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Isomorphic substitution and the hydration behavior of alinite cement

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Abstract

Zn and/or Fe substituted alinite cement was synthesized using reagent grade chemicals, and its formation and hydration behavior were investigated. Mg, which is known to be essential for alinite formation, was completely replaced by Zn. XRD, FT-IR, and ^{29}Si MAS NMR results indicated that a Zn substituted alinite was a nearly single phase and was easy to grind compared to Mg-alinite. In addition, partially or fully Zn substituted alinite had superior hydration characteristics, and NMR results showed that most of the alinite was hydrated after 100 days. Fe substitution of Al was not effective for alinite formation and its hydration properties were similar to Mg-alinite. Cl^- ions leached out during alinite hydration, but the exsolution of Zn and Fe was below the detection limit.

Keywords: Alinite; Cement; Chlorine ion; Hydration

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1. Introduction

Recently, the use of industrial wastes such as scrap tyres, waste oils, fly ash, and slag residues as fuels and raw materials in cement manufacturing has increased substantially.[1–5] From an environmental and recycling point of view, cement has been recognized as being one of the more effective and promising solutions for waste treatment disposal and energy recovery, and is widely used to solidify and stabilize industrial hazardous wastes.[6–10] Based on the use of waste products, a new class of cement that is emerging is the chlorine bearing alinite cement.[11]

Alinite cement (general formula: $Ca_{10}Mg_{(1-x)/2}V_{x/2}[(SiO_4)_{3+x}(AlO_4)_{1-x}O_2Cl]$, V: a lattice vacancy) has characteristics of a low clinkering temperature, comparable or even superior hydraulic properties, and easy grindability when compared to ordinary Portland cement.[12–14] Alinite has a comparable or even higher capacity of isomorphic substitution than alite (3–4%),[15] which has been attributed to vacancies on the Ca and Mg position and no specific distribution of Mg ions and vacancies over the three crystallograpically different Ca positions.[16–18] Mg^{2+} is known to be replaceable by Ni^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+}, and Si^{4+} is fully replaceable by Ge^{4+}.[16] The hydrates of alinite have a capability to fix heavy metals in the crystal lattice. Therefore, alinite cement can be used to immobilize hazardous waste materials.[11]

In the process of recycling the sewage sludge into cementitious materials, the chemical composition analysis indicates that incinerated solid residues contain alkali and heavy metals such as Cr, Cu, Zn, and Pb as well as chlorine. These heavy metals are known to have remarkable effects on both the clinkering process and the hydration of Portland cement.[19–21] Thus, it is worth investigating the effects of these elements on the alinite clinkering and its hydration.

In the previous work,[22] Mg-alinite was successfully synthesized and its phase evolution and hydration behavior were investigated. In this study, Zn and/or Fe substituted alinite clinkers were synthesized using reagent grade chemicals based on the composition reported by Neubauer and Pollmann.[23] The influence of the substituted elements on alinite clinker formation and its hydration was examined.

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2. Experimental procedures

The reagent grade chemicals, CaO, SiO_2, Al_2O_3, MgO, $CaCl_2$, ZnO, and Fe_2O_3, were used as starting materials. The composition of alinite was based on the formula reported by Neubauer and Pollmann;[23] $Ca_{10}Mg_{1-x/2}V_{x/2}[(SiO_4)_{3+x}(AlO_4)_{1-x}O_2Cl]$ (V: a lattice vacancy). In this study, x in the above formula was fixed as 0.4, and Mg^{2+} and Al^{3+} ions were partially or fully substituted by Zn^{2+} and Fe^{3+} ions, respectively. The raw materials were mixed in isopropyl alcohol, ball-milled for 24 h, and then dried in an oven for 24 h. The dried mixtures were calcined at 1300 °C for 3 h. To minimize the chlorine loss, a double crucible method was employed during calcination.[22] The calcined powder (cement clinker) was ground by hand in a high purity alumina mortar and stored in a N_2 atmosphere until required.

For comparing the hydration rates among the single phase alinite cements, the calcined powder was mixed with distilled water at a water/cement ratio of 0.5 and the pastes were cast into plastic vials. The vials were stored in a sealed container containing water. Samples were demolded after fixed times, and hydration was quenched by immersing the crushed samples in methanol for a week with subsequent drying in a N_2 atmosphere.

