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**Understanding the sulfate attack of Portland cement-based materials exposed to applied electric fields: Mineralogical alteration and migration behavior of ionic species**

Chen Li <sup>a,b</sup>, Zhengwu Jiang <sup>a,\*</sup>, Rupert J. Myers <sup>c,d</sup>, Qing Chen <sup>a</sup>, Mengxue Wu <sup>a,e</sup>, Jiaqi Li <sup>b</sup>, Paulo J. M. Monteiro <sup>b,f</sup>

<sup>a</sup> Key Laboratory of Advanced Civil Engineering Materials of Ministry of Education, Tongji University, 4800 Cao'an Road, Shanghai, 201804, China

<sup>b</sup> Department of Civil and Environmental Engineering, University of California, Berkeley, California, 94720, United States

<sup>c</sup> School of Engineering, University of Edinburgh, Edinburgh, EH9 3FB, United Kingdom

<sup>d</sup> Current address: Department of Civil and Environmental Engineering, Imperial College London, London, SW7 2AZ, United Kingdom

<sup>e</sup> Administration for Market Regulation of Chengdu, Sichuan, 610044, China

<sup>f</sup> Material Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States

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\* Corresponding author

E-mail address: jzhw@tongji.edu.cn (Z. Jiang).

## Abstract

The magnesium and sodium sulfate attacks on Portland cement paste in the presence of applied electric fields were studied, and the mineralogical alterations were investigated by both experiments and thermodynamic modeling. When an electric current flows out of the cement paste, the electric migration of ions induced sulfate ingress and decalcification. Compared with the specimen exposed to  $\text{Na}_2\text{SO}_4$ , that exposed to  $\text{MgSO}_4$  for 28 d proceeded to a later degradation stage, which is characterized by the decomposition of ettringite, portlandite, and AFm phases, and the formation of  $\text{CaSO}_4$ . Thermodynamic modeling indicates a neutralization process induced by the electric migration of  $\text{OH}^-$ , which is potentially responsible for the decomposition of ettringite. When an electric current flows into the cement paste, the  $\text{Mg}^{2+}$  and  $\text{Na}^+$  showed different migration behavior.  $\text{Mg}^{2+}$  was incorporated to form brucite and M-S-H-like products in a shallow area ( $\sim 100\text{ }\mu\text{m}$ ) on the surface of the specimen, whilst a part of the  $\text{Na}^+$  could be bonded to form Na-rich silica gel with the other part penetrating through the specimen. By coupling the pore solution chemistry obtained from thermodynamic modeling with the Nernst-Planck equation, the migration behaviors of the ionic species ( $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$ ) were analyzed.

## Keywords

Sulfate attack; Mineralogical alteration; Thermodynamic modeling; Nernst-Planck equation; Applied electric field

## 1 Introduction

Cement-based materials are porous and consist of multiple phases. The hydration products (solid phase) form the

skeleton of the pore structures, and the pore solution (aqueous phase) and air (gaseous phase) fill inside the pores. In a fully hydrated cement paste, the hydration products are approximately at equilibrium with the pore solution. However, this state will be affected by the ionic exchange between the pore solution and the external environment. Such a process usually induces mineralogical alterations and is described as a chemical attack. The attack is affected by the type, rate, and direction of the ion exchange, as well as the chemical reactions that occur.

The ingress of external sulfate will cause sulfate attack, which is one of the most widely recognized and well-studied chemical attacks. In Portland cement systems, sulfate attacks are usually characterized by the formation of ettringite, and by the expansion, cracking, and strength loss thereafter [1-3]. Recent theories relate the expansion to the crystallization pressure caused by the formation of ettringite from oversaturated solution in small pores [4-6]. The crystals growing in confined pores, e.g., in the C-S-H gel, generate crystallization pressure and thus expansive stress [7,8], whilst those growing in unrestrained pore spaces do not. Gypsum usually forms at the late stage of sulfate attack. There was once a debate on whether the formation of gypsum is a cause [9-11] or an effect [12,13] of the expansion and cracking. Recent studies proposed that the presence of gypsum induces a high supersaturation with respect to ettringite, and thus a high crystallization pressure and more expansion [2,14,15].

The type of cation that coincides with sulfate greatly influences the degradation process. When the cation is  $\text{Mg}^{2+}$ , surface erosion occurs in addition to expansion [15-17]. This phenomenon is induced by the formation of brucite and magnesium silicate hydrate (M-S-H) [2,16], and is the most important characteristic to distinguish magnesium sulfate attack from sodium sulfate attack. It was also reported that the co-existence of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  can reduce surface erosion and expansion in the  $\text{MgSO}_4$  attack [2,16]. When the sulfate is provided by an acidic environment, neutralization can take place in the pore solution, and the  $\text{Ca}^{2+}$  can diffuse towards the external environment due to

the concentration gradient. Under this circumstance, calcium leaching or decalcification will also occur together with the sulfate attack [18-20].

In most cases, the ionic exchange between cement-based materials and the external environment is driven by the concentration gradient, and this process is known as diffusion. In certain field conditions, the exposed surface of a structure is subjected to strong evaporation conditions. The moisture gradient between the external environment and cement-based materials induces capillary suction, and the ionic species will be transported by advection [21]. Under an applied electric field, the ionic species in the pore solution can also migrate, which is known as electric migration [22-24]. The transportation of ionic species—their diffusion, advection, and electric migration in cement-based materials is described by the Nernst-Planck equation [22-25]. During the ionic transportation, chemical reactions can take place. For example,  $\text{SO}_4^{2-}$  can react with monosulfate to form ettringite [1,20,26]. This reaction impacts not only the mass transport of  $\text{SO}_4^{2-}$  but also the strength of  $\text{Ca}^{2+}$  and  $\text{AlO}_2^-$  by disturbing the equilibrium between the hydration products and the pore solution. In this respect, the concurrent chemical reactions and ionic transportation both play significant roles in the ingress of sulfate.

In some cases, cement-based materials are directly exposed to applied electric fields, e.g., the DC stray current that is present in underground metro tunnels [27-29]. Electric migration can accelerate the ingress of aggressive ions from the external environment and remove the calcium and alkali metals from the pore solution [30,31]. Electric fields are also applied in some modern concrete techniques, e.g., chloride extraction, realkalinization, cathodic protection, and electrochemical deposit [32-35]. In these techniques, certain types of ions are designed to migrate, but the migrations of other ions have to be considered because they may induce side effects [36]. Electric migration is also a useful tool for laboratory acceleration tests, e.g., the chloride ion penetration tests (ASTM C1202), calcium

leaching acceleration tests [37,38], etc. Recent studies proposed that electric migration tests can be potentially used in the acceleration of sulfate attacks [39-41]. However, a deeper understanding of the mineralogical alterations and the degradation mechanism under such circumstances will be needed to evaluate the validity of this technique.

In a conventional sulfate attack caused by diffusion, both the cations and anions in the external solution diffuse into the cement-based materials, while the ions in the pore solution, e.g.  $\text{Ca}^{2+}$ ,  $\text{OH}^-$ , and alkali metal ions diffuse outward. In contrast, under applied electric fields, the cations and anions migrate in different directions, and thus the degradation behavior and mechanism may differ from the diffusion-induced sulfate attacks. This paper studies the  $\text{MgSO}_4$  and  $\text{Na}_2\text{SO}_4$  attacks on Portland cement paste in the presence of applied electric fields. The chemical and mineralogical alterations during the degradation process were analyzed by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS), X-ray diffractometry (XRD), and thermogravimetric analysis (TGA). The results suggest different degradation behaviors between the areas near the cathode and anode, and between the specimens exposed to different sulfate sources. To better understand the degradation mechanism, an approach was proposed to simplify the electric migration processes, and changes of the phase assemblages during the simplified electric migration processes were then calculated by thermodynamic modeling. By combining the pore solution chemistry obtained in the thermodynamic modeling with the Nernst-Planck equation, the migration behaviors of various ionic species were analyzed to explain the different degradation behaviors observed experimentally.

## 2 Experimental

### 2.1 Cement paste specimens

Cement paste specimens were prepared using Portland cement and deionized water at a water-to-cement ratio of 0.5. The chemical composition of the Portland cement was tested by X-ray fluorescence spectrometry (XRF), and the mineralogical composition was measured by XRD and analyzed by Rietveld refinement, as shown in Table 1. The specimens were cast into cylindrical molds that were 100 mm in diameter and 50 mm in height, cured at  $20\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ ,  $\text{RH} > 95\%$  and unmolded after 24 h. The top of the cylinders, which was not in contact with the molds, was polished by P240 (58  $\mu\text{m}$ ) sandpaper to make it flat and smooth. The specimens were then cured in saturated limewater at  $20\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$  until 28 d.

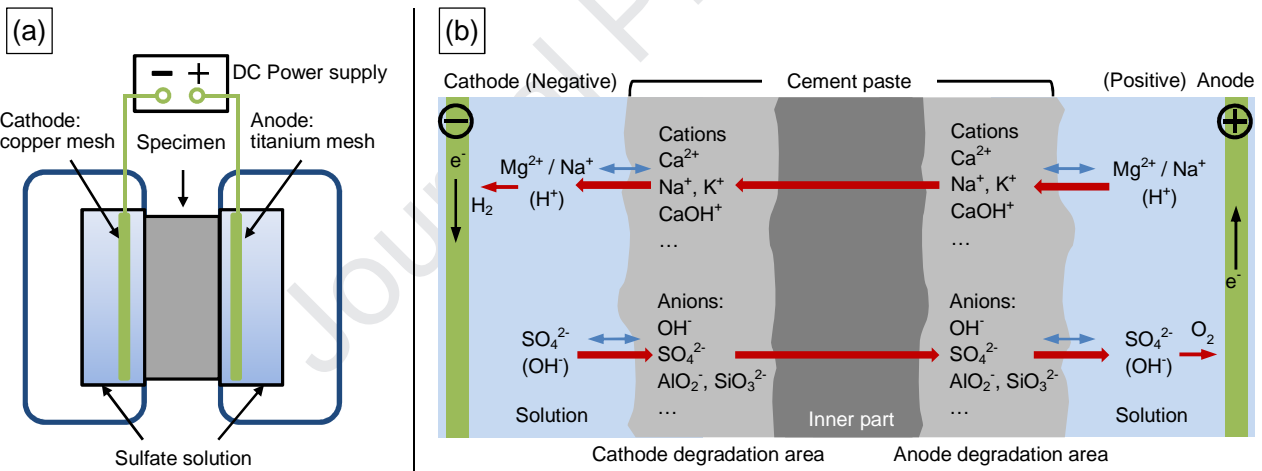
**Table 1** Chemical and mineralogical compositions of the Portland cement (wt. %).

Chemical composition		Mineralogical composition	
$\text{Na}_2\text{O}$	0.04	$\text{C}_3\text{S}$	58.32
$\text{MgO}$	0.76	$\text{C}_2\text{S}$	11.64
$\text{Al}_2\text{O}_3$	4.55	$\text{C}_3\text{A}$	3.96
$\text{SiO}$	20.8	$\text{C}_4\text{AF}$	8.03
$\text{P}_2\text{O}_5$	0.11	Calcite	4.58
$\text{SO}_3$	2.92	Anhydrite	0.76
$\text{K}_2\text{O}$	0.74	Bassanite	3.67
$\text{CaO}$	64.8	Gypsum	0.01
$\text{TiO}_2$	0.23	Lime	0.35
$\text{Cr}_2\text{O}_3$	0.02	Portlandite	0.58
$\text{MnO}$	0.11	$\text{CF}_2$	1.53
$\text{Fe}_2\text{O}_3$	3.27	Goergeyite	3.30
$\text{CuO}$	0.02	Perovskite	1.79
$\text{ZnO}$	0.05	Periclase	0.85
$\text{SrO}$	0.03	Dolomite	0.13
LOI	2.58	Quartz	0.21

## 2.2 Electric field application

The electric field was applied by electrolytic cells similar to those for the chloride ion penetration tests described in ASTM C1202 (Fig. 1a). The anode was a titanium mesh, and the cathode was a copper mesh. A constant electric

current of 30.0 mA (equal to  $\sim 4.71 \text{ A/m}^2$ ) was maintained by a DC power supply. The cells on both sides were filled with the same sulfate solution, either 0.5 mol/L  $\text{MgSO}_4$  or 0.5 mol/L  $\text{Na}_2\text{SO}_4$ . This concentration is slightly higher than the one used in the sulfate expansion tests in ASTM C1012 (5%  $\text{Na}_2\text{SO}_4$ ,  $\sim 0.35 \text{ mol/L}$ ). The solutions were prepared using deionized water and sodium sulfate anhydrous (Sinopharm, purity > 99.0%) or magnesium sulfate heptahydrate (Sinopharm, purity > 99.0%), and were refreshed every three days. An estimation based on charge conservation shows that the concentration of the sulfate solutions can remain higher than  $\sim 0.34 \text{ mol/L}$  during the experiment (see Supplementary Data). For either  $\text{MgSO}_4$  or  $\text{Na}_2\text{SO}_4$ , three sets of electrolytic cells were set up. The specimens were taken out after exposure to the applied electric fields for 7, 14, and 28 days. The deposits formed on the electrodes were cleaned every six days.



**Fig. 1.** Test setup to apply electric fields: (a) overview of the test setup and (b) schematic of ionic motion where thickness and velocity are not to scale. The ionic motion is driven by electric migration (red arrows) and diffusion (blue arrows).

Figure 1b illustrates the motion of ionic species in the test setup. The anode is connected to the positive output of the power supply and has a higher electric potential compared with the cathode. The cations in the anodic solution ( $\text{Mg}^{2+}$  or  $\text{Na}^+$ ) migrate towards the cement paste and enter the specimen from the surface near the anode. Meanwhile, the cations in the pore solution ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , etc.) migrate towards the cathode and leave the



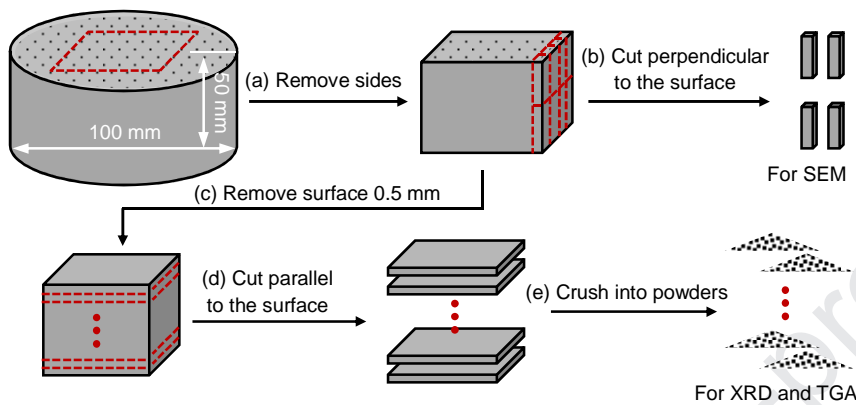
specimen from the nearby surface. The anions migrate in the opposite direction. Diffusion also occurs in addition to electric migration. The ionic species in the external solution ( $\text{SO}_4^{2-}$  and  $\text{Na}^+/\text{Mg}^{2+}$ ) diffuse towards the specimen on both sides, and the ions in the pore solution also diffuse towards the external solutions.

Similar test setups are also used in [39-41] for accelerating sulfate attacks in the laboratory. The current density was not reported in those literatures, and the estimated values were between one and several  $\text{A/m}^2$  based on the voltage and size of the specimen (assuming the resistivity of water-saturated cement mortar is around  $10 \text{ k}\Omega\cdot\text{cm}$ ). For studying the effects of DC stray current on reinforcement corrosion and concrete degradation, the current densities of 1 and  $10 \text{ A/m}^2$  were chosen in [27,42]. The current density used in this paper ( $\sim 4.71 \text{ A/m}^2$ ) is comparable to these reported values.

### 2.3 Test method

After the exposures to the applied electric fields for certain durations, the specimens were removed from the test setups and cut into pieces according to the procedures in Fig. 2. Small patches that contain all the depth from the exposure surface (0 mm) to  $\sim 25 \text{ mm}$  were prepared for SEM. A face perpendicular to the exposure surface was used for observation. These samples were impregnated with epoxy resin, polished on SiC discs and diamond suspension-sprayed discs (Buehler), carbon-coated, and observed using a Quanta 200 FEG microscope in the backscattered electron mode. The hydration products on the surface of the specimens usually showed clear features (brightness and morphology), and the chemical composition of such well-resolved hydration products was analyzed based on at least five EDS measurements. EDS point analyses were also conducted randomly in the well hydrated areas (where the hydration products mingle and cannot be identified easily) to reflect the chemical composition of

the hydration products in such areas. The average chemical composition in several  $50\ \mu\text{m} \times 50\ \mu\text{m}$  areas was measured to represent the distribution of elements along the depth from the exposure surface. The microstructure were analyzed by observing a 5-mm-wide area parallel to the surface.



