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The influence of calcium lignosulphonate–sodium bicarbonate on the status of ettringite crystallization in fly ash cement paste

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Abstract

Calcium lignosulphonate (CL)–sodium bicarbonate (SB) (a total of 0.7% by weight of cement and CL to SB ratio of 1:1.8) will cause the fluidity of fly ash cement paste to decrease rapidly. It is the variation of the status of ettringite crystallization that causes this phenomenon. Experimental results show that CL–SB affects the liquid-phase composition of fly ash cement paste remarkably. As a result, ettringite crystallizes out in the shape of needles from the solution. These needle-like crystal particles are distributed in the solution at a certain distance from the surface of clinker particles. At the initial hydration stage, the crystallization of ettringite is stronger in fly ash cement with calcined gypsum than in fly ash cement with gypsum. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Calcium lignosulphonate–sodium bicarbonate; Cement paste; Rheology; Ettringite

1. Introduction

Since Lukjanova and Renbinder [1] began to study the effects of lignosulphonate–alkali carbonate on the hydration of ground silicate clinker in 1957, a succession of work about this system has been carried out by Brunauer [2], Odler et al. [3], Jawed [4] and Škvára and Ševčík [5]. The range of the research has been broadened into a system that contains gypsum, besides lignosulphonate, alkali carbonate and silicate clinker. In present experiments, when calcium lignosulphonate–sodium bicarbonate is added into the fly ash cement paste, a remarkable water-reducing effect will be gained, normal setting time can be achieved, and both early strength and long-term strength can be improved considerably as long as both the total amount of CL–SB and the proportion of CL to SB are appropriate. However, if the added amount of CL–SB is smaller, the fluidity of fly ash cement paste will decrease rapidly at the initial hydration stage. It is the variation of the status of ettringite crystallization in cement paste that causes this phenomenon. In this paper, the influence of CL–SB on the status of ettringite crystallization is investigated and the reasons for the change in the status of ettringite crystallization are analyzed.

2. Experimental materials and methods

The chemical constituents of materials used in this test are listed in Table 1. The calcined gypsum (CG) was obtained by burning gypsum (G) at 1050 °C for 3 h in an electric furnace. The proportions of the different materials in cement E with gypsum and cement S with the calcined gypsum are given in Table 2. Calcium lignosulphonate–sodium bicarbonate was added into both cements E and S, which are labeled as $E_{0.7}$ and $S_{0.7}$, respectively. The amount of CL–SB added was 0.7% by weight of the cement and CL

Table 1
The chemical composition of materials (wt.%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Loss
Clinker	19.88	4.81	2.10	67.72	1.81		
Fly ash	51.20	33.18	6.10	2.48	1.64	0.32	7.73
Blast furnace slag	35.45	9.69	1.66	31.49	12.88		
Gypsum						32.56	

Table 2
The proportion of the different materials in cement (wt.%)

Cement	Clinker	Fly ash	Gypsum or calcined gypsum	Blast furnace slag
E	53.86	35.00	6.14	5.00
S	54.95	35.00	5.05	5.00

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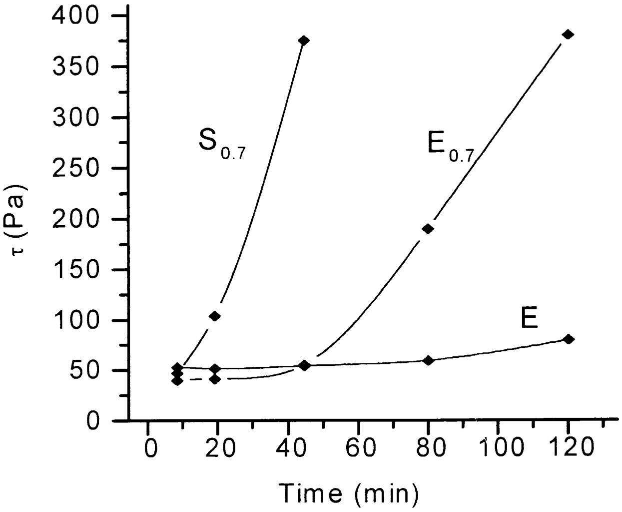


Fig. 1. Yield value of cement paste.

to SB ratio was 1:1.8. In each cement sample, Blaine specific surface ranged from 430 to 435 m^2/kg.

The yield value of cement paste (W/C = 0.6) was measured with an NXS-11 rotational viscometer (measure system B). In order to study the hydrate the cement was watered to mix round into the paste according to water demand of standard consistency and the molded. Samples were cured in tap water at 20 ± 2 °C and the curing was stopped at different hydration ages by absolute ethyl alcohol. The hydration products were studied with XRD, SEM and DTA. The liquid-phase composition of cement paste was analyzed, and the tested solution was collected according to the following procedure: prepare cement paste (W/C = 2.5