss on ignition 1000 °C

Fig 1

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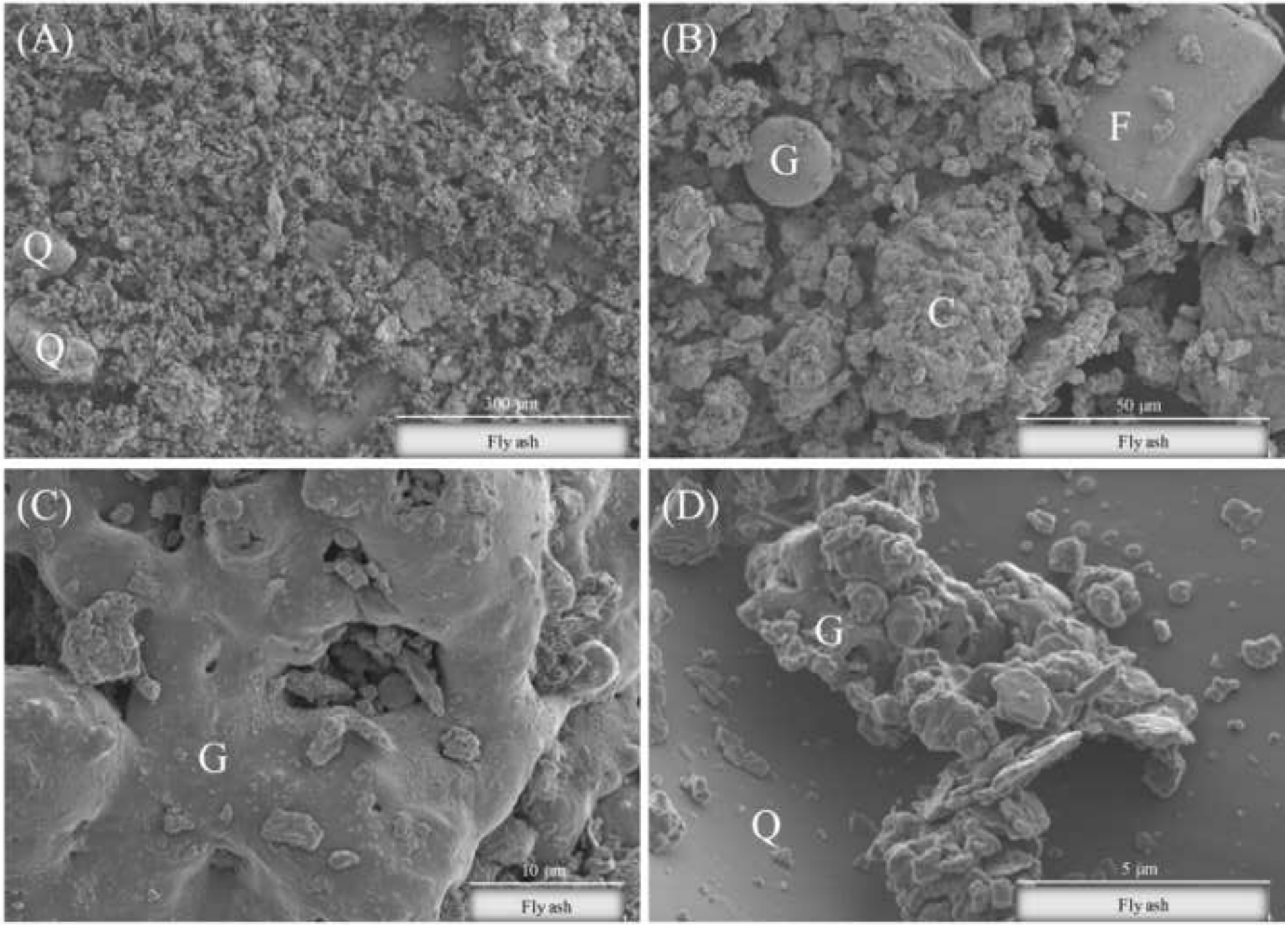
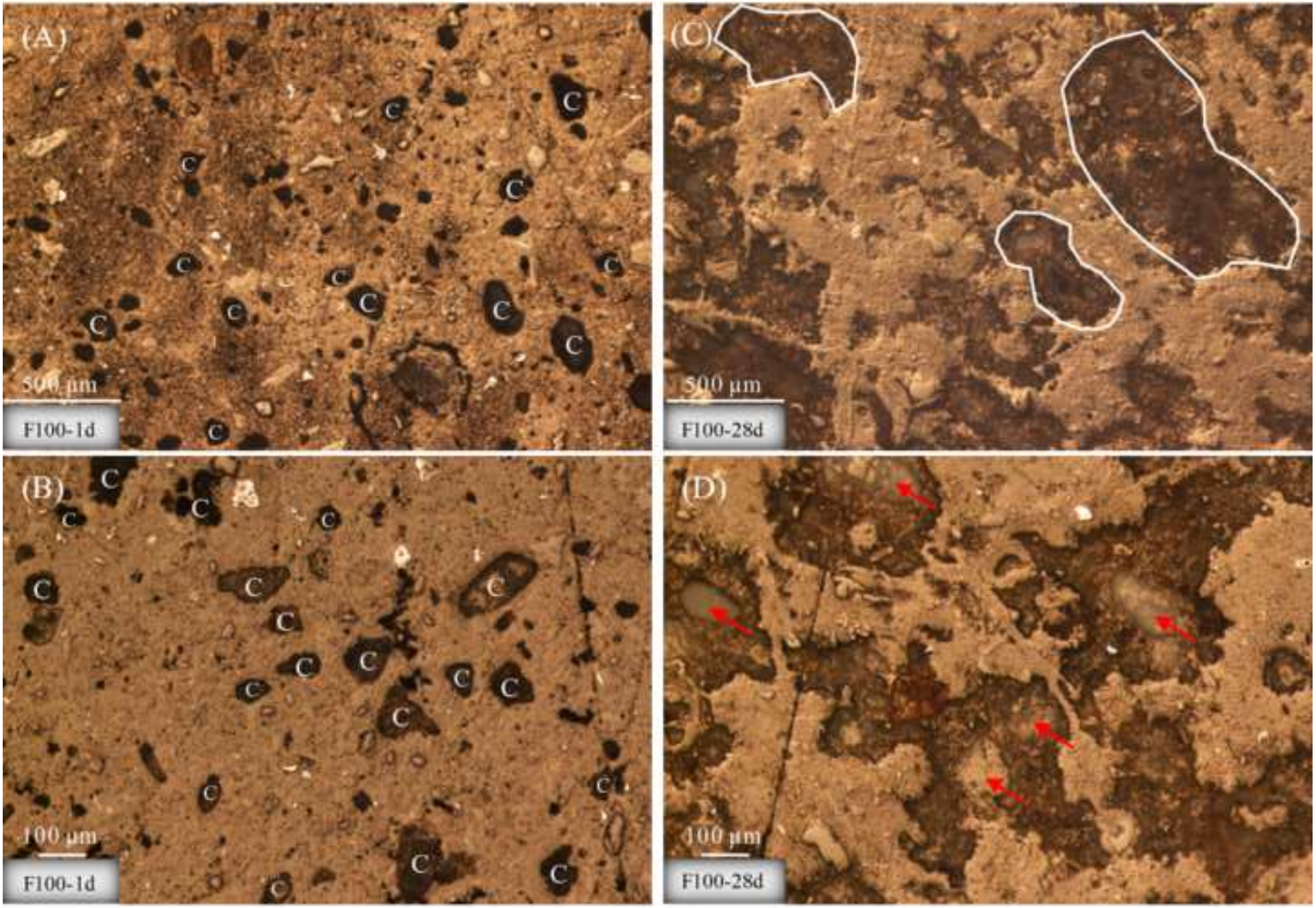


Fig 2



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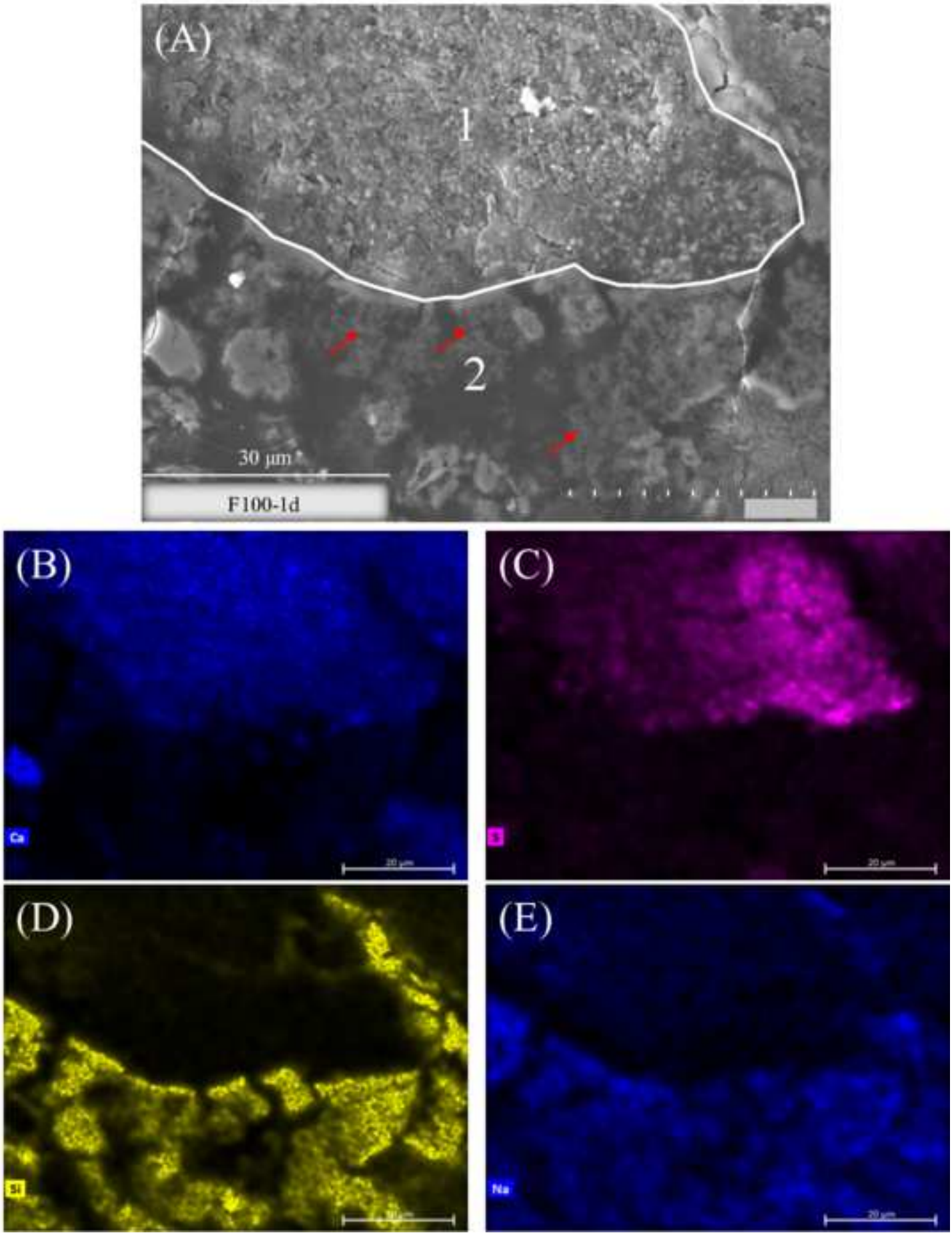

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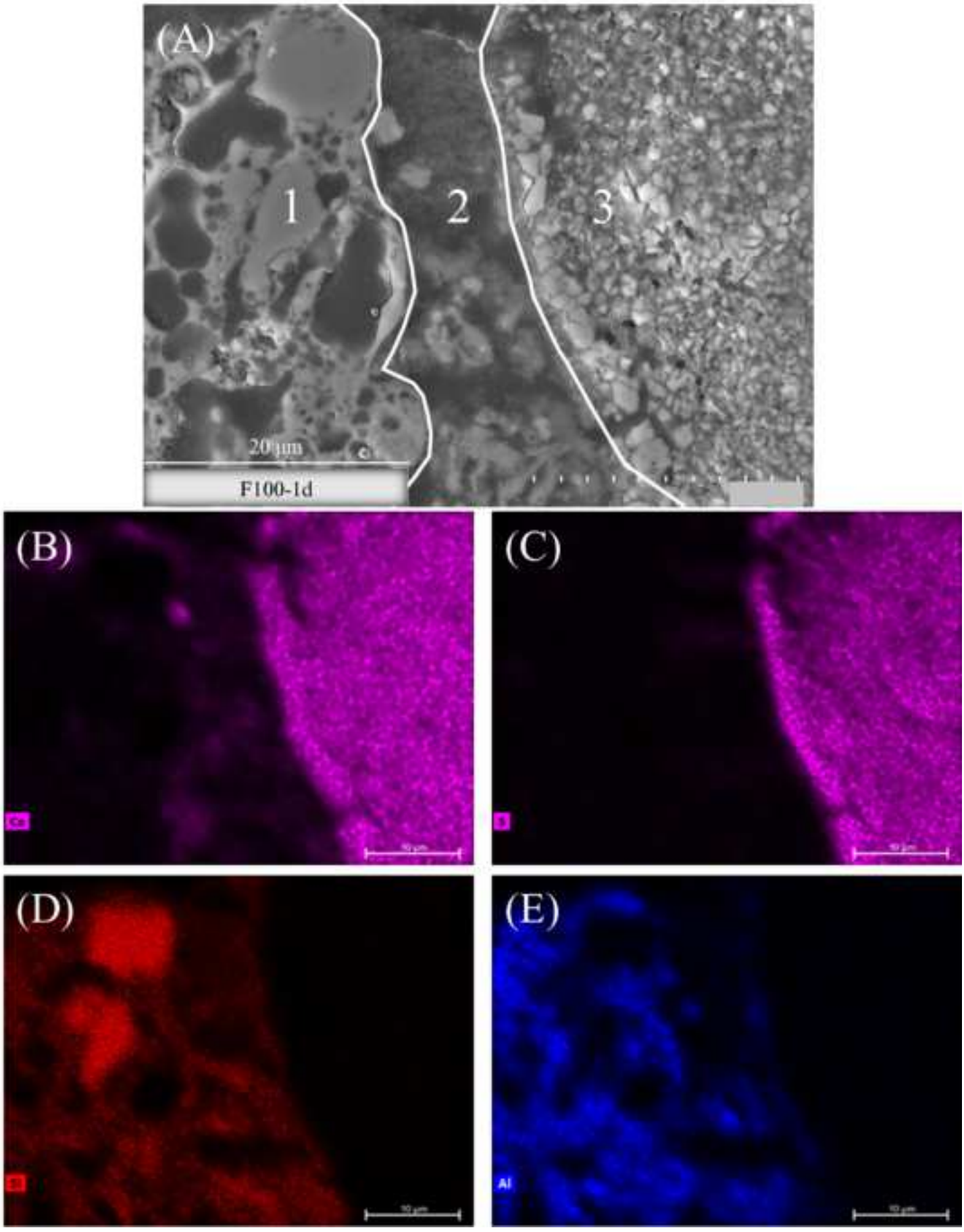
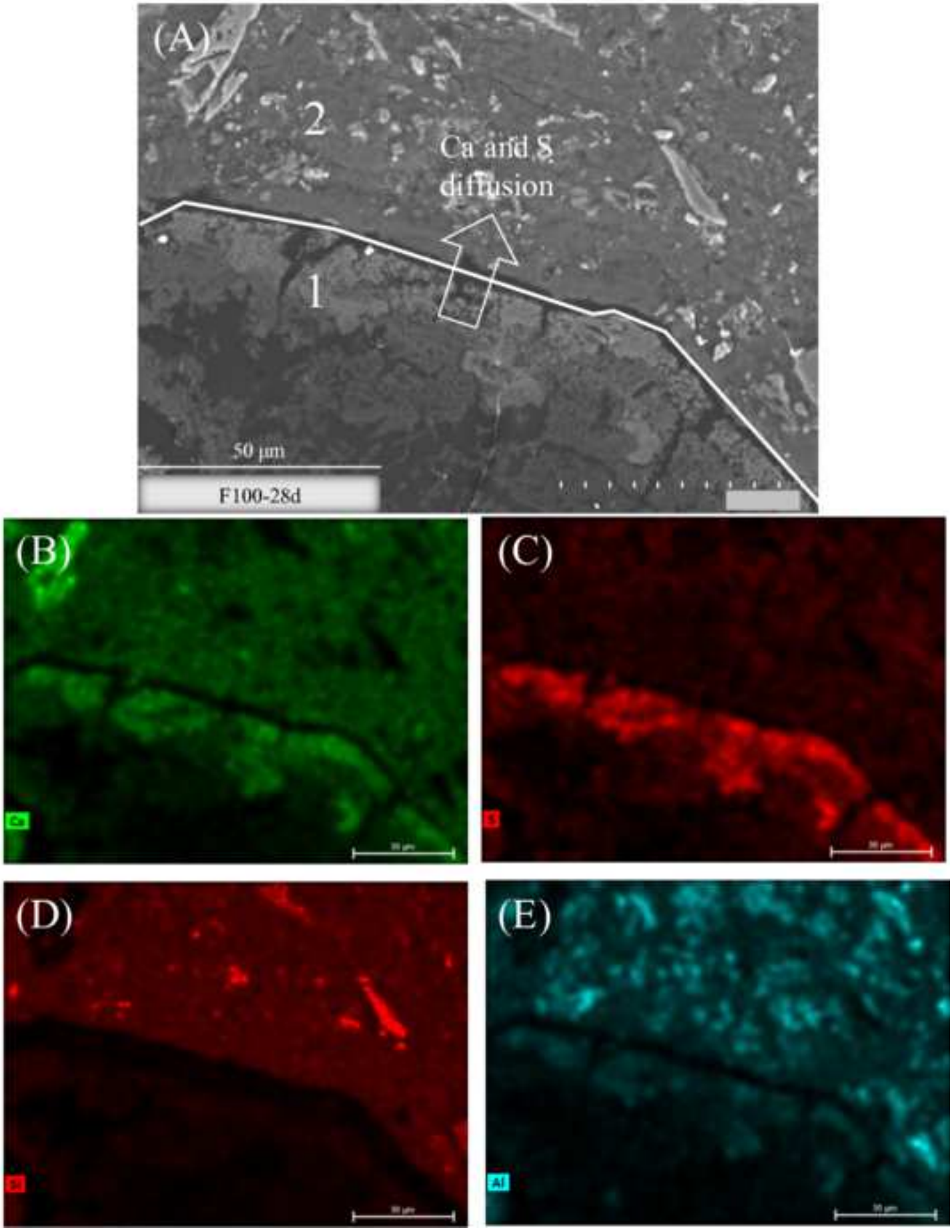