The phase of the calcined powder and the hydrates was determined by XRD (Rigaku D/max-B) and FT-IR (Perkin Elmer 1725X8700). The lattice parameters were calculated by a least square refinement of the data collected with an internal Si standard using the TREOR program. ^{29}Si MAS NMR spectra were recorded at 79.50 MHz on Bruker DSX400 solid-state NMR spectrometer with a magnetic field of 9.4 T and a spin rate of 12∼13 kHz. The specific surface area of the calcined powder was measured by BET (ASAP 2010, Micromeritics). The morphology of the calcined powder and the hydrates was observed in SEM (JSM-5600, JEOL). To determine the Zn^{2+}, Fe^{3+}, and Cl^- ion exsolution during alinite hydration, the samples were immersed in distilled water (w/c = 10) for a predetermined time and the ion concentrations of the filtered suspension were measured by ion chromatography (Dionex Series 4500i, American Hi-tech).

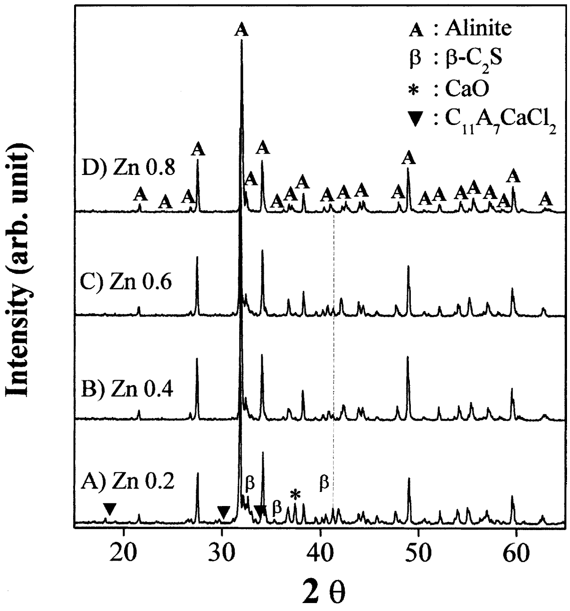

Fig. 1. XRD patterns of the alinite powders (Al = 0.6) calcined at 1300 °C for 3 h (a) Zn = 0.2, (b) Zn = 0.4, (c) Zn = 0.6, and (d) Zn = 0.8.

3. Results and discussion

Fig. 1 shows the XRD patterns taken from the only Zn substituted alinite powders. The amount of Zn was varied from 0.2 to 0.8 mol without Mg addition while the values of Si and Al were kept constant as in the original formula (Al = 0.6). At Zn = 0.2 mol substitution, an alinite phase formed along with additional phases such as β-C_2S, $C_{11}A_7CaCl_2$, and unreacted CaO [Fig. 1(A)]. As the amount of Zn substitution increased, unreacted CaO and $C_{11}A_7CaCl_2$ disappeared rapidly with a gradual decrease of β-C_2S [Fig. 1(B) and (C)]. At Zn = 0.8 mol, a single-phase alinite was obtained [Fig. 1(D)]. As reported previously,[16] Mg^{2+} ions were fully replaceable by Zn^{2+} ions in the alinite structure, and this fact can be further rationalized by the similar ionic radii of Mg^{2+} (0.72Å) and Zn^{2+} (0.745Å).[24] Therefore, the partial substitution of Mg by Zn was also possible and pure alinite was formed at the composition of Mg = 0.4 and Zn = 0.4 mol (Al = 0.6). The lattice parameters of Zn = 0.8 mol substituted alinite were determined to be a = 10.534(1) Å and c = 8.509(2) Å, which was slightly different from the reported values.[18]

The XRD pattern of the sample (Mg = 0.8) in which Al was fully replaced by Fe (Fe = 0.6) revealed that unreacted CaO, β-C_2S, $C_{11}A_7CaCl_2$, and $Ca_2Fe_2O_5$ were major phases with alinite as a minor phase. The partial replacement of Al by Fe resulted in the alinite, but unreacted CaO and β-C_2S still remained in the pattern (Fig. 2). The more Al was substituted by Fe, the more additional phases were produced. The inability of isomorphous substitution might be due to the ionic size difference between Al^{3+} (0.39 Å) and Fe^{3+} (0.49 Å).[24]

