



# Article Hydration of Calcium Sulfoaluminate-Based Binder Incorporating Red Mud and Silica Fume

## Yubin Jun <sup>1</sup>, Jae Hong Kim <sup>1</sup> and Taewan Kim <sup>2</sup>,\*

- <sup>1</sup> Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Korea; ssjun97@gmail.com (Y.J.); jae.kim@kaist.ac.kr (J.H.K.)
- <sup>2</sup> Department of Civil Engineering, Pusan National University, Busan 46241, Korea
- \* Correspondence: ring2014@naver.com; Tel.: +82-51-510-7681

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**Abstract:** This study investigated the properties of hardened pastes made with calcium sulfoaluminate expansive agent (CSA), red mud, and silica fume. Five different ratios of 10:90, 20:80, 30:70, 40:60, and 50:50 were applied as the weight ratios of CSA and red mud. Red mud was replaced with 0, 5, and 10% silica fume by weight. Compressive strength, drying shrinkage, XRD, MIP, and SEM/EDS of the hardened pastes were performed. The results indicated that as the amount of CSA increased (i.e., as the amount of red mud decreased) up to 30%, sample strengths showed a tendency to increase. The main reaction product of the pastes was expansive ettringite, which was formed from the consumption of ye'elimite, anhydrite, gypsum, and Ca(OH)<sub>2</sub>. It was expected that C-S-H would be formed by the reaction of  $C_2S$  in red mud; however, C-S-H phase was not present, and the pozzolanic activity due to the use of silica fume did not occur. The increase of CSA replacement level of CSA induced excessive expansion, leading to the reduction in strength. It was found that the excessive expansion in the sample was reduced by the addition of silica fume.

Keywords: calcium sulfoaluminate; red mud; silica fume; by-product; ettringite; ye'elimite

## 1. Introduction

The production of Portland cement clinker results in considerable CO<sub>2</sub> emission, and the Portland cement industry is therefore actively looking for ways to reduce greenhouse gas emissions [1]. Calcium sulfoaluminate is finely ground calcium sulfoaluminate clinker, which is manufactured at about 100–200 °C lower than Portland cement clinker [1–5]. It reduces the amount of fossil fuel needed in a furnace, contributing to lower fuel-derived CO<sub>2</sub> emissions compared with Portland cement. In this respect, calcium sulfoaluminate has been known as a low-CO<sub>2</sub> alternative to Portland cement. Calcium sulfoaluminate consists mainly of ye'elimite ( $C_4A_3\overline{S}$ ), which exhibits rapid strength gain and controlled expansion [6–8]. It is known that ye'elimite hydrates to form ettringite ( $C_6A\overline{S}_3H_{32}$ ), which can give expansion [4]. Calcium sulfoaluminate cement. Calcium sulfoaluminate cement is applied as a binder for concrete, and CSA is known as a shrinkage compensating additive in concrete mixtures. Many previous studies reported that calcium sulfoaluminate cement had rapid setting and hardening, although expansion and strength depended on its calcium sulfoaluminate content and the amount of added gypsum [9–11]. Lin et al. [12] reported that CSA is effective in controlling concrete shrinkage.

Red mud (denoted as RM) is an industrial by-product obtained from ore bauxite during the Bayer alumina producing process [13]. RM is classified as a hazardous waste because it is highly alkaline (pH > 10), and RM can contaminate soil and groundwater when added to landfills. The

disposal of RM is therefore a significant environmental issue, and the re-utilization of RM should receive more attention.

Several studies have explored the possible reuse of RM in the production of cementitious or pozzolanic material-based binders [14–16]. Yao et al. [15] have studied the mechanical properties of composed samples with RM, coal refuse, fly ash, cement, and gypsum. They reported that the combined sample met the requirement of ASTM standards in physical and mechanical tests, and concluded that the sample could be used as ordinary Portland cement (OPC) substitute material. Manfroi et al. [16] reported the pozzolanic properties of dry and calcined RM, and showed that OPC replaced by RM contained the hydration products of C-S-H, ettringite, monosulfate, and C-A-H. They described how SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> contained in RM contribute to the pozzolanic activity. Some studies have used RM as an alkali activator for the synthesis of geopolymers or alkali-activated slag because RM generally has high alkalinity [17,18]. Choo et al. [17] proposed that RM could provide solid alkali activation for making a fly ash-based geopolymer.