**Fig. 2.** Preparation of samples: (a) the sides of a cylindrical specimen that were not well exposed to sulfate solutions were cut off, (b) small patches that were perpendicular to the exposure surface was cut for SEM, (c) the surface part (0.5 mm) of the remainder was removed, (d) the specimen was cut parallel to the exposure surface into 5-mm thick slices, and (e) the slices were crushed into powders (particle size  $<75\ \mu\text{m}$ ) for XRD and TGA.

The powder samples for XRD and TGA were soaked in ethanol for 5 days to stop the hydration and then dried at  $40\ ^\circ\text{C}$  for 24 h. XRD was conducted on a D/max2550VB3+/PC diffractometer equipped with  $\text{Cu K}\alpha_1$  radiation and a graphite monochromator. The X-ray generator was operated at 40 kV and 250 mA, the scanning range was  $2\theta = 5\text{--}75^\circ$ , and the step size and counting time were  $0.02^\circ$  and 2 s, respectively. TGA was conducted on a NETZSCH STA 449C simultaneous thermal analyzer. The samples were heated under  $\text{N}_2$  atmosphere from  $40\ ^\circ\text{C}$  to  $950\ ^\circ\text{C}$  with a heating rate of  $10\ ^\circ\text{C}/\text{min}$ . The data were expressed as differential thermogravimetry, and the peaks were assigned according to [43]. Note that the specimens for XRD and TGA did not include the surface part ( $\sim 0.5\ \text{mm}$ ), because this part was quite different in composition from the other parts according to SEM but its material amount was not sufficient for these tests.

#### 2.4 Rietveld refinement

Corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, Aladdin, purity > 99.99%) was used as an internal standard. It was mixed with the dried powder samples at a mass ratio of 10 to 90. The Rietveld refinement was conducted using TOPAS Academic V5. The crystallographic models were obtained from the Inorganic Crystal Structure Database (ICSD), see Supplementary Data. The optimized parameters included the background coefficient, zero-shift error, crystal size L, and lattice parameters (restrained within  $\pm 0.5\%$ ). The peak shape was described by the fundamental parameter (FP) approach employed in TOPAS. The March-Dollase ellipsoidal preferred orientation correction algorithm [44] was employed for Alite-M3 (606) [45], portlandite (001) [46], and calcite (104) [45]. Two peaks using fundamental parameters were added near  $2\theta = 29.3^\circ$  and  $50.0^\circ$  to simulate the broad peaks produced by C-S-H [47,48]; and the scale factor, crystal size L, and position of the peaks were refined.

#### 2.5 Simplifications in the thermodynamic modeling of the degradation process

In order to gain insight into the chemical and mineralogical aspects of the degradation process and study the degradation mechanism, a simplified approach was proposed to represent the main processes of electric migration. Based on this simplified approach, the phase assemblage during degradation was further studied by thermodynamic modeling. Here, electric migration is assumed to be the only driving force for the ionic motion and described by the Nernst-Planck equation [22-25] as

$$J_{i,e} = -D_i^a \cdot \frac{z_i F}{RT} C_i \frac{\partial \Psi}{\partial x} \quad (1)$$

where  $J_{i,e}$  (mol·m<sup>-2</sup>·s<sup>-1</sup>) is the bulk flux of ionic species  $i$  at location  $x$ ;  $D_i^a$  (m<sup>2</sup>·s<sup>-1</sup>) is the apparent diffusion coefficient;  $z_i$  is the charge number;  $C_i$  (mol·m<sup>-3</sup>) is the ionic strength;  $F = 9.648 \times 10^4$  C·mol<sup>-1</sup> is the Faraday

constant;  $R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  is the gas constant;  $T$  (K) is the absolute temperature; and  $\Psi$  (V) is the electric potential. The apparent diffusion coefficient usually has a positive relationship with the corresponding diffusion coefficient in free water ( $D_i^0$  in  $\text{m}^2 \cdot \text{s}^{-1}$ ), and this relationship is impacted by the pore structure characterized by porosity ( $\varphi$ ) and tortuosity ( $\tau$ ) as [23]

$$D_i^a = \frac{\varphi}{\tau^2} D_i^0 \quad (2)$$

When an electric field is applied, the migration rate of an ion depends on its charge number, concentration, and diffusion coefficient in free water. The diffusion coefficient in free water can be obtained from the chemistry handbook [49], and the concentration of ions in the cement paste before exposure to electric fields can be calculated by thermodynamic modeling (see Supplementary Data), as shown in Table 2.

**Table 2** Concentration of ions in the pore solution before degradation and diffusion coefficient in free water ( $D_i^0$ ).

	Concentration mol/L	Diffusion coefficient $10^{-9} \text{ m}^2/\text{s}$	Direction
$\text{OH}^-$	$2.05 \times 10^{-1}$	5.273	Cathode $\rightarrow$ inner part $\rightarrow$ anode $\rightarrow$ anodic solution
$\text{SO}_4^{2-}$	$6.79 \times 10^{-4}$	1.065	
$\text{AlO}_2^-$	$4.25 \times 10^{-5}$	n.a. <sup>1</sup>	
$\text{SiO}_3^{2-}$	$9.94 \times 10^{-6}$	n.a. <sup>1</sup>	
$\text{CO}_3^{2-}$	$4.66 \times 10^{-5}$	n.a. <sup>1</sup>	
$\text{HCO}_3^-$	$2.27 \times 10^{-8}$	1.185	Anode $\rightarrow$ inner part $\rightarrow$ cathode $\rightarrow$ cathodic solution
$\text{Ca}^{2+}$	$1.01 \times 10^{-3}$	0.792	
$\text{Ca(OH)}^+$	$9.09 \times 10^{-4}$	n.a. <sup>1</sup>	
$\text{Mg}^{2+}$	$1.11 \times 10^{-10}$	0.706	
$\text{Na}^+$	$2.34 \times 10^{-3}$	1.334	
$\text{K}^+$	$2.01 \times 10^{-1}$	1.957	

<sup>1</sup> Not available in [49].

As illustrated in Fig. 1b, it is assumed that each specimen contains two degradation areas that are located on the exposure surfaces and are affected by the chemical attack, while the inner part between these two degradation areas is not affected. At the beginning of degradation, the pore solution chemistry and pore structure are similar in all

parts across the cement paste, and the electric gradient is uniform. In the pore solution, ionic species  $i$  at different positions will migrate at the same rate according to Eq. 1. In the degradation area near the cathode, the cations are released into the cathodic solution due to electric migration, but they are also supplemented by those migrating from the inner part of the specimen at the same rate. The anions in the pore solution migrate towards the inner part and are replaced by those from the cathodic solution. However, the migration rate of the anions from the cathodic solution into the cement paste is difficult to determine, because the electric gradient and pore structure are different between the surface of a specimen and its interior. Here, it is assumed that the replacement of the anions in the degradation area near the cathode maintains the charge balance. Similarly, the main process in the degradation area near the anode is the replacement of cations in the pore solution by those from the anodic solution in a charge-balanced manner. These processes are similar to those reported in numerical simulation studies of the rapid chloride migration test [23,50]. Here, they are defined as the “basic state” of electric migration, which is a transient state when the concentration of the ions in the pore solution is similar to that before degradation initiates. The duration of the basic state depends on whether the concentration of the ionic species in the pore solution remains stable during the ionic exchange and the relevant chemical reactions.

In the pore solution, the concentration of  $\text{OH}^-$  is higher than the other anions by three orders of magnitude (Table 2), and the main anion in the cathodic solution (a neutral  $\text{Na}_2\text{SO}_4$  or  $\text{MgSO}_4$  solution) is  $\text{SO}_4^{2-}$ . According to Eq. 1, these two ionic species migrate much faster than the others in the pore solution and the cathodic solution, respectively. Moreover, the decomposition of portlandite can somewhat help maintain the ionic strength of  $\text{OH}^-$  in the pore solution, which is known as the buffering effect [51]. Therefore, the electric migration process near the cathode is simplified to the replacement of each two moles of  $\text{OH}^-$  by one mole of  $\text{SO}_4^{2-}$ .

In the area near the anode,  $K^+$  and  $Na^+$  are the most easily migrated ionic species. However, they will be removed quickly due to their low contents in the hydrated cement paste [23,50], indicating that this state is short-lived. Afterward,  $Ca^{2+}$  will be the main ionic species to migrate. ( $CaOH^+$  will also migrate, but its effect on the mineralogical alteration is similar to that of  $Ca^{2+}$ .) Its ionic strength can be maintained by the buffering effect, suggesting a possibly longer duration. Therefore, the electric migration process in this state is simplified by replacing each mole of  $Ca^{2+}$  with one mole of  $Mg^{2+}$  or two moles of  $Na^+$ , based on a hydrated system without K and Na.

## 2.6 Thermodynamic modeling

Thermodynamic modeling was performed using the geochemical code GEMS 3.3 [52] with the Nagra/PSI database [53] and CEMDATA 18 database (version 18.01) [54]. The CSHQ model was selected. The solid solutions of AFt and AFm were not considered. Siliceous hydrogarnet ( $C_3AS_{0.8}H_{4.4}$ ) and thaumasite usually form at slow kinetics at the ambient temperature [55,56]. The presence of electric fields does not significantly impact the slow formation kinetics of thaumasite [57], but it remains unknown whether the formation kinetics of  $C_3AS_{0.8}H_{4.4}$  will be influenced. These products were both suppressed in the modeling.

First, the phase assemblage before sulfate ingress was calculated. The following hydration degrees were assumed based on the XRD results at an age of 28 d: 95% for  $C_3S$ , 65% for  $C_2S$ , 100% for  $C_3A$ , and 70% for  $C_4AF$ . The  $Na_2O$  and  $K_2O$  in the cement were assumed to dissolve completely, while the  $MgO$  was assumed to dissolve by 90%. Calcite was set to react freely [58].

The hydration phase assemblage during the electric migration process was then calculated by changing the input recipe according to the simplified approach (see Supplementary Data). In order to further analyze the migration rate of the ionic species in the pore solution during degradation, the theoretical flux of  $\text{OH}^-$  in the pore solution at the beginning of degradation was considered as a reference. Provided that the pore structure in Eq. 2 does not change significantly during degradation, the relative flux ( $R$ ) of a type of ionic species  $i$  is hereby defined as

$$R = \frac{J_{i,e}}{J_{\text{OH},e}} = \frac{D_i^0 z_i C_i}{D_{\text{OH}}^0 z_{\text{OH}} C_{\text{OH}}^0} \quad (3)$$

At a given time during the electric migration process, an ion with higher relative flux migrates faster, provided that the flux is uniform in the cross-section. In addition to their migration, the concentration of ions in the pore solution may also be affected by the phase changes induced by electric migration, and the manner of ionic migration may thus deviate from the description of the simplified processes. This effect can also be represented by the changes in the relative flux.

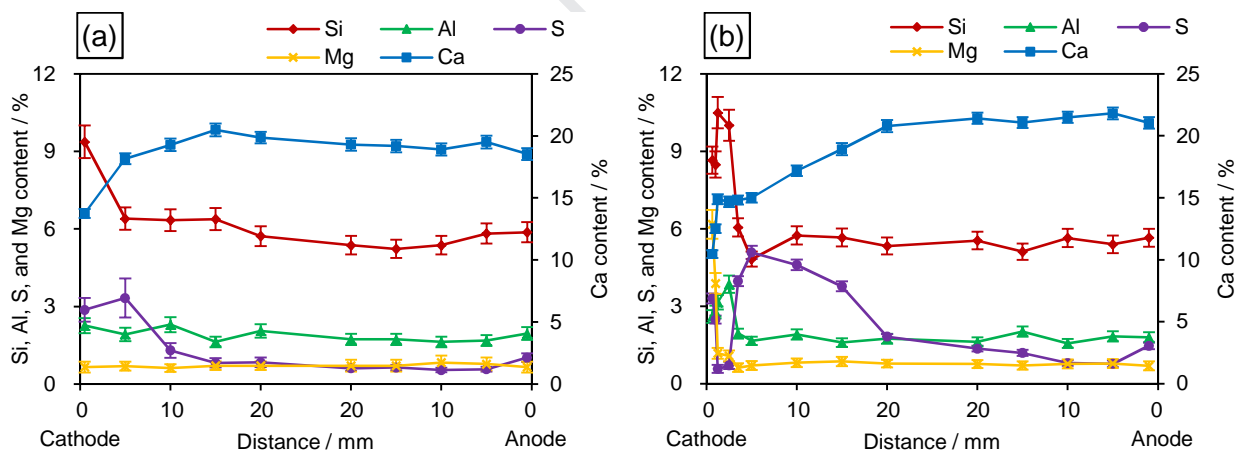
### 3 Results

#### 3.1 Test results of $\text{MgSO}_4$ exposure

##### 3.1.1 Chemical composition and microstructural alterations

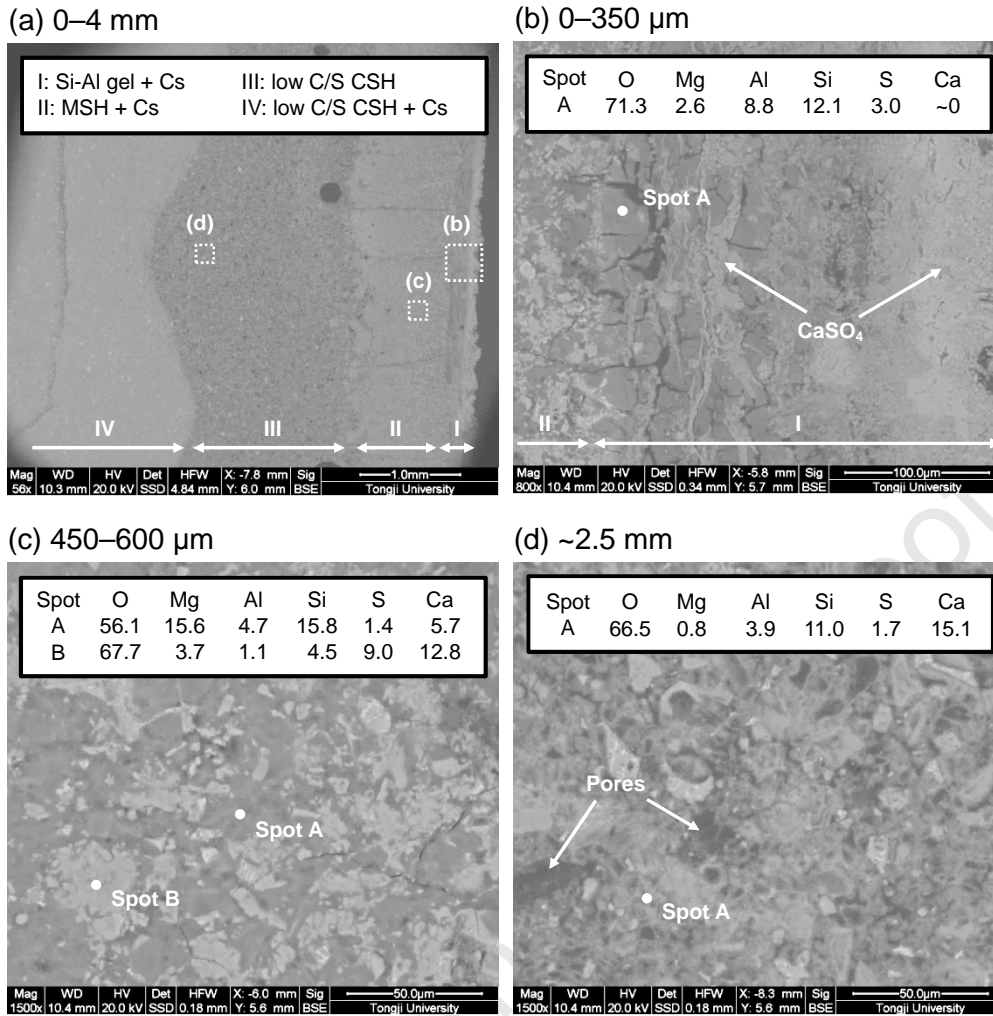
Near the cathode, an exposure to  $\text{MgSO}_4$  in the presence of applied electric fields increased the S content of the cement paste (Fig. 3, see from the left). The S content near the surface (e.g., 0.1–10 mm) increased with the exposure time and became higher than that of the inside part (e.g., 20 mm). In addition, the Ca content near the surface decreased whilst the Si and Al contents increased. An enrichment of Mg was observed at a depth of 0.1–0.25 mm after an exposure time of 28 d (Fig. 3b). In addition to the chemical composition alteration, the surface

area near the cathode (0–3 mm) showed a layered microstructure (Fig. 4a). In the outermost layer (0–300  $\mu\text{m}$ , area I), a large amount of  $\text{CaSO}_4$  formed on the surface of the specimen, and the hydration products decalcified to form silica-alumina gel (e.g., Spot A of Fig. 4b). Deeper inside the cement paste (300–1000  $\mu\text{m}$ , area II), the hydration products were affected by both decalcification and magnesium ingress. The silica-alumina gel showed a high Mg content (Spot A of Fig. 4c), which agrees with the Mg enrichment in this area (Fig. 3b).  $\text{CaSO}_4$  was also present in this area (Spot B of Fig. 4c). About 1–3 mm from the surface (area III), the hydration products were not impacted by the ingress of either magnesium or sulfate. The cement paste was porous (Fig. 4d). The Ca/Si ratio of the hydration products in this area was typically smaller than 1.5, which coincides with the chemical composition shown in Fig. 3b. From 3 mm inside (area IV), the cement paste started to show continuous alterations without layered structures.