The full substitution of Mg by Zn and Al by Fe was not possible for the pure alinite formation and resulted in second phases [Fig. 3(A)]. However, a half replacement by each element yielded the single-phase alinite [Fig. 3(B)]. It is believed that the lattice distortion from the ionic radius difference could be accommodated by partial substitution. Preliminary results indicated that Mn^{2+} (0.67Å)[24] was able to replace Mg^{2+} but only in a narrow range due to the larger ionic size difference (6.9%). It was confirmed that alinite has a capability over a wide range of isomorphic substitutions if the lattice distortion is not too great. The chemical compositions for the single-phase alinite obtained from the XRD studies were given in Table 1 together with the specific surface area. All the subsequent discussions will be focused on the alinite cements with the compositions shown in Table 1.

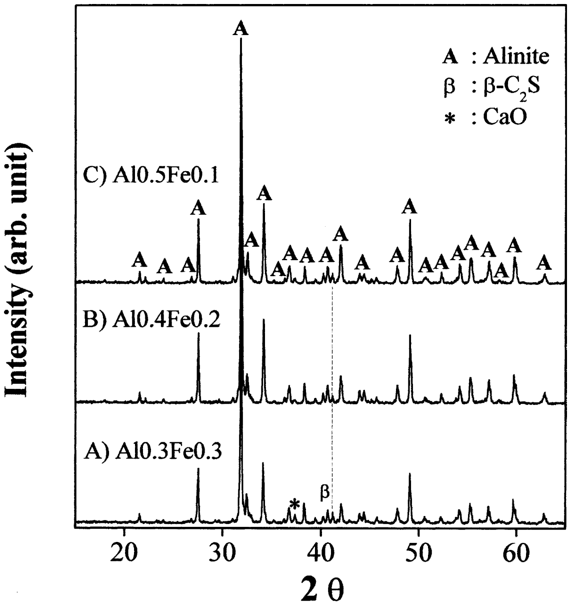

Fig. 2. XRD patterns of the alinite powders (Mg = 0.8) calcined at 1300 °C for 3 h (a) Al = 0.3, Fe = 0.3, (b) Al = 0.4, Fe = 0.2, and (c) Al = 0.5, Fe = 0.1.

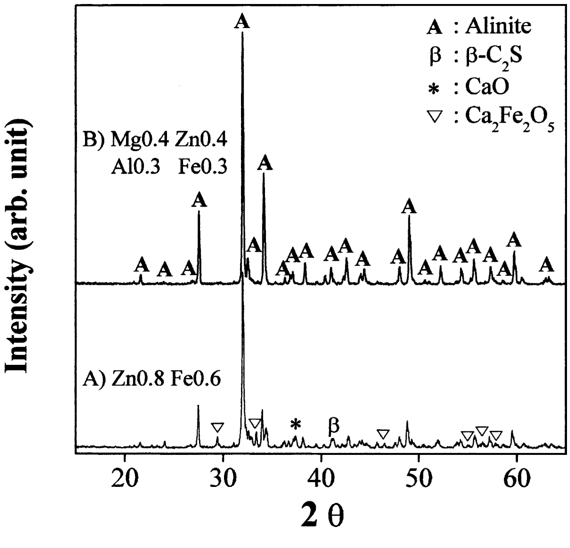

Fig. 3. XRD patterns of the alinite powders calcined at 1300 °C for 3 h (a) Zn = 0.8, Fe = 0.6 and (b) Mg = 0.4, Zn = 0.4, Al = 0.3, Fe = 0.3.