Molineux et al. [19] used RM for the manufacture of lightweight aggregate as a replacement for pulverized fuel ash. They showed that the manufactured lightweight aggregate had good physical characterizations: compressive strength, density, and water holding capacity. It was expected that the produced lightweight aggregate made with RM could be used in concrete and other construction products [19,20]. Lin and Poon [20] reported that RM used with cement, fly ash, and sand would be effective in reducing autogenous shrinkage of self-compacting mortar.

Silica fume (denoted as SF) is a pozzolanic material that is a by-product in the manufacture of silicon metal. Due to its high surface area and microparticles, SF is used to enhance the strength and durability of concrete [21,22]. It contributes to the permeability reduction of concrete as a pore filler.

As mentioned above, several studies have reported on the characteristics of CSA, RM, and SF, which are a low-carbon material and an industrial by-product. From the viewpoint of resources recycling and environmental pollution, further studies will be needed to use by-products in a variety of ways. The objective of this study is to develop eco-friendly ternary blended binders made of CSA, RM, and SF. In this study, compressive strength and drying shrinkage as well as the results of X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) with energy dispersive spectroscopy (EDS), and mercury intrusion porosimetry (MIP) of hardened samples with CSA, RM, and SF were analyzed.

### 2. Materials and Methods

#### 2.1. Materials

RM was supplied by KC Corporation in South Korea; it has a density of 0.00321 g/mm<sup>3</sup> and a Blaine fineness of 2350 m<sup>2</sup>/kg. CSA was produced by Ssangyong Cement Industrial Co., Ltd., Boryeong, South Korea; it has a density and Blaine fineness of 0.00295 g/mm<sup>3</sup> and 250 m<sup>2</sup>/kg, respectively. SF from Elkem Materials was used. Its Blaine fineness and density were 22,000 m<sup>2</sup>/kg and 0.002 g/mm<sup>3</sup>, respectively. The chemical composition of the CSA, RM, and SF was determined by X-ray fluorescence (XRF) spectrometry, and is tabulated in Table 1. Figure 1 shows the X-ray diffraction (XRD) spectra of the raw materials.

		Oxide Composition (wt.%)						Density	Blaine Fineness	Ig-loss	
	SiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	(g/mm <sup>3</sup> )	$(g/mm^3)$ $(m^2/kg)$ (9	
CSA	4.85	13.46	0.27	1.13	49.84	0.17	0.21	29.17	0.00295	250	2.36
RM	19.21	20.92	32.74	0.81	3.87	0.27	13.15	0.26	0.00321	2350	9.41
SF	95.50	1.00	0.30	0.50	0.40	1.00	-	-	0.00200	22,000	2.00

 Table 1. Chemical composition and physical properties of raw materials.

Note. CSA: calcium sulfoaluminate expansive agent; RM: red mud; SF: silica fume.



**Figure 1.** XRD patterns of raw materials (CSA: calcium sulfoaluminate expansive agent; RM: red mud; SF: silica fume). E: ettringite (98-002-7039), G: gypsum (98-040-9581), P: portlandite (01-084-1265), A: anhydrite (01-080-0787), Y: ye'elimite (98-002-8480), C: calcite (00-003-0596), K: cancrinite (98-015-6526), S: sodalite (98-041-0158), B: boehmite (00-001-1283), H: hematite (00-006-0502), V: vaterite (98-016-2480), L: larnite ( $C_2S$ , 98-002-4640), R: perovskite (98-007-4212), T:  $C_3A$  (98-015-1369). The numbers in parentheses are ICDD (International Center for Diffraction Data) PDF-2 or ICSD (Inorganic Crystal Structure Database) data numbers for identified phases.

## 2.2. Mixture Proportions, Sample Preparation, and Curing

The mix design of the samples is presented in Table 2, in which each sample is denoted with a specific letter, "C", "R", and "S" representing CSA, RM, and SF, respectively. The number following the specific letter indicates the weight percent of each material. The weight ratio of the water to the ternary compound material (CSA + RM + SF) was 0.5. Five different ratios of 10:90, 20:80, 30:70, 40:60, and 50:50 were selected as the weight ratios of the raw materials between CSA and RM. RM was replaced with 0%, 5%, and 10% SF by weight. Fifteen mixtures were made to produce sample pastes.