**Fig. 3.** Chemical composition at different distances from the surface (cathode on the left and anode on the right) after exposure to  $\text{MgSO}_4$  for (a) 7 d and (b) 28 d. Each data point represents the average over a  $50 \mu\text{m} \times 50 \mu\text{m}$  area measured by EDS. Error bars indicate the standard error in ZAF matrix correction schemes. The sampling points nearest to the surfaces are 0.1 mm from the surface.

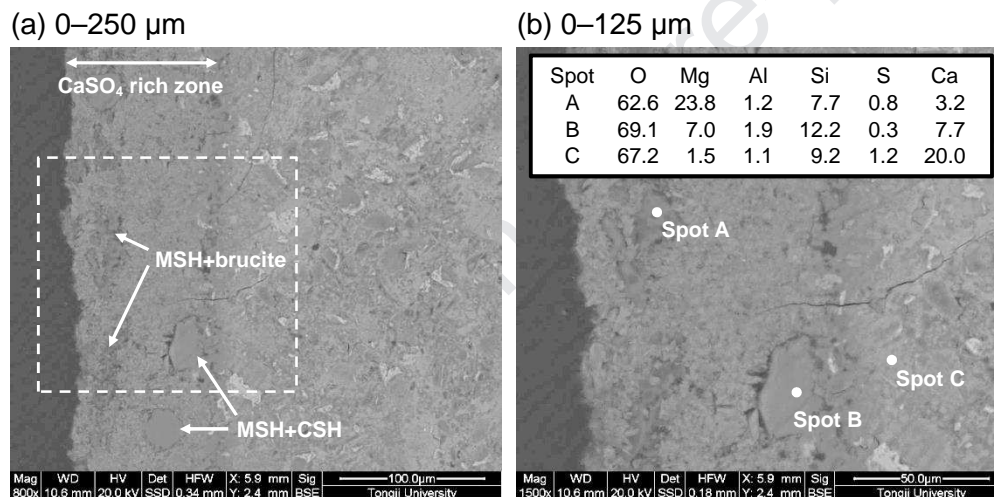




**Fig. 4.** Microstructure of the surface area (0–4 mm) near the cathode after 28 d exposure to  $\text{MgSO}_4$ : (a) an overview, and (b) to (d) enlargements of the squared areas. Surface on the right.

The cement paste near the anode did not show significant alterations on both chemical composition (Fig. 3, see from the right) and microstructure (Fig. 5). A very small increase of the S content was observed in the surface area (0.1 mm from the surface). Considering the direction of electric migration (Fig. 1b), the increased S content is mainly induced by diffusion [39,40]. The  $\text{Mg}^{2+}$  in the anodic solution should theoretically move towards the cement paste due to electric migration (Fig. 1b). However, the ingress of  $\text{Mg}^{2+}$  was constrained within a depth of  $\sim 100 \mu\text{m}$  according to SEM. (Fig. 5). This  $100\text{-}\mu\text{m}$ -zone was rich in  $\text{CaSO}_4$ , and two types of Mg-containing products with different brightness and Mg/Si ratio were found. Closer to the surface, some Mg-containing products in clusters were embedded in the  $\text{CaSO}_4$ . These products were darker than the hydration products nearby. The Mg/Si ratio was

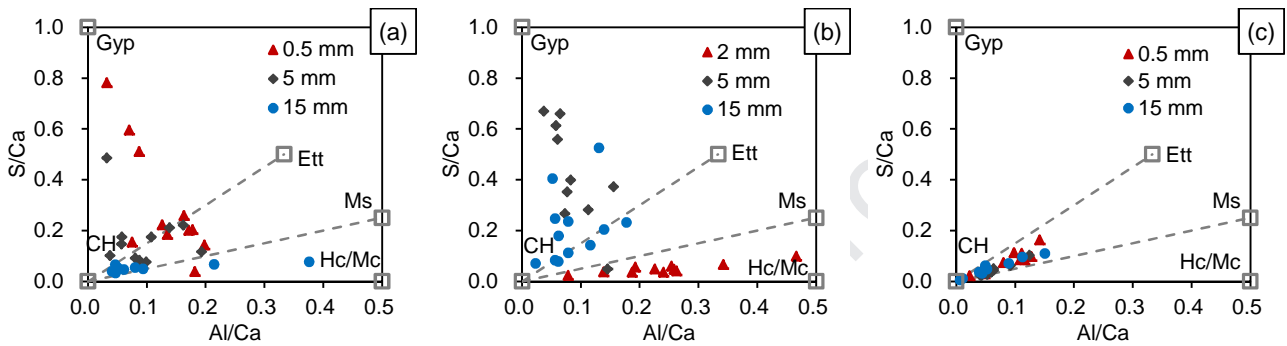
higher than 3 (Spot A), which potentially indicates a mixture of M-S-H and brucite on the microscale. Similar products were also reported to form on the surface of the cement mortar after the magnesium sulfate attack in the absence of applied electric fields [15,16]. Farther from the exposure surface, there were some larger particles (Spot B). Compared with the Mg-containing products in clusters (Spot A), the Mg/Si ratio of these particles was much lower, and the Ca content was higher. This chemical composition led to a slightly higher brightness and may represent a mixture of M-S-H and C-S-H, or an M-C-S-H [59]. Next to the  $\text{CaSO}_4$ -rich zone, the Ca/Si ratio of the hydration products was typically higher than 1.5, and no magnesium-containing products were observed, which is also verified in Fig. 3b.



**Fig. 5.** Microstructure of the surface area (0–250  $\mu\text{m}$ ) near the anode after 28 d exposure to  $\text{MgSO}_4$ : (a) an overview and (b) enlargement of the squared area. Surface on the left.

EDS spot analyses were conducted randomly at certain depths, and the S/Ca is plotted against the Al/Ca in Fig. 6. After an exposure time of 7 d (Fig. 6a), the chemical composition of the hydration products indicates the presence of  $\text{CaSO}_4$  and ettringite at the depths of 0.5 mm and 5 mm from the cathode. A small amount of ettringite may exist at the depth of 15 mm. After an exposure time of 28 d (Fig. 6b), the hydration products at 2 mm from the cathode (area III, Fig. 4a) showed very small S/Ca and relatively high Al/Ca to the other groups, coinciding with the

decalcification observed in Spot A, Fig. 4d.  $\text{CaSO}_4$  was suggested to be the dominant sulfate-bearing phase at 5 mm from the cathode (area IV, Fig. 4a), and a large amount of  $\text{CaSO}_4$  with ettringite in a minor proportion may be present at 15 mm from the cathode. In the areas that are 0.5 mm, 5 mm, and 15 mm from the anode (Fig. 6c), the hydration products may contain a mixture of ettringite, monosulfate, C-S-H, and portlandite.

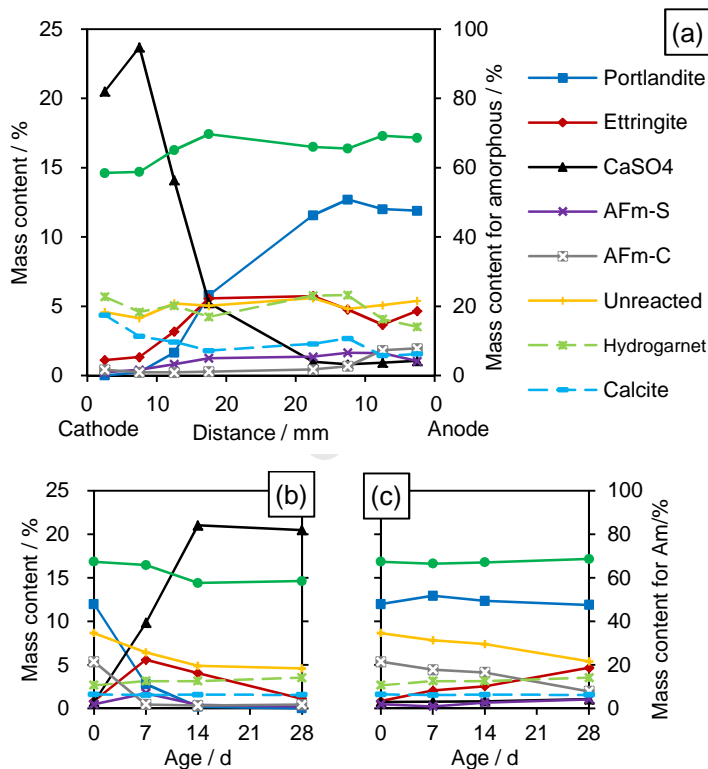


**Fig. 6.** Atom ratio plots of S/Ca against Al/Ca at different depths from the surface after exposures to  $\text{MgSO}_4$ : (a) and (b) the cathode areas exposed to  $\text{MgSO}_4$  for 7 d and 28 d, respectively; (c) the anode areas exposed to  $\text{MgSO}_4$  for 28 d. CH = Portlandite (and C-S-H at a similar position), Ett = Ettringite, Ms = Monosulfate, Hc/Mc = Hemihydrate or monohydrate, Gyp =  $\text{CaSO}_4$ .

### 3.1.2 Mineralogical alteration

In the cement paste near the cathode, the formation of sulfate-bearing products and decomposition of portlandite were observed. After 28 d exposure to  $\text{MgSO}_4$ , the cement paste nearest to the surface (0.5–5 mm) contained almost no portlandite or ettringite, but a large amount of  $\text{CaSO}_4$  (Fig. 7a, see from the left). The  $\text{CaSO}_4$  content was slightly higher at 5–10 mm than that of the surface part, and started to decrease beyond this depth. Portlandite and ettringite were detected beyond the depth of 10 mm, and their contents increased with the depth. In addition to the decomposition of portlandite, the amorphous content in the cement paste near the cathode also showed a reduction. Fig. 7b shows that the formation of ettringite and  $\text{CaSO}_4$  started even before 7 d, during which the decomposition of portlandite had been significant. Between 7–14 d, the formation of  $\text{CaSO}_4$  continued while ettringite started to

decompose. Almost no portlandite could be detected by 14 d, and the  $\text{CaSO}_4$  content remained almost constant afterward. Monocarbonate and hemicarbonate were observed due to the hydration of limestone [56,58]. These products had formed before the exposure to  $\text{MgSO}_4$  but started to decompose after the exposure. Almost no AFm phases remained near the cathode after an exposure time of 7 d (Fig. 7b). Magnesium-bearing products were not observed in XRD, which agrees with the small penetration depth of  $\text{Mg}^{2+}$  shown in Fig. 3 and Fig. 4. However, brucite was observed to form in the cathodic solution, which mingles with other products and forms a thick layer of deposits on the electrode. The deposits collected on the 28th exposure day and tested by XRD suggested a mixture of 40.2% brucite, 41.1% gypsum, 14.5% portlandite, 3.3% anhydrite, and 0.8% calcite.



**Fig. 7.** Mineralogical composition of the specimen exposed to  $\text{MgSO}_4$  obtained by XRD and Rietveld refinement: (a) all the depths after 28 d exposure time; (b) and (c) phase alteration of the 0.5–5 mm area near the cathode and anode, respectively, after different exposure time.  $\text{CaSO}_4$  = anhydrite + bassanite + gypsum, AFm-S = monosulfate, AFm-C = monocarbonate + hemicarbonate, hydrogarnet = katoite + hydrogrossular.

In the anode area, the ettringite content in the 0.5–5 mm area increased slowly with the exposure time, and the

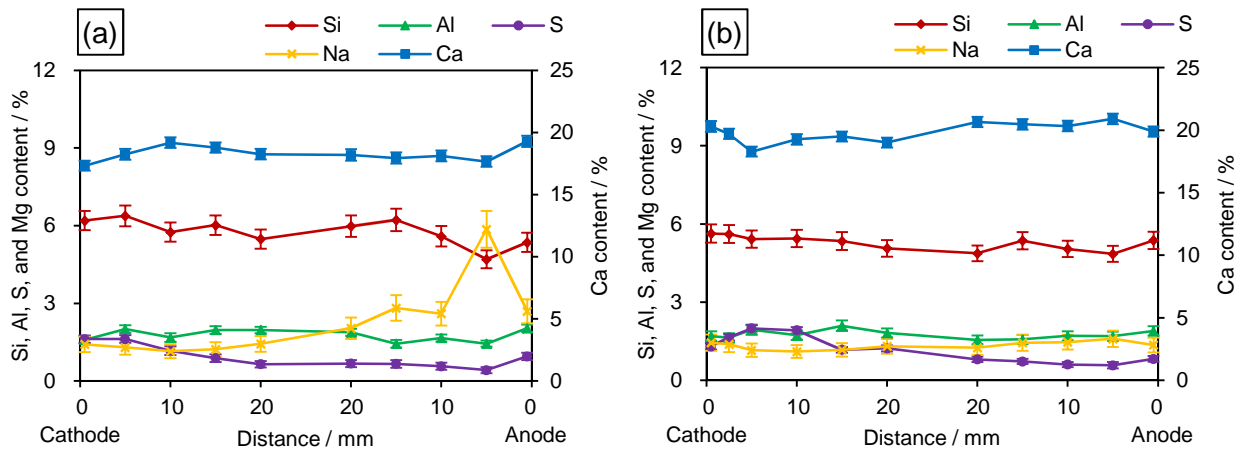
contents of monocarbonate and hemiacarbonate decreased (Fig. 7c). After 28 d, the ettringite content in this area was slightly higher than that of the 5–10 mm area (Fig. 7a, see from the right). No other significant mineralogical alterations could be observed in the 0.5–5 mm area, which also agrees with the SEM observations (Fig. 3, Fig. 5, and Fig. 6c). The XRD analyses did not include the outer surface (~0.5 mm) and thus no Mg-bearing product, e.g., brucite, was detected. No brucite deposits could be found in the anodic solution, either.

The XRD results are also confirmed by TGA, as detailed in Supplementary Data.

### 3.2 Test results of $\text{Na}_2\text{SO}_4$ exposure

#### 3.2.1 Chemical composition and microstructural alterations

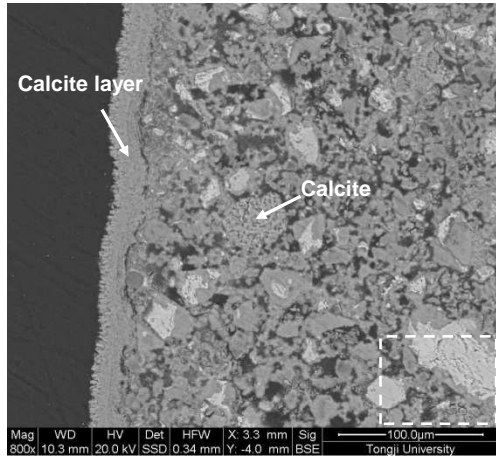
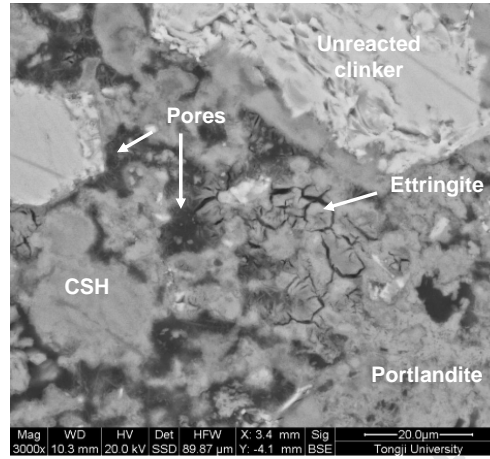
Near the cathode, an exposure to  $\text{Na}_2\text{SO}_4$  in the presence of applied electric fields also induced an increased S content (Fig. 8, see from the left), but to a much lower extent compared with the situation of the  $\text{MgSO}_4$  exposure (Fig. 3). The S content in the 0.5–10 mm area after 28 d exposure to  $\text{Na}_2\text{SO}_4$  (Fig. 8b) was even lower than that of the same area exposed to  $\text{MgSO}_4$  for 7 d (Fig. 3a). Different from the situation of  $\text{MgSO}_4$  exposure, the loss of  $\text{Ca}^{2+}$  in this area could not be clearly observed. After an exposure time of 28 d, the Ca content on the surface even showed a small increase (Fig. 8b). The microstructure of the cement paste after the exposure to  $\text{Na}_2\text{SO}_4$  showed different features compared with that of the  $\text{MgSO}_4$  exposure. The cement paste in the 0–600  $\mu\text{m}$  area was porous (Fig. 9a). Portlandite and large ettringite crystals could be observed (Fig. 9b). A calcite shell covered the surface of the specimen, and calcite could also be found inside the cement paste.



