

# The Effects of Alkali Sulfate on the Hydration of a $C_3A-CaSO_4 \cdot 2H_2O$ System

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## ABSTRACT

The hydration mechanism of the  $3CaO \cdot Al_2O_3 - CaSO_4 \cdot 2H_2O$  system in the presence of alkali sulfates has been investigated. The early hydration rate of  $3CaO \cdot Al_2O_3$  was accelerated by the addition of  $Na_2SO_4$  and  $K_2SO_4$ . This is closely related to the formation of syngenite ( $CaSO_4 \cdot K_2SO_4 \cdot H_2O$ ), and the U-phase added  $K_2SO_4$  and  $Na_2SO_4$  in the  $3CaO \cdot Al_2O_3 - CaSO_4 \cdot 2H_2O$  system, respectively. The formation of the rigid syngenite and U-phase structure led to rapid setting and decreases the sulfate content in the liquid phase of the hydrating cement to the extent that it cannot adequately retard the hydration of  $3CaO \cdot Al_2O_3$ . In case of the alkali sulfate not added to the  $3CaO \cdot Al_2O_3 - CaSO_4 \cdot 2H_2O$  system, the ettringite was transformed to monosulfoaluminate immediately after the consumption of gypsum. However, when the alkali sulfates were added to this system, the ettringite did not transform to monosulfoaluminate immediately even though the gypsum was completely consumed. There was a stagnation period to transform to the monosulfoaluminate after the consumption of gypsum because the syngenite and U-phase remained as the sulfate source.

**Key words :** Alkali sulfate, Hydration, U-phase, Syngenite, Phase composition

## 1. Introduction

Alkalis are inevitably introduced in minor quantities into Portland cement clinkers. In general, the alkalis in Portland cement clinkers are found partly as soluble sulfates and partly as constituents of the clinker minerals. When an alkali-containing cement is mixed with water, the alkali metal ion dissolves in the liquid phase of the hydrating system and affects the rate of cement hydration, the morphology of the hydration products, and the rheological properties of the fresh cement.<sup>1-4</sup> As the alkali content increases, the early strengths increase while the corresponding 28-day strengths decrease. Furthermore, the initial hydration increases while the later hydration decreases.<sup>5-7</sup> It is well known that cements containing alkali sulfates usually exhibit poor rheological behavior. Recently, there have been many papers regarding the rheological properties of cement pastes with alkali sulfates and superplasticizers.<sup>8-10</sup> Alkalis have been known to promote flash setting, however the promotion mechanism of the setting time for fresh cement was unclear. The research related to the early setting and hardening behavior have been studied. Odler and Wonnemann reported the rapid setting to form syngenite ( $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ ) by adding  $K_2SO_4$ , but the effects of  $Na_2SO_4$  was unclear.<sup>11-15</sup> Also, there were several reports regarding the hydration mechanism of the  $3CaO \cdot$

$Al_2O_3 - CaSO_4 \cdot 2H_2O$  system containing alkali sulfates.

The purpose of this research is to clarify the effects of the alkali sulfates on the hydration of the  $3CaO \cdot Al_2O_3 - CaSO_4 \cdot 2H_2O$  system by investigating the effect of  $Na_2SO_4$  and  $K_2SO_4$  on hydration.

## 2. Experimental Procedure

### 2.1. Materials

$Ca_3Al_2O_6$  ( $3CaO \cdot Al_2O_3$ ) was synthesized by sintering at 1350°C for three hours for stoichiometric mixtures of reagent grade  $Al_2O_3$  and  $CaCO_3$ . The process was repeated two times and the sample was ground to a specific surface area of 0.48 m<sup>2</sup>/g. The reagent grade of  $CaSO_4 \cdot 2H_2O$  with a specific surface area of 0.4 m<sup>2</sup>/g was used as Gypsum and the reagent grades of  $Na_2SO_4$  and  $K_2SO_4$  were used as alkali sulfates.

### 2.2. Specimen Preparation

The molar ratio of  $3CaO \cdot Al_2O_3 : CaSO_4 \cdot 2H_2O$  was 1:2/3 for the standard ratio of  $3CaO \cdot Al_2O_3$  and gypsum in OPC.  $Na_2SO_4$  and  $K_2SO_4$  were the alkali sulfates, which were added 0.13 mole respecting  $3CaO \cdot Al_2O_3$ , respectively. This ratio was approximately same in the OPC as in  $R_2O$ . Hydration was carried out at 20°C with water/solid=0.6 and cured in sealed polyethylene bottles for the desired hydration time. To characterize the hydration products, the hydration was stopped by washing with acetone and dried using an aspirator for 3 h.