The samples were prepared in a laboratory according to ASTM C305 [23]. After mixing, samples of  $50 \times 50 \times 50 \text{ mm}^3$  and  $40 \times 40 \times 160 \text{ mm}^3$  were cast for the determination of compressive strength and drying shrinkage, respectively. The samples for the MIP and SEM tests were cast in cubic molds with dimensions of  $25 \times 25 \times 25 \text{ mm}^3$ . All samples were placed in a humidity chamber at  $95 \pm 5\%$  relative humidity and  $20 \pm 2^{\circ}$ C temperature for 24 hrs. After demolding, the samples were stored in the same chamber until the testing age.

Group	Sample ID	CSA	RM	SF	Testing					
		(wt.%)	(wt.%)	(wt.%)	С	D	X	Μ	S	
	C10R90S0	10	90	0		$\checkmark$	$\checkmark$			
	C20R80S0	20	80	0	$\checkmark$	$\checkmark$				
Ι	C30R70S0	30	70	0	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		
	C40R60S0	40	60	0	$\checkmark$	$\checkmark$				
	C50R50S0	50	50	0	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		
	C10R85S5	10	85	5	$\checkmark$	$\checkmark$	$\checkmark$			
	C20R75S5	20	75	5	$\checkmark$	$\checkmark$				
II	C30R65S5	30	65	5	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	
	C40R55S5	40	55	5	$\checkmark$	$\checkmark$				
	C50R45S5	50	45	5	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	
	C10R80S10	10	80	10	$\checkmark$	$\checkmark$	$\checkmark$			
	C20R70S10	20	70	10	$\checkmark$	$\checkmark$				
III	C30R60S10	30	60	10	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		
	C40R50S10	40	50	10	$\checkmark$	$\checkmark$				
	C50R40S10	50	10	10	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		

**Table 2.** Mixture proportions of samples.

Abbreviations. CSA: calcium sulfoaluminate expansive agent; RM: red mud; SF: silica fume; C: compressive strength; D: drying shrinkage; X: XRD; M: MIP; S: SEM; √: test conducted.

The compressive strength of the samples was determined at 1, 3, 7, and 28 days in accordance with ASTM C109 [24]. Each strength value was the average of three samples. The XRD, MIP, and SEM tests were carried out on the samples cured for 28 days. Fractured specimens after strength testing were ground finely, and the particles that passed through sieve No. 200 were used for XRD analysis. The XRD analysis was carried on an X-ray diffractometer (Empyrean, PANalytical, Netherlands) using Cu K $\alpha$  radiation with 20 scan from 5° to 60°. For the MIP test, 5 × 5 × 5 mm<sup>3</sup> cubic pieces were obtained from the central inner part of the samples. MIP measurement was conducted using an AutoPore IV 9500 mercury porosimetry (Micromeritics, USA). An FE-SEM (Supra 40 VP, Zeiss, Germany) secondary electron (SE) image was used to observe the surface morphology, and energy dispersive X-ray spectroscopy (EDS) was performed to determine the elemental compositions of a few spots on the samples. Cross sections with a thickness of 5 mm along the length of the samples were prepared using a rock saw. The cross sections were coated with a thin film of gold before the SEM observation.

The drying shrinkage test was conducted in accordance with ASTM C596 [25]. The samples were stored in a chamber with a controlled temperature of  $23 \pm 1$  °C and a relative humidity of  $50 \pm 5\%$  for 91 days.

#### 3. Results and Discussion

#### 3.1. Compressive Strength Development

The compressive strengths of the paste mixes are shown in Figure 2. The 1-day and 28-day strength values from Figure 2 are tabulated in Table 3. As can be seen in Figure 2, the compressive strength of all paste mixes generally increased with curing time. When the CSA replacement level was increased up to 30%, the compressive strength also increased for each group. However, when the CSA content was 40%, the compressive strength value tended to be similar to or slightly higher than the 30% content, and the content of 50% CSA showed lower strength than the 40% content.