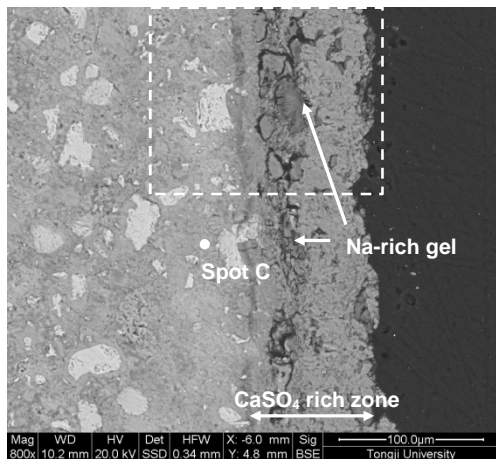
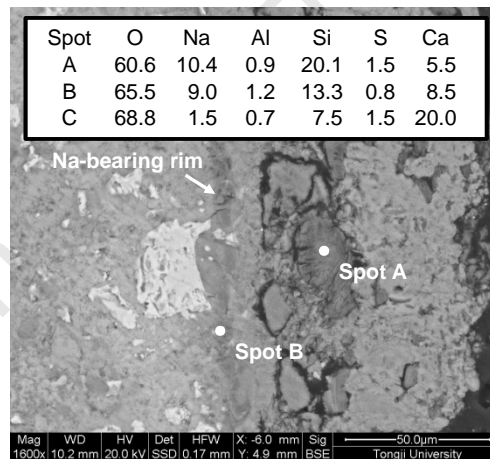
**Fig. 8.** Chemical composition at different distances from the surface (cathode on the left and anode on the right) after exposure to  $\text{Na}_2\text{SO}_4$  for (a) 7 d and (b) 28 d.

The surface area near the anode (0.5 mm) showed slightly higher S content compared with the areas inside the specimen (Fig. 8, see from the right), which is similar to the situation of  $\text{MgSO}_4$  exposure. Different from  $\text{Mg}^{2+}$  whose penetration depth is less than 100  $\mu\text{m}$ ,  $\text{Na}^+$  could penetrate deeper into the specimen from the anode, as indicated by its increased content at a depth of 5–15 mm near the anode in Fig. 8a. There are two possible causes for the Na enrichment: a) a continuous accumulation during seven days, or b) a quick accumulation during the day before testing, after the sulfate solution was just refreshed. When we chose not to refresh the solution on the 27th day, no Na enrichment was observed in the specimen on the 28th day (Fig. 8b). This observation supports the second hypothesis and indicates that the migration of  $\text{Na}^+$  under electric fields was fast. The microstructure of the surface area after  $\text{Na}_2\text{SO}_4$  exposure showed some similar features compared with that of  $\text{MgSO}_4$  exposure. A  $\text{CaSO}_4$ -rich zone also formed (Fig. 10a), and silica gel that is rich in Na can be observed (Spot A of Fig. 10b). Between the  $\text{CaSO}_4$ -rich zone and the cement paste, there is a Na-bearing rim (Spot B of Fig. 10b). Comparing the chemical composition of the rim with that of the Na-rich silica gel, the former owned a slightly lower Na content and a higher Ca content. Next to the  $\text{CaSO}_4$ -rich zone, the Ca/Si ratio of the hydration products was also higher than 1.5. The Ca/Si ratio became stable beyond this depth ( $\sim 100 \mu\text{m}$ ), as also verified in Fig. 8b.



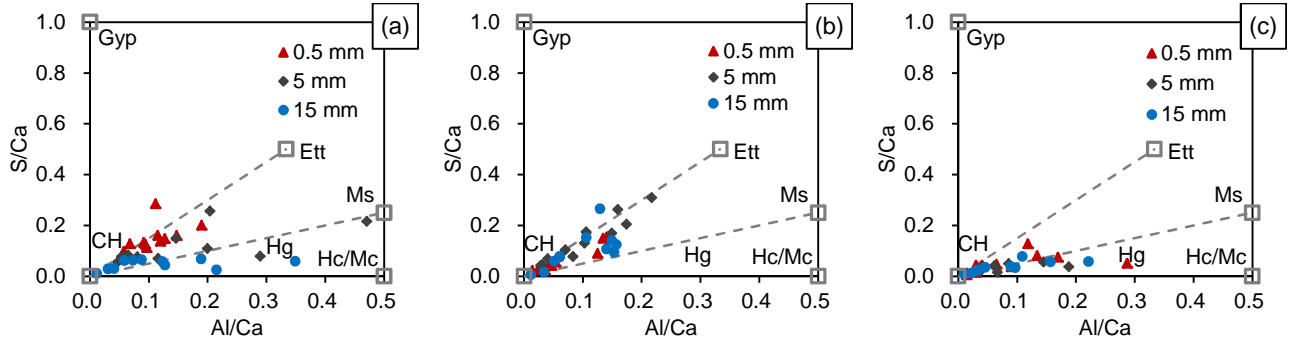
(a) 0–250  $\mu\text{m}$ (b) ~250  $\mu\text{m}$ 

**Fig. 9.** Microstructure of the surface area (0–250  $\mu\text{m}$ ) near the cathode after 28 d exposure to  $\text{Na}_2\text{SO}_4$ : (a) an overview and (b) enlargement of the squared area. Surface on the left.

(a) 0–250  $\mu\text{m}$ (b) 0–125  $\mu\text{m}$ 

**Fig. 10.** Microstructure of the surface area (0–250  $\mu\text{m}$ ) near the anode after 28 d exposure to  $\text{Na}_2\text{SO}_4$ : (a) an overview and (b) enlargement of the squared area. Surface on the right.

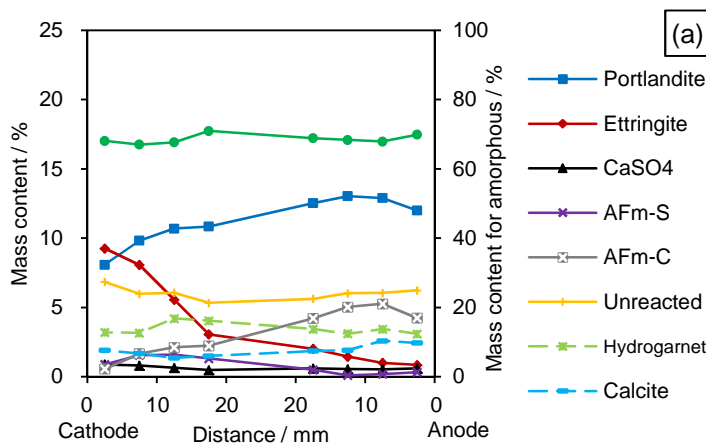
The S/Ca plotted against Al/Ca indicates the presence of ettringite in large amounts at 0.5 mm and 5 mm depths from the cathode when the specimen is exposed to  $\text{Na}_2\text{SO}_4$  for 7 d (Fig. 11a). After an exposure time of 28 d, ettringite was suggested to form at 0.5 mm, 5 mm, and 15 mm depths from the cathode (Fig. 11b), whilst a small amount of ettringite may also be present at the 0.5 mm area from the anode (Fig. 11c).



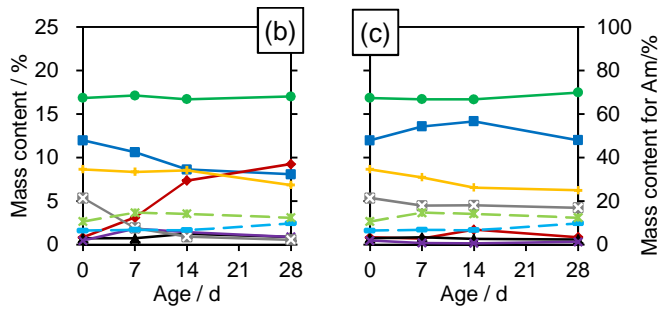
**Fig. 11.** Atom ratio plots of S/Ca against Al/Ca at different depths from the surface after exposures to  $\text{Na}_2\text{SO}_4$ : (a) and (b) the cathode areas exposed to  $\text{Na}_2\text{SO}_4$  for 7 d and 28 d, respectively; (c) the anode areas exposed to  $\text{Na}_2\text{SO}_4$  for 28 d. CH = Portlandite (and C-S-H at a similar position), Ett = Ettringite, Ms = Monosulfate, Hc/Mc = Hemiacarbonate or monocarbonate, Gyp =  $\text{CaSO}_4$ .

### 3.2.2 Mineralogical alteration

When the specimen is exposed to  $\text{Na}_2\text{SO}_4$ ,  $\text{CaSO}_4$  did not form in large amounts near the cathode (e.g., 0.5–20 mm, Fig. 12a, see from the left) even after an exposure time of 28 d. Instead, the ettringite content in this area was high, and it decreased with the distance from the surface. Furthermore, the decomposition of portlandite and AFm (especially monocarbonate and hemiacarbonate) after  $\text{Na}_2\text{SO}_4$  exposure was not as significant as the situations in the  $\text{MgSO}_4$  exposure (comparing Fig. 12a to Fig. 7a). The decomposition of portlandite and AFm, and the formation of ettringite showed a positive relationship with time (Fig. 12b).







**Fig. 12.** Mineralogical composition of the specimen exposed to  $\text{Na}_2\text{SO}_4$  obtained by XRD and Rietveld refinement: (a) all the depths after 28 d exposure time; (b) and (c) phase alteration of the 0.5–5 mm area near the cathode and anode, respectively, after different exposure time.  $\text{CaSO}_4$  = anhydrite + bassanite + gypsum, AFm-S = monosulfate, AFm-C = monocarbonate + hemiacarbonate, hydrogarnet = katoite + hydrogrossular.

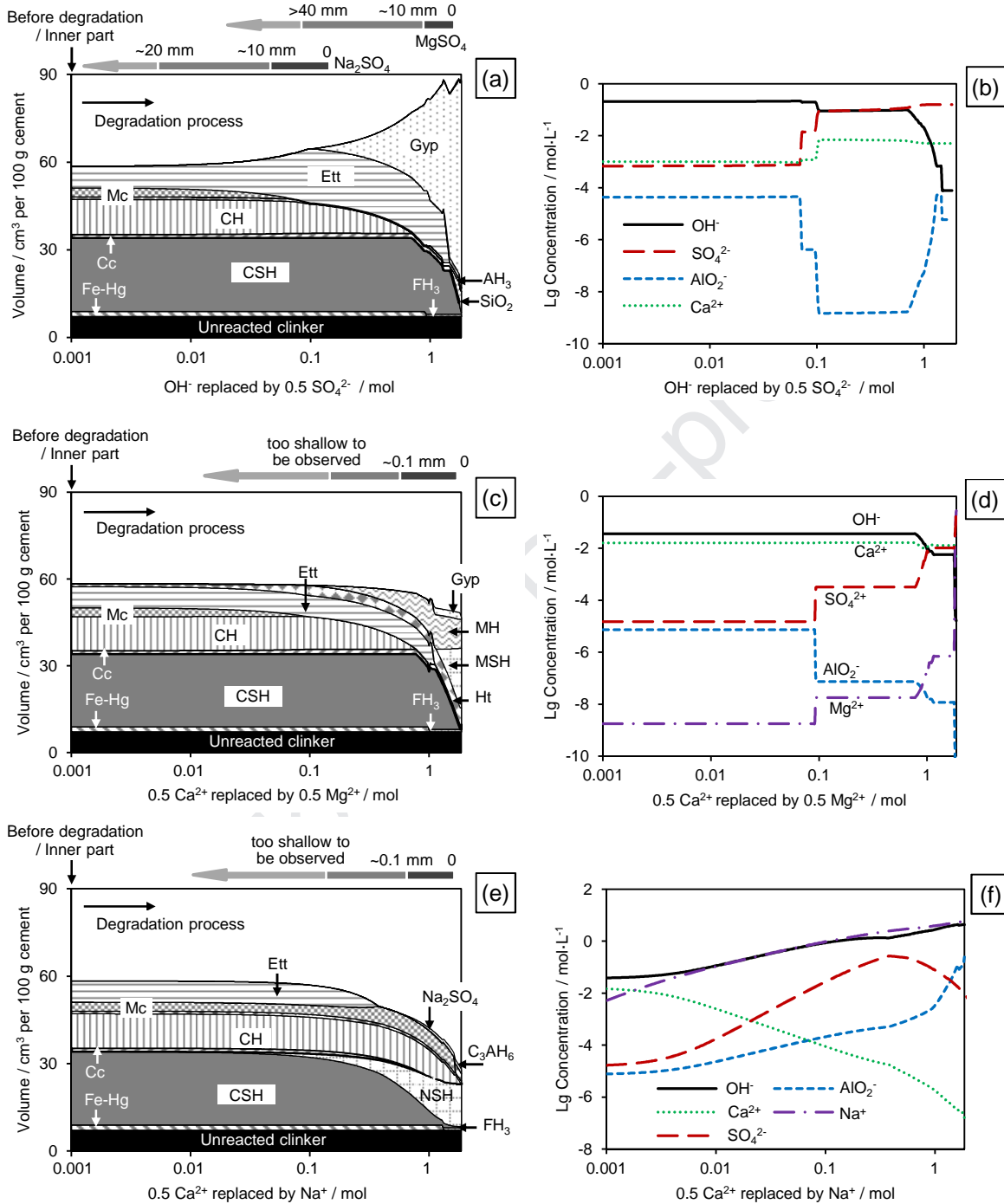
In the surface area near the anode (0.5–5 mm), no significant mineralogical alterations could be observed except for a small increase in the ettringite content and a decrease in the contents of monocarbonate and hemiacarbonate. Similar to the situation of  $\text{MgSO}_4$  exposure, these phenomena are assigned to the effects of  $\text{SO}_4^{2-}$  diffusing from the anodic solution (Fig. 12c). The Na enrichment after 7 d exposure to  $\text{Na}_2\text{SO}_4$  did not form any products that can be detected by XRD. Moreover, no deposits formed in the cathodic and anodic solutions.

### 3.3 Results of thermodynamic modeling

#### 3.3.1 Phase assemblage and pore solution chemistry

The phase assemblage and pore solution chemistry during the simplified electric migration processes were calculated by thermodynamic modeling. For the electric migration near the cathode (Fig. 13a),  $\text{SO}_4^{2-}$  initially stabilized ettringite in favor of monocarbonate. After the complete consumption of monocarbonate, gypsum was stabilized in favor of portlandite and C-S-H. During these processes, the  $\text{SO}_4^{2-}$  concentration in the pore solution showed an increase, whilst the  $\text{OH}^-$  concentration kept decreasing (Fig. 13b). In addition to gypsum, amorphous

SiO<sub>2</sub> and AH<sub>3</sub> were predicted as the stable phases at the last stage of the electric migration process.