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### 2.3. Test Measurement

An X-ray quantitative analysis (CuK  $\alpha$  radiation, Ni filter) and a scanning electron microscope (SEM) were used to investigate the hydration reaction. First, we synthesized the standard hydrates sample for  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\text{-CaSO}_4\cdot 2\text{H}_2\text{O}$ -alkali systems. In these systems, the primary crystallized hydrates were ettringite, monosulfoaluminate, and U-phase (calcium sulfate hydrate containing  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ ). The fabrication of standard samples and the method of X-ray quantitative analysis have been explained in earlier papers.<sup>16-18)</sup> The hydrated sample and internal standard sample were carefully mixed and ground until the mean diameter reached  $5\ \mu$  in order to avoid the effect of preferred orientation and microabsorption of X-rays. MgO was selected as the internal standard because the main peak does not overlap with the main hydrated peak in the systems. In a mixture, each crystalline component possesses a unique pattern of diffraction peaks and the intensity of each peak is directly proportional to the component's weight fraction in the mixture, excluding the absorption effects. The unwanted absorption effects can be satisfactorily removed by introducing an internal standard.

## 3. Results and Discussion

To survey the effects of the alkali sulfates on the hydration mechanism for the  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\text{-}2/3\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  system, the hydration rate of  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  was first investigated using an X-ray quantitative analysis and the result is shown in Fig. 1. It can be seen that the early hydration rate of  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  increased by adding alkali sulfates, however

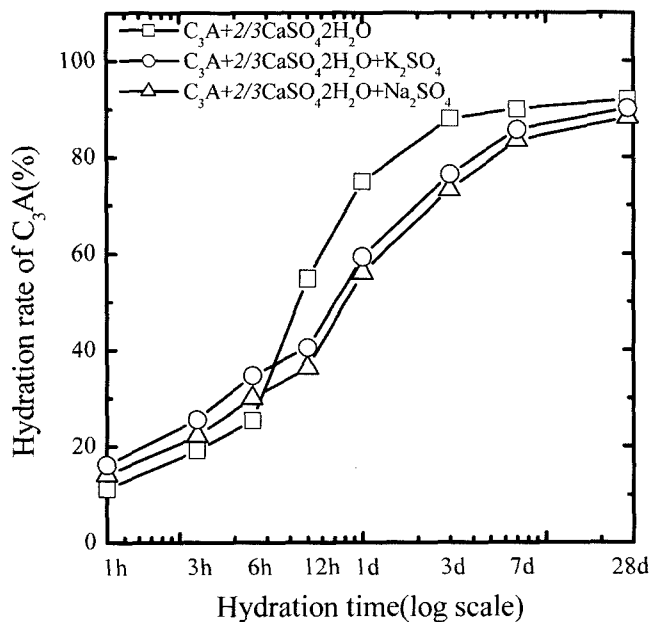


Fig. 1. Hydration rate of  $\text{C}_3\text{A}$  for  $\text{C}_3\text{A}+2/3\text{CaSO}_4\cdot 2\text{H}_2\text{O}+\text{alkalies}$  system.

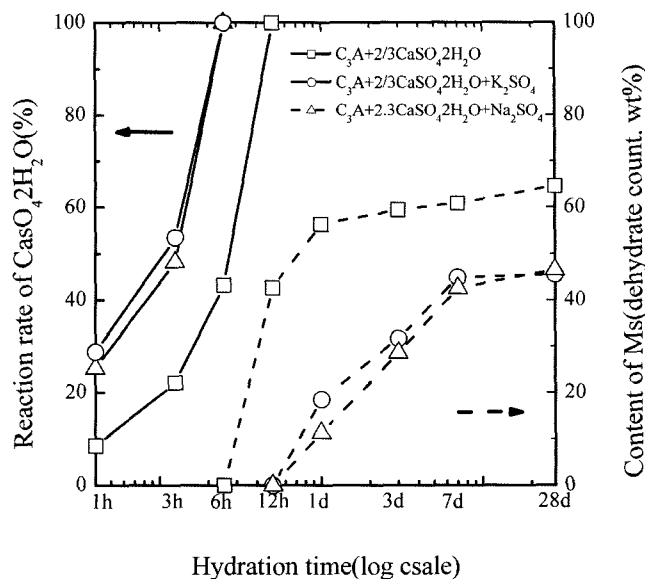


Fig. 2. Reaction rate of  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  and Content of Ms for  $\text{C}_3\text{A}+2/3\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  with alkalies (Ms: monosulfoaluminate).

after 6 h, the later hydration rate was decreased. Furthermore, for the  $\text{K}_2\text{SO}_4$  addition, the increasing effect of hydration was higher than that of the  $\text{Na}_2\text{SO}_4$  addition.