Table 1
Chemical compositions for single phase alinite and specific surface areas of alinite powders calcined at 1300 °C for 3 h

Sample no.	Composition	Surface area (m^2/g)
#1	$Ca_{10}Mg_{0.8}V_{0.2}\{(SiO_4)_{3.4}(AlO_4)_{0.6}O_2Cl\}$[a]	0.29
#2	$Ca_{10}Mg_{0.4}Zn_{0.4}V_{0.2}\{(SiO_4)_{3.4}(AlO_4)_{0.6}O_2Cl\}$	0.55
#3	$Ca_{10}Zn_{0.8}V_{0.2}\{(SiO_4)_{3.4}(AlO_4)_{0.6}O_2Cl\}$[a]	0.35
#4	$Ca_{10}Mg_{0.4}Zn_{0.4}V_{0.2}\{(SiO_4)_{3.4}(AlO_4)_{0.3}(FeO4)_{0.3}O_2Cl\}$	0.97

[a] Composition by Neubauer and Pollmann.[23]

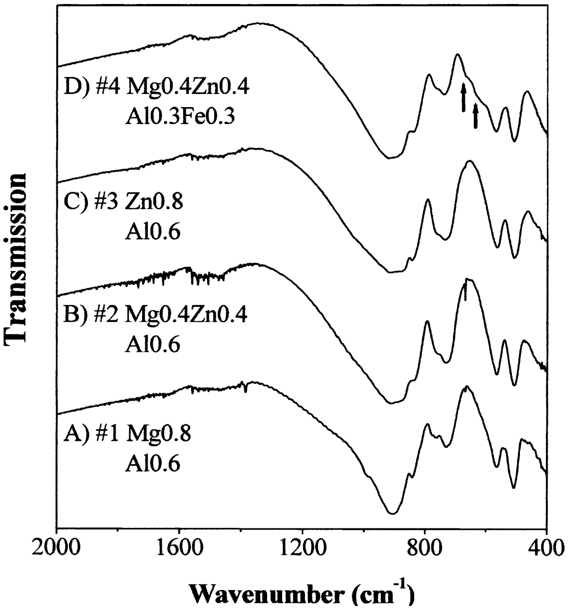

Fig. 4. FT-IR absorption spectra of single phase alinite listed in Table 1.

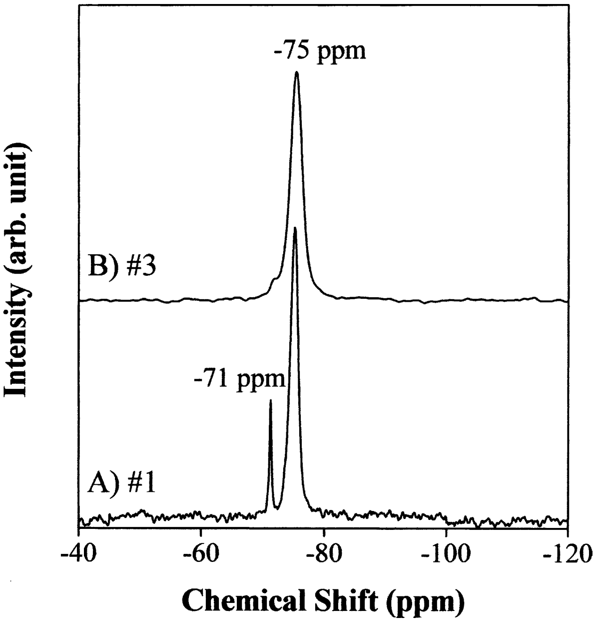

Fig. 5. ^{29}Si MAS NMR spectra of the alinite powders (a) #1 and (b) #3.

The substituted alinite structures were further investigated by both FT-IR (Fig. 4) and ^{29}Si MAS NMR (Fig. 5). All the FT-IR spectra obtained were similar and closely matched the previously reported alinite spectra.[25,26] The broad absorption band at approximately 910 cm^{-1} and the bands between 500 and 600 cm^{-1} correspond to the tensile and bending vibrations of the silicon-oxygen tetrahedra $(SiO_4)^{4-}$, respectively, whereas the weak doublet at 730–770 cm^{-1} is associated with the tensile vibration of the aluminum-oxygen tetrahedra $(AlO_4)^{5-}$. The additional weak bands at 630 and 670 cm^{-1} in Zn and Fe substituted alinite are attributed to the Fe^{3+} in a tetrahedral coordination [Fig. 4(D)]. The ^{29}Si MAS NMR spectra for the Mg and Zn substituted samples exhibited a strong peak at −75 ppm and a weak peak or shoulder at −71 ppm (Fig. 5). The chemical shift of −75 ppm could be assigned to alinite based on the crystal structure reported by Ilyukhin et al.,[27] which revealed one unique Si position in an isolated tetrahedron. The weak −71 ppm peak is believed to be due to the presence of β-C_2S[22] although it was not well identified in the XRD patterns. Considering the NMR results, Zn substitution was more efficient for producing a single phase alinite than Mg addition.