**Fig. 13.** Phase assemblage and pore solution chemistry during the simplified electric migration process, calculated by thermodynamic modeling: (a) and (b) the degradation process near the cathode; (c) and (d) the degradation process near the anode after MgSO<sub>4</sub> exposure; (e) and (f) the degradation process near the anode after Na<sub>2</sub>SO<sub>4</sub> exposure. The horizontal-axis can be interpreted into the alteration in a certain position with time or the distribution of products after a certain exposure time. A logarithmic axis is used for better comparison with thermodynamic modeling studies on diffusion-induced sulfate attacks [1,2,11,14-16]. The arrows above the figures illustrate the

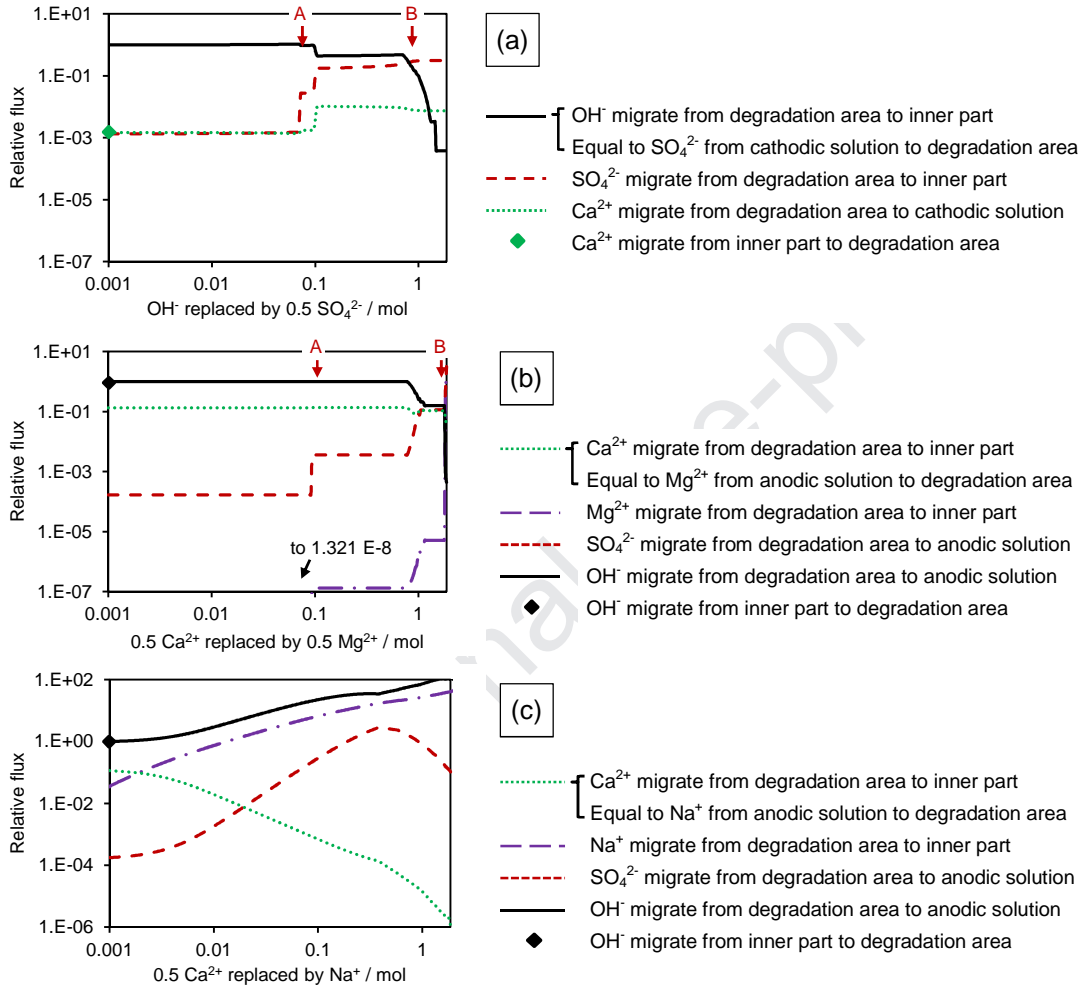
approximate distribution of hydration products after 28 d exposure time (experimental results). CH = portlandite, Ett = ettringite, Mc = monocarbonate, Gyp = gypsum, Cc = calcite, Fe-Hg =  $C_3FS_{0.84}H_{4.32}$  and/or  $C_3F_{1.34}H_{3.32}$ , Ht = hydrotalcite, MH = brucite, MSH = M-S-H gel, and NSH = the Na end-member,  $[(NaOH)_{2.5}SiO_2H_2O]_{0.2}$  included in the CSHQ model.

In the anode area exposed to  $MgSO_4$  (Fig. 13c), the incorporated  $Mg^{2+}$  stabilized hydrotalcite and ettringite in favor of monocarbonate at an initial stage. Brucite formed when all the monocarbonate was consumed, during which portlandite decomposed. At the last stage of the electric migration process, M-S-H and gypsum were stabilized in favor of C-S-H and ettringite, respectively. In contrast, exposure to  $Na_2SO_4$  induced continuous Na uptake in the C-S-H (Fig. 13e). By separating the Na end-member from the C-S-H phase in the CSHQ model, the Na uptake can be clearly observed. Portlandite kept stable until the depletion of C-S-H. Ettringite and monocarbonate were predicted to destabilize during the electric migration process.

### 3.3.2 Migration of ionic species

The simplified electric migration process assumes that the phase changes are restricted in a certain “degradation area” on the surface of a specimen (see Fig. 1b). The relative flux of a certain ion is thus interpreted as its migration rate from the degradation area towards a certain direction which depends on the ion’s polarity. In the degradation area near the cathode, when degradation initiated  $OH^-$  had the highest relative flux among all the ionic species (Fig. 14a). This phenomenon demonstrates that the replacement of  $OH^-$  by  $SO_4^{2-}$  from the external solution was the most significant process that occurred. The relative flux of  $SO_4^{2-}$  turned higher when all the monocarbonate decomposed (point A), and exceeded that of  $OH^-$  when portlandite started to decompose and gypsum started to form (point B). From this point on,  $SO_4^{2-}$  would take the place of  $OH^-$  as the main ionic species that migrated towards the inner part of the specimen. The replacement of  $OH^-$  by  $SO_4^{2-}$  in the degradation area, represented by the relative flux of  $OH^-$ ,

thus slowed down, and the degradation remained stable at point B. During the degradation process, the relative flux of  $\text{Ca}^{2+}$  showed an increase (point A), indicating that the loss of  $\text{Ca}^{2+}$  from the degradation area to the external solution will be faster than the compensation from the inner part of the specimen.



**Fig. 14.** The relative flux of ionic species: (a) the cathode area; (b) and (c) the anode area exposed to  $\text{MgSO}_4$  and  $\text{Na}_2\text{SO}_4$ , respectively. The cations and anions migrate in different directions, see Fig. 1b. Certain ionic species are compensated by those from the inner part of the specimen, and the compensation rate is marked by a diamond (provided that the ionic strength in the inner part of the specimen remains stable). The square bracket indicates the ionic species in the external solution is transported into the degradation area with the same relative flux to certain ions based on the assumption of charge balance.

For the anode area that is exposed to  $\text{MgSO}_4$  (Fig. 14b), the relative flux of  $\text{OH}^-$  remained the highest for a long period during the electric migration process. This phenomenon indicates that the outflow of  $\text{OH}^-$  to the external

solution, as well as the compensation of  $\text{OH}^-$  from the inner part, was faster than the migration of all the other ions. The relative flux of  $\text{Ca}^{2+}$  was at a lower level, indicating that the  $\text{Ca}^{2+}$  in the degradation area would be replaced by the  $\text{Mg}^{2+}$  from the external solution at a slow rate. The relative flux of  $\text{Mg}^{2+}$  was even lower than that of  $\text{Ca}^{2+}$ , indicating that the  $\text{Mg}^{2+}$  in the degradation area could hardly migrate towards the inner part. The relative flux of  $\text{SO}_4^{2-}$  showed an increase during the electric migration process (point A). This phenomenon will theoretically lead to a loss of  $\text{SO}_4^{2-}$  in the degradation area, but this effect may be offset by the diffusion of  $\text{SO}_4^{2-}$  from the external solution in the experiments. At the last degradation stage (point B), the relative flux of  $\text{Mg}^{2+}$  increased sharply, the penetration of  $\text{Mg}^{2+}$  started, and the entire electric migration process repeated stepwise in a slightly deeper area from the surface. The degradation phase assemblage thus kept stable at point B.

When the anode was exposed to  $\text{Na}_2\text{SO}_4$  (Fig. 14c), the relative flux of  $\text{OH}^-$  remained the highest among all the ionic species during the entire electric migration process. The relative flux of  $\text{Na}^+$  was lower than that of  $\text{OH}^-$ , but much higher than that of  $\text{Mg}^{2+}$  in the specimen exposed to  $\text{MgSO}_4$ . This phenomenon indicates that  $\text{Na}^+$  will migrate into the cement paste at a much higher rate than  $\text{Mg}^{2+}$ . The relative flux of  $\text{Ca}^{2+}$  was at a low level during the electric migration process, suggesting that the replacement of  $\text{Ca}^{2+}$  by  $\text{Na}^+$  in the degradation area will be slow, and most  $\text{Na}^+$  will migrate towards the inner part of the specimen.

## 4 Discussions

### 4.1 Comparison between test results and thermodynamic modeling

The mineralogical alterations that occurred near the cathode agreed well with the thermodynamic modeling, as indicated by the arrows in Fig. 13a. After exposure to  $\text{MgSO}_4$  for 28 d,  $\text{CaSO}_4$  was observed to form in the outer

part of the specimen (0–10 mm) where almost no portlandite or ettringite existed (XRD, Fig. 7a). The silica-alumina gel found on the surface of the specimen (SEM, Fig. 4b) corresponds to the amorphous  $\text{SiO}_2$  and  $\text{AH}_3$  in the thermodynamic modeling [14], and the reduction of the amorphous content coincides with the decomposition of C-S-H predicted by thermodynamic modeling. Deeper inside the specimen (10–40 mm), the content of  $\text{CaSO}_4$  gradually decreased, while those of portlandite and ettringite increased (XRD, Fig. 7a). In comparison, the specimen exposed to  $\text{Na}_2\text{SO}_4$  for 28 d remained at an earlier degradation stage, when  $\text{CaSO}_4$  did not form in large amounts. The different degradation stages between the specimens also coincide with the amount of S that has been transported from the cathodic solution into the cement paste (EDS, cf. Fig. 3b and Fig. 8b).

The mineralogical alterations occurred in a shallow depth ( $\sim 0.1$  mm) in the cement paste near the anode, but had proceeded to the last degradation stage in both exposure conditions when comparing the test results with the thermodynamic modeling (Fig. 13c and 13e). For the  $\text{MgSO}_4$  exposure, the presence of Mg-containing products (brucite and M-S-H, SEM, Fig. 5) agrees with the thermodynamic calculation, while for the  $\text{Na}_2\text{SO}_4$  exposure, the Na-rich silica gel (Fig. 10) coincides with the Na uptake by C-S-H in the thermodynamic modeling. A  $\text{CaSO}_4$ -rich zone was observed in both exposure conditions no matter if  $\text{CaSO}_4$  is predicted to be stable. The diffusion of  $\text{SO}_4^{2-}$  from the anodic solution is believed to be responsible for this phenomenon (see also Fig. 1b).

#### 4.2 Migration behavior of $\text{Mg}^{2+}$ , $\text{Na}^+$ , and $\text{SO}_4^{2-}$

The degradation near the cathode and anode proceeded in different ways. Near the cathode, the anions from the external solution (mainly  $\text{SO}_4^{2-}$ ) migrated into a deep area, and the mineralogical alteration proceeded gradually following the prediction of thermodynamic modeling. For the anode area exposed to  $\text{MgSO}_4$ , the incorporation of

$\text{Mg}^{2+}$  occurred in a shallow area with the mineralogical alteration proceeding directly to the late degradation stage. In contrast,  $\text{Na}^+$  could penetrate deep into the cement paste, but the mineralogical alteration occurred also in a shallow area. The different migration behaviors of the ionic species can be explained by the relative flux which is obtained from the solution chemistry calculated by thermodynamic modeling.

According to section 3.3.2, an ion's capability for migration under electric fields depends on its relative flux, while its accumulation rate in a degradation area depends on the relative flux of the other ion that is being replaced. For the degradation process near the cathode, the high relative flux of  $\text{OH}^-$  suggests a fast accumulation of  $\text{SO}_4^{2-}$  at an early degradation stage, whilst the increased relative flux of  $\text{SO}_4^{2-}$  indicates an accelerated migration rate towards the inner part of the specimen (Fig. 14a). In contrast, for the degradation process near the anode, the smaller relative flux of  $\text{Ca}^{2+}$  than that of  $\text{OH}^-$  suggests a slower accumulation rate of the cations ( $\text{Mg}^{2+}$  or  $\text{Na}^+$ ) than the outflow of  $\text{OH}^-$  (Fig. 14b and 14c), which coincides with the shallow depth of  $\text{Mg}^{2+}$  and  $\text{Na}^+$  incorporation (Fig. 5 and 10). The strengths of  $\text{Na}^+$  and  $\text{Mg}^{2+}$  in the pore solution (Fig. 13d and 13f) and thus their relative fluxes (Fig. 14b and 14c) were different after the chemical reactions. As a result,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  showed different migration behaviors (also compare Fig. 3 and Fig. 8). The different migration behaviors of  $\text{SO}_4^{2-}$  and  $\text{Mg}^{2+}$  were once realized when using thermodynamic modeling to study the magnesium sulfate attack simply caused by diffusion [15,16]. It was reported that the penetration depth of  $\text{Mg}^{2+}$  is usually overestimated compared to that of  $\text{SO}_4^{2-}$ . According to the findings in this paper, this can be explained by the low concentration of  $\text{Mg}^{2+}$  in the pore solution and thus its slower diffusion rate than  $\text{SO}_4^{2-}$ .

The electric migration of the cations and anions can also influence each other because both processes carry electric charges. The experiment was conducted under a constant electric current. The same amount of charges should pass

through the specimen during the same period of time, no matter the specimen was exposed to  $\text{MgSO}_4$  or  $\text{Na}_2\text{SO}_4$ . In the cathode side,  $\text{SO}_4^{2-}$  was migrated from the cathodic solution into the cement paste. It penetrated through the specimen together with  $\text{OH}^-$  (and other anions) in the pore solution. In the meanwhile, the  $\text{Ca}^{2+}$  in the pore solution were released into the cathodic solution, but this process carried less electric charges due to the low relative flux of  $\text{Ca}^{2+}$  than the anions. In the anode side exposed to  $\text{MgSO}_4$ , the migration of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  towards the inner part of the specimen were at low rates. The electric charges were mainly carried by the  $\text{OH}^-$  migrating from the inner part of the specimen towards the anode side, and finally into the anodic solution. In contrast, in the case of  $\text{Na}_2\text{SO}_4$  exposure,  $\text{Na}^+$  could penetrate through the specimen much more easily than  $\text{Mg}^{2+}$ , and its electric migration can carry much more electric charges. Under such circumstance, the electric migration of anions ( $\text{SO}_4^{2-}$  and  $\text{OH}^-$ ) will carry fewer charges, and thus the sulfate ingress will proceed on a lower rate compared with the situation of  $\text{MgSO}_4$  exposure. Similar results were also reported in [41] but no convincing explanations were ever given.

#### *4.3 Comparison with the sulfate attack induced by diffusion*

To compare with the sulfate attack in the absence of electric field (induced by diffusion), the main mineralogical alterations of Portland cement (Type I with limestone addition) mortars under  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  attacks [11,15] and the results obtained in this paper are summarized in Table 3. This section focuses on the sulfate ingress and decalcification near the cathode because a) these effects influenced a much wider area than the phase alterations near the anode and b) similar processes also occur in the diffusion-induced sulfate attacks.

In the diffusion-induced  $\text{Na}_2\text{SO}_4$  attack, the ingress of sulfate leads to the formation of ettringite followed by that of gypsum. In the  $\text{MgSO}_4$  attack, nevertheless,  $\text{Mg}^{2+}$  reacts with  $\text{OH}^-$  in the pore solution to form brucite, reducing the



solution pH to ~10.5 and inducing the decomposition of ettringite [60,61]. The decomposition of ettringite was also observed here when the specimen is exposed to  $\text{MgSO}_4$ . This phenomenon can be also attributed to a reduction of the pore solution alkalinity, but the presence of  $\text{Mg}^{2+}$  may not be a decisive factor considering the shallow depth of the Mg transportation (Fig. 3b). During the sulfate ingress, the  $\text{OH}^-$  in the pore solution near the cathode was theoretically transported towards the inner part of the specimen by the electric field. This process is used as a basic assumption in the thermodynamic modeling and it is shown that the decomposition of ettringite and the formation of gypsum occurred simultaneously with the decrease of  $\text{OH}^-$  concentration in the pore solution (Fig. 13b). According to the test results, the presence of  $\text{CaSO}_4$  in the cement paste near the cathode (Fig. 7) indicates sufficient ionic strengths of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  for the stabilization of ettringite [2,14,15], whilst the Al content in the hydration products did not show any apparent reduction (Fig. 3). It can be thus inferred that the decomposition of ettringite was most probably caused by a neutralization process as assumed in the thermodynamic modeling. A similar neutralization process was also observed when accelerating thaumasite sulfate attacks by applied electric fields, and this process was also believed to destabilize ettringite according to [62].

**Table 3** Mineralogical alterations of sulfate attacks induced by electric migration (this paper) and diffusion (obtained from [11,15]).

Process	Formation phase	Decomposition phase
Electric migration, cathode	Ettringite $\rightarrow$ Gypsum + Si-Al gel	Monocarbonate $\rightarrow$ Portlandite $\rightarrow$ Ettringite $\rightarrow$ C-S-H
Electric migration, anode, $\text{Na}_2\text{SO}_4$ <sup>1</sup>	Na-rich silica gel + Gypsum (surface)	Not clearly observed in the experiments
Electric migration, anode, $\text{MgSO}_4$ <sup>1</sup>	M-S-H + Brucite + Gypsum (surface)	Not clearly observed in the experiments
Diffusion, $\text{Na}_2\text{SO}_4$	Ettringite $\rightarrow$ Gypsum <sup>2</sup>	Monocarbonate $\rightarrow$ Portlandite $\rightarrow$ C-S-H
Diffusion, $\text{MgSO}_4$	Ettringite $\rightarrow$ Brucite $\rightarrow$ Gypsum $\rightarrow$ M-S-H	Monocarbonate $\rightarrow$ Portlandite $\rightarrow$ Ettringite $\rightarrow$ C-S-H

<sup>1</sup> Only the experimentally verified phases are listed in the formation column. The decomposition order of the hydration products was not clearly observed in the experiments and thus is not listed in the decomposition column.