(c)

**Figure 2.** Compressive strength developments on paste samples with various mixes: (a) Group I (10–50% CSA + 90–50% RM + 0% SF), (b) Group II (10–50% CSA + 85–45% RM + 5% SF), and (c) Group III (10–50% CSA + 80–40% RM + 10% SF). The numbers above each column indicate compressive strength testing result in MPa.

	C10R90S0	C10R85S5	C10R80S10
1-day	3.9 (1.12)	4.0 (0.86)	4.2 (1.15)
28-day	6.2 (1.57)	6.7 (1.22)	6.9 (1.34)
	C20R80S0	C20R75S5	C20R70S10
1-day	7.7 (0.86)	11.3 (1.05)	10.8 (1.02)
28-day	11.7 (1.20)	20.3 (1.04)	19.8 (1.25)
	C30R70S0	C30R65S5	C30R60S10
1-day	18.3 (0.80)	18.6 (0.74)	16.4 (1.13)
28-day	24.6 (0.87)	36.6 (0.88)	34.8 (1.05)
	C40R60S0	C40R55S5	C40R50S10
1-day	18.4 (1.05)	18.3 (0.88)	15.2 (0.86)
28-day	32.1 (1.32)	41.4 (1.38)	36.9 (1.11)
	C50R50S0	C50R45S5	C50R40S10
1-day	10.9 (0.85)	10.9 (1.03)	8.4 (1.16)
28-day	28.6 (1.14)	34.7 (1.39)	29.6 (0.75)

Table 3. Strength (standard deviation) of samples at 1 and 28 days (MPa).

Earlier studies have reported that the incorporation of SF is effective in enhancing compressive strength due to its fine particles as a filler and its pozzolanic reactions [26,27]. In this study, for the same CSA replacement level, the 10% CSA content samples (i.e., C10R90S0, C10R85S5, and C10R80S10) showed no significant strength change due to the addition of SF. The C10R90S0, C10R85S5, and C10R80S10 pastes developed 3.9, 4.0, and 4.2 MPa compressive strength at an early age, respectively. After 28 days of hydration, the strengths of the pastes were 6.2, 6.7, and 6.9 MPa, respectively (Table 3). This shows that the hydration reaction of mixtures was insufficient and that hydration products were not properly formed under the above mixture conditions. Senff et al. [28] reported that when RM content is higher, the compressive strength of a sample could decrease. They stated that since RM particles can absorb a little water, the required amount of water for hydration reaction might be insufficient.

In the case of other CSA replacement levels, the compressive strength was affected by SF addition. The sample with SF addition yields a lower or higher early-age strength but higher later-age strength than that without SF. With respect to the amount of SF addition, 5% addition gives better strength development than 10% addition.

#### 3.2. Drying Shrinkage

The results of drying shrinkage or length change of the samples are presented in Figure 3. With respect to the amount of SF addition, Figure 3a shows that, at a given SF content (0% SF addition), drying shrinkage is reduced as the CSA content in the sample is increased. When 5% SF is added, there is no significant difference in the drying shrinkage behavior of samples as the CSA content in samples is increased or decreased, except for the C50R45S5 sample. All samples with 5% SF have an almost constant drying shrinkage after 28 days. The addition of 10% SF indicates that there is no consistency in terms of the CSA content for drying shrinkage.

Previous studies [21,29] found that the addition of SF influences the drying shrinkage of samples and that drying shrinkage increases with increase in SF content. This was also confirmed for the samples with 40% CSA content in this study. The drying shrinkage of the sample increased with increasing the amount of SF. The opposite result was observed in the samples with 10–30% CSA content. That is, the drying shrinkage of the samples tends to decrease with increasing amounts of SF. Rao [21] and Mazloom et al. [29] reported that the increase in shrinkage of samples is influenced by the pore size refinement and pozzolanic reaction due to the SF content. Mazloom et al. [29] also reported that the refinement of pore size leads to increase in capillary tension, causing the increase of shrinkage.



**Figure 3.** Drying shrinkage for the paste samples with various mixes: (a) Group I (10–50% CSA + 90–50% RM + 0% SF), (b) Group II (10–50% CSA + 85–45% RM + 5% SF), and (c) Group III (10–50% CSA + 80–40% RM + 10% SF).

In the case of the 50% CSA replacement level, the sample with 0% SF addition showed expansion during the testing period. When 5% SF was added, the sample showed reduced expansion; however, its length change was still positive. The sample with 10% SF addition showed shrinkage after 24 days.