Fig 5



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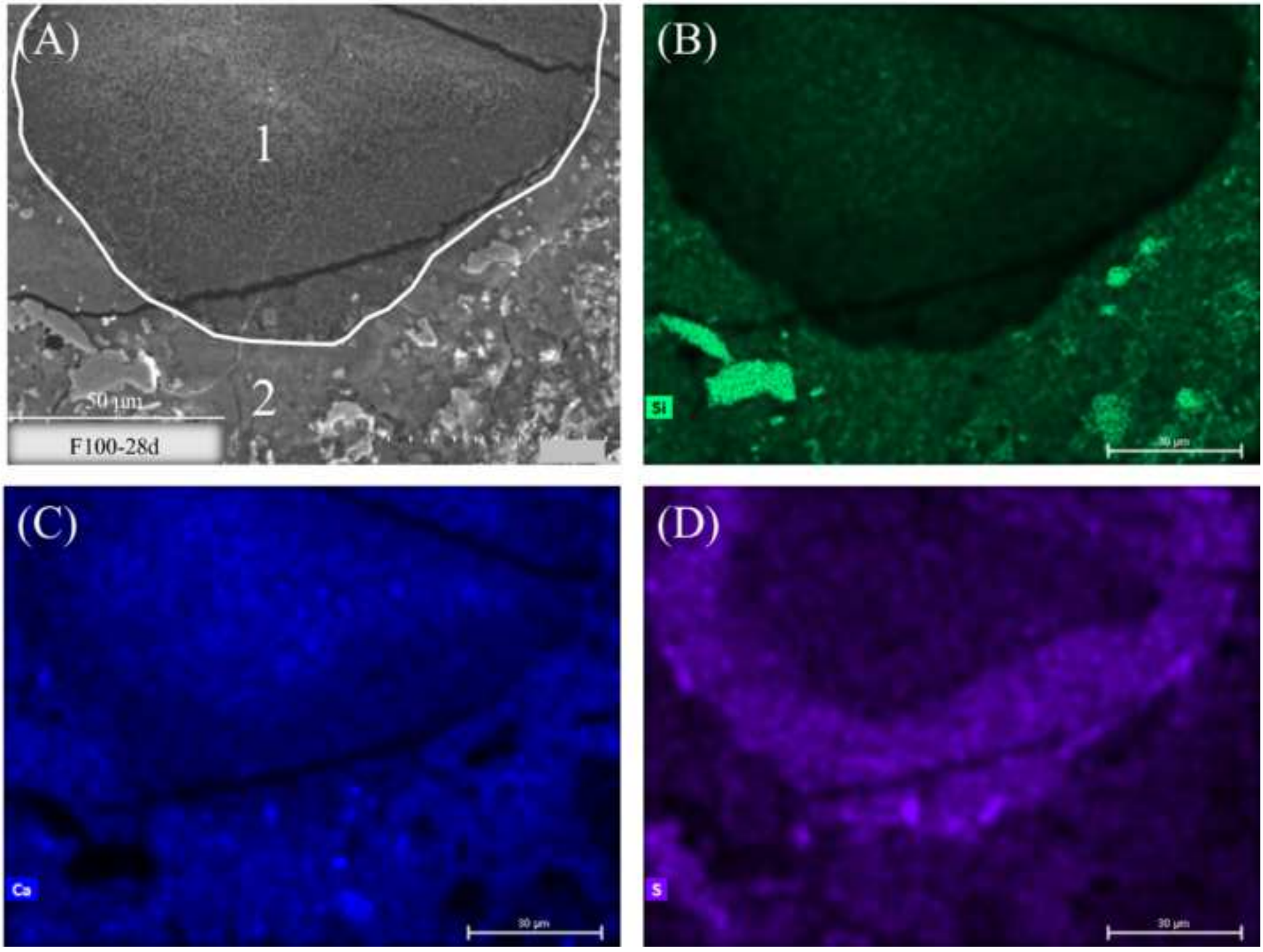

Fig 7

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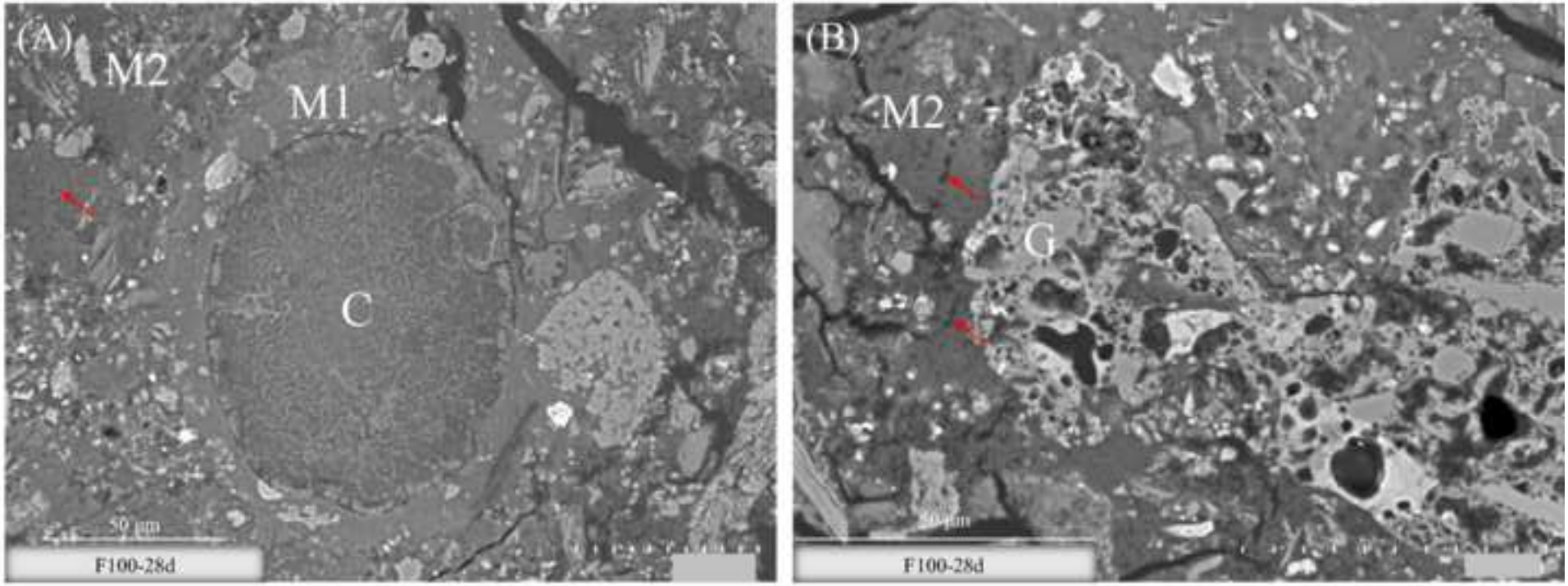

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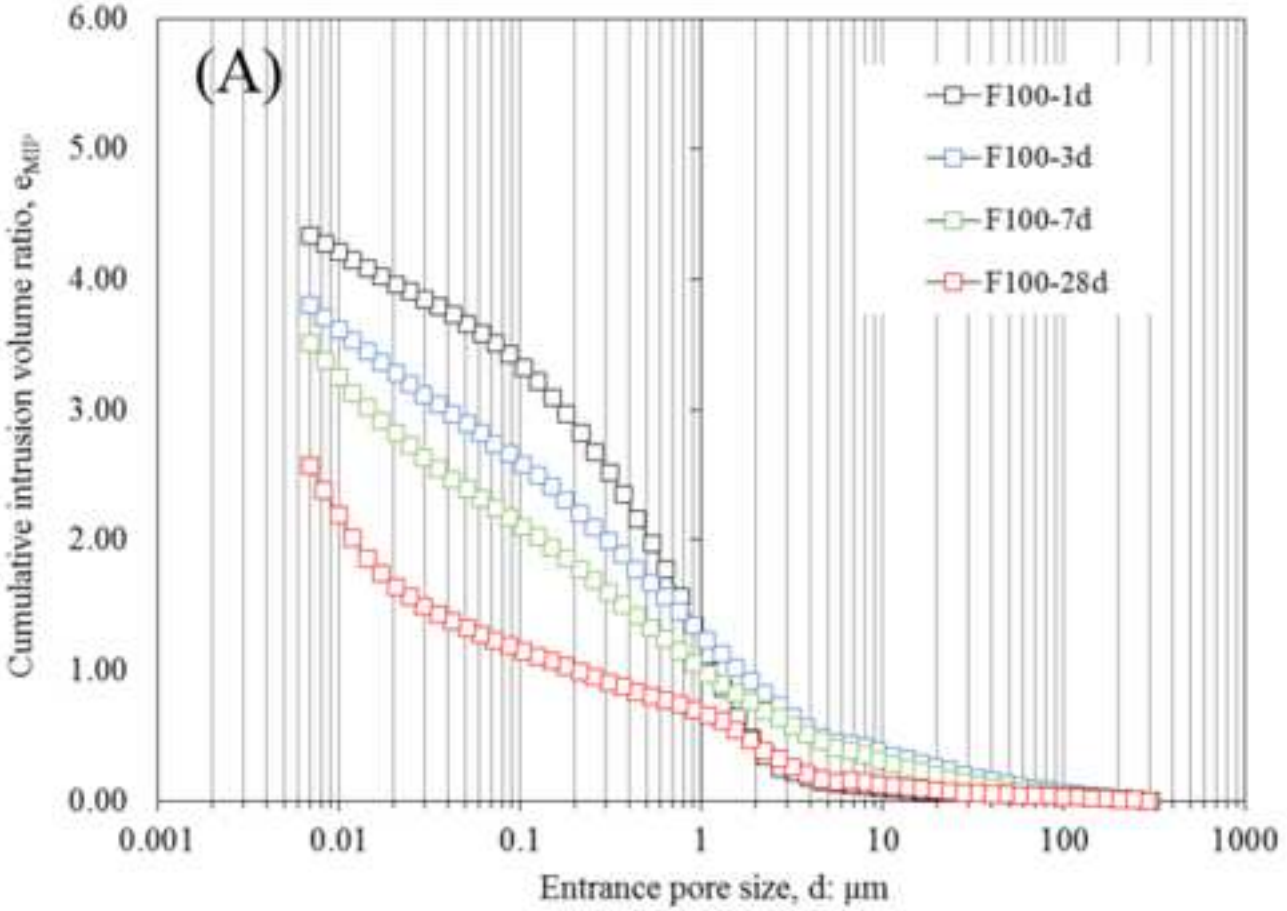

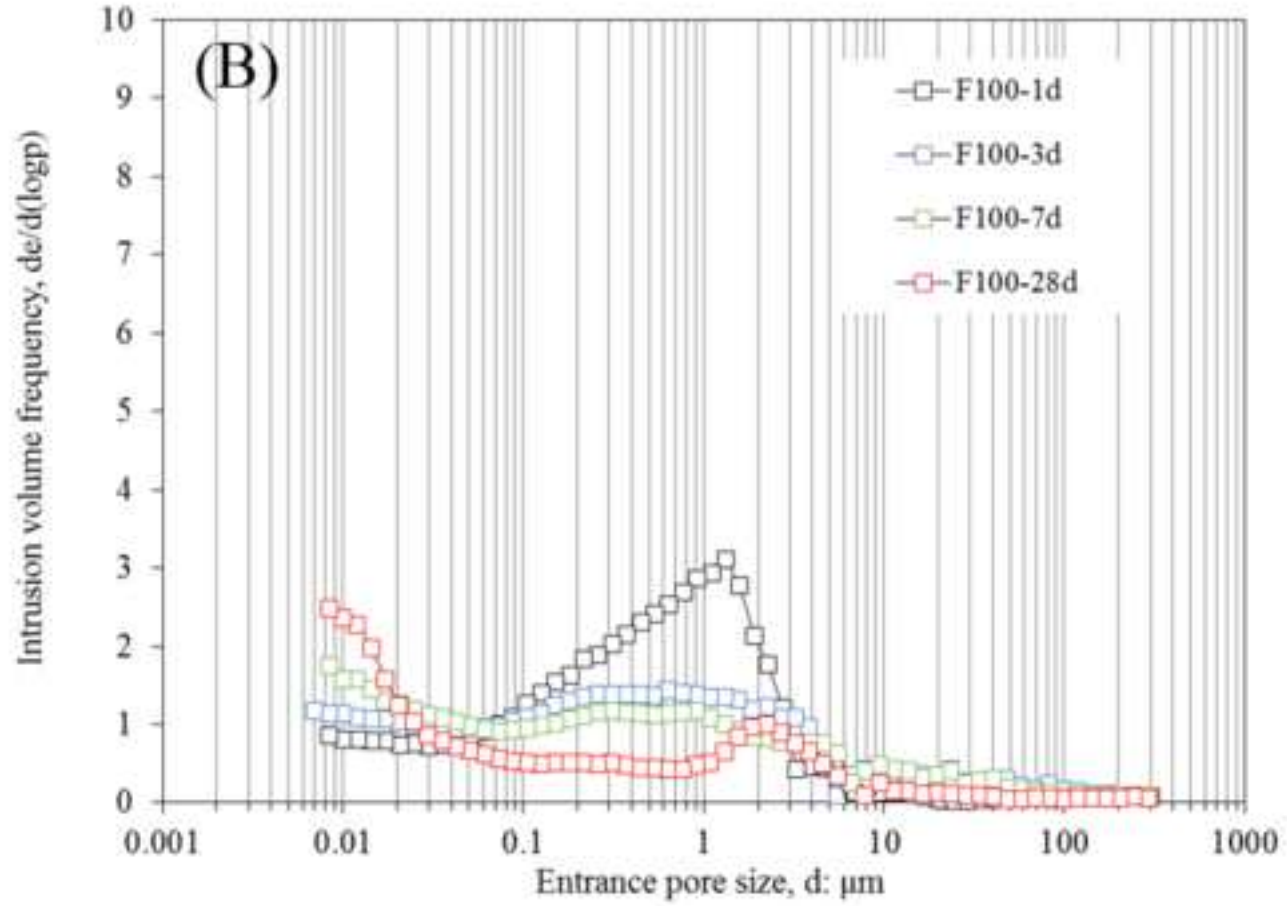

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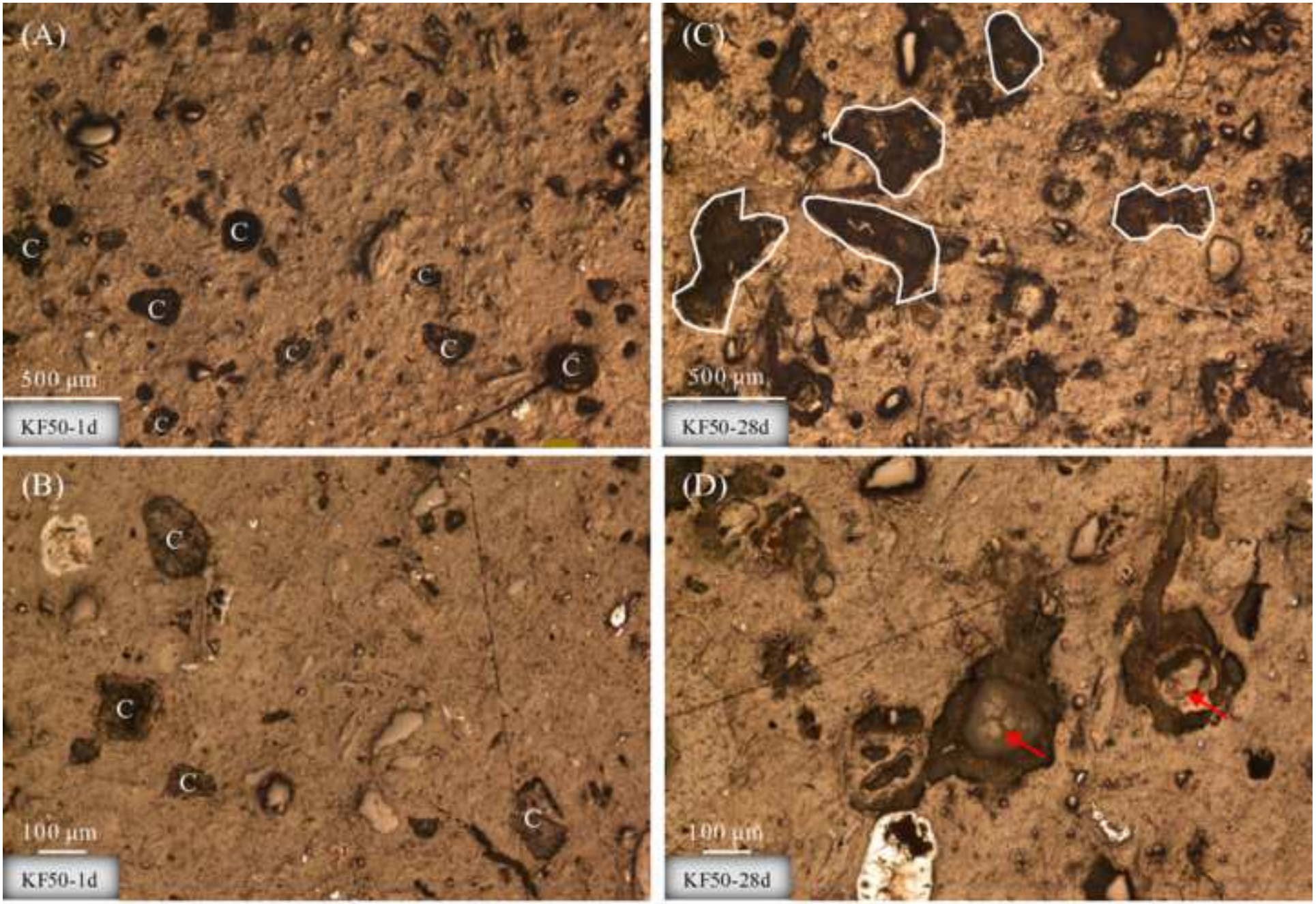