Fig. 2 shows the reaction rate of  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  and the formation rate of the monosulfoaluminate hydrate for  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\text{-}2/3\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ -alkali sulfate system with the hydration time. The reaction rate of  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  increased by adding alkali sulfates. The reaction rate of the  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  added to the  $\text{K}_2\text{SO}_4$  was slightly higher than that of  $\text{Na}_2\text{SO}_4$ . In general, after consuming the  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ , the ettringite began to transform into monosulfoaluminate in the alkali sulfate-free  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\text{-}2/3\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  system. However, for the added alkali sulfates, the ettringite did not transform into monosulfoaluminate immediately, even though the gypsum was completely consumed. Therefore, it is clear that the presence of alkali sulfates leads to the retardation of the transformation reaction of ettringite into monosulfoaluminate.

To understand the hydration mechanism for the  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\text{-}2/3\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  system, the behavior of the ettringite hydrate is very important. Fig. 3 shows the formation rate of the ettringite for the  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\text{-}2/3\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ -alkali sulfate system with the hydration time. When the alkali sulfate was added, the formation rate of ettringite was higher than that of the alkali sulfate free formation for the  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\text{-}2/3\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  system. The content of ettringite began to decrease after 6 h in the alkali sulfates free  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\text{-}2/3\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  system: it is the same time for the complete consumption of  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  as shown in Fig. 2. However for the alkali sulfate addition, the  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  disappeared at 6 h as shown in Fig. 2 and the ettringite did not decrease even after the consumption of  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ . There was a stagnation period between 6 h and 12 h.

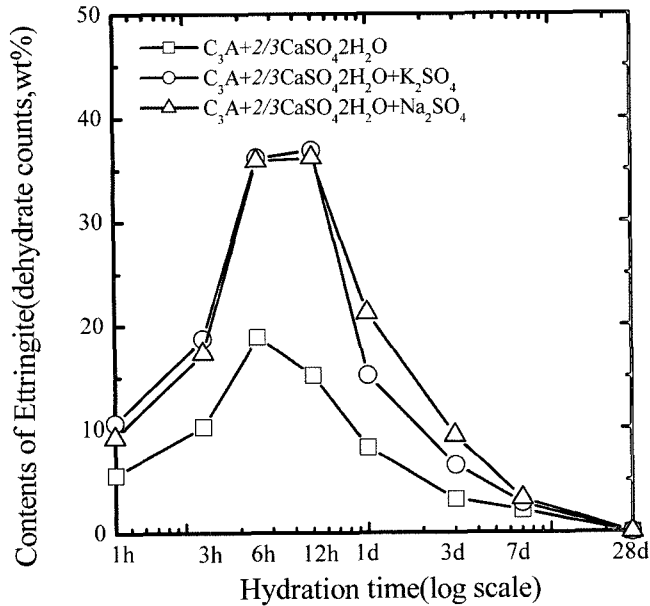


Fig. 3. Contents of ettringite for  $C_3A-2/3CaSO_4 \cdot 2H_2O$  system with alkali.