#### 3.3. XRD

Figure 4 represents the XRD patterns of the 28-day samples with 10, 30, and 50% CSA content for each group (Table 2). In all of the samples, most identified phases were already present in the raw materials (i.e., CSA and RM) such as ettringite (PDF 98-002-7039), sodalite (PDF 98-041-0158), cancrinite (PDF 98-015-6526), boehmite (PDF 00-001-1283), hematite (PDF 00-006-0502), anhydrite (PDF 01-080-0787), vaterite (PDF 98-016-2480), calcite (PDF 00-003-0596), larnite (C<sub>2</sub>S, PDF 98-002-4640), C<sub>3</sub>A (PDF 98-015-1369), perovskite (PDF 98-007-4212), and ye'elimite (PDF 98-002-8480).

Yang and Xiao [30] reported that C-S-H and calcium hydroxide are formed from the hydration of  $C_2S$  in RM. In this study, C-S-H gel and calcium hydroxide were not identified in XRD patterns of the hardened samples. This result suggests that  $C_2S$  in RM was unhydrated, and the pozzolanic activity of SF would not occur. Generally, SF is used as a pozzolanic material, which reacts with calcium hydroxide and forms C-S-H. In this study, it can be seen that SF did not react chemically, but it is expected that SF would associate with a physical filler effect.

Note that in each group, the reflection intensity of ettringite increased with the CSA replacement level. This observation suggests that the main reaction product of the hardened samples is ettringite. The degrees of reaction could be compared between the samples by comparing the intensities of ettringite reflections in XRD.

It was reported that ettringite could be formed from  $C_3A$  in RM with gypsum and water [30]. However, it is difficult to assess whether the presence of ettringite (Figure 4) in this study was formed by the hydration of  $C_3A$ . The residual unhydrated  $C_3A$  (denoted as T) in Figure 4 is not easily identified because the strongest peak of  $C_3A$  (33.210° 2 $\theta$ ) overlaps with hematite (denoted as H, 33.280° 2 $\theta$ ) and perovskite (denoted as R, 33.114° 2 $\theta$ ) peaks. Furthermore, as  $C_3A$ , hematite, and perovskite are contained in the raw RM, their peaks decrease with decreasing RM.

From this study, it can be seen that ettringite forms from the consumption of ye'elimite, anhydrite, gypsum, and Ca(OH)<sub>2</sub> in the curing process, and that the formed ettringite is expansive. Earlier studies reported that ye'elimite hydrates to form monosulfoaluminate [6,9], and ye'elimite combined with anhydrite and/or gypsum results in non-expansive ettringite ( $C_6A\bar{S}_3H_{32}$ ) [4]. It was also reported that in the presence of calcium hydroxide, ye'elimite combined with anhydrite and/or gypsum produces expansive ettringite ( $3C_6\bar{S}_3H_{32}$ ) [4,6]. In this study, gypsum and calcium hydroxide contained in the raw CSA were not observed in the hardened samples with 10, 30, and 50% CSA replacement level, indicating that those were consumed in the curing process. It can be observed from Figure 4 that anhydrite was not fully depleted in the samples. The residual anhydrite in the samples with 0% SF (~S0) was very similar to each other with respect to the CSA content; however, in the case of 5% SF addition (~S5), the peak of anhydrite in the sample with 50% CSA content (C50R45S5) was significantly higher than those with 10 and 30% CSA content (C10R85S5, C30R55S5). When 10% SF was added (~S10), the residual anhydrite was increased with the CSA replacement level.

For each group (~S0, ~S5, and ~S10), it seems that ye'elimite is completely converted into ettringite in the sample with 10% CSA replacement level. This is because the peak of ye'elimite was not detected in the samples. Unhydrated ye'elimite existed in the mixes with 30 and 50% CSA, and the ye'elimite was increased with the CSA replacement level.

Bizzozero et al. [31] reported that the complete hydration of binder with 50 wt.% of ye'elimite and 22 wt.% of anhydrite and gypsum did not occur in the water/binder ratio of 0.4. They indicated that higher water/binder ratio (about 0.6) would be required for the complete reaction of ye'elimite, gypsum, and water [31,32]. In this study, all mixtures were made with a water to ternary compound material (CSA + RM + SF) ratio of 0.5. It should be mentioned that the quantity of mixing water was not sufficient for complete hydration of ye'elimite and anhydrite in the mixtures.