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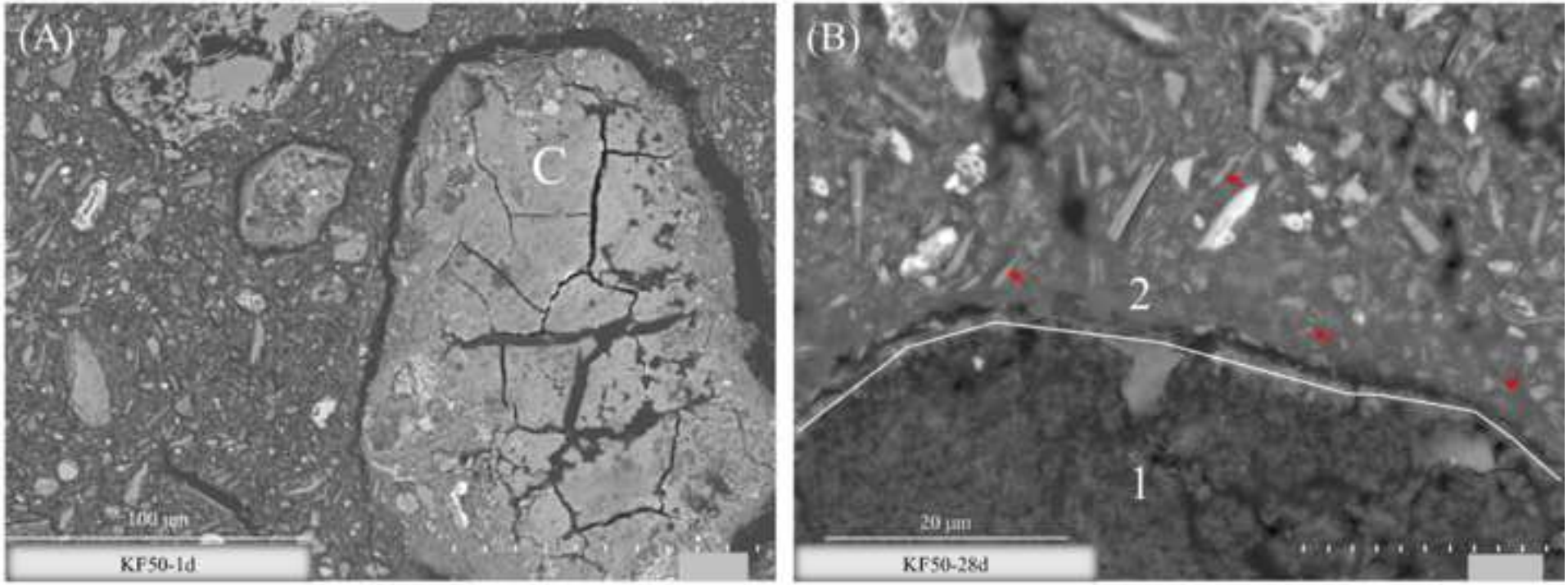

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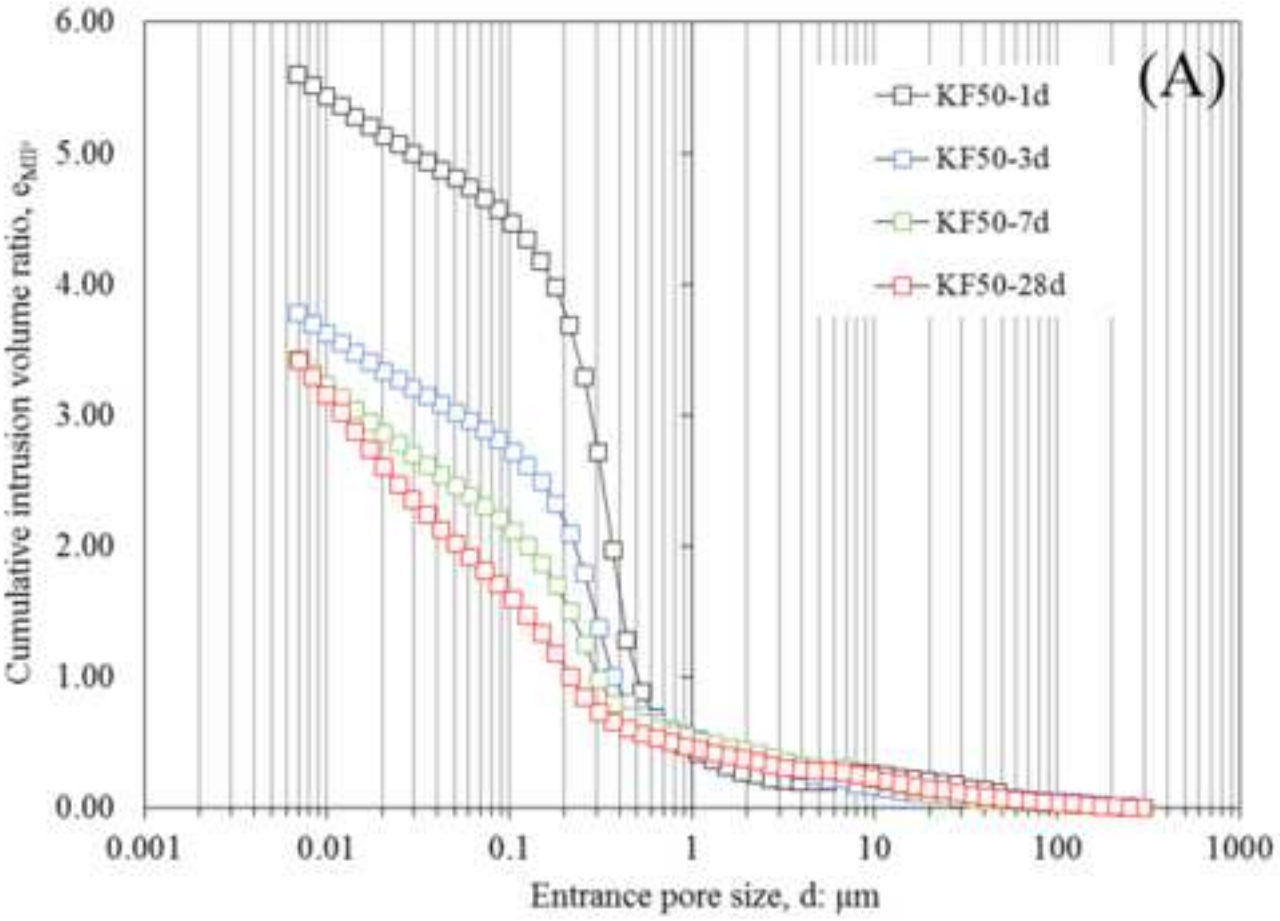

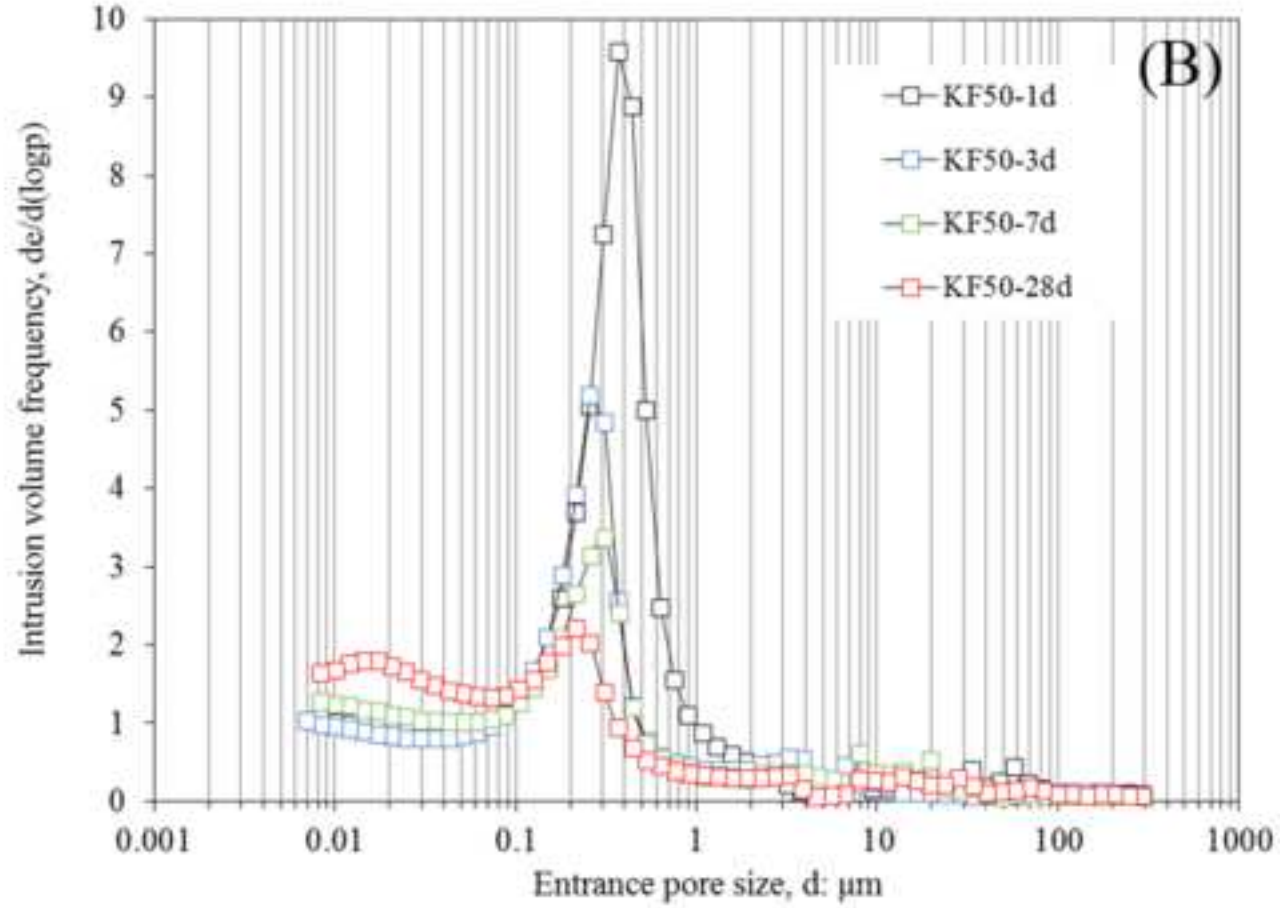

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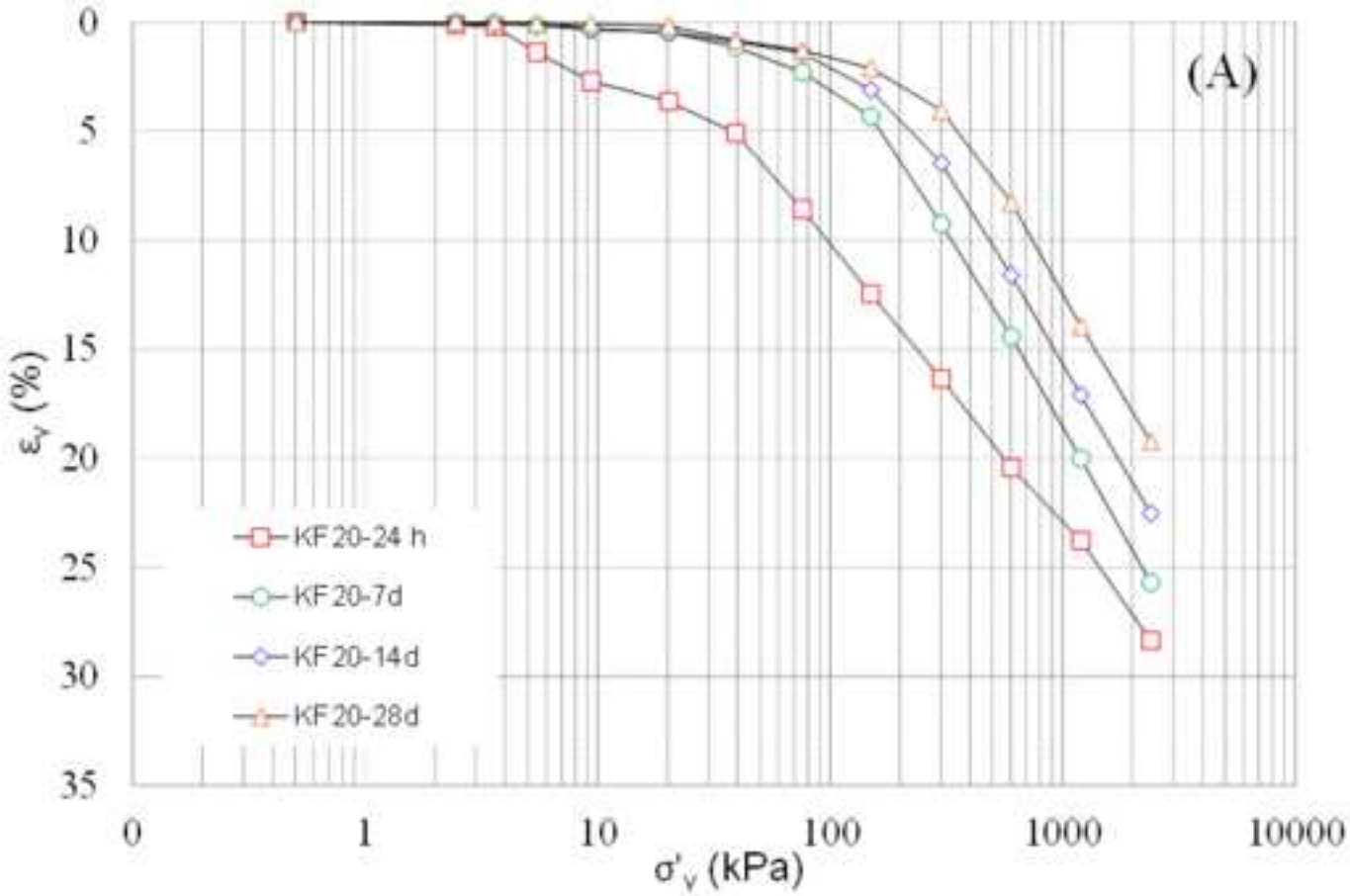