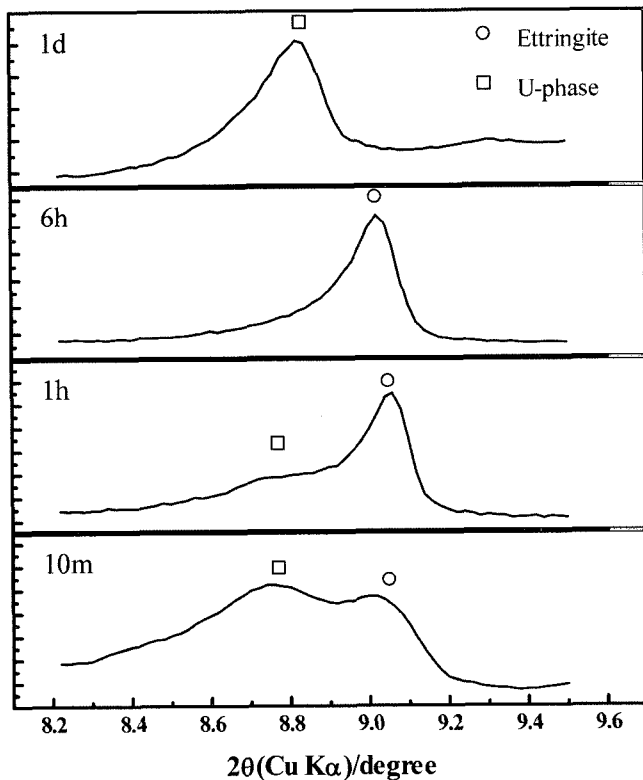


Fig. 4. XRD patterns of  $C_3A-2/3CaSO_4 \cdot 2H_2O-Na_2SO_4$  system with hydration time.

The early hydration rate of  $3CaO \cdot Al_2O_3$  was accelerated by the addition of  $Na_2SO_4$  and  $K_2SO_4$  as shown in Fig. 1. It is assumed that there is a difference of initial hydrates between the alkali-free system and alkali sulfates addition system. Figs. 4 and 5 show the XRD patterns of the  $3CaO \cdot Al_2O_3-2/3CaSO_4 \cdot 2H_2O-Na_2SO_4$  and  $3CaO \cdot Al_2O_3-2/3$

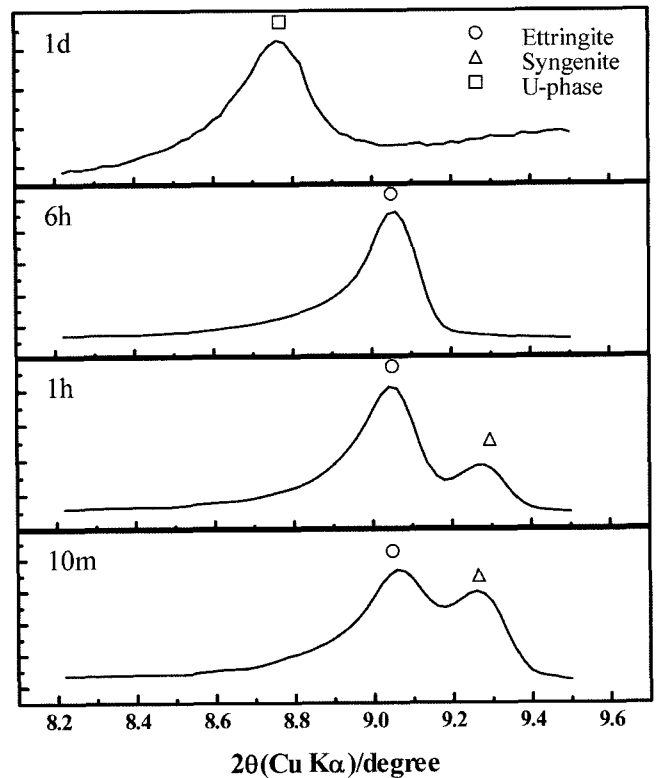
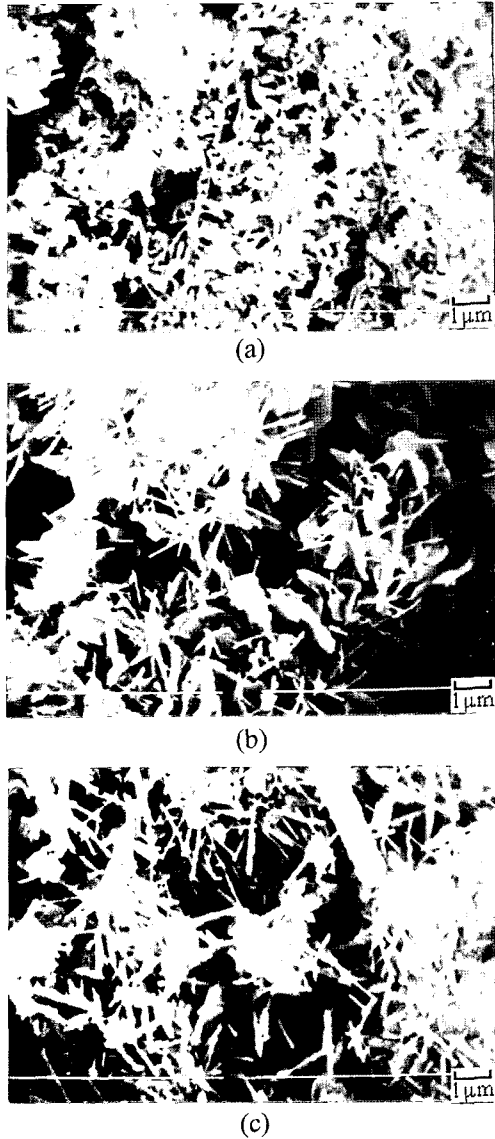