The SEM micrographs of the calcined powders at 1300 °C for 3 h are shown in Fig. 6. The morphology of alinite in Neubauer and Pollmann's composition (Mg = 0.8 mol and Al = 0.6) was irregular and plate-like [Fig. 6(A)]. However, the other alinite powders were smaller and rather spherical. Although it was very qualitative, the substituted alinite clinkers were easily grindable and had slightly higher specific surface areas as shown in Table 1. The reasons for the different morphologies depending on the substituted ions were not clearly understood, but it appeared to be closely related to the grindability of the clinkers. The effect of zinc oxide (ZnO) on the grindability of the alinite clinker was different from the previous results[28] in that Portland cement clinker containing ZnO had the lower grindability due to an increase in the melt content and a decrease in the clinker porosity.

The XRD patterns of 100 day hydrated alinite pastes are shown in Fig. 7. The main hydration products were C–S–H gels, $Ca(OH)_2$, and a Friedel's salt-like phase. The composition of the Friedel's salt-like phase proposed by Neubauer and Pollmann was $C_3A{\cdot}CaY_2{\cdot}10H_2O$ ($Y = 1/2CO_3^{2-}$, $(OH)^-$, Cl^-).[23] The unhydrated alinite still remained in all the pastes, but

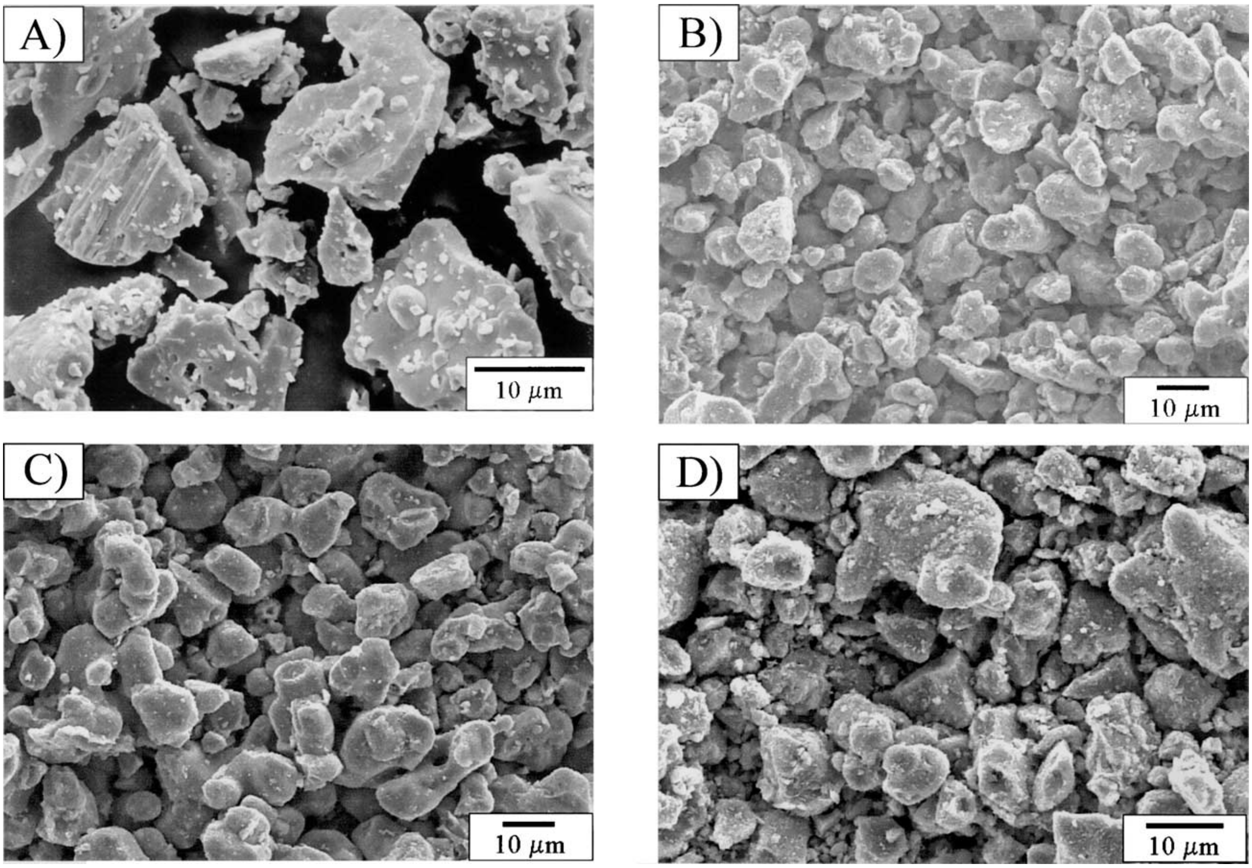

Fig. 6. SEM micrographs of the alinite powders (a) #1, (b) #2, (c) #3, and (d) #4.

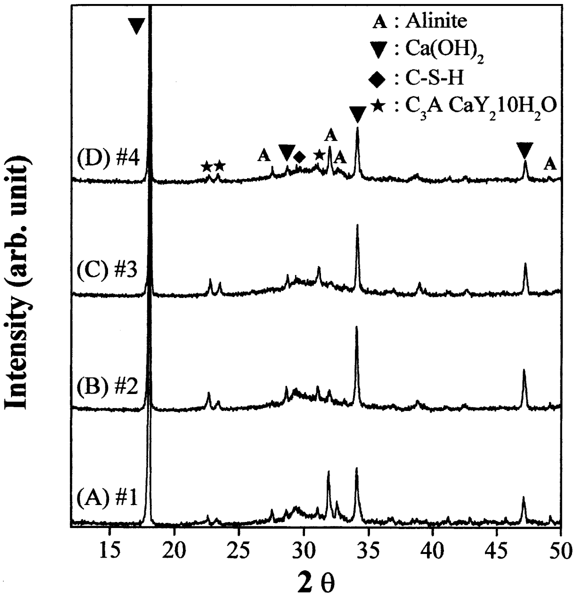

Fig. 7. XRD patterns of the hydrated alinite pastes cured for 100 days (a) #1, (b) #2, (c) #3, and (d) #4.

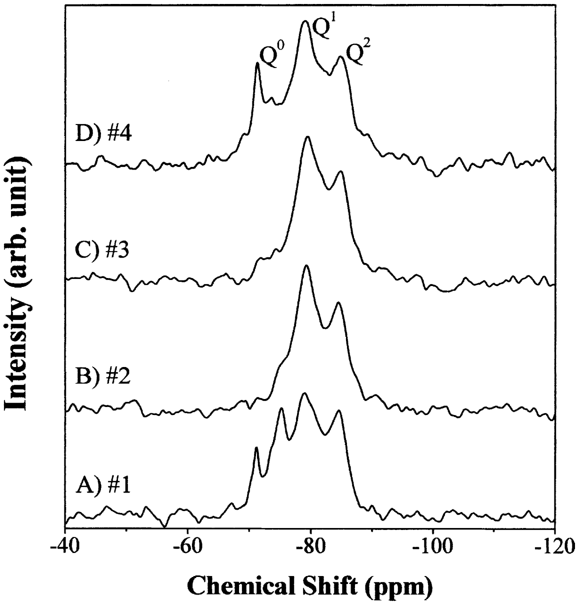

Fig. 8. ^{29}Si MAS NMR spectra of the hydrated alinite pastes cured for 100 days (a) #1, (b) #2, (c) #3, and (d) #4.

the peak intensity of alinite in the Zn substituted pastes was relatively weak. In particular, the peak intensity of the alinite in the Zn = 0.8 mol substituted paste was negligible indicating a nearly full hydration [Fig. 7(C)]. It has been reported that Zn had a retardation effect on the early hydration of C_3S and Portland cement,[19,29,30] but it appears that Zn substitution instead of Mg accelerated the alinite hydration. The possible reason for the accelerated hydration in the Zn substituted alinite is that Zn substitution produced the single-phase alinite without second phases confirmed by ^{29}Si MAS NMR (Fig. 5). Furthermore, there might be some contributions from the higher specific surface area in the Zn substituted alinite.