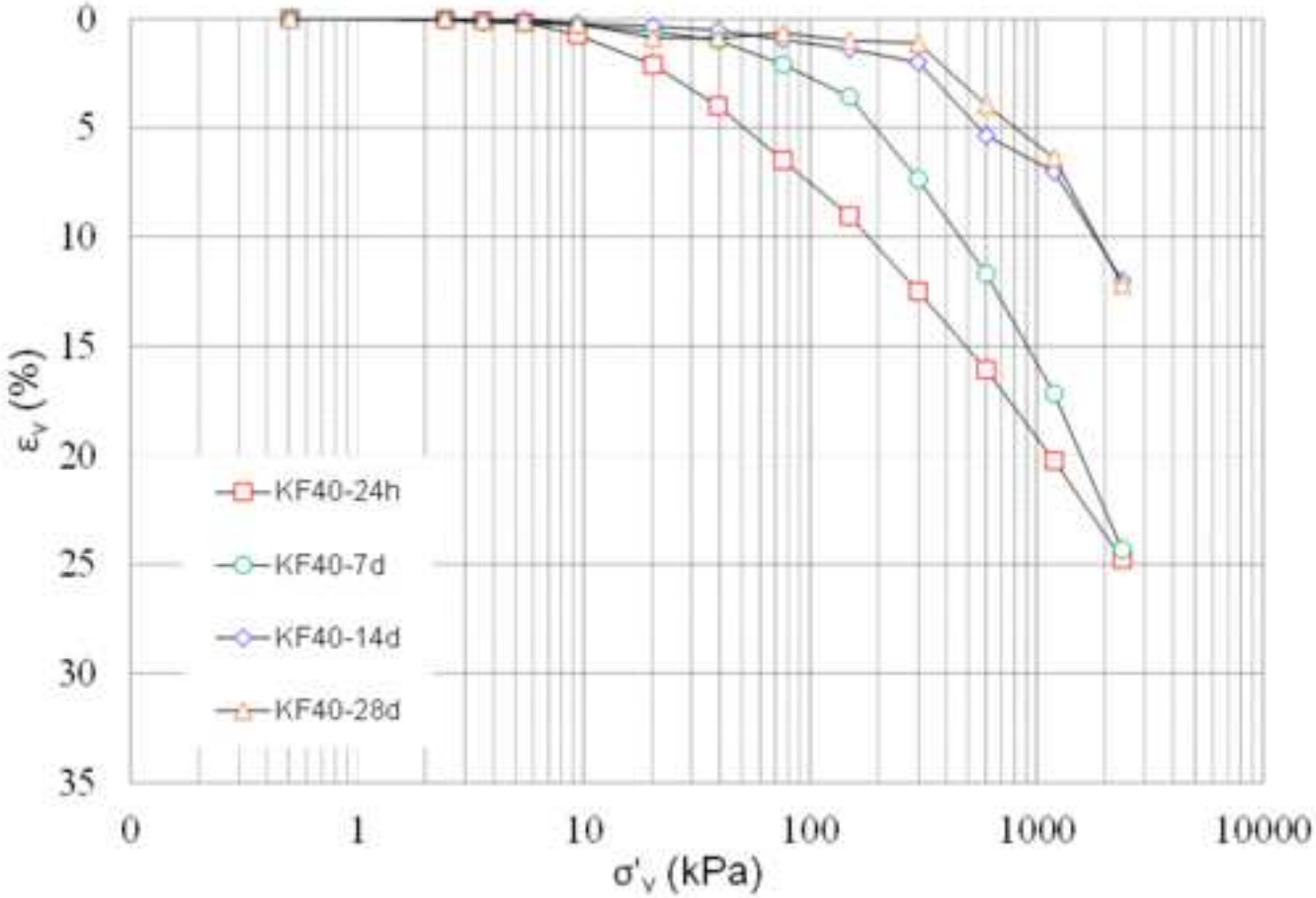

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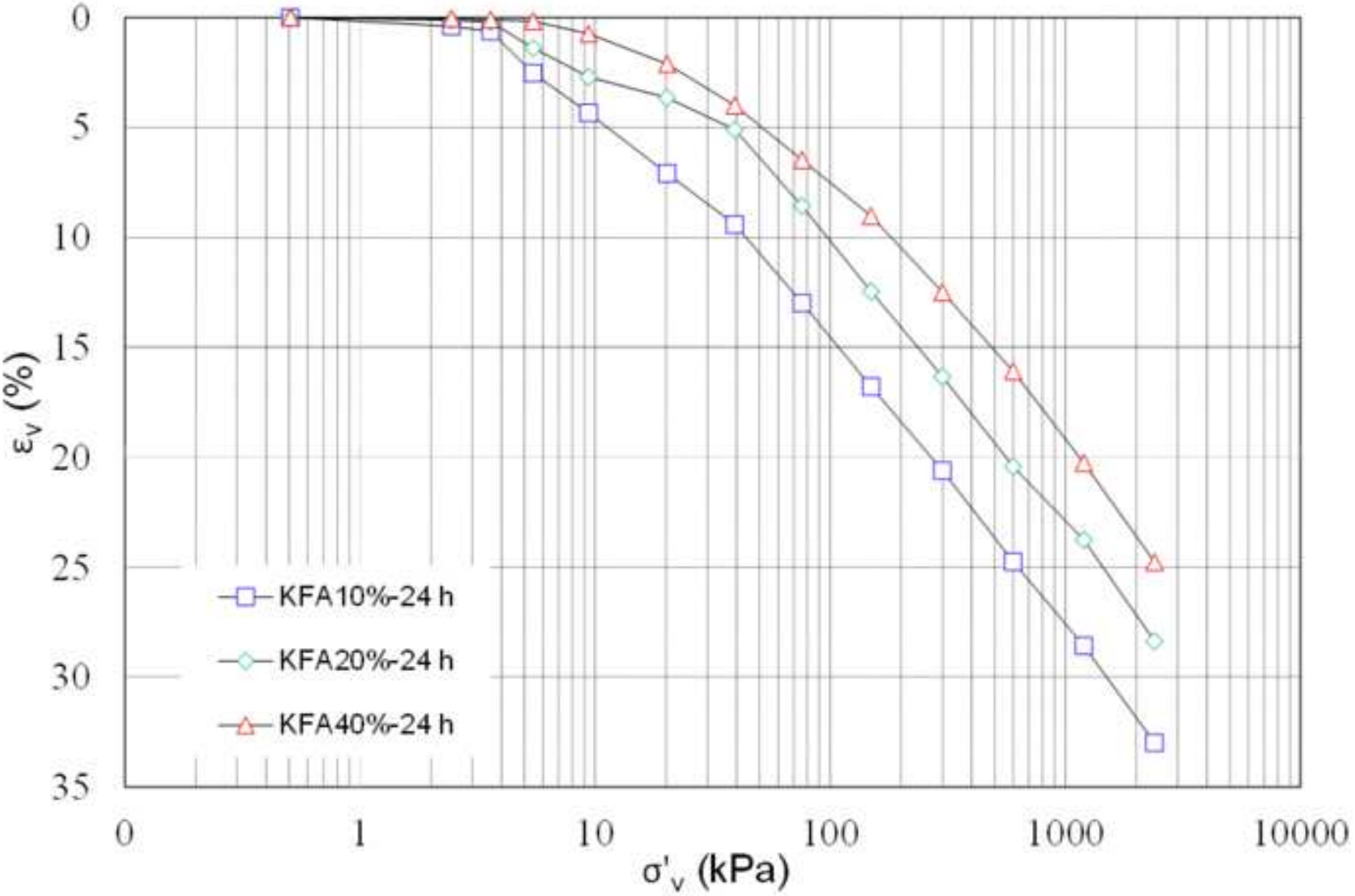

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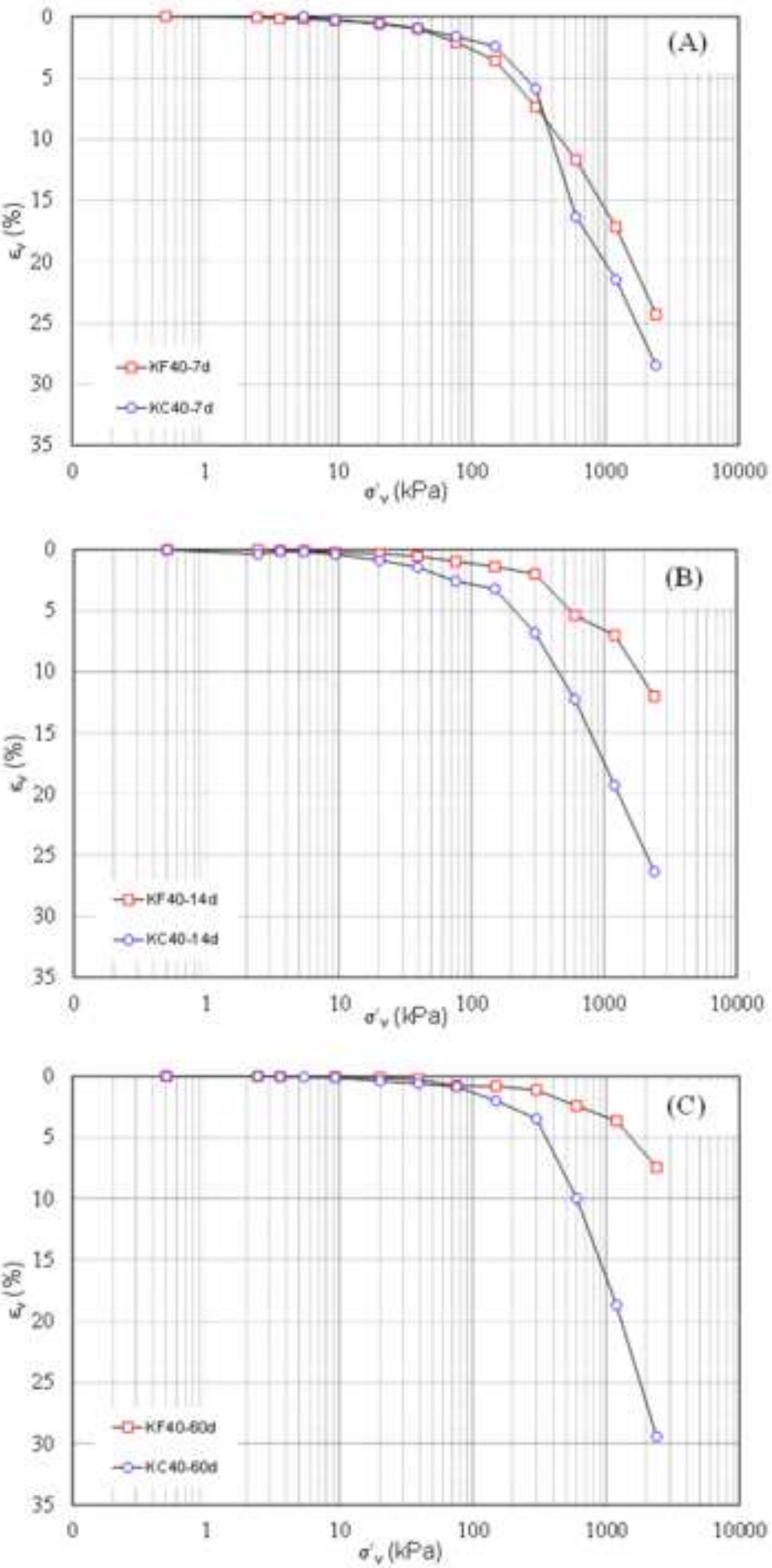

ANSWERS TO EDITOR COMMENTS

We would like to thank the Editor for giving us the opportunity of revising the paper

EDITOR

Note that "mechanical behavior of the alkali activated binder treated soils" needs to be included in this study. We do not want salami sliced papers! Your "Use of alkali activated High-calcium fly ash binder for kaolin clay soil stabilisation: Physicochemical evolution" has already been accepted. I would suggest that you combine the remaining two of three structural levels (namely, microstructure level, and volume element level), into this paper

Authors' Reply

It was not our intention to produce salami papers, the mechanical part was not included simply because we had no mechanical tests at the time of submission on the 'reconstituted' material, which is the object in this paper and the previous one already published. However, we agree with the editor that adding a mechanical part makes the paper more robust. We have therefore conducted additional mechanical tests (one-dimensional compression) and the revised version of the paper now combines the microstructure level with experimental evidence at volume element level.

As a result:

1) the title of the paper has been amended as follows:
   "MICROSTRUCTURAL EVOLUTION AND MECHANICAL BEHAVIOUR OF ALKALI ACTIVATED FLY ASH BINDER TREATED CLAY"

2) one Author has been added, namely Dr Enza Vitale (University of Naples Federico II), who conducted the additional mechanical tests reported in the paper.

3) Text with marked changes has been uploaded for highlights the added parts.

Highlights

- alkali activated fly ash-based binder enhances engineering characteristics of soft clay-rich soils
- microstructural evolution of a calcium-rich fly ash from coal combustion-based binder activated by a sodium-based alkaline solution has been investigated
- microstructural changes occur around calcium-containing phases derived from fly ash which are the reactive phases of the system
- evolution of the pore network over time is characterized by a progressive filling of capillary pores by new compounds
- relevant improvement of mechanical performances of soil treated by alkali activated fly ash-based binder have been detected

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Credit Author Statement

Elodie Coudert: Data curation; Investigation; Methodology; Roles/Writing - original draft; Writing - review & editing. **Dimitri Deneele:** Conceptualization; Data curation; Investigation; Methodology; Supervision. **Giacomo Russo:** Conceptualization; Data curation; Methodology; Supervision; Roles/Writing - original draft; Writing - review & editing. **Alessandro Tarantino:** Conceptualization; Methodology; Supervision.

Title page

MICROSTRUCTURAL EVOLUTION AND MECHANICAL BEHAVIOUR OF ALKALI ACTIVATED FLY ASH BINDER TREATED CLAY

MICROSTRUCTURAL EVOLUTION AND MECHANICAL BEHAVIOUR OF ALKALI ACTIVATED FLY ASH BINDER TREATED CLAY

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Abstract

This work focusses on the use of alkali activated fly ash-based binder to enhance engineering characteristics of soft clay-rich soils and as a substitute to standard stabilisers (e.g., ~~that are~~ lime or cement). Especially, it examines the microstructural evolution of a calcium-rich fly ash from coal combustion-based binder activated by a sodium-based alkaline solution. To this end, the processes generating the microstructure and the evolution of the pore network over time are investigated. A second point addressed by this study is how the presence of ~~small sized~~ kaolin particles ~~soil~~ affects the microstructural features of the binder. The microstructure has therefore been investigated by considering the binder alone and the binder mixed with kaolin. The effects of microstructural evolution have been observed at macroscopic level by means of one-dimensional compression tests.

The combination of completing techniques has been used including Optical microscopy, Scanning Electron Microscopy and Mercury Intrusion Porosimetry in order to gain an overview of the complex pore structure.

Microstructural changes occur around calcium-containing phases derived from fly ash which are the reactive phases of the system. Namely, the dissolution of calcium-rich grains leads to the formation of new compounds that first cover the grain surfaces and then further grow into the available space. Furthermore, the evolution of the pore network over time is characterized by a progressive filling of capillary pores by new compounds while small nanometric pores are being formed and associated with the newly formed silicate-calcium chains. Similar tendencies are observed when the binder is mixed with the soil although the general porosity is lesser due to the filling of pores by small-sized kaolinite platelets. Experimental evidences at microscale level have been linked to the macroscopic behaviour of treated soil.

Keywords: Kaolin, Fly ash, Soil treatment, Alkali activated material, Microstructure, Mechanical Behaviour

1. Introduction

Soft clay-rich soils are frequently encountered in construction sites. Their poor mechanical performances represent a critical issue in engineering projects and are commonly improved by using either Ordinary Portland Cement or lime as a soil stabiliser. Nevertheless, those conventional stabilisers are associated with high carbon dioxide emissions and energy intensive processes, significantly increasing the worldwide carbon footprint (Scrivener and Kirkpatrick, 2008, Xi et al. 2016). The anthropogenic carbon emissions have been increasingly recognized to be one of the main responsible of climate changes and environmental degradation (United Nations, 2004). In the low carbon agenda, it is then of outmost relevance the development of cost- and carbon-efficient technologies. In the construction sector, for which cement production contributes to at least 5–8% of global carbon dioxide emissions (Scrivener and Kirkpatrick, 2008), alternative industrial by-products (e.g. high-calcium fly ash, rice husk ash, silica fume) have been successfully used as cementing agents in soil improvement resulting in environmental and economic benefits (Basha et al. 2003, Nalbantoğlu 2004, Sargent 2015, James & Pandian 2016).

As an alternative, the use of Alkali Activated Material (AAM) as a soil stabiliser is gaining more and more attention over the past ten years. Alkali Activated Materials are defined as any binder system derived by the reaction of an alkali metal source (usually alkali hydroxide and alkali silicate solutions) with a solid aluminosilicate powder (commonly metakaolin, fly ash, blast furnace slag or natural pozzolan) (Buchwald et al., 2003; Shi et al., 2006). It gives a hardened material at room temperature with mechanical properties potentially suitable for Portland cement replacement. Alkali Activated Materials could constitute a viable sustainable soil binder because of their lower CO_2 emission process compared to traditional Portland cement (Duxson et al. 2007; McLellan

et al. 2011, Zhang et al. 2014). Furthermore, recent studies have shown a positive potential and feasibility results of using alkali activated binders for soil improvement, and this not only for different types of soil i.e. clayey soil (Wilkinson et al., 2010; Singhi et al., 2016; Vitale et al. 2017, Vitale et al. 2019; Vitale et al. 2020a, 2020b), sandy clay (Cristelo et al., 2011), marl, marlstone (Cristelo et al., 2012), silty sand (Rios et al., 2016) or else road aggregates (Tenn et al., 2015); but also for different applications i.e. in deep soft soil (Cristelo et al., 2011), at shallow depth (Zhang et al., 2013) or in rammed earth construction (Silva et al., 2013).

Works on alkali activated binder treated soils are relatively recent and constitute a novel domain of application. Our study particularly focuses on the use of a calcium-rich fly ash from coal combustion activated by sodium-based alkaline solution as a binder for clay kaolin stabilisation. Kaolin was selected as a model soil that represent a wide class of clays encountered in engineering projects and for maintaining the system simple. Kaolinite being not reactive to alkaline activation at ambient temperature, a more reactive aluminosilicate source is required for chemical reactions to occur. For that purpose, a calcium-rich fly ash was selected in the context of resource-saving being an industrial waste. The main aim is to assess the feasibility of using this novel binder for soil treatment.

When addressing the feasibility of using a class of material for a novel application, there are several important parameters to consider such as the composition, microstructure and processing which all ultimately affect the performance-to-cost ratio of a material (Askeland et al., 2011). A detailed understanding of both the composition but also the structure of the binder across length scales is therefore required in order to control materials properties through its processing.

Two main length scales of investigation can be distinguished with relevant importance. A first one is the particle scale and corresponds to the identification of the different phases constituting particles in terms of chemical composition and crystal structure. Important properties of particles depend on the arrangements of atoms and types of bonding within each phase (Clemens et al., 2008). A second scale of observation is at the level of group of particles, or microstructure. Microstructural investigations for alkali activated materials are of prime importance as their physical properties depend largely on their pore network characteristics and microstructure (Nath et al., 2016; Lawrence and Jiang, 2017). This is associated with the fact that the microstructure controls the transport properties of the binder and the stability of the matrix when exposed to aggressive agents (van Deventer et al., 2015).

In our previous study the physicochemical evolution of similar systems than those herein studied was carried out i.e. identification and evolution of the constitutive phases until 28 days of curing time at an atomic level. It showed that the soil i.e. kaolin was not reactive. Whereas, fly ash was partly reactive. Some of its phases such as the vitreous phase and quartz were mainly unreactive, while calcium-containing phases represented the reactive phases. The new compounds formed were an amorphous silicate consisting of chains combined with calcium probably incorporating three-dimensional four-fold aluminium environments and thenardite Na_2SO_4 (Coudert et al., 2019).

The present work ~~therefore constitutes a complementary study and~~ focusses on the ~~next level that is the~~ microstructural description~~. It particularly aims at providing a first step towards an understanding of the microstructural evolution~~ taking into account the knowledge gained about the physicochemical evolution of the system.

The study was designed in three stages. An initial stage consisted in the identification of the phases present in the reactive aluminosilicate source i.e. the original calcium-rich fly ash and description of their structure, shape and size distribution. The different constituents of fly ash being inhomogeneously reactive (Provis and Deventer, 2009), it was important to identify the reactive phases around which microstructural changes were predominant. A second stage focussed on the investigation of the microstructural evolution of the alkali activated fly ash binder during the first 28 days of curing, including (i) a description of the dispersion and arrangement of phases, (ii) an understanding of which processes generate the microstructure over time and (iii) a pore network characterisation. Fly ash being a highly inhomogeneous material (Provis and Deventer, 2009), a key point was to determine the homogeneity of processes across the sample at a microscopic level. Besides, a particular emphasis was put at understanding microstructural changes and processes around calcium particles which are the main reactive phases. A third stage focussed on the interaction of the fly ash-based binder with the kaolin clay to understand how the presence of kaolin modifies the microstructural features of the system. As previously stated, kaolinite is unreactive during the alkaline activation. However, because of its small size kaolinite acts as a filler of the porosity (Coudert et al., 2019) and undoubtedly plays a role on the microstructural evolution. The effects at macroscopic level have been highlighted with reference to one dimensional compression results, showing the improvement of the mechanical performances of the treated soil as function of binder percentage and curing time. A final comparison between the performance of cement treated soil with alkali activated binder treated soil has shown for highlighting the effectiveness of the improvement.

2. Material and methods

2.1 Materials

A Polish fly ash derived from hard coal and coal slime combustion in fluidised bed boiler was used. Its chemical analysis is given in Table 1, and consists primarily of SiO_2, Al_2O_3 and CaO. The fly ash contains, approximately, 52% of particles sized lower than 45 µm and 41% lower than 10 µm.

Speswhite kaolin provided by Imerys Minerals UK, and whose chemical composition is given in Table 1 was used. It is mainly constituted of kaolinite (95%) and secondarily of muscovite (4%) (Chemeda, 2015). The kaolin contains, approximately, 100 % of particles sized lower than 10 µm and 80 % lower than 2 µm.

A unique alkaline solution was used: a sodium silicate with a mass ratio SiO_2/Na_2O of 1.7 and a dry mass percentage of 44%; supplied by Woellner Group and named GEOSIL 34417.