Figure 4. Cont.



**Figure 4.** XRD patterns of the 28-day samples with 10, 30, and 50% CSA replacement level for (**a**) Group I (0% SF addition), (**b**) Group II (5% SF addition), and (**c**) Group III (10% SF addition). E: ettringite, S: sodalite, K: cancrinite, B: boehmite, H: hematite, A: anhydrite, V: vaterite, C: calcite, L: larnite ( $C_2S$ ), R: perovskite, T:  $C_3A$ , Y: ye'elimite.

Bagheri et al. [33] reported that the use of SF had increased the water demand in mixtures, and the water demand increased with increasing the content of SF. When comparing the samples with or without SF, the mix with 10% CSA replacement level indicated that there is little difference in the ettringite formation and unhydrated anhydrite due to the SF addition (Figure 5a). When comparing the 30% CSA replacement level before and after the addition of SF, it was observed that the peak of ettringite is similar, and more unhydrated anhydrite and ye'elimite remain after the addition of SF (Figure 5b).



Figure 5. Cont.



**Figure 5.** Ettringite (E), ye'elimite (Y), and anhydrite (A) phases in 5-30° 2θ of (**a**) 10% CSA content sample, (**b**) 30% CSA content sample, and (**c**) 50% CSA content sample on the amount of SF addition.

In the case of 50% CSA replacement level, when SF was added, the peaks of anhydrite and ye'elimite were higher than without SF added (Figure 5c). Furthermore, those peaks increased with increasing SF. At the same time, the peak of ettringite was significantly reduced. It may be that the use of SF in 50% CSA replacement level has an impact on water losses in the hydration of ye'elimite and anhydrite to form ettringite. However, it may rather serve as an advantage to prevent excessive formation of ettringite. In this study, when 0% or 5% SF was added in 50% CSA replacement level (C50R50S0 and C50R45S5 samples), the samples showed expansion at the age of 28 days in the drying shrinkage test. This appears to be due to excessive ettringite formation, which may cause expansion. However, when 10% SF was added (C50R40S10), the intensity of ettringite reflections in XRD reduced, and the sample did not show expansion at 28 days in the drying shrinkage test.

## 3.4. MIP

The pore size distributions of the samples subjected to the XRD analysis were measured using MIP at the age of 28 days, except for the C10R90S0, C10R85S5, and C10R80S10 samples. The MIP tests for the C10R90S0, C10R85S5, and C10R80S10 samples were not performed due to poor compressive strength (i.e., 6.2 MPa, 6.7 MPa, and 6.9 MPa). Figures 6 and 7 represent the pore size distribution of samples with 30 and 50% CSA replacement level on the amount of SF addition.



Figure 6. Pore size distribution of 30% CSA content sample on the amount of SF addition.



Figure 7. Pore size distribution of 50% CSA content sample on the amount of SF addition.

As shown in Figure 6, the pore structure of the sample with 30% CSA level showed that as SF was added, the pore size distribution shifted toward a finer distribution, and the average pore diameter and total porosity reduced. The 50% CSA content sample showed that the average pore diameter and total porosity decreased with an increase in SF content.

Given that smaller-sized pores induce an increase in the strength of samples [34], in this study the compressive strength should increase with the addition of SF because the pore size distribution and average pore diameter decreased with an increase in SF content. However, in the compressive strength results, the 5% addition of SF offered better strength development than 10% addition. This shows that the pore volume in the samples did not contribute to the strength.

As mentioned previously in the XRD analysis, the pozzolanic activity of SF did not occur in the samples. Furthermore, the sample with 30% CSA replacement level did not show any significant difference in reaction product (i.e., the formation of ettringite). It seems that the pore-size refinement is not due to the formation of reaction product but the filler effect of SF.

The C50R50S0 and C50R45S5 samples displayed an increase of the micrometer-sized pores around 10  $\mu$ m compared with the C50R40S10 sample. It should be noted that the C50R50S0 and C50R45S5 samples indicated a higher ettringite peak intensity than the C50R40S10 sample, and the length change of the C50R50S0 and C50R45S5 samples at 28 days for drying shrinkage was about 0.25% and 0.12%, respectively. It can be inferred that expansion due to the ettringite formation had occurred in the samples, and the expansion had led to cracking.