The corresponding ^{29}Si MAS NMR spectra are shown in Fig. 8. The Q^0 peaks (−71 and −75 ppm) for anhydrous materials and the Q^1 (−79 ppm) and Q^2 (−84 ppm) peaks for hydrated materials can be clearly seen in the Mg = 0.8 mol paste [Fig. 8(A)]. The progress of hydration, estimated by the intensity ratio of NMR peaks, $\{(Q_1+Q_2)/(Q_0+Q_1+Q_2)\}\times 100$,[31] was ~80%. With Zn substitution, the intensity of the Q^0 peaks progressively decreased and only weak Q^0 peaks were observed in the Zn = 0.8 mol paste [Fig. 8(C)]. The extent of hydration in the Zn substituted specimen was calculated to be 97~98%. Consistent with the XRD results, Zn substitution promoted the alinite hydration. In contrast, Fe substitution had little influence on the alinite hydration although Fe substituted alinite had the highest specific surface area [Fig. 8(D)].

SEM micrographs of the fracture surfaces in the alinite cement pastes hydrated for 100 days are shown in Fig. 9. All the microstructures consisted of portlandite [$Ca(OH)_2$] and C-S-H phase as well as unhydrated spherical alinite particles. The plate-like $Ca(OH)_2$ was predominant and reticular C–S–H was occasionally observed. The Zn substituted pastes [Fig. 9(B) and (C)] appear to have dense microstructures, which implies more hydration in Zn substituted samples consistent with the previous XRD and NMR results.

The Fe^{2+} and Zn^{2+} ion concentrations in the filtered suspension measured by ion chromatography were under detection limit. It was confirmed that the alinite hydrates were capable of fixing these ions into the crystal lattice. Heavy metals can enter the structures of the Afm- and Aft-phases[7] and various stabilization and solidification mechanisms of heavy metals using Portland cement have been proposed.[32,33] However, no detailed information for alinite cement has yet been published. The Cl^- ion exsolution from the alinite pastes was significant as shown in Fig. 10. The substituted alinite released the Cl^- ions slowly, but the Cl^- concentrations in all the samples were saturated at approximately 1200 ppm (~0.034 mol/l) after 14 days. The pH of the solutions decreased slightly with curing time and was 12±0.25. The estimated Cl^-/OH^- ratio was in the range of 1~3. It was reported that the protective oxide film was no longer stable and the embedded steel was corroded when the Cl^-/OH^- molar ratio was higher than 0.6.[34] Although the Cl^- exsolution was accelerated by using a w/c ratio of 10 and avoiding the cement hardening, the steel reinforcement exposed to the alinite cement is more likely to be corroded.