Table 1 - Chemical composition (wt. %) of raw fly ash and kaolin.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	CaO_{free}[a]	MgO	SO_3	Na_2O	K_2O	H_2O	L.o.I.
Fly ash	39.4	19.8	7.4	18.6	5.2	1.8	4.1	2.0	1.8	0.0	1.7[b]
Kaolin	49.2	34.5	1.2	0.0	0.0	0.2	0.0	0.1	1.7	13.1	12.0[c]

[a] Free calcium oxide content
[b] L.o.I = Loss on ignition 900 °C
[c] L.o.I = Loss on ignition 1000 °C

2.2 Sample preparation

Sample preparation consisted in (i) mix of liquid sources i.e. silicate and water (ii) mix of aluminosilicate powders i.e. fly ash and kaolin in the case of soil-source sample (iii) mix of (i) and (ii) previously prepared.

For microstructural analyses, two types of mixes were studied and named F100 and KF50. F100 is the fly ash-based alkali activated binder. It corresponds to a solid phase made of fly ash only, whereas KF50 is the alkali activated binder treated soils and corresponds to a solid phase made of 50% of fly ash and 50% of kaolin in mass.

To ensure a good workability, the amount of added water with respect to the solid mass (e.g. mass of kaolin and fly ash) was fixed to 50% for all the samples. Additionally, the mass ratio of alkaline solution to fly ash was fixed to 50% for all the samples, giving the initial molar ratios (considering that kaolin is unreactive): Si/Al = 2.0, Si/Na = 3.5 and Al/Na = 1.8. The Al/Na ratio was not fixed to one because of the presence of calcium ions in high quantity in our system playing a role of charge compensation as well as sodium.

The paste obtained was poured in closed plastic molds and cured at room temperature (20 °C). Samples were finally demoulded and freeze-dried at curing times of 24 hours, 3, 7 or 28 days.

Samples for one dimensional compression tests were prepared with the described technique. Three mixes have been considered in the study, namely KF10, KF20 and KF40 corresponding to a solid phase made of 10%, 20% and 40% of fly ash with reference to dry mass of solids (fly ash+ kaolin). Remoulded samples were prepared by hand mixing solids, alkaline solution and water at their liquid limits (i.e. w_L=67% for KF10, w_L=60% for KF20, w_L=55% for KF40). Samples were poured in the mould and placed in

oedometer cell without compaction. Treated samples were cured for 24 hours, 7, 14, 28 and 60 days before mechanical testing.

2.3 Methods

Samples were studied by Optical and Scanning Electron Microscope from polished section. Freeze-dried samples were impregnated under a vacuum with an acrylic resin (LR White). The polymerisation of the resin was performed in an oven at 60 °C over 48 h. The samples were then polished with diamond powder. The observations from Optical Microscopy were done with a Nikon LV100 polarizing optical microscope combined with a ccd Nikon DS-2Mv camera and the NIS Element BS software. Whereas the observations from Scanning Electron Microscope were done with a HITACHI SU5000 scanning electron microscope equipped with an energy-dispersive X-ray analyser (Quantax microanalyser system composed of X-Flash® SDD detector and the Esprit software). The polished samples were coated with carbon before the observation. The microscope was operated at an accelerating voltage of 20 kV and working distances of 10 mm.

MIP tests were performed by a double chamber Micromeritics Autopore III apparatus. In the filling apparatus (dilatometer) samples were outgassed under vacuum and then filled by mercury allowing increase of absolute pressure up to ambient one. Using the same unit the intrusion pressure was than raised up to approximately 200 kPa by means of compressed air. The detected entrance pore diameters ranges between 134 µm and 7.3 µm (approximately 0.01 MPa - 0.2 MPa for a mercury contact angle of 139°). After depressurisation to ambient pressure, samples were transferred to high-pressure unit, where mercury pressure was increased up to 205 MPa following a previously set intrusion

program. The smallest detected entrance pore diameter was about 7 nm. Corrections to pore-size distribution due to compressibility of intrusion system were applied performing a blank test.

One dimensional compression tests have been performed in standard oedometer cells, where vertical stress was conventionally applied in successive steps ($\Delta\sigma v/\sigma v = 1$) within the stress interval 10 ÷ 2400 kPa. Micrometer dial gauges with an accuracy of 0.001 mm have been used to measure vertical displacements.

3. Results and discussion

The first section of results presents the general characteristics of the raw fly ash which constitutes the reactive aluminosilicate source of the mixes. The second part examines the microstructural evolution of the binder. ~~Finally,~~ The third part focusses on the description of system made by kaolin and the alkali activated binder and its mechanical performance.

3.1 Raw fly ash

The fly ash used here contains various components. Its composition consisting of (i) a vitreous phase and (ii) various crystalline phases i.e. calcium-containing minerals: anhydrite $CaSO_4$, calcite $CaCO_3$ and portlandite $Ca(OH)_2$, and other minerals: quartz SiO_2, feldspar $(K,Na,Ca)(Si,Al)_4O_8$, hematite Fe_2O_3 and muscovite $(Si_3Al)O_{10}(Al_2)(OH)_2K$ (Coudert et al., 2019).

Its particle size distribution reflects this diversity with 52 % of particles lower than 45 µm, 41 % of particles lower than 10 µm and 12 % of particles lower than 2 µm.

Figure 1 confirms this great variety also detectable by Scanning Electron Microscopy. In fact, the fly ash presents an extremely heterogeneous microstructure with particles of different shapes and ranging from 1 µm to more than 200 µm. The vitreous phase is itself heterogeneous and made of (i) some spherical particles (see G Figure 1B), (ii) bigger unshaped particles (see G Figure 1C) and (iii) aggregates of small particles primarily (see G Figure 1D).

Some crystallised angular shaped minerals can also be distinguished and correspond to quartz (see Q Figure 1A&D) or feldspar (see F Figure 1B).

Finally, regarding calcium-rich phases, our previous study showed that calcium-containing minerals i.e. anhydrite $CaSO_4$, calcite $CaCO_3$ and portlandite $Ca(OH)_2$ are interlaced together (Coudert et al., 2019). Especially, they are interlinked within a nodule shape structure generally of 50 to 200 µm size as seen on Figure 1B (particle labelled C).

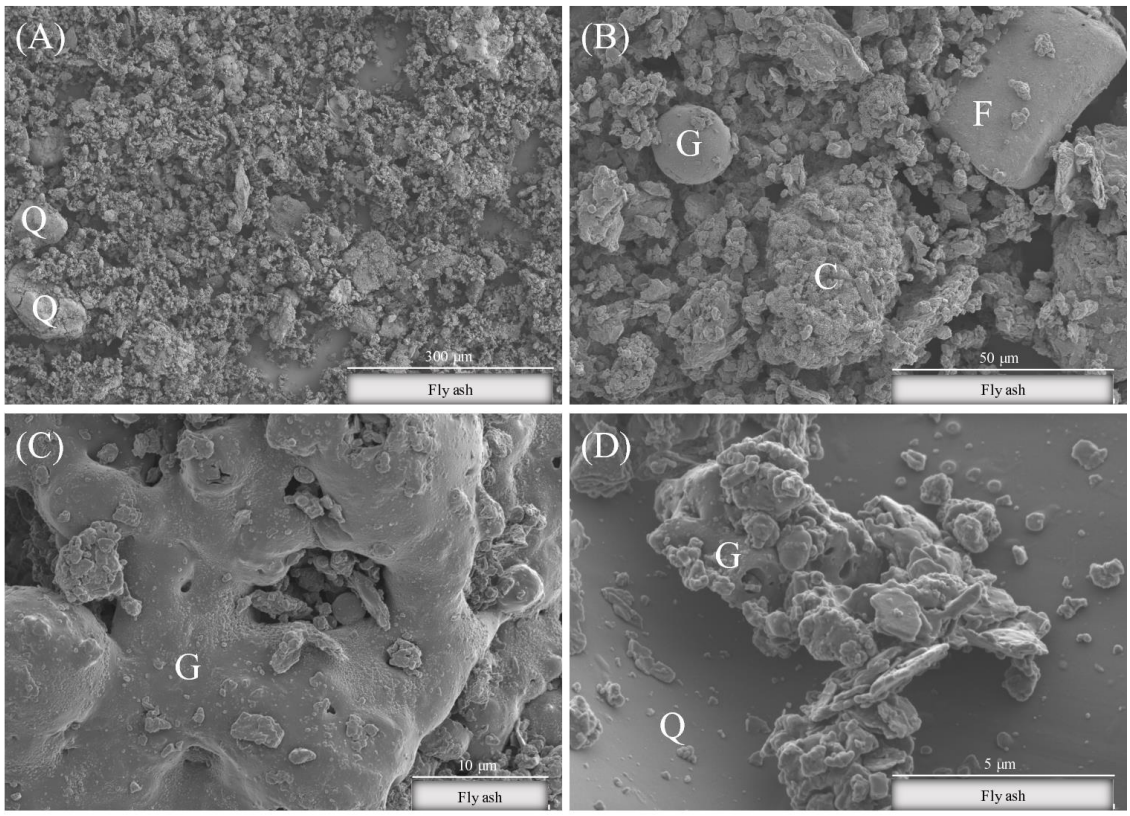

Fig. 1 SEM micrographs of the raw fly ash; C=calcium-rich particle; F=feldspar; G=glass; Q=quartz.

3.2 Alkali activated fly ash binder

3.2.1 Optical Microscopy

Figure 2 shows the microstructural evolution of the alkali activated fly ash binder over time by optical microscopy. Observations were carried out until 28 days as chemical reactions are fully developed at that curing time (Coudert et al., 2019).

After 24 hours of curing, dispersed dark spots of around 50 µm to 200 µm size are seen across the overall sample (see particles labelled C on Figure 2A&B), and correspond to reactive calcium-rich nodules by analogy with the previous observations of the raw fly ash constituents (section 3.1). They represent approximatively 15 % of the mixture. Whereas the brown matrix includes the vitreous phase and calcium-free minerals from fly ash.

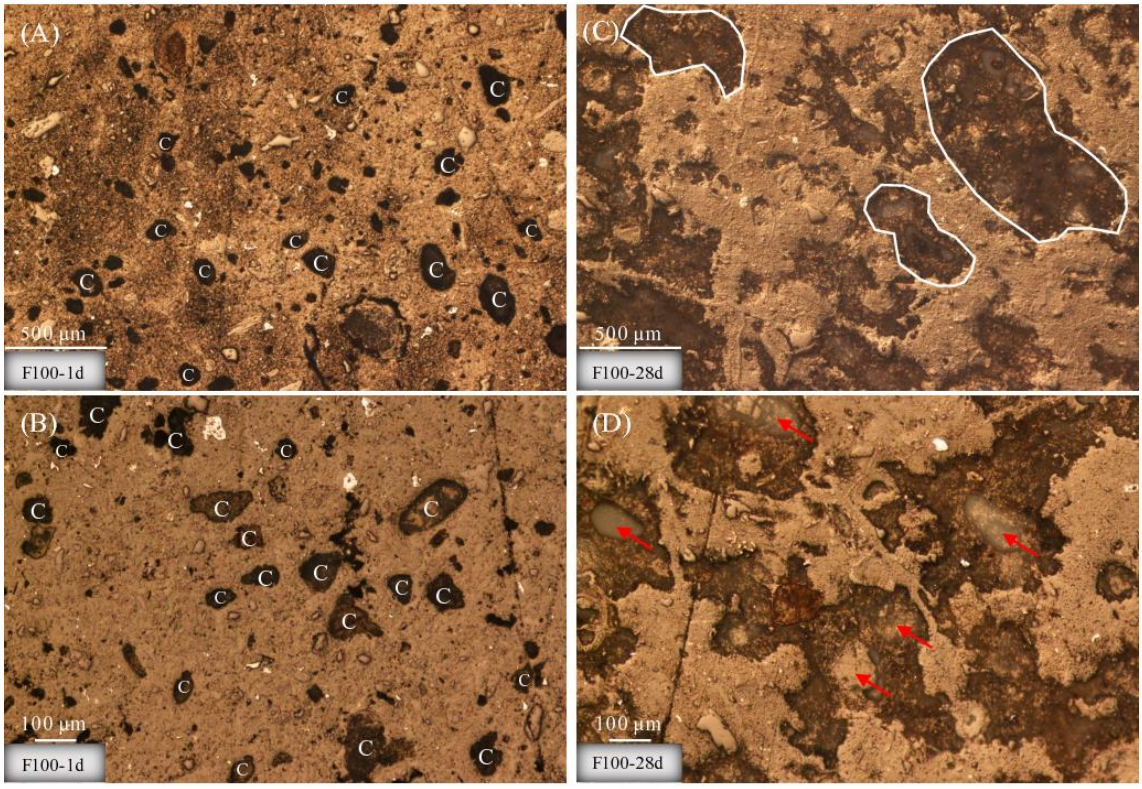

Fig. 2 Optical microscopy images of the alkali activated fly ash binder F100 (A) and (B) after 24 hours, (C) and (D) at 28 days*;* C=calcium-rich particle.

By comparison, at 28 days, no dark spots are visible but instead large dark zones whose edges are less well defined (see encircled areas on Figure 2C), and correspond to new products formed. Figure 2D shows a closer observation of those large dark reactive areas. The initial nodule shapes can still be distinguished at 28 days but instead of a dark spot as observed at 24 hours it is a hollowed greyish structure that is seen as shown by the red arrow (Figure 2D). This structure is associated with dissolution features over time of the calcium-rich phase, and in accordance with the previous results about the physicochemical evolution which indicate that calcium-containing phases are the main reactive phases. New compounds corresponding to dark areas are therefore formed around the hollowed dissolved calcium nodules. Those new compounds have been identified in a previous study as thenardite Na_2SO_4, and an amorphous silicate consisting of chains combined with calcium probably incorporating three-dimensional four-fold aluminium environments (Coudert et al., 2019).

As a consequence of those observations, the spreading of the darker areas at 28 days gives an idea of the extent of the reaction and widening of the new compounds formation across samples. In this system, half of the sample encompasses the new compounds and is hence reactive whereas the initial calcium nodules represented only 15 % of the sample. Besides, those new compounds seem homogeneously spread across the sample which likely could give a homogeneously reinforced material at the macroscopic scale.

Results from optical microscopy therefore match with the observed physicochemical evolution i.e. principal changes occur around calcium-rich reactive particles. That is why

the next session focusses on the in-situ microstructural transformation of calcium-rich phases induced by the alkaline solution.

3.2.2 Scanning Electron Microscopy (SEM)

Figure 3 shows microstructural observations from a polished section and combined chemical mappings of the alkali activated fly ash binder after 24 hours of curing. Chemical mappings on Figure 3B&C indicate the presence of a calcium-rich nodule labelled 1 on Figure 3A and predominantly made of calcium and sulphur. Additionally, those calcium-rich particles display a granular aspect on their surface.

Surrounding this calcium-rich particle, the area labelled 2 on Figure 3A corresponds to a porous zone distinguishable by the presence of dense black areas characteristic of the filling resin of low atomic mass. Chemical mappings of that porous zone show an enrichment in silicon and sodium (Figure 3D&E) indicating the presence of the sodium-silicate Na_2SiO_3 alkaline solution at that short curing time. Additionally, filament like structures are observed within that area (see red arrow on Figure 3A), and considered as the beginning of the secondary phases formation i.e. the amorphous silicate consisting of chains combined with calcium and potentially aluminium. In fact, a former study about cementitious microstructures has shown the formation of similar arrangements associated with Calcium Silicate Hydrates whose structure strongly resembles the one of our newly formed chains (Scrivener, 2004). Moreover, it appears that those filament structures are stacked around particles corresponding to the initiation of the reaction process after 24 hours of curing.

Figure 4 also shows microstructural observations of the alkali activated fly ash binder after 24 hours of curing, and particularly illustrates the microstructural difference

between a calcium-rich particle and a particle from the vitreous phase both originally present in the fly ash. They can both be distinguished by SEM by their chemical composition and microstructural features. Regarding calcium-rich particles, they present a nodule shape with a granular surface (see 3 on Figure 4A) as previously observed (Figure 3A). Whereas particles from the vitreous phase display a vesicular structure (see 1 on Figure 4A) and can be distinguished using chemical mappings by their enrichment in silicon and aluminium (Figure 4D&E).

In between those two particles, a porous area labelled 2 on Figure 4A and with filament like structures can once again be observed and evidences the initiation of the reaction processes. Consequently, from Figure 3 as from Figure 4 it is noticeable that the alkali activated binder after 24 hours of curing presents a high porosity created by the fly ash grains of various sizes and that is filled by water, alkaline solution, and the new product starting to be formed.

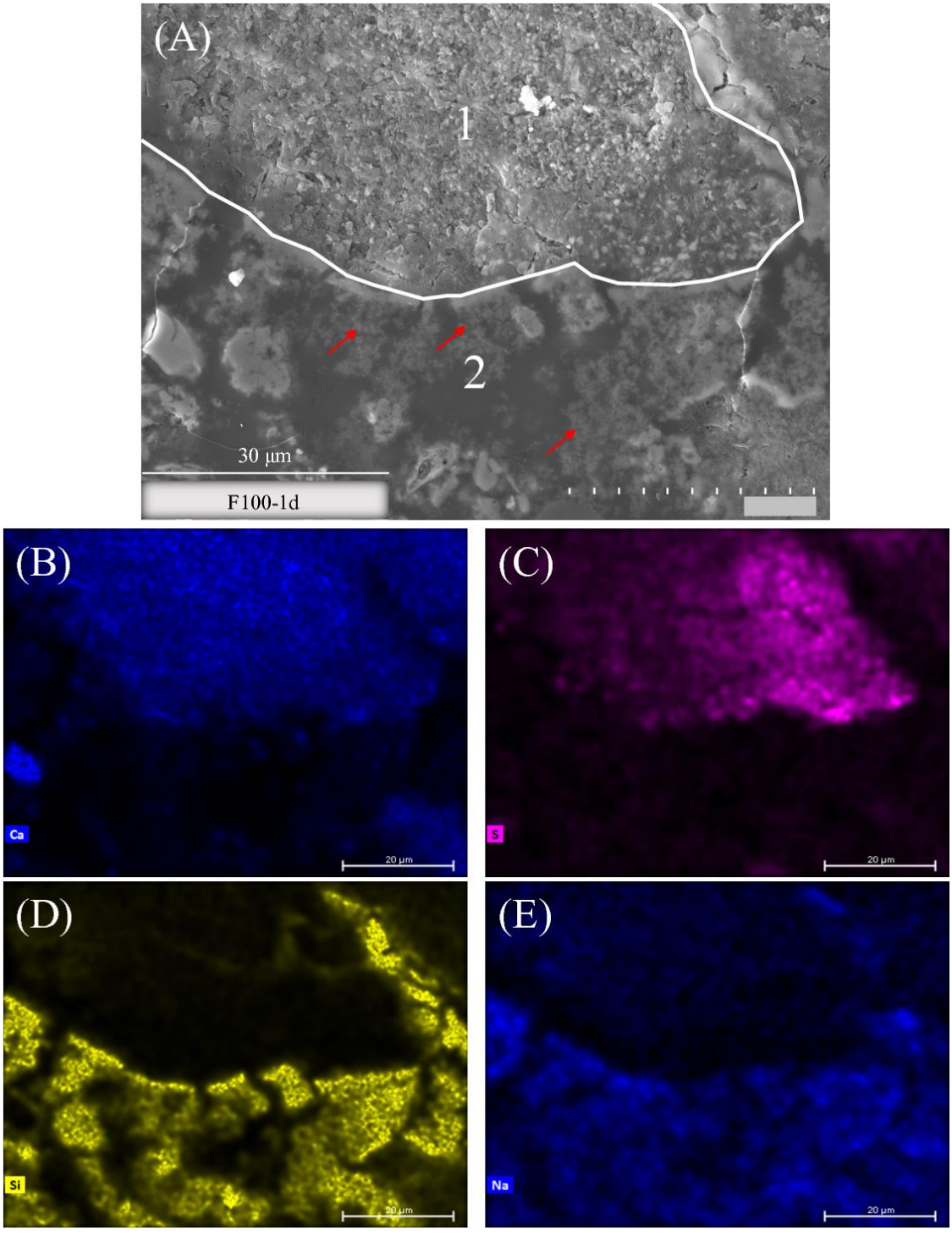

Fig. 3 SEM observations of the alkali activated fly ash binder F100 after 24 hours of curing: (A) SEM micrograph, and chemical mappings of: (B) calcium, (C) sulphur, (D) silicon and (E) sodium.