## 3.5. SEM/EDS Analysis

Figure 8a,c,e shows representative SEM micrographs of cross sections taken from the C10R85S5, C30R65S5, and C50R45S5 samples at the age of 28 days. The samples exhibited a large number of needle-like crystals in the matrix areas. The EDS analysis of the crystals (see white arrows and dashed ellipse in Figure 8a,c,e is shown in Figure 8b,d,f. These display representative EDS spectra for the needle-like crystals in the C10R85S5, C30R65S5, and C50R45S5 samples. As seen in Figure 8b,d,f, relatively high concentrations of Ca, Al, and S were detected in all the crystals. This indicates that the needle-like crystals are ettringite, which was clearly identified in the XRD analysis for the samples. It was mentioned above that ettringite formed in this study could be expansive because it forms from the consumption of ye'elimite, anhydrite, gypsum, and Ca(OH)<sub>2</sub> [4,6]. Other studies [35,36] reported that there are two types of ettringite with different morphologies, which are ball-type and needle-like crystals. It was reported that ball-type ettringite crystals do not cause any expansion, and needle-like crystals cause expansion.



Figure 8. Cont.





**Figure 8.** SEM secondary electron (SE) images of saw-cut surfaces of (**a**) C10R85S5, (**c**) C30R65S5, and (**e**) C50R45S5 samples. The graphs of (**b**), (**d**), and (**f**) show representative EDS spot analyses for ettringite in the samples.

The C50R45S5 sample indicated expansion at the age of 28 days in the drying shrinkage test, and the peak intensity of ettringite was higher in the C50R45S5 sample compared with the ettringite peaks in the C10R85S5 and C30R65S5 samples. The SEM image of the C50R45S5 sample showed a difference in the formation of ettringite crystals in comparison with other samples. It was observed that the matrix of the C50R45S5 sample was extensively covered with ettringite crystals, while clusters of ettringite were observed in the C10R85S5 and C30R65S5 samples.

The results of the SEM SE image and EDS analysis for samples with 10, 30, and 50% CSA content in Groups I and III (Table 2) were confirmed to have a similar tendency to those for samples with 10, 30, and 50% CSA content in Group II (i.e., C10R85S5, C30R65S5, and C50R45S5).

#### 4. Conclusions

The following conclusions were drawn from the results of this experimental investigation.

The main reaction product of the hardened samples was expansive ettringite, which was formed from the consumption of ye'elimite, anhydrite, gypsum, and Ca(OH)<sub>2</sub> in raw CSA material. The intensities of ettringite in XRD patterns increased with the CSA replacement level. The C-S-H or ettringite was expected to be formed by the reaction of  $C_2S$  or  $C_3A$  in raw RM; however, C-S-H phase was not present in XRD patterns, and it cannot be determined in the XRD results if the  $C_3A$  had been reacted or not. Additionally, although pore-size refinement for representative samples was confirmed by the addition of SF, it seems that was not due to the pozzolanic activity but instead due to the filler effect of SF.

Regardless of the SF content, as the amount of CSA increased (i.e., as the amount of RM decreased) up to 30%, the strength of the samples showed a tendency to increase. However, the strength of the sample containing 40% CSA replacement level was similar to or higher than that of the sample with 30% CSA, and the sample containing 50% replacement level of CSA showed lower strength development than that with 40% CSA. With respect to the SF content, the overall strength development was higher in the samples containing 5% SF than those containing 10% SF.

For the samples containing no SF, the increase of CSA content was effective for controlling the drying shrinkage of the samples. However, it was shown that 50% replacement level of CSA induced excessive expansion, leading to the reduction in compressive strength. It was found that the excessive expansion in the sample with 50% CSA was reduced by the addition of SF. Based on representative samples, it was indicated that ettringite in the 10% or 30% CSA sample was clustered, while ettringite in the 50% CSA sample was spread out evenly on the matrix.

It is expected that the experimental results of this study could provide a starting point as a basic data for the manufacture of eco-friendly binders mixing CSA and other industrial by-products except for RM and SF.

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