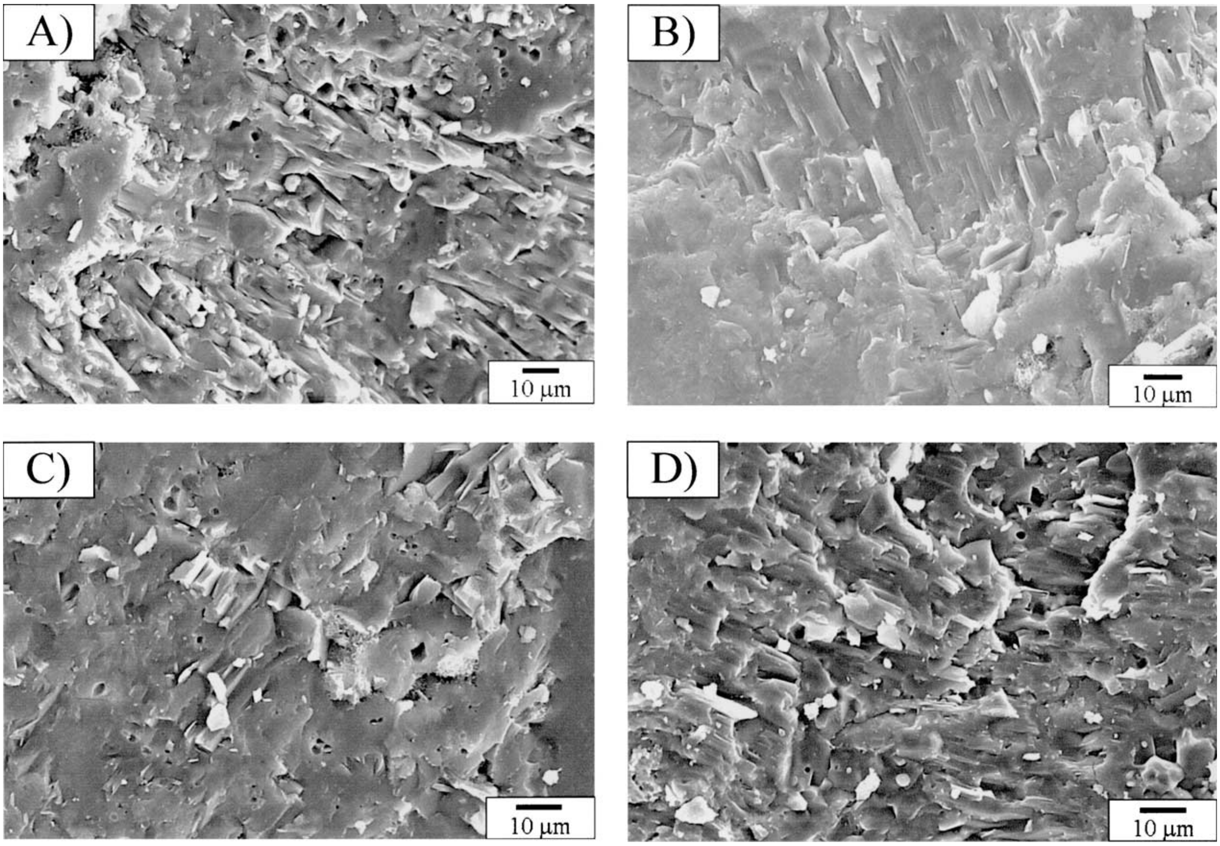

Fig. 9. SEM micrographs of the hydrated alinite pastes cured for 100 days (a) #1, (b) #2, (c) #3, and (d) #4.

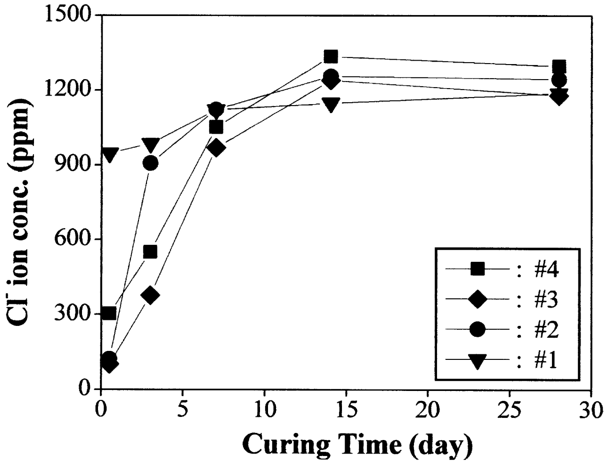

Fig. 10. Chlorine ion exsolution from the alinite pastes during hydration with a w/c ratio of 10.

4. Summary

Mg was completely replaced by Zn for a single phase alinite. The Zn substituted alinite was easy to grind and had a higher specific surface area. The partially or fully Zn substituted alinite hydrated rapidly and for 100 day hydration, most of the unhydrated alinite phase disappeared. Furthermore, the Zn substituted alinite pastes showed a dense microstructure. Al was partially replaceable by Fe probably due to the size difference, and alinite formation and the hydration characteristics of the Fe substituted alinite were similar to those of unsubstituted Mg-alinite. The exsolution of Zn^{2+} and Fe^{3+} ions upon alinite hydration was negligible confirming that alinite hydrates could fix hazardous elements in its crystal structure. However, the release of Cl^- ions was significant, which could lead to the reinforcement corrosion. The effects of other hazardous elements such as Mn, Cr, Cu, and Pb on alinite formation and hydration are still under investigation.

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