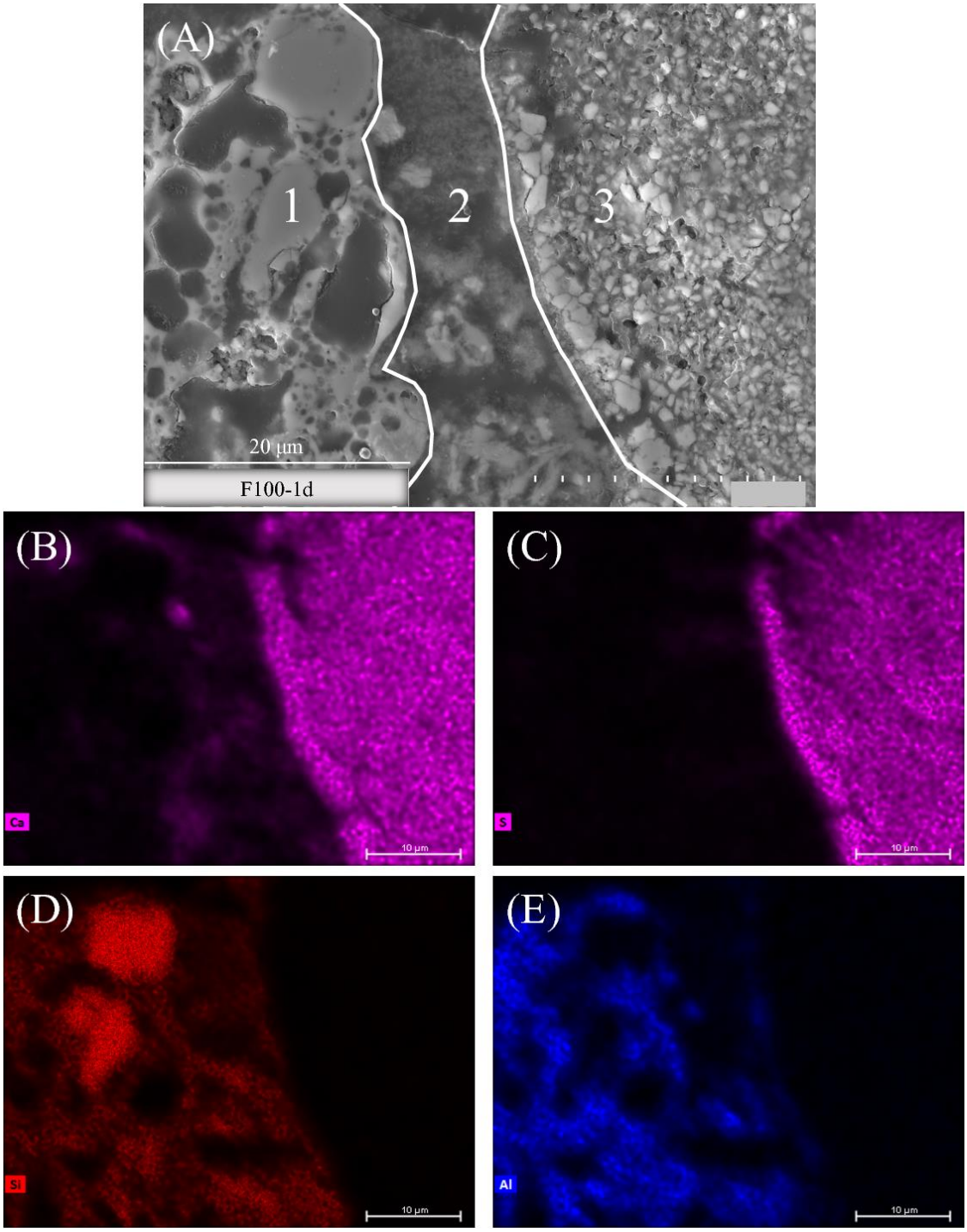

Fig. 4 SEM observations of the alkali activated fly ash binder F100 after 24 hours of curing: (A) SEM micrograph, and chemical mappings of: (B) calcium, (C) sulphur, (D) silicon and (E) aluminium

Figure 5 shows SEM observations and combined chemical mappings of the alkali activated fly ash binder after 28 days of curing. It especially focuses on the interface between a calcium-rich nodule labelled 1 and the surrounding matrix labelled 2.

Regarding the calcium-rich nodule, it displays a hollowed structure, especially in its centre, and as similarly observed previously by optical microscopy in section 3.2.1. In addition, those hollowed structures show dense black zones indicating the presence of filling resin and therefore porosity. Those structural characteristics strongly contrast with calcium nodules after 24 hours presenting a granular surface, and are attributed to the dissolution of calcium-rich phases over time leaving behind a porous body. It is supported by chemical mappings on Figure 5B&C showing a strong impoverishment in calcium and sulphur in the hollowed area with respect to nodules after 24 hours.

An enrichment in calcium and sulphur is seen in the outer part of the nodule suggesting a mechanism of dissolution of calcium and sulphur moving from the calcium nodules to the matrix. Moreover, few silicon supplied in that system by the alkaline solution is detected above the edges of the calcium nodule and inside implying that the alkaline solution penetrates through the calcium-nodule accelerating its dissolution. The coloration due to the silicon presence inside the nodule is few marked as unreactive quartz which corresponds to intensely coloured and well defined edges spots on the silicon chemical mapping (Figure 5D) are present in the matrix and induces a rescaling of the silicon coloration.

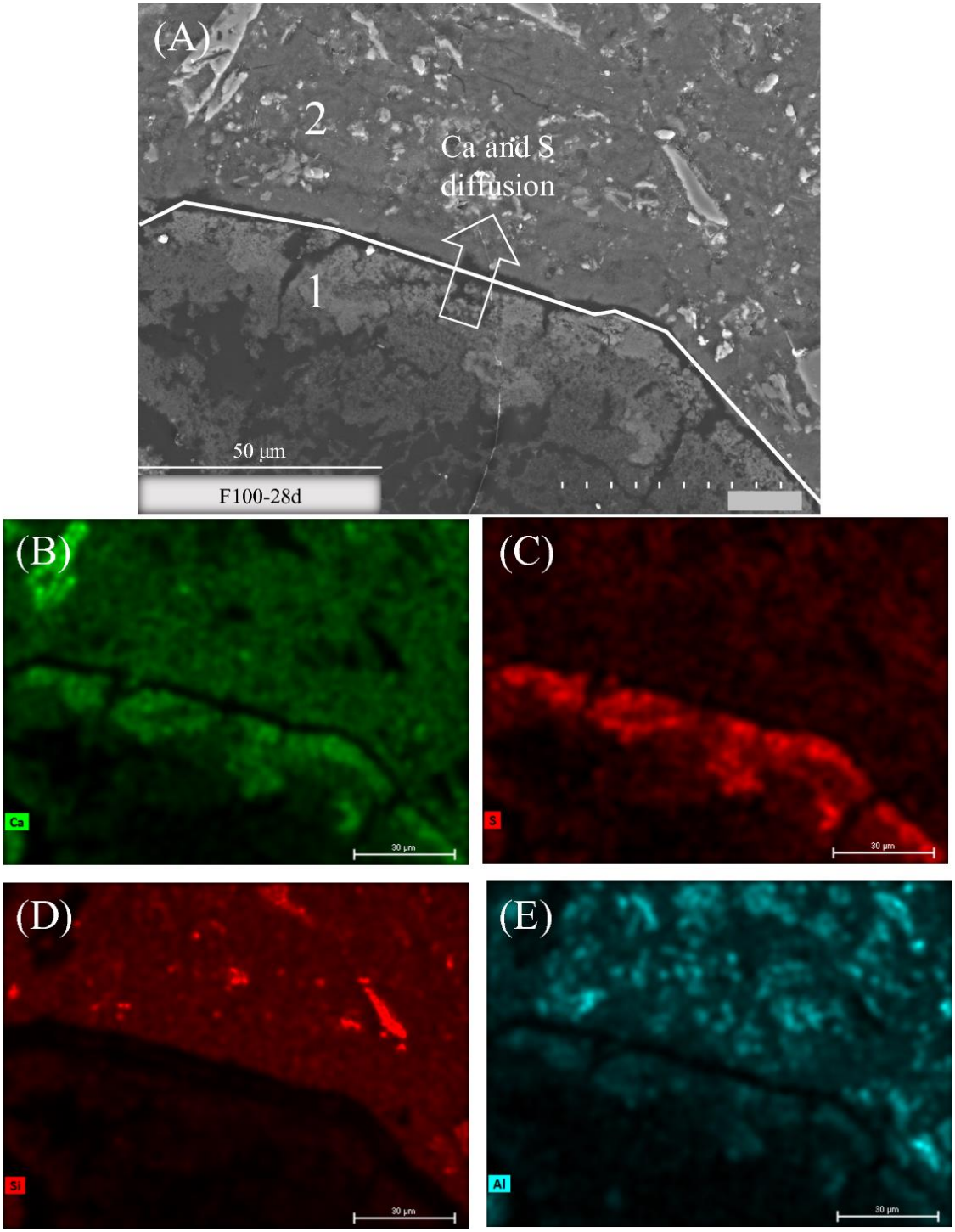

Fig. 5 SEM observations of the alkali activated fly ash binder F100 at 28 days: (A) SEM micrograph, and chemical mappings of: (B) calcium, (C) sulphur, (D) silicon and (E) aluminium.

Regarding the area surrounding the calcium nodule labelled 1, it is massive and presents a low porosity compared to the binder after 24 hours. It corresponds to the area where

new products are formed. Its chemical mappings show a high content of calcium and silicon which is in accordance with the physicochemical investigation that showed the formation of silicate chains combined with calcium over time. The wide diffusion of calcium into the matrix is clearly seen from Figure 5 when compared to the binder after 24 hours of curing for which calcium is contained and restrained to the nodule surface (see Figure 3 and Figure 4). Concerning sulphur elements, as well initially present in the nodule in the form of anhydrite $CaSO_4$, its dissolution occurs in a lesser extent and seems stopped to the outer part of the nodule at 28 days (Figure 5C). The physicochemical evolution of this system showed that dissolved sulphur combine with sodium to form thenardite Na_2SO_4 at 28 days (Coudert et al., 2019). Consequently, the presence of thenardite is restrained to small areas around the calcium-rich particles, whereas silicate two-dimensional chains combined with calcium are widely spread all around the calcium nodules. The formation of this thenardite crust limited around calcium nodules can be explained by the low amount of sulphur elements compared to calcium (see chemical composition of the raw fly ash in Table 1), that already all precipitated in this small area. The conjoint chemical mapping of sodium to localise thenardite is not shown here as sodium is a volatile element for which it is difficult to get a chemical mapping showing a reliable representativeness of sodium dispersion.

Finally, important crackings are observed around calcium-rich particle as seen on Figure 5 and are associated with shrinkage processes frequently observed for alkali activated materials (Fang et al., 2018).

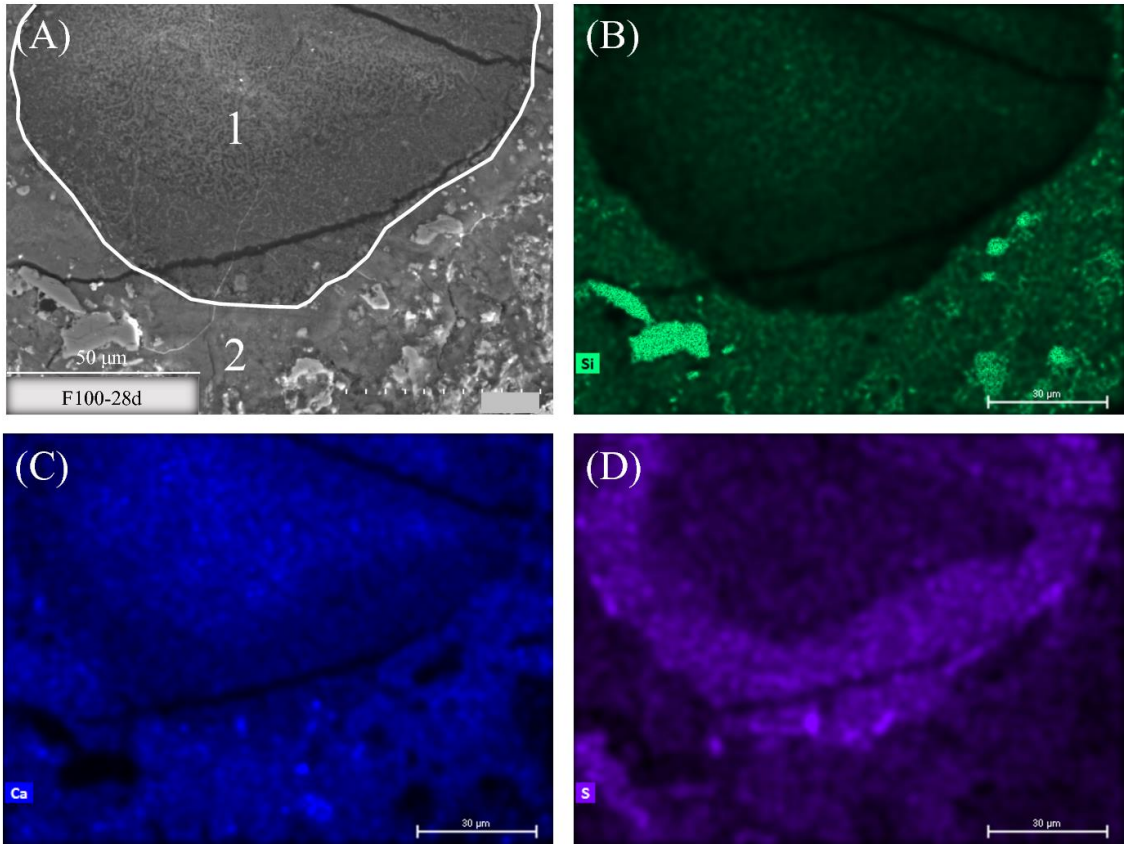

Fig. 6 SEM observations of the alkali activated fly ash binder F100 at 28 days: (A) SEM micrograph, and chemical mappings of: (B) silicon, (C) calcium and (D) sulphur.

Figure 6 shows the alkali activated fly ash binder at 28 days, and more particularly a calcium-rich reactive nodule labelled 1 surrounded by a dense matrix comprising both new products and non-reactive phases such as quartz or aluminium containing minerals. However, in that case the extent of dissolution of the calcium nodule appears lower as the hollowed structure is not seen but rather a granular microstructure similar of those observed after 24 hours. Chemical mappings show that the dissolution of that nodule did start as calcium is widely diffused into the matrix, and an enrichment in sulphur is once again seen in the outer part of the nodule. Nevertheless, the dissolution is at a different stage as calcium is still strongly detected in the centre of the nodule and no hollowed structure is noticed. Consequently, the extent of reaction of a calcium-rich nodule varies

locally. A lesser porosity of the calcium nodule could for instance moderates its dissolution. Its size, its content in calcium and sulphur or else the amount of water locally available are also all parameters that may locally affect the extent of reaction.

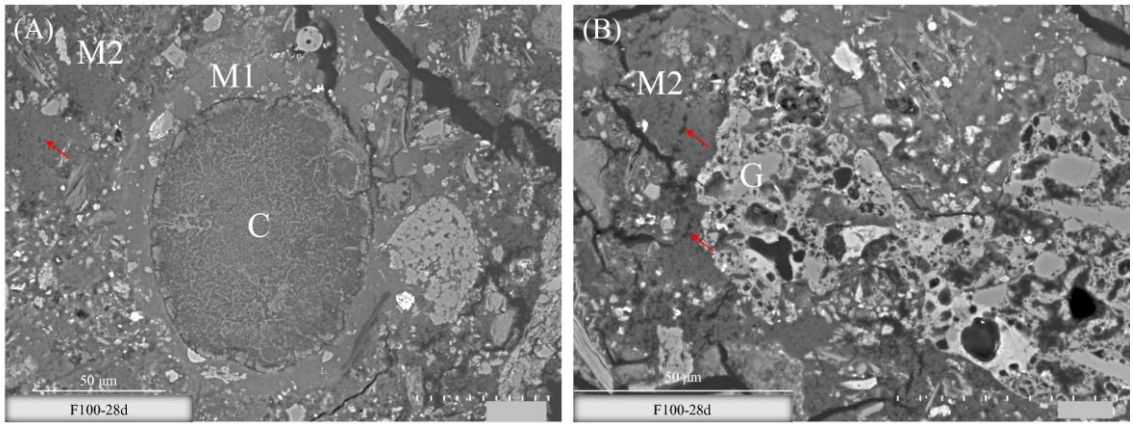

Fig. 7 Comparing SEM microstructural changes of the alkali activated fly ash binder F100 at 28 days around: (A) a calcium-rich nodule labelled C, and (B) a particle from the vitreous phase labelled G; M1 = dense matrix; M2 = porous matrix

Figure 7 shows micrographs of the alkali activated binder after 28 days, and more particularly the difference between microstructural changes occurring (A) around a calcium rich particle identified as the dark reactive zones in optical microscopy, and around a glassy particle identified as the brown matrix in optical microscopy.