<sup>2</sup> Gypsum forms when the  $\text{Na}_2\text{SO}_4$  concentration is high, e.g., 44 g/L in [11].

In the diffusion-induced sulfate attack, decalcification usually occurs on the surface of a specimen and is

characterized by the decomposition of portlandite and the decrease of the Ca/Si in C-S-H [1,63,64]. In the presence of bicarbonate, gypsum will be the only stable sulfate-bearing product in the decalcification zone, and amorphous  $\text{SiO}_2$  and  $\text{AH}_3$  are predicted as the stable phases by thermodynamic calculation [14,15]. Similar results are also obtained in this paper (e.g., the  $\text{MgSO}_4$  exposure for 28 d), but a different mechanism can be proposed when the decalcification is induced by electric migration. According to the thermodynamic modeling, the relative flux of  $\text{Ca}^{2+}$  migrating from the cement paste to the external solution accelerated during the degradation process (Fig. 14a). This suggests that the loss of  $\text{Ca}^{2+}$  in the cement paste near the cathode cannot be fully compensated by the  $\text{Ca}^{2+}$  migrating from the inner part of the specimen. The  $\text{Ca}^{2+}$  content near the cathode decreased (Fig. 3 and 8), thus leading to the decalcification and the decomposition of hydration products. The decalcification near the cathode may also have accelerated the transportation of  $\text{Mg}^{2+}$  through diffusion (Fig. 3b and Fig. 4c), as also reported in concrete exposed to field conditions [65,66]. But the presence of Mg is not likely to be the cause of decalcification here considering the depths of these processes (Fig. 4, Area III showed decalcification but very small Mg content).

The Ca/Si ratio (cf. Fig. 3 and Fig. 8) and portlandite content (cf. Fig. 7 and Fig. 12) indicate that the specimen exposed to  $\text{MgSO}_4$  had a higher degree of decalcification than that exposed to  $\text{Na}_2\text{SO}_4$ . On one hand, the decalcification process is induced by the electric migration of  $\text{Ca}^{2+}$ . It will be impacted by the electric migration of other cations ( $\text{Mg}^{2+}$  and  $\text{Na}^+$ ), and thus the degree of decalcification coincides with that of sulfate ingress. On the other hand, this process is also impacted by alterations of ionic strength in the external sulfate solution near the cathode, which is a potential drawback of the test setup. When the specimen was exposed to  $\text{Na}_2\text{SO}_4$ ,  $\text{H}^+$  in the solution would be reduced to  $\text{H}_2$  on the cathode, thus producing  $\text{OH}^-$  in the solution [40] (Fig. 1b). Both  $\text{OH}^-$  and  $\text{SO}_4^{2-}$  could carry electric charges and would migrate into the cement paste near the cathode. The  $\text{OH}^-$  migrating towards the specimen may react with the  $\text{Ca}^{2+}$  that was driven out of the paste to form a surface layer consisting of

portlandite. When the  $\text{Na}_2\text{SO}_4$  solution was refreshed (every 3 d), the portlandite might carbonate, forming a calcite layer as observed in the SEM (Fig. 9). This hypothesis explains the slight increase of the Ca content near the cathode area in Fig. 8b and a better protection from carbonation may help with its verification. In contrast, in the  $\text{MgSO}_4$  solution, the  $\text{OH}^-$  produced on the cathode precipitated with  $\text{Mg}^{2+}$  to form brucite in the external solution (section 3.1.2). Owing to the precipitation of  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$  was the main anion migrating into the specimen, and thus  $\text{CaSO}_4$  formed on the surface of the specimen instead of calcite (Fig. 4b).

#### 4.4 Comparison with coupled reactive-transport modeling

As stated in [1], the coupled reactive-transport modeling and the pure thermodynamic modeling presented comparable results in revealing the phase alterations of a diffusion-induced sulfate attack. The pure thermodynamic modeling is usually easy to use and provides fast results, but the results do not correspond directly with the real exposure time or the depth from the exposure surface. In comparison, coupled reactive-transport modeling provides the information of time and depth, but the accuracy depends strongly on the preciseness of models (e.g., transportation equation, fluid transport, charge balance) [21,67] and parameters (e.g., diffusion coefficient) [1]. This paper proposed a simplified approach for the pure thermodynamic modeling study of electric-migration-induced sulfate attacks. Such an approach focuses on the chemical and mineralogical aspects and clarifies alterations of the hydration products. Although the real distribution of the products was not presented, this information can be reflected by the relative flux that is proposed here. The advantages and validity of this approach will be further demonstrated in an upcoming paper investigating the effect of supplementary cementitious materials in the same situation.

The thermodynamic modeling calculation conducted in this paper is based on the assumption that the kinetics of the chemical reactions is much faster than the transportation of ionic species, and that the hydration system is close to an equilibrium state. As reviewed in [68], this assumption is usually valid in most practical cases involving the diffusion of ions in saturated systems, and thus it is widely accepted by the existing pure thermodynamic modeling studies [1,2,11,14-16]. In contrast, electric migration usually induces a quicker ionic motion, and thus the equilibrium state is more difficult to be reached [24]. When studying the electric migration of chloride by coupled reactive-transport models, an equilibrium state was assumed in [69] and the test results agree well with the modeling. The results of this paper also show that the migration behavior of ionic species coincides with the solution chemistry (relative flux) under the assumption of equilibrium. It can be thus inferred that the real solution chemistry in the hydrated cement paste is similar to that under the equilibrium state and that the equilibrium assumption is likely to be valid in the case of electric migration.

The electric migration behavior of ionic species can be represented by the relative flux, which depends on the ion's diffusion coefficient and concentration in the pore solution. The diffusion coefficients of different ions are usually at the same order of magnitude, as shown in Table 2. However, their concentrations can span several orders of magnitude, which induces wide differences in the relative fluxes and is responsible for the different migration behavior of  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$  under applied electric fields. In this respect, for a reactive-transport process, it is sometimes acceptable to suppose the same diffusion coefficient for different ionic species, as was done in [16,70,71]. Nevertheless, the effect of chemical reactions on the concentration and thus the migration of ionic species should be carefully considered.

#### *4.5 Comparison with real-life situations*

683

684 This setup simulates both processes when electric current flows into and out of the cement-based materials  
685 simultaneously. In contrast, in the case of DC stray current, these two processes occur separately. The electric  
686 current enters the concrete at a certain location, goes through the reinforcement, and then flows out of the concrete  
687 at another location [29]. The ionic exchange between the external environment and cement-based materials induced  
688 by the inflow and outflow of electric current can be represented by the anode area and cathode area in this setup,  
689 respectively, but the behavior of the reinforcements, e.g., anodic corrosion or hydrogen evolution, is not simulated.  
690 Moreover, this paper focused on the chemical and mineralogical aspects of sulfate attacks and thus the physical and  
691 microstructural aspects, including expansion and cracking, were not investigated. During the electric migration  
692 tests, the specimens did not show significant cracking, which agrees with the focus of this paper but may possibly  
693 differ from the real situation. The test results (Fig. 7) and thermodynamic modeling (Fig. 13a) both indicate the  
694 decomposition of ettringite at the late degradation stage, probably suggesting the absence of expansion at that stage.  
695 However, thermodynamic modeling predicted an increased volume of hydration products near the cathode, which  
696 may yet cause expansion. Based on the results of this paper, it is difficult to determine whether expansion and  
697 cracking will occur under such circumstances.

698

699 The concentration of ions in the external solution will change with time, and this will be the other difference  
700 between the test setup and the real-life situation. Although the concentration of the sulfate solution theoretically  
701 remains above  $\sim 0.34$  mol/L due to the 3-day periodically refreshment (see section 2.2 and Supplementary Data), it  
702 seems that the alterations of the ionic strength in the external sulfate solution have still impact the products formed  
703 on the surface of the specimens (see section 4.3). Increasing the volume of the external solutions and shortening the  
704 refreshing cycle can be solutions to this problem.

The test setup used here has been proposed for the purpose of laboratory acceleration tests [39-41]. The discussion in section 4.3 demonstrates that the electric migration of ionic species near the cathode not only induce the ingress of sulfate, but also cause a neutralization process in the pore solution and a decalcification process (see also Table 3). These effects should be considered when interpreting the mineralogical alterations obtained by such test setups, especially when a)  $\text{MgSO}_4$  attack is investigated and the degradation proceeds to the late-stage quickly and b) a long exposure time is investigated in the case of  $\text{Na}_2\text{SO}_4$  attack and the degradation may proceed to a later stage compared with that in this paper. After an exposure time of 28 d,  $\text{SO}_4^{2-}$  from the cathodic solution had penetrated through most of the specimen and even influenced the area that is 5–10 mm deep from the anode, as indicated by the distribution of hydration products (Fig. 7 and Fig. 12). Specimens with greater height are thus recommended for such tests, especially in the case of long duration (e.g., > 28 d exposure time), in order that the real penetration depth of  $\text{SO}_4^{2-}$  can be accurately identified from an uncontaminated area.

In addition to the situations mentioned above, we believe that the simplified approach for the thermodynamic modeling study proposed in this paper can be more broadly applied in investigating the behavior of cement-based materials under applied electric fields. Future studies may involve the use of this approach in accelerated electrochemical leaching tests [37,38], other types of chemical attacks, and in concrete technologies involving electrochemical methods (e.g., chloride extraction, realkalinization, and electrochemical deposit [32-34]).

## 5 Conclusions

When an electric current flows out of a Portland cement paste (in the cathode area of the specimen), the electric

migration of ionic species induced the ingress of sulfate from the external solution. Ettringite formed at the initial stage but decomposed to form gypsum at a later stage. Thermodynamic modeling indicates that the alkalinity of the pore solution decreased during this process, which is most probably responsible for the decomposition of ettringite. In addition to the sulfate ingress, decalcification also occurred in this area, which is characterized by the decomposition of portlandite followed by that of C-S-H. When the specimen was exposed to  $\text{MgSO}_4$ , the sulfate ingress and decalcification proceeded to a later stage and occurred in a deeper area compared with the specimen exposed to  $\text{Na}_2\text{SO}_4$ .

Near the anode, electric current flows into the cement paste, and the electric charges were mainly carried by the electric migration of  $\text{OH}^-$  from the pore solution towards the external solution. The  $\text{Ca}^{2+}$  originally in the pore solution migrated towards the inner part of the specimen at a much lower rate than that of  $\text{OH}^-$ , and thus the incorporation of the cations from the external solution ( $\text{Mg}^{2+}$  or  $\text{Na}^+$ ) was slow. The incorporation of  $\text{Mg}^{2+}$  formed brucite and M-S-H-like products. Thermodynamic modeling indicates that this process induced a low  $\text{Mg}^{2+}$  concentration in the pore solution, and thus  $\text{Mg}^{2+}$  would not effectively migrate into the inner part of the specimen. In contrast, the incorporation of  $\text{Na}^+$  formed Na-rich silica gel, during which the  $\text{Na}^+$  concentration in the pore solution was much higher. As a result,  $\text{Na}^+$  showed a better capability of migration and can penetrate through the cement paste easily. Since both cations and anions can carry electric charges, the different migration behaviors of  $\text{Mg}^{2+}$  and  $\text{Na}^+$  are attributed to inducing the different degrees of sulfate ingress near the cathode.

A simplified approach based on thermodynamic modeling and the ionic transportation equation were newly proposed to provide insights into the degradation processes of the sulfate attacks that are induced by electric migration. In addition to calculating the degradation phase assemblage, the migration behavior of ionic species

under electric fields can be represented by the relative flux. We believe this approach can be more broadly applied to predict the behavior of cement-based materials under electric fields.

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## Appendix A. Supplementary Data

- 1 Estimating the concentration range of the sulfate solution
- 2 Rietveld refinement
- 3 Input recipes for thermodynamic modeling
- 4 Mineralogical alterations of cement paste tested by TGA

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916

**Table 1** Chemical and mineralogical compositions of the Portland cement (wt. %).

Chemical composition		Mineralogical composition	
Na <sub>2</sub> O	0.04	C <sub>3</sub> S	58.32
MgO	0.76	C <sub>2</sub> S	11.64
Al <sub>2</sub> O <sub>3</sub>	4.55	C <sub>3</sub> A	3.96
SiO	20.8	C <sub>4</sub> AF	8.03
P <sub>2</sub> O <sub>5</sub>	0.11	Calcite	4.58
SO <sub>3</sub>	2.92	Anhydrite	0.76
K <sub>2</sub> O	0.74	Bassanite	3.67
CaO	64.8	Gypsum	0.01
TiO <sub>2</sub>	0.23	Lime	0.35
Cr <sub>2</sub> O <sub>3</sub>	0.02	Portlandite	0.58
MnO	0.11	CF <sub>2</sub>	1.53
Fe <sub>2</sub> O <sub>3</sub>	3.27	Goergeyite	3.30
CuO	0.02	Perovskite	1.79
ZnO	0.05	Periclase	0.85
SrO	0.03	Dolomite	0.13
LOI	2.58	Quartz	0.21



**Table 2** Concentration of ions in the pore solution before degradation and diffusion coefficient in free water ( $D_i^0$ ).

	Concentration mol/L	Diffusion coefficient $10^{-9} \text{ m}^2/\text{s}$	Direction
$\text{OH}^-$	$2.05 \times 10^{-1}$	5.273	Cathode $\rightarrow$ inner part $\rightarrow$ anode $\rightarrow$ anodic solution
$\text{SO}_4^{2-}$	$6.79 \times 10^{-4}$	1.065	
$\text{AlO}_2^-$	$4.25 \times 10^{-5}$	n.a. <sup>1</sup>	
$\text{SiO}_3^{2-}$	$9.94 \times 10^{-6}$	n.a. <sup>1</sup>	
$\text{CO}_3^{2-}$	$4.66 \times 10^{-5}$	n.a. <sup>1</sup>	
$\text{HCO}_3^-$	$2.27 \times 10^{-8}$	1.185	Anode $\rightarrow$ inner part $\rightarrow$ cathode $\rightarrow$ cathodic solution
$\text{Ca}^{2+}$	$1.01 \times 10^{-3}$	0.792	
$\text{Ca(OH)}^+$	$9.09 \times 10^{-4}$	n.a. <sup>1</sup>	
$\text{Mg}^{2+}$	$1.11 \times 10^{-10}$	0.706	
$\text{Na}^+$	$2.34 \times 10^{-3}$	1.334	
$\text{K}^+$	$2.01 \times 10^{-1}$	1.957	

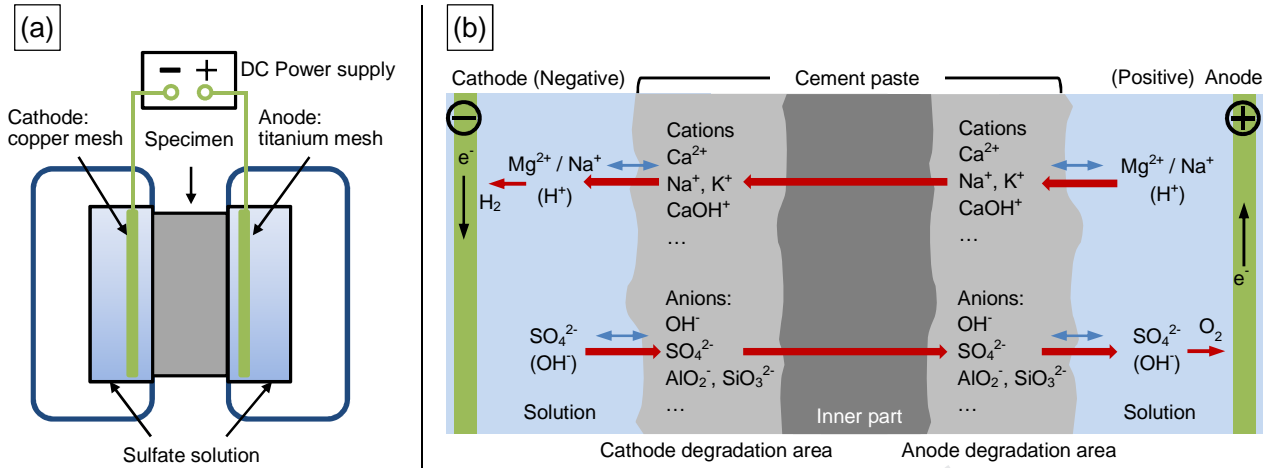
<sup>1</sup> Not available in [49].

**Table 3** Mineralogical alterations of sulfate attacks induced by electric migration (this paper) and diffusion (obtained from [11,15]).