Fig. 5. XRD patterns of  $C_3A-2/3CaSO_4 \cdot 2H_2O-K_2SO_4$  system with hydration time.

$CaSO_4 \cdot 2H_2O-K_2SO_4$  systems. In general, the crystallized initial hydrate is ettringite in the alkali-free  $3CaO \cdot Al_2O_3-2/3CaSO_4 \cdot 2H_2O$  system. However, in the case of the  $Na_2SO_4$  addition for the  $3CaO \cdot Al_2O_3-2/3CaSO_4 \cdot 2H_2O$  system, not only the ettringite but also the U-phase (calcium mono-sulfoaluminate containing  $Na_2SO_4$ ) was formed initially. It is reported that the initial hydration rate may be controlled by sulfate ions in the hydrated solution. The U-phase formation in addition to ettringite may lead to a deficiency of sulfate ions in the hydrated solution. Therefore, it is considered that the reaction of  $CaSO_4 \cdot 2H_2O$  and  $3CaO \cdot Al_2O_3$  is further accelerated with alkali sulfate additions compared with the alkali-free system as shown in Figs. 1 and 2. The U-phase disappeared at 6 h, but after 1 day, the U-phase appeared again, as shown Fig. 4.

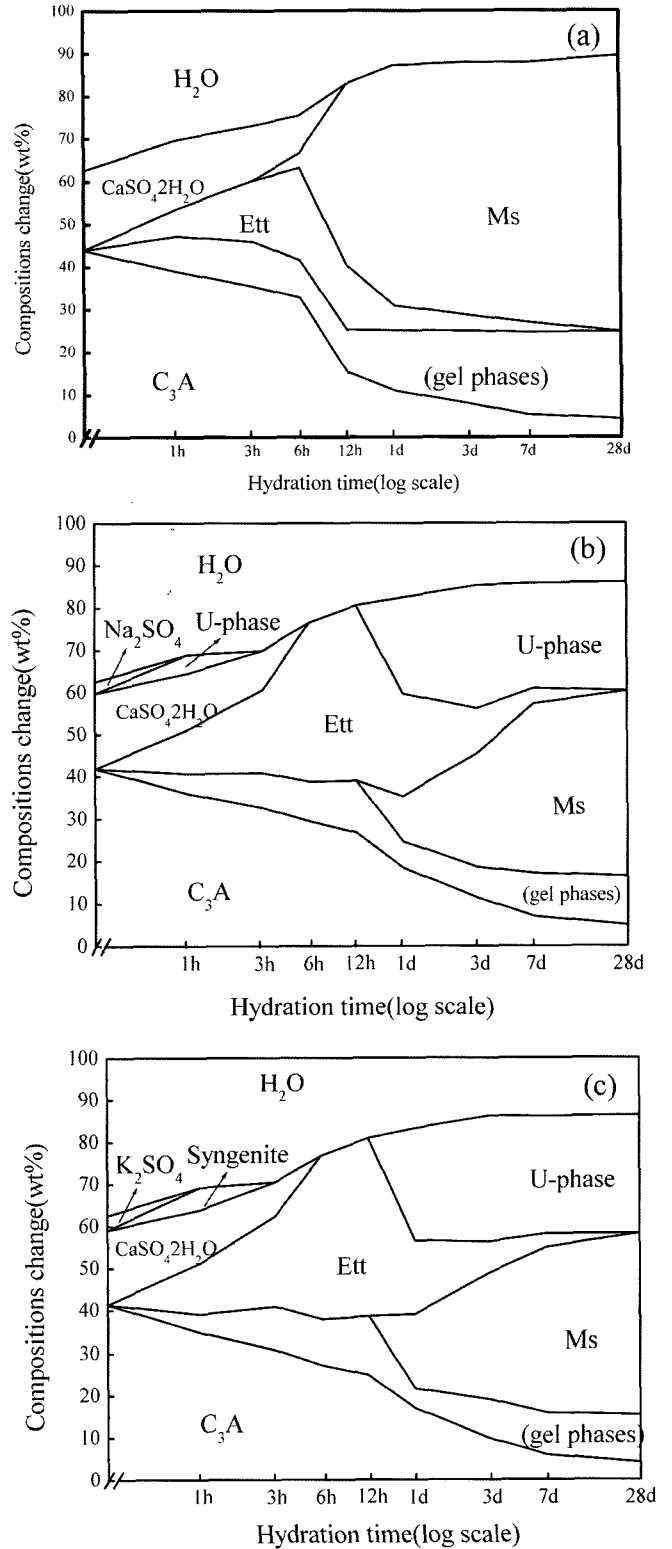
Otherwise, in case of the  $K_2SO_4$  addition for the  $3CaO \cdot Al_2O_3-2/3CaSO_4 \cdot 2H_2O$  system as shown in Fig. 5, the ettringite and syngenite ( $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ ) were formed initially. The U-phase did not form at the initial stage in this system because  $K_2SO_4$  prefers to react with  $CaSO_4 \cdot 2H_2O$  to form the syngenite. The reaction of  $CaSO_4 \cdot 2H_2O$  and  $3CaO \cdot Al_2O_3$  is accelerated more than the alkali-free system due to the above-mentioned reasons. The syngenite disappeared after 6 h and the U-phase did not form at the initial stage as mentioned above, but after 1 day, the U-phase was also formed.