It is worth noting that although amorphous and extremely porous the vesicular glassy phases reaction is negligible as its vesicular structure remains similar to the one after 24 hours (see Figure 4A, particle labelled 1). This observation is in accordance with our previous study about the physicochemical evolution of that system which shows that the vitreous phase mainly remains unreactive (Coudert et al., 2019). It is well known that the rate of reaction of the aluminosilicate vitreous phases of fly ash at ambient temperature following alkaline activation is slow and takes several days (Provis and Deventer, 2009; Wardhono et al., 2015). Whereas the calcium-rich particles in our mixes are extremely

and quickly reactive as the formation of new products containing calcium already starts after 24 hours as seen previously in Figure 3. Hence, the faster reaction of calcium-rich particles leads to the formation of dense products (as seen in Figure 7A) freezing the system and preventing the later reaction of the aluminosilicate glassy phases.

Massive and dense areas are observed around calcium-rich nodules (see Figure 7A), while a more porous matrix is seen around vesicular glassy phases (see Figure 7B). The comparison in Figure 7 hence evidences that there are different matrices forming the alkali activated treated soil: (i) a first circularly-shaped matrix identified around calcium-rich particles and presenting a high density labelled M1 on Figure 7A, and (ii) a more porous matrix less bonded labelled M2 on Figure 7A&B whose pores are shown by red arrows, and located around glassy phases of lower reactivity. A previous investigation of that system by Nuclear Magnetic Resonance showed the signature of only one type of silicate chains combined with calcium and spreaded into the matrix as a new compound (Coudert et al., 2019). Therefore, Scanning Electron Microscopy provides an additional information: although the atomic structure of the silicate chain remains similar, the arrangement of those phases in the matrix varies following the local environment. Similarly to the great heterogeneity of fly ash, the matrix formed is also highly heterogeneous.

3.2.3 Mercury Intrusion Porosimetry (MIP)

Figure 8A shows cumulative curves of mercury intrusion porosimetry tests of the alkali activated fly ash binder over time. The longer the curing time, the lower is the cumulative intrusion volume ratio implying a progressive decrease of the overall porosity over time, and in accordance with the general tendencies observed by SEM in section 3.2.2. It is

owed to the progressive filling of pores by the new compounds formed i.e. calcium-silicate two-dimensional chains and thenardite.

Figure 8B shows the frequency distributions of pore entrance diameters belonging to the alkali activated fly ash binder over time. Samples at 24 hours, 3 and 7 days all show one broad modal pore sizes between 0.05 µm and 3 µm. However, from 24 hours to 7 days the frequency of those pores progressively decreases due to their filling by newly formed compounds. Whereas, at 28 days a narrower modal pore size at about 2 µm is observed. By analogy with SEM pictures, those remaining pores at 2 µm could correspond to either the size of the cracks seen around calcium particles and associated with shrinkage as previously observed on Figure 5, the porosity formed within calcium nodules after their dissolution also seen on Figure 5, or else pores that have not been filled by new compounds within the more porous matrix previously identified and labelled M2 on Figure 7.

Finally, in the area of lower pore size i.e. below 20 nm the increase of frequency over time corresponds to the formation of a new class of pores inside the matrix. It is associated with the formation of the silicate two-dimensional chains combined with calcium, whose structure resembles those of Calcium-Silicate Hydrates (i.e. C–S–H phases commonly found in Portland cement) known for possessing an intrinsic porosity of a nanometer size (Muller, 2014). However, this small new class of pores cannot be fully probed by MIP technique whose detection limit in the small entrance pore size is of 7 nm.

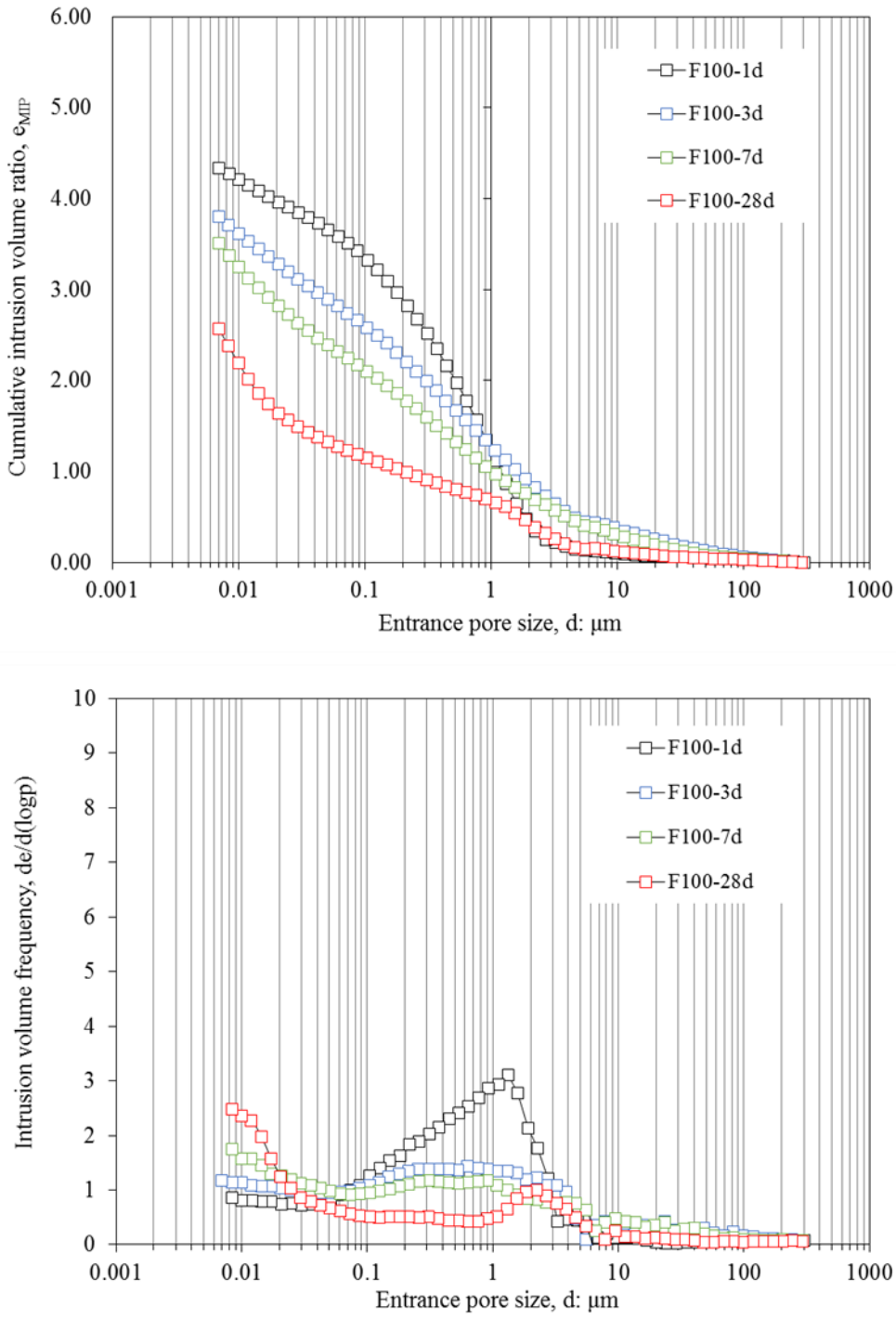

Fig. 8 Comparing mercury intrusion porosimeter tests of the alkali activated fly ash binder F100 over time and in terms of (A) cumulative intrusion volume ratios, (B) intrusion volume frequency ratios as a function of entrance pore size.

3.3 Interaction between the alkali activated fly ash binder and kaolin

The following section aims at understanding the interaction between kaolin and the alkali activated fly ash binder previously described. Our former study focussing on the physicochemical evolution of the same mixes herein studied showed that kaolin was not reactive during alkaline activation and did not modify the reaction sequence when compared to the one of the alkali activated fly ash binder alone (Coudert et al., 2019). Accordingly, similar mechanisms of ions dissolution precipitation from the calcium-rich particles into the matrix leading to the formation of new products also occur in the alkali activated fly ash binder treated soil as previously described for the binder in section 3.2.2, and hence will not be detailed here.

Regarding the pore network structure, our previous study also showed that kaolinite platelets were homogeneously spread across the matrix. This section consequently aims at giving a deeper insight of the influence of kaolin on the microstructure with respect to the binder alone.

Figure 9 shows microstructural observations of the alkali activated fly ash binder treated soil over time by optical microscopy. Similarly, to the alkali activated fly ash binder, after 24 hours of curing, dispersed dark spots corresponding to calcium-rich nodules are seen across the overall sample, whereas at 28 days larger dark zones encompassing the newly formed compounds have grown around those nodules. Hollowed greyish nodule structures at 28 days can also be distinguished as for the binder and associated with the dissolution of calcium-rich particles.

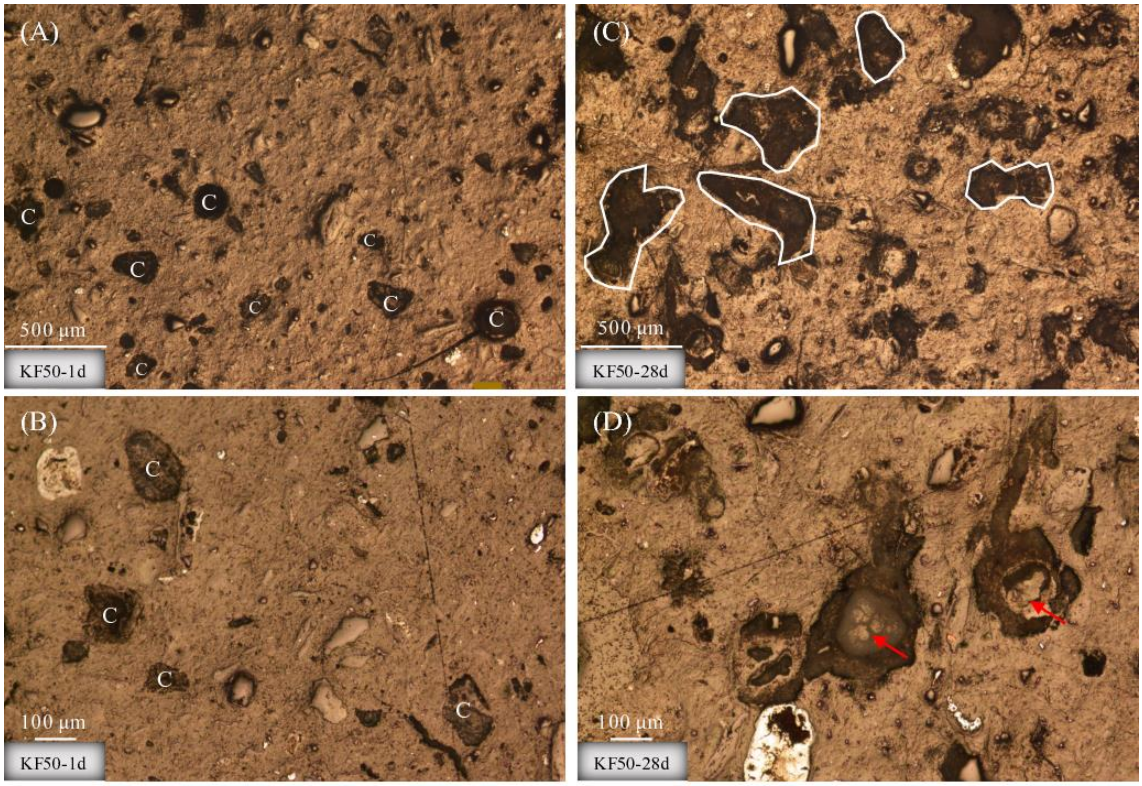

Fig. 9 Optical microscopy images of the alkali activated fly ash binder treated soil KF50 (A) and (B) after 24 hours, (C) and (D) at 28 days, C=calcium-rich particle.

The widening of darker zones which indicates the extent of reaction is lesser than the binder and represents around ¼ of the sample. This is consistent with the proportions of aluminosilicate solid considering that half of fly ash containing the reactive calcium nodules has been replaced by non-reactive kaolin in this soil-binder mixture. Consequently, the growth and development of new products into the available spaces does not seem influenced by the presence of kaolin.

Figure 10 shows micrographs of the alkali activated binder treated soil. After 24 hours crackings around and inside calcium nodules are seen (see particle C on Figure 10A), and associated to shrinkage similarly to the alkali activated fly ash binder at 28 days. The treated soil at 28 days however shows less marked crackings as shown on Figure 10B which focusses on the interface between a calcium-rich nodule labelled 1 and the

surrounding dense matrix labelled 2. It is attributed to the presence of kaolinite acting as a filler at the periphery of the calcium-rich nodules (see red arrows on Figure 10B showing kaolinite platelets).

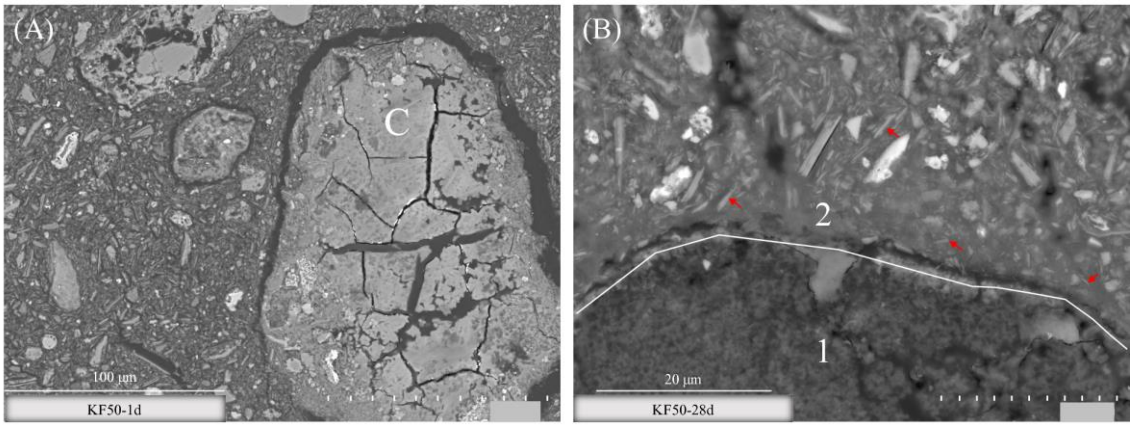

Fig. 10 SEM micrographs of the alkali activated fly ash binder treated soil KF50 at (A) 24 hours and (B) 28 days.

Figure 11A shows cumulative curves of mercury intrusion porosimetry tests of the alkali activated fly ash binder treated kaolin over time. Similarly to what was observed for the alkali activated binder, a decrease of the total porosity is detected over time.

Figure 11B shows the frequency distributions of pore entrance diameters belonging to the treated soil over curing time. Similarly to the alkali activated fly ash binder, the treated soil at 24 hours shows one modal pore sizes. Nevertheless, compared to the binder it is associated with a lower entrance pore size value around 0.4 µm and a much thinner peak. The non-presence of a wide class of pores between 0.05 µm and 3 µm at 24 hours as seen for the alkali activated fly ash binder is associated with the filling of the spaces between the coarse grains of fly ash by the small sized kalinite platelets. At 24 hours, kaolin therefore leads the organisation of the system microstructure as the typical pattern of kaolin (i.e. a monomodal curve with a peak around 0.4 µm) is shaping the curve.

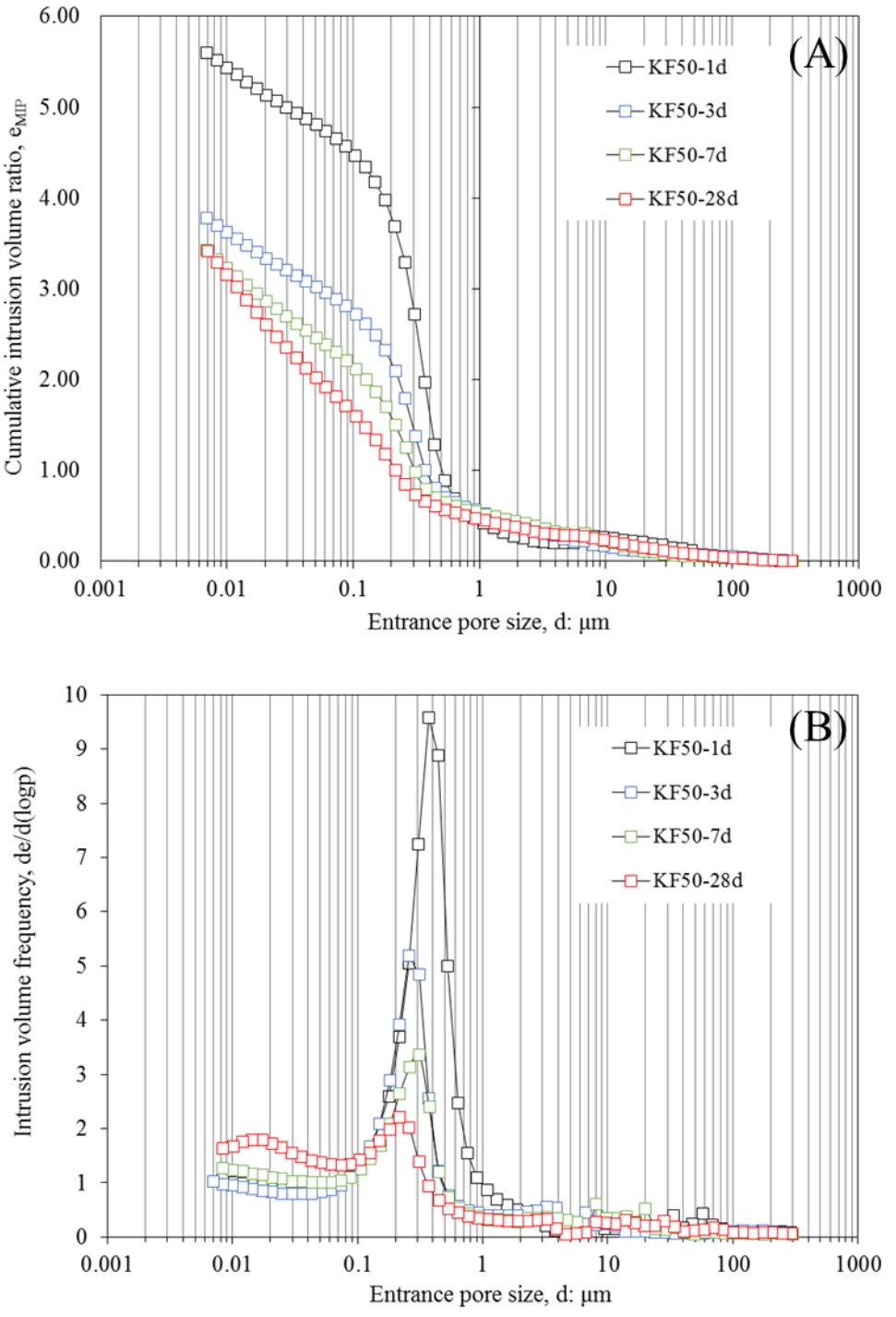

Fig. 11 Comparing mercury intrusion porosimeter tests of the alkali activated fly ash binder treated soil KF50 over time and in terms of (A) cumulative intrusion volume ratios, (B) intrusion volume frequency ratios as a function of entrance pore size.