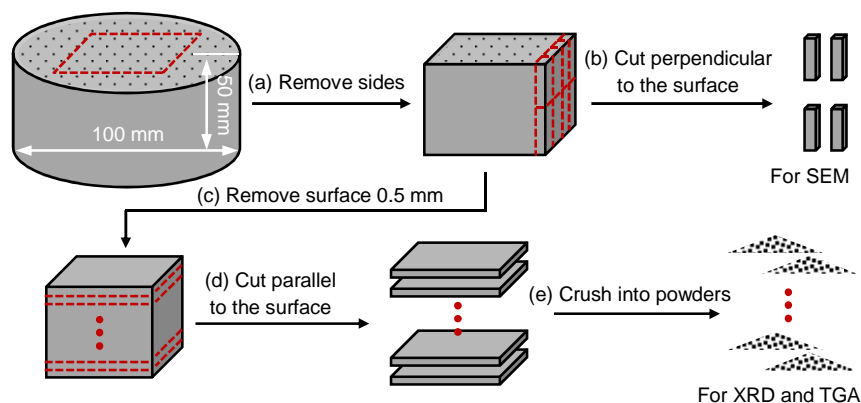
Process	Formation phase	Decomposition phase
Electric migration, cathode	Ettringite → Gypsum + Si-Al gel	Monocarbonate → Portlandite → Ettringite → C-S-H
Electric migration, anode, Na <sub>2</sub> SO <sub>4</sub> <sup>1</sup>	Na-rich silica gel + Gypsum (surface)	Not clearly observed in the experiments
Electric migration, anode, MgSO <sub>4</sub> <sup>1</sup>	M-S-H + Brucite + Gypsum (surface)	Not clearly observed in the experiments
Diffusion, Na <sub>2</sub> SO <sub>4</sub>	Ettringite → Gypsum <sup>2</sup>	Monocarbonate → Portlandite → C-S-H
Diffusion, MgSO <sub>4</sub>	Ettringite → Brucite → Gypsum → M-S-H	Monocarbonate → Portlandite → Ettringite → C-S-H

<sup>1</sup> Only the experimentally verified phases are listed in the formation column. The decomposition order of the hydration products was not clearly observed in the experiments and thus is not listed in the decomposition column.

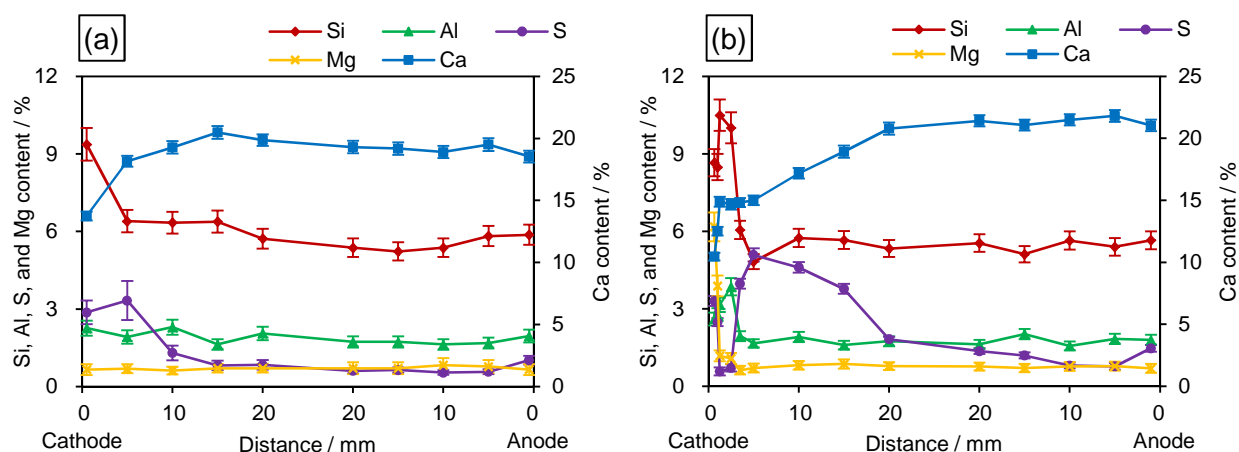
<sup>2</sup> Gypsum forms when the Na<sub>2</sub>SO<sub>4</sub> concentration is high, e.g., 44 g/L in [11].



**Fig. 1.** Test setup to apply electric fields: (a) overview of the test setup and (b) schematic of ionic motion where thickness and velocity are not to scale. The ionic motion is driven by electric migration (red arrows) and diffusion (blue arrows).

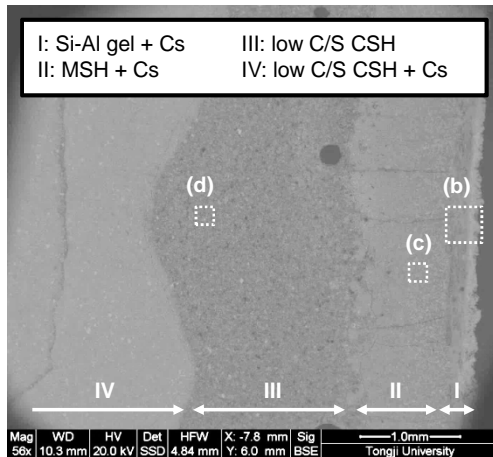
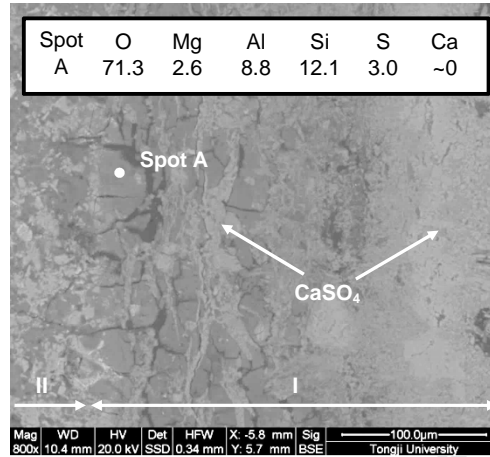
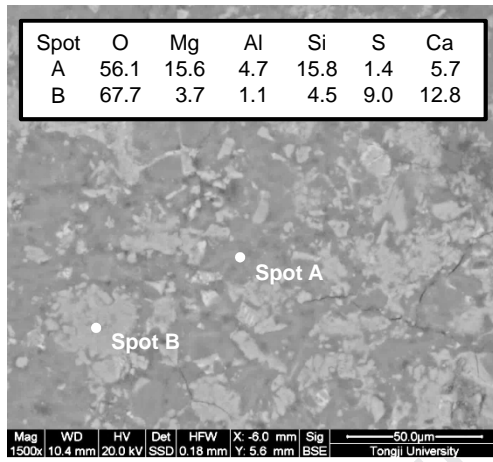


**Fig. 2.** Preparation of samples: (a) the sides of a cylindrical specimen that were not well exposed to sulfate solutions were cut off, (b) small patches that were perpendicular to the exposure surface was cut for SEM, (c) the surface part (0.5 mm) of the remainder was removed, (d) the specimen was cut parallel to the exposure surface into 5-mm thick slices, and (e) the slices were crushed into powders (particle size  $<75 \mu\text{m}$ ) for XRD and TGA.

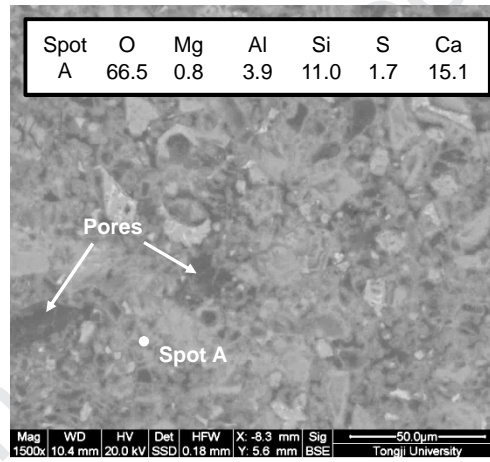


**Fig. 3.** Chemical composition at different distances from the surface (cathode on the left and anode on the right) after exposure to  $\text{MgSO}_4$  for (a) 7 d and (b) 28 d. Each data point represents the average over a  $50 \mu\text{m} \times 50 \mu\text{m}$  area measured by EDS. Error bars indicate the standard error in ZAF matrix correction schemes. The sampling points nearest to the surfaces are 0.1 mm from the surface.

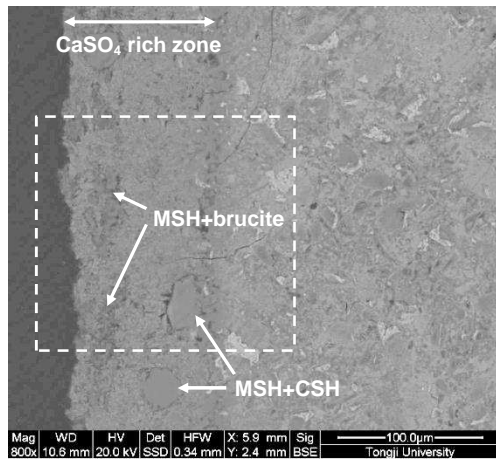
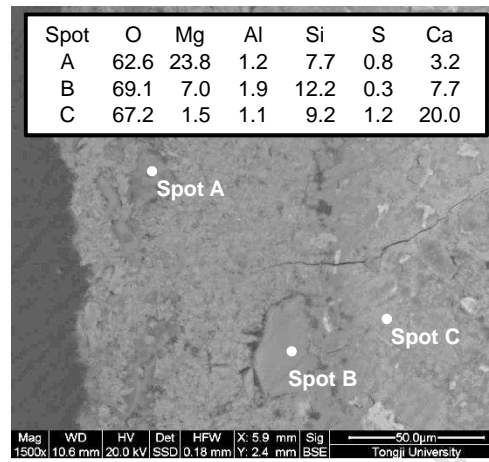
(a) 0–4 mm

(b) 0–350  $\mu\text{m}$ (c) 450–600  $\mu\text{m}$ 

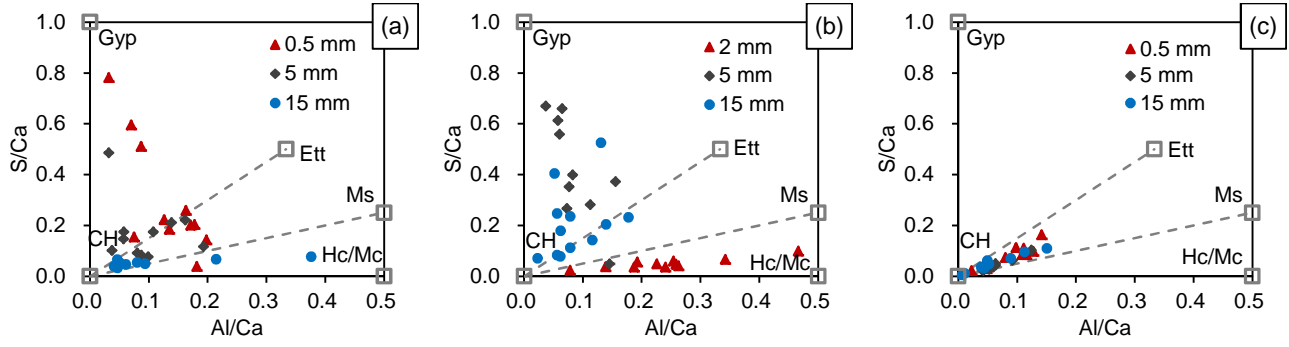
(d) ~2.5 mm



**Fig. 4.** Microstructure of the surface area (0–4 mm) near the cathode after 28 d exposure to  $\text{MgSO}_4$ : (a) an overview, and (b) to (d) enlargements of the squared areas. Surface on the right.

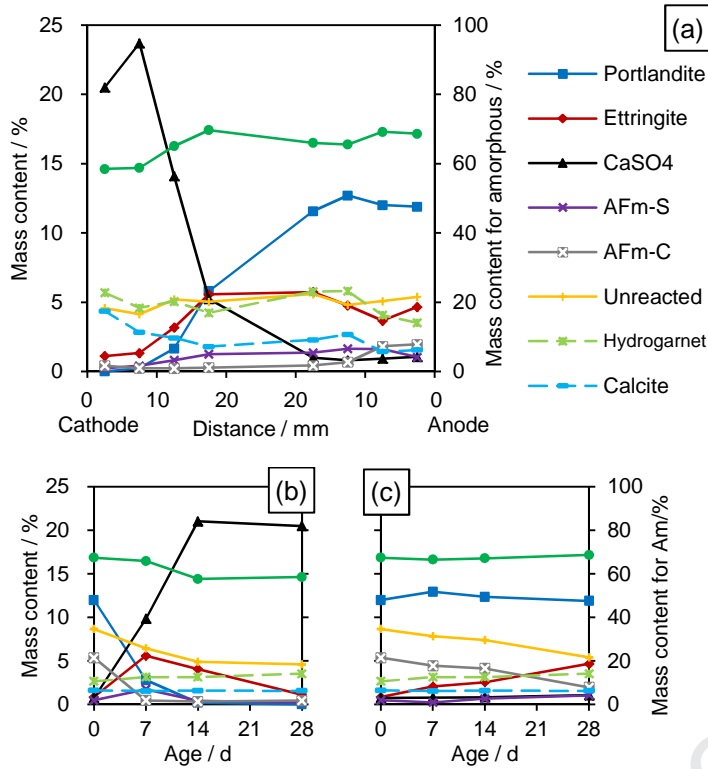
(a) 0–250  $\mu\text{m}$ (b) 0–125  $\mu\text{m}$ 

**Fig. 5.** Microstructure of the surface area (0–250  $\mu\text{m}$ ) near the anode after 28 d exposure to  $\text{MgSO}_4$ : (a) an overview and (b) enlargement of the squared area. Surface on the left.

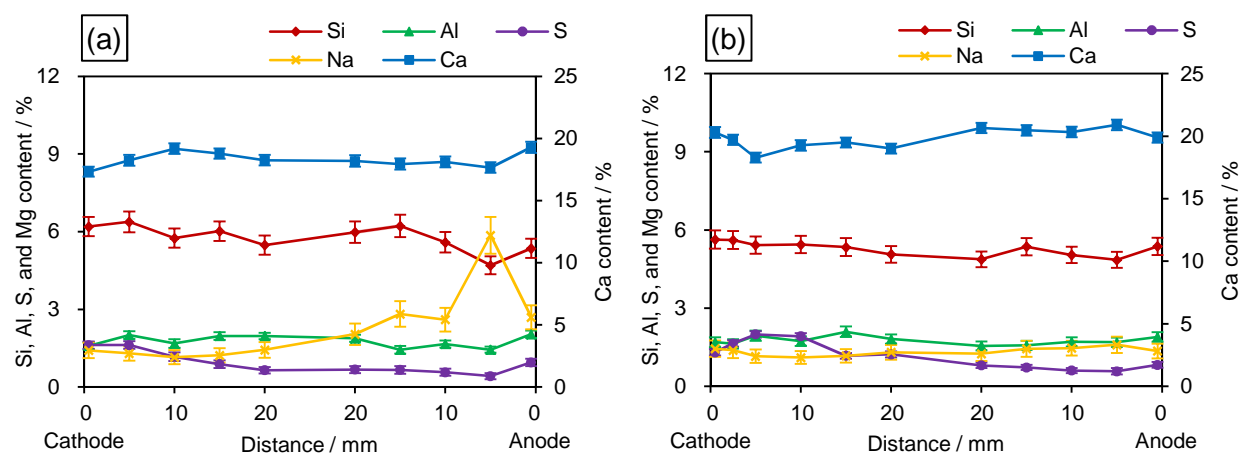


**Fig. 6.** Atom ratio plots of  $S/Ca$  against  $Al/Ca$  at different depths from the surface after exposures to  $MgSO_4$ : (a) and (b) the cathode areas exposed to  $MgSO_4$  for 7 d and 28 d, respectively; (c) the anode areas exposed to  $MgSO_4$  for 28 d. CH = Portlandite (and C-S-H at a similar position), Ett = Ettringite, Ms = Monosulfate, Hc/Mc = Hemicarbonate or monocarbonate, Gyp =  $CaSO_4$ .