Fig. 6 shows the scanning electron microscopes of the  $3CaO \cdot Al_2O_3-2/3CaSO_4 \cdot 2H_2O$ -alkali sulfate system at 1 h.



**Fig. 6.** SEM photographs for  $C_3A-2/3CaSO_4 \cdot 2H_2O$ -alkali sulfate system at 1 h.  
 (a)  $C_3A-2/3CaSO_4 \cdot 2H_2O$   
 (b)  $C_3A-2/3CaSO_4 \cdot 2H_2O-Na_2SO_4$   
 (c)  $C_3A-2/3CaSO_4 \cdot 2H_2O-K_2SO_4$

In the alkali-free  $3CaO \cdot Al_2O_3-2/3CaSO_4 \cdot 2H_2O$  system, as shown in Fig. 6(a), only the needle-shaped small ettringite crystal appeared. However, in the case of the  $Na_2SO_4$  addition for the  $3CaO \cdot Al_2O_3-2/3CaSO_4 \cdot 2H_2O$  system (Fig. 6(b)), plate-shaped and needle-shaped crystals were formed. At this time, the crystallized hydrates are the U-phase and ettringite, as shown in Fig. 4. Because the hydration was accelerated, the needle-shaped ettringite crystal size was larger than the alkali-free system. This is the reason that the formation of the U-phase led to a deficiency of sulfate ions in the hydrating solution, so the hydration was accelerated as mentioned above. In the case of the  $K_2SO_4$  addition to the  $3CaO \cdot Al_2O_3-2/3CaSO_4 \cdot 2H_2O$  system (Fig. 6(c)), the crystallized hydrates are ettringite and syngenite, as shown



**Fig. 7.** Compositions change of  $C_3A-2/3CaSO_4 \cdot 2H_2O$ -alkali sulfate system.  
 (a)  $C_3A-2/3CaSO_4 \cdot 2H_2O$   
 (b)  $C_3A-2/3CaSO_4 \cdot 2H_2O-Na_2SO_4$   
 (c)  $C_3A-2/3CaSO_4 \cdot 2H_2O-K_2SO_4$

in Fig. 5. A large needle-shaped ettringite was formed com-

pared with the alkali-free system.

As mentioned above, it is assumed that due to the formation of syngenite ( $CaSO_4 \cdot K_2SO_4 \cdot H_2O$ ) in the case of the  $K_2SO_4$  addition and the U-phase in the case of the  $Na_2SO_4$  addition, the early hydration was accelerated. The formation of a rigid syngenite and U-phase structure not only led to quick setting, but also decreased the sulfate content in the liquid phase of the hydrating cement to the extent that it cannot adequately retard the hydration of  $3CaO \cdot Al_2O_3$ .

The compositions change was determined by an X-ray quantitative analysis to confirm the above results. In the  $3CaO \cdot Al_2O_3$ - $2/3CaSO_4 \cdot 2H_2O$ -alkali sulfate system, the crystallized hydrated products are ettringite, monosulfoaluminate, U-phase, and syngenite. The gel phases were calculated by the difference in the balance of the materials between the reaction rate of the reactants and produced hydrates. First, in the alkali-free  $3CaO \cdot Al_2O_3$ - $2/3CaSO_4 \cdot 2H_2O$  system, the compositions changed as shown in Fig. 7(a). The gel phase and the ettringite were initially formed by the reaction of  $3CaO \cdot Al_2O_3$  and  $CaSO_4 \cdot 2H_2O$ . At almost the same time as the consumption of the  $CaSO_4 \cdot 2H_2O$ , the ettringite began to transform to monosulfoaluminate and the ettringite was completely transformed to monosulfoaluminate after 28 days. Figure 7(b) shows the phase compositions with hydration times for the  $3CaO \cdot Al_2O_3$ - $2/3CaSO_4 \cdot 2H_2O$ - $Na_2SO_4$  system. In this system, the U-phase in addition to gel phases and ettringite were formed initially. This U-phase disappeared after 6 h, but after 1 day, it reappeared. As shown in Fig. 1, the early hydration rate was accelerated by addition of alkali sulfates. This may be closely related to the sulphate ions in the hydrating solution, which are deficient due to the U-phase formation in addition to the ettringite and cannot lead to adequate retardation for the  $3CaO \cdot Al_2O_3$  initial hydration. In the case of the alkali sulfate free system, the ettringite is transformed to monosulfoaluminate immediately after the consumption of the gypsum. However, in the case of the added alkali sulphates, the ettringite does not transform into monosulfoaluminate immediately even though the gypsum was consumed. There is a stagnation period to transform into monosulfoaluminate after consumption of gypsum, and the ettringite transformed into not only monosulfoaluminate but also a U-phase after 1 day. Figure 7(c) shows the phase compositions with hydration times for the  $3CaO \cdot Al_2O_3$ - $2/3CaSO_4 \cdot 2H_2O$ - $K_2SO_4$  system. In this system, the syngenite phase in addition to the gel phases and ettringite were initially formed differ to those with the  $Na_2SO_4$  addition. The early hydration rate was also accelerated by adding  $K_2SO_4$  with the  $Na_2SO_4$  addition, as shown in Fig. 1. It is also considered that the sulphate ions in the hydrating solution will be in deficient states due to the syngenite phase and ettringite formation. There is also a stagnation period to transform the monosulfoaluminate after the consumption of gypsum because the syngenite phase remains as a sulfate source.

## 4. Conclusions

The effect of  $Na_2SO_4$  and  $K_2SO_4$  on the hydration of the  $3CaO \cdot Al_2O_3$ - $CaSO_4 \cdot 2H_2O$  system was investigated. The early hydration rate of  $3CaO \cdot Al_2O_3$  was accelerated by the addition of  $Na_2SO_4$  and  $K_2SO_4$ . This is closely related to the initial formation of syngenite ( $CaSO_4 \cdot K_2SO_4 \cdot H_2O$ ) and the U-phase in addition to ettringite. A formation of the rigid syngenite and U-phase structure not only led to quick setting, but also decreased the sulfate content in the liquid phase of the hydrating cement to the extent that it could not adequately retard the hydration of  $3CaO \cdot Al_2O_3$ . In case of alkali sulfate not being added to the  $3CaO \cdot Al_2O_3$ - $CaSO_4 \cdot 2H_2O$  system, the ettringite was transformed into monosulfoaluminate immediately after consuming the gypsum. However, in case of the alkali sulfates addition for the  $3CaO \cdot Al_2O_3$ - $2/3CaSO_4 \cdot 2H_2O$  system, the ettringite did not transform into monosulfoaluminate immediately even though the gypsum was completely consumed. There was a stagnation period in the transformation to monosulfoaluminate after the consumption of gypsum because the syngenite and U-phase remain as a sulfate source. After the syngenite and U-phase disappeared, the ettringite began to transform into monosulfoaluminate and/or U-phase (calcium mono-sulfoaluminate hydrates containing sodium sulfate) again.

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