Increasing the curing time, the filling of largest pores around the peak is seen as for the binder and due to the progressive filling of those pores by the newly products formed. A little shift of the residual peak towards smaller entrance diameters is also observed.

Finally, the formation of a new class of pores in the area of lower pore size i.e. below 30 nm is observed between 7 and 28 days of curing. Similarly to the binder, it is associated with the intrinsic porosity of the newly formed silicate-calcium chains. The delay in detection compared to the binder is due to the lower amount of phases formed for that system.

Figure 12 shows the results of one dimensional compression tests on KF20 and KF40 treated samples at increasing curing times, namely 24h, 7, 14 and 28 days. Addition of alkali activated binder induces an overall reduction of compressibility of the treated samples, with reduced volume strains for reference vertical stresses. The reduction is more relevant for increasing curing times, showing the stiffer behaviour of the treated sample. Coupled with the reduction of compressibility, an increase of yield stress of the samples is observed. The transition from a reversible behaviour to an irreversible one is shifted (yield stress) to higher vertical stresses. The shift is more relevant for higher amount of binder and at increasing curing time, revealing the reactivity of the binder to promote an improvement of the mechanical response of the treated soil. For stress levels higher than yield stress, treated samples show a higher compressibility coefficient (i.e. slope of the compressibility curve), depending on the destructuration stage induced by load increase, more evident for longer curing times and higher binder content. As a confirmation, in Figure 13 the compressive behaviour of treated samples is reported as function of binder contents. Sample prepared at 10%, 20% and 40% of alkali activated fly ash and cured for 24 hours before testing show a progressive improvement mainly

related to the amount of new compounds forming over time. Compressibility curves show a reduction of compressibility evidenced by the relevant decrease of volume strains and an increase yield stresses of the treated samples, whose extent depends on binder content.

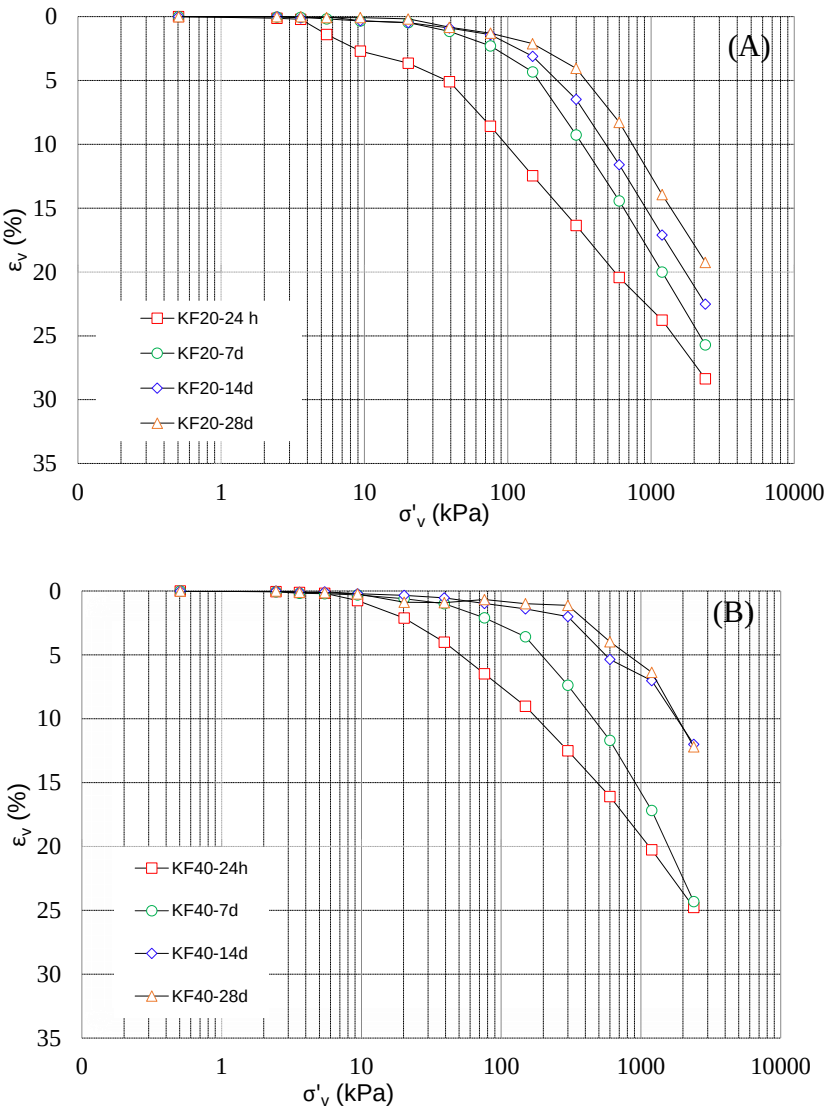

Fig. 12 One dimensional compression curves of alkali activated binder treated samples at 24 h, 7, 14 and 28 days of curing: (A) KF20; (B) KF40.

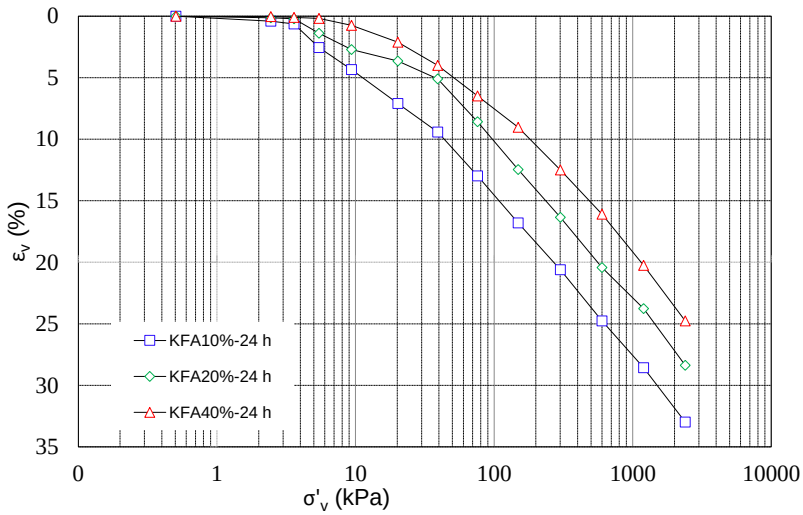

Fig. 13 One dimensional compression curves of treated samples as function of binder contents (i.e. KF10, KF20, KF40) at 24 hours of curing.

3.4 Comparison with Portland cement

This last section focusses on a comparison with microstructural development in Portland cement for which the mechanisms involved appear alike. This comparison particularly helps at providing a better understanding of (i) how microstructures are formed and (ii) interpreting the short and long-term performances of the treated soil regarding the evolution of the binder over time. At macroscopic level, the effectiveness of alkali activated binder soil treatment has been highlighted by comparison with mechanical performance induced by Portland cement.

3.4.1 Processes generating the microstructure

In cement systems, the dissolution of cement particles releases ions into the pore solution which then combine with water to form mainly Calcium Silicate Hydrates C–S–H (Muller, 2014). In a similar way, in our alkali activated binder, the dissolution of calcium-rich particles from fly ash releases calcium cations into the pore solution which then combine with water and silicon anions from the alkaline solution to form silicate two-

dimensional chains combined with calcium. A former investigation by Nuclear Magnetic Resonance nevertheless showed that the chains structure is slightly different from C–S–H, namely they are not well organized, of high length and may incorporate aluminum in a three dimensional environment which has not been described in literature yet (Coudert et al., 2019).

Secondly, it was reported for cement systems that the first Calcium Silicate Hydrates C–S–H cover cement grains and further grow into the available space. All cement grains are therefore surrounded by a shell of C–S–H (Scrivener, 2004). Again similarly in this study, optical microscopy images clearly show the development and growth of new products around calcium-rich reactive particles suggesting a similar mechanism.

Furthermore, Scrivener (2004) shows that as the cement grains dissolve, this might leave a hollow shell (Scrivener, 2004). The various extent of reaction of individual cement grains depends on their sizes: small cement grains hydrate completely in the first stages and remain as hollow shells of hydration product; whereas big grains further hydrate which forms denser hydration products and which fill in the gap between shell and grain (Muller, 2014). In this study it is also noticeable that calcium-rich reactive phases react at different rates: some completely dissolve after 28 days leaving a hollow shell while other remain with their initial structure and still contain calcium. Consequently, and similarly to what is described in the literature, depending on the calcium nodule size, the local products formed slightly differ which could lead to local variation of the inherent material properties.

3.4.2 Pore network characteristics

Regarding the pore network characteristics of cement systems, two populations of pores are generally distinguished: (i) capillary pores which correspond to space not being filled by solid products of hydration, and (ii) small pores called gel pores associated to the intrinsic porosity of Calcium Silicate Hydrates C–S–H. Over time, while chemical reactions proceed the population of capillary pores decreases whereas the population of gel pores increases, which may lead to the formation of disconnected spaces (Jennings et al., 2008). Our alkali activated binder shows similar tendencies that is a progressive decrease of intermediate pores or capillary pores while a new class of pores associated with silicate-calcium chain products is detected using Mercury Intrusion Porosimetry.

3.4.3 Macroscopic behaviour according to the microstructure evolution

Since both the processes generating the microstructure and the evolution of the pore network over time of our alkali activated binder are similar to cement systems, a similar influence of the microstructure on the short and long-term performances can be expected. Changes in the pore network strongly influence transport properties that govern the rate of all major deterioration processes and the service life of building materials (Wong et al., 2006). Namely the formation of gel pores inside the capillary spaces tends to decrease the connectivity of the pore network inhibiting the transport of aggressive substances such as acids, carbonate or chloride through concrete and therefore enhancing the material durability (van Deventer et al., 2010; Muller, 2014).

Finally, despite the great inhomogeneity of the reactive fly ash the growth and widening of new products appear to occur homogeneously across the sample at a millimetric scale in our alkali activated materials which would benefit the formation of a homogeneously reinforced material.

At volume scale of the sample, a comparison between the mechanical performance induced by alkali activated binder (KF40) and by ordinary Portland cement (KC40) is shown in Figure 14 for samples prepared with the same binder content and cured for 7, 14 and 60 days. No relevant changes in the compressibility curves are observed for KF40 and KC40 samples cured for 7 days before testing (Figure 14A). For longer curing times, results show a higher compressibility reduction and yield stress increase for KF40 treated samples compared to cement treated samples (Figures 14B and 14C). The post-yield behaviour induced by ordinary Portland cement shows the highest slope of the compressibility curve, highlighting a more evident destructuration stage for cement treated samples at increasing vertical stresses.

~~Experimental evidences, not reported in this study, confirm the improved mechanical behaviour of the alkali activated binder treated soils, with a relevant increase of stiffness compared to the not treated soil, an increase of the range of stresses to which the soil is subjected to limited strains under reversible behaviour, as well a destructuration stage beyond that stress level. An improved shear resistance is also clearly visible after 28 days of curing and associated to contractile behaviour~~.

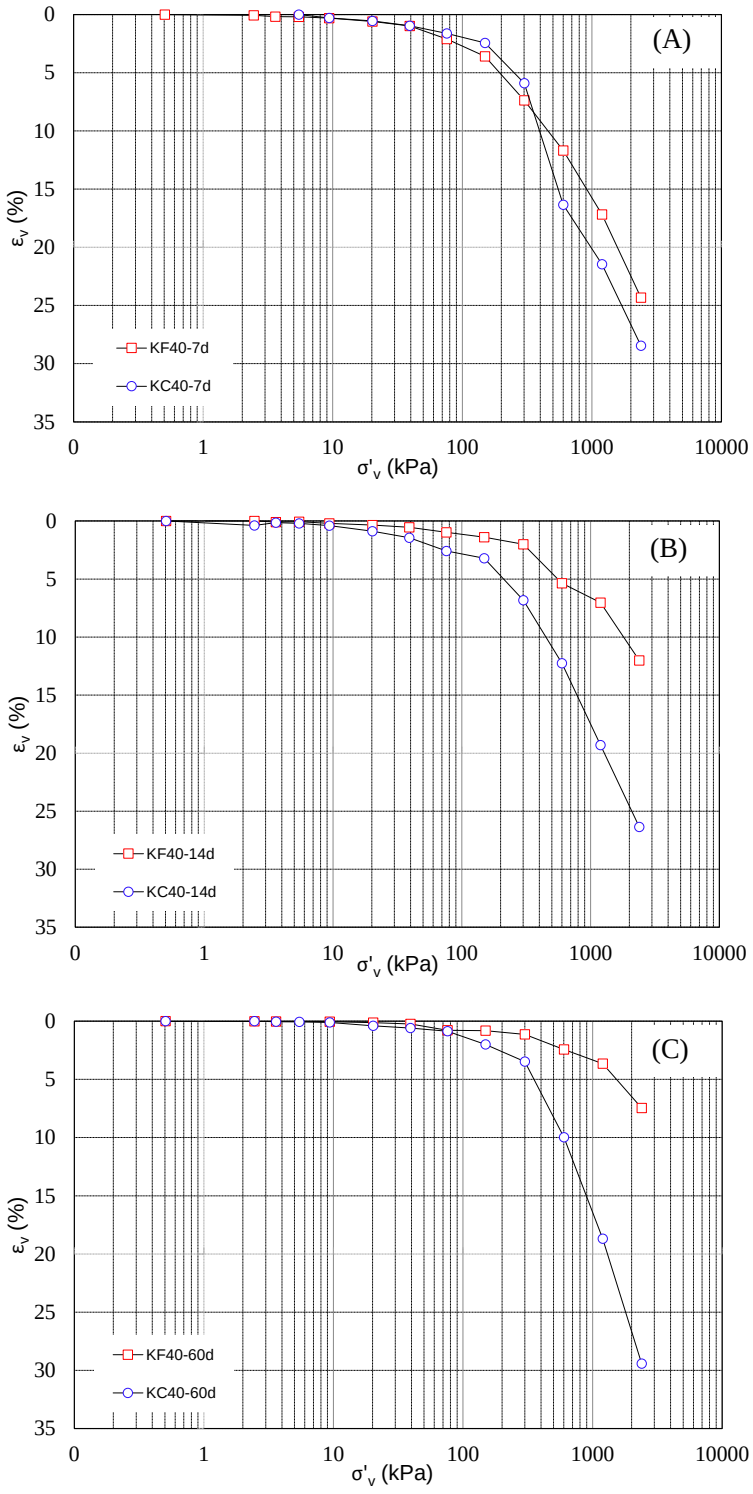

Fig. 14 One dimensional compression curves of treated samples as function of binder type (i.e. KF40 vs. KC40): (A) 7 days of curing; (B) 14 days of curing; (C) 60 days of curing

3 Conclusions

The development of a novel binder that is an alkali activated calcium-rich fly ash for clay soil stabilisation was investigated. The study of its microstructural evolution showed that structural changes occur around calcium-bearing minerals from fly ash which constitute the reactive phases, and whose dissolution leads to the formation of new compounds on its surface first and then growing into the available space. Capillary pore spaces are progressively filled by new compounds (i.e thernadite and silicate-calcium chains) over time. Whereas the newly formed silicate-calcium chains possess an intrinsic porosity of nanometric size conducting to the formation of a new class of small pores over time. Different heterogenous matrices of various porosity and arrangement are however observed across the material and owed to the high heterogeneity of fly ash whose particles locally react differently.

The interaction between the binder and kaolin showed that small sized kaolinite platelets fill the spaces between coarser grains from fly ash. Kaolin is therefore leading the microstructural organisation, that is, the pore network is characterised by pores ranging in lower size compared to the binder. Nevertheless, the microstructural changes remain similar over time i.e. filing of capillary pores and appearance of nanometric pores from silicate-calcium chains.

One-dimensional compression tests performed on treated sample highlighted the effectiveness of alkali activated binders to promote an improvement of the mechanical behaviour of treated soil. A reduction of compressibility and increase of the yield stress soil was observed since the very short term.

The observed microstructural evolution is similar to the one of cement system and should therefore conducts to akin performances that is an increase in strength and ability to resist

to aggressive substances due to changes in transport properties. It has been confirmed by observing the similarities of the mechanical performance of alkali activated binder treated samples with cement treated ones for short curing time. A marked improvement of the mechanical behaviour of soil is induced by alkali activated binder starting from 14 days of curing, representing a viable sustainable alternative to the use of ordinary stabilizing agent for soil improvement.

However, regarding the complexity of both cement and alkali activated systems which are multi-components systems, a coupling of those microstructural observations with mechanical performances and transport properties is of further interest. Namely, a complementary three-dimensional characterisation of the pore network using for instance microtomography would greatly help to assess the connectivity and tortuosity of the pore network which are primordial parameters to understand properly transport properties and therefore durability. Using micro-indentation coupled with Scanning Electron Imaging would also allow to measure local hardness variations following the extent of reaction of calcium particles and therefore help to apprehend how significant are the local microstructural variations for the mechanical performances at a macroscopic scale.

Acknowledgements

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