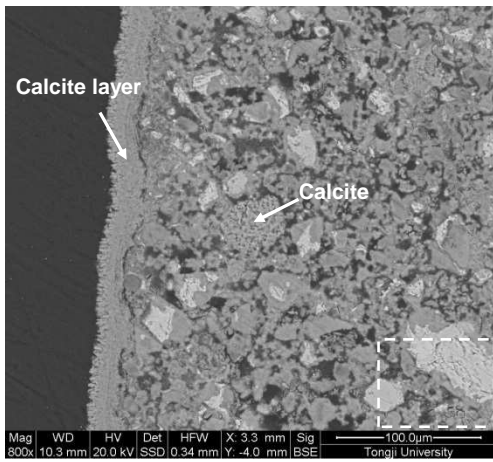
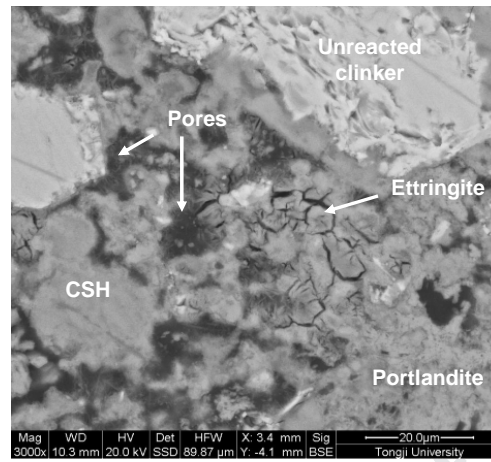




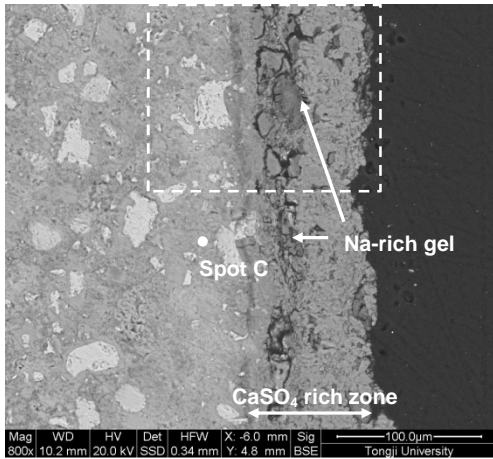
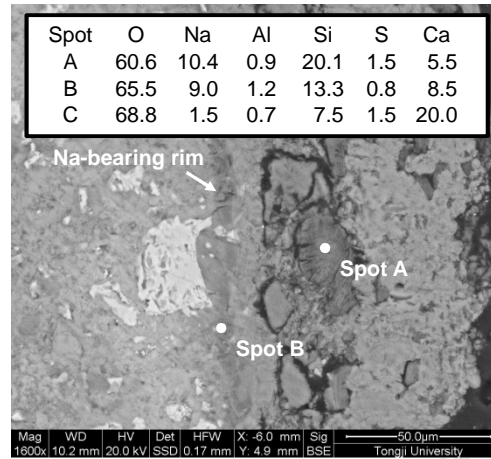
**Fig. 7.** Mineralogical composition of the specimen exposed to  $\text{MgSO}_4$  obtained by XRD and Rietveld refinement: (a) all the depths after 28 d exposure time; (b) and (c) phase alteration of the 0.5–5 mm area near the cathode and anode, respectively, after different exposure time.  $\text{CaSO}_4$  = anhydrite + bassanite + gypsum, AFm-S = monosulfate, AFm-C = monocarbonate + hemiacarbonate, hydrogarnet = katoite + hydrogrossular.



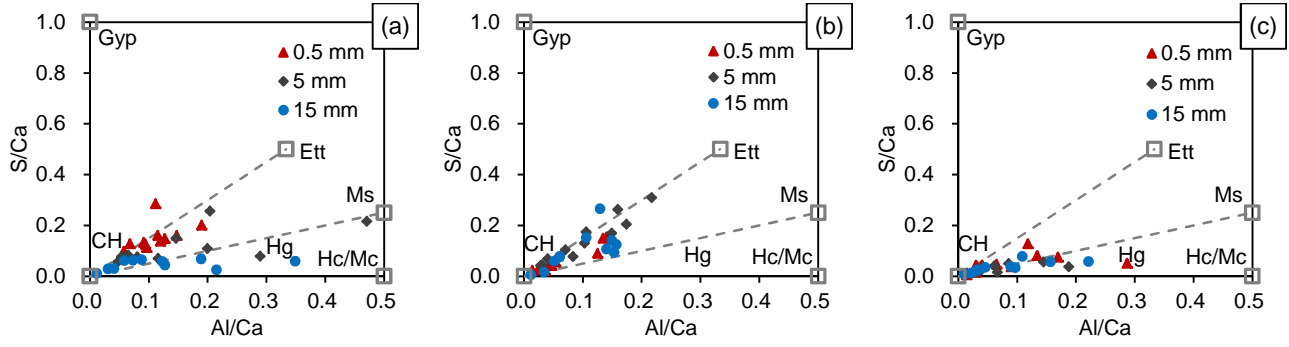
**Fig. 8.** Chemical composition at different distances from the surface (cathode on the left and anode on the right) after exposure to  $\text{Na}_2\text{SO}_4$  for (a) 7 d and (b) 28 d.

(a) 0–250  $\mu\text{m}$ (b) ~250  $\mu\text{m}$ 

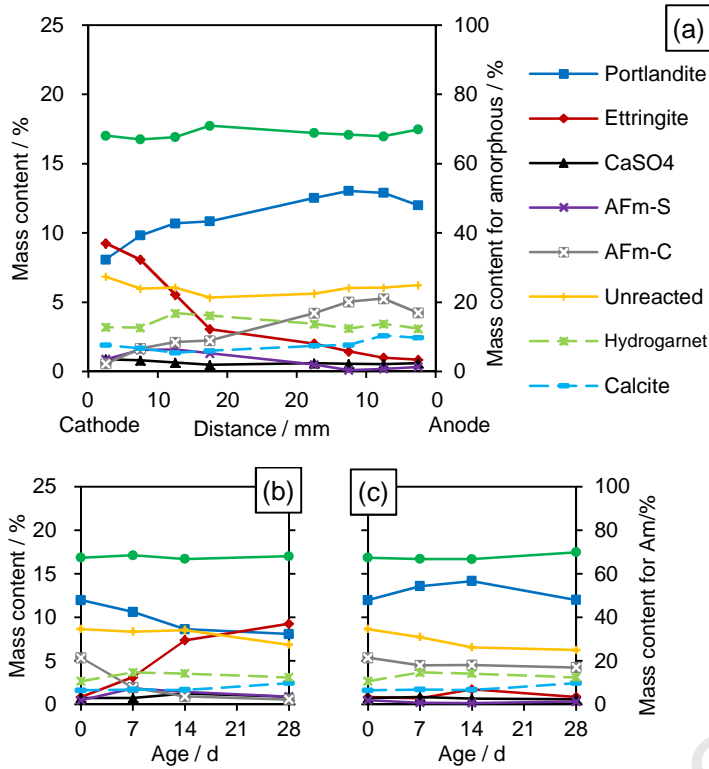
**Fig. 9.** Microstructure of the surface area (0–250  $\mu\text{m}$ ) near the cathode after 28 d exposure to  $\text{Na}_2\text{SO}_4$ : (a) an overview and (b) enlargement of the squared area. Surface on the left.

(a) 0–250  $\mu\text{m}$ (b) 0–125  $\mu\text{m}$ 

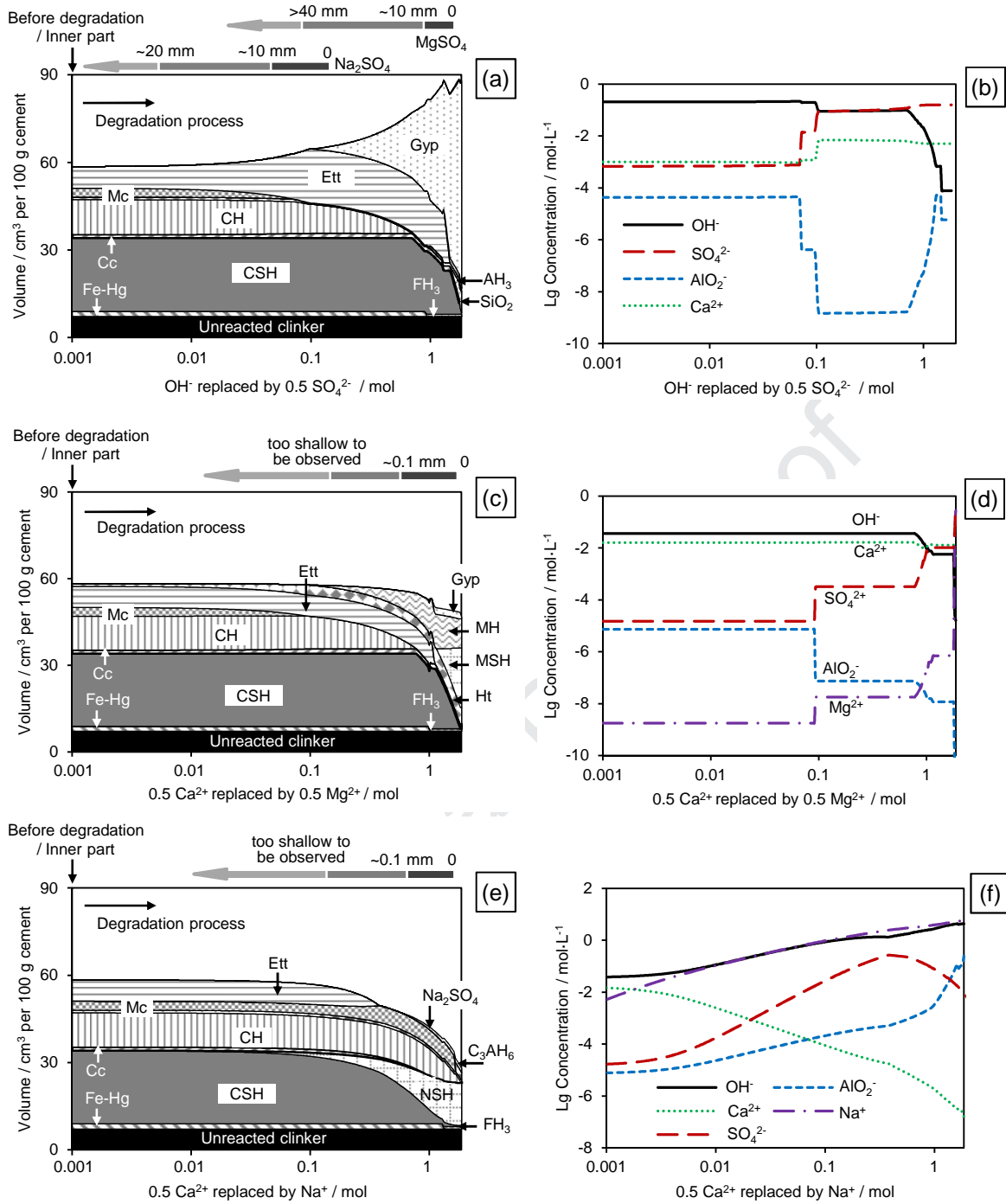
**Fig. 10.** Microstructure of the surface area (0–250  $\mu\text{m}$ ) near the anode after 28 d exposure to  $\text{Na}_2\text{SO}_4$ : (a) an overview and (b) enlargement of the squared area. Surface on the right.



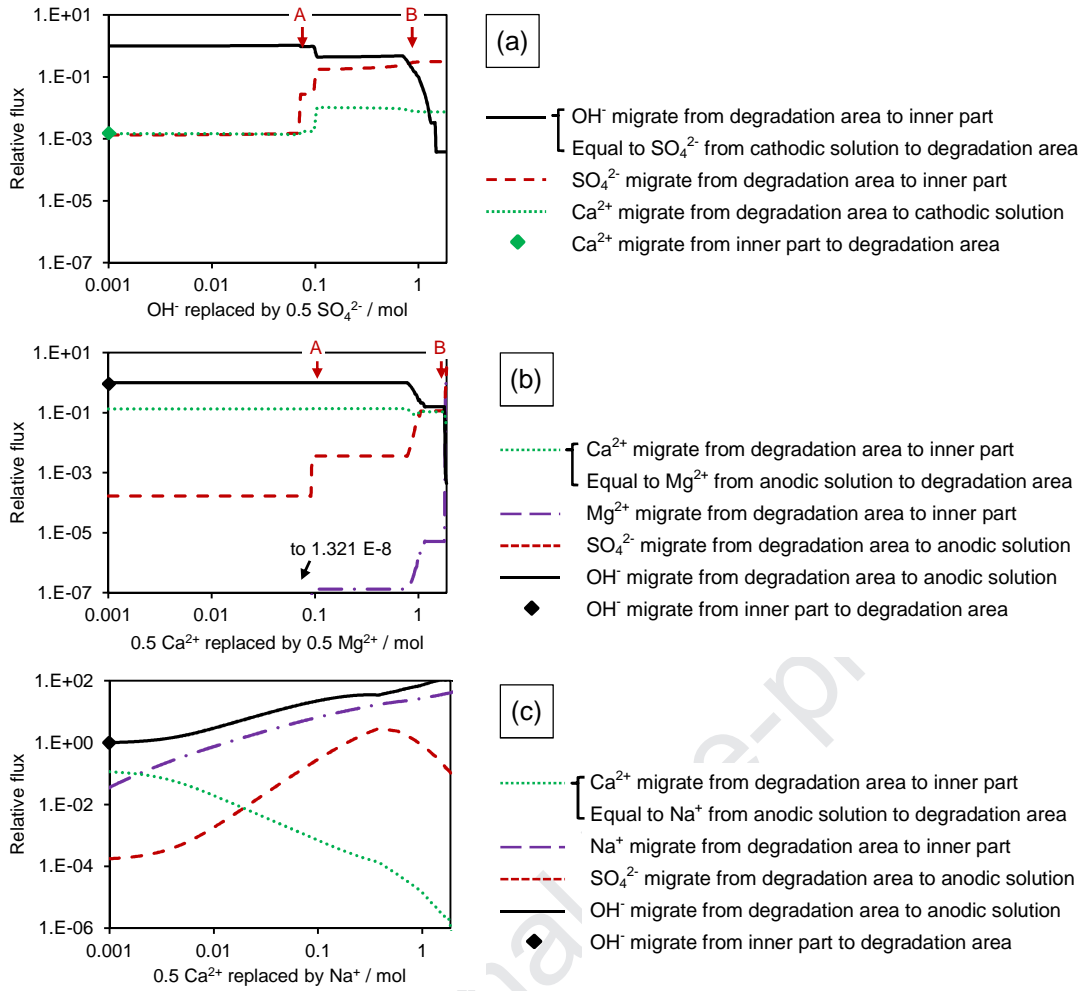
**Fig. 11.** Atom ratio plots of S/Ca against Al/Ca at different depths from the surface after exposures to  $Na_2SO_4$ : (a) and (b) the cathode areas exposed to  $Na_2SO_4$  for 7 d and 28 d, respectively; (c) the anode areas exposed to  $Na_2SO_4$  for 28 d. CH = Portlandite (and C-S-H at a similar position), Ett = Ettringite, Ms = Monosulfate, Hc/Mc = Hemicarbonate or monocarbonate, Gyp =  $CaSO_4$ .



**Fig. 12.** Mineralogical composition of the specimen exposed to  $\text{Na}_2\text{SO}_4$  obtained by XRD and Rietveld refinement: (a) all the depths after 28 d exposure time; (b) and (c) phase alteration of the 0.5–5 mm area near the cathode and anode, respectively, after different exposure time.  $\text{CaSO}_4$  = anhydrite + bassanite + gypsum, AFm-S = monosulfate, AFm-C = monocarbonate + hemiacarbonate, hydrogarnet = katoite + hydrogrossular.



**Fig. 13.** Phase assemblage and pore solution chemistry during the simplified electric migration process, calculated by thermodynamic modeling: (a) and (b) the degradation process near the cathode; (c) and (d) the degradation process near the anode after MgSO<sub>4</sub> exposure; (e) and (f) the degradation process near the anode after Na<sub>2</sub>SO<sub>4</sub> exposure. The horizontal-axis can be interpreted into the alteration in a certain position with time or the distribution of products after a certain exposure time. A logarithmic axis is used for better comparison with thermodynamic modeling studies on diffusion-induced sulfate attacks [1,2,11,14-16]. The arrows above the figures illustrate the approximate distribution of hydration products after 28 d exposure time (experimental results). CH = portlandite, Ett = ettringite, Mc = monocarbonate, Gyp = gypsum, Cc = calcite, Fe-Hg = C<sub>3</sub>FS<sub>0.84</sub>H<sub>4.32</sub> and/or C<sub>3</sub>F<sub>1.34</sub>H<sub>3.32</sub>, Ht = hydrotalcite, MH = brucite, MSH = M-S-H gel, and NSH = the Na end-member, [(NaOH)<sub>2.5</sub>SiO<sub>2</sub>H<sub>2</sub>O]<sub>0.2</sub> included in the CSHQ model.



**Fig. 14.** The relative flux of ionic species: (a) the cathode area; (b) and (c) the anode area exposed to MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>, respectively. The cations and anions migrate in different directions, see Fig. 1b. Certain ionic species are compensated by those from the inner part of the specimen, and the compensation rate is marked by a diamond (provided that the ionic strength in the inner part of the specimen remains stable). The square bracket indicates the ionic species in the external solution is transported into the degradation area with the same relative flux to certain ions based on the assumption of charge balance.



**Conflict of interest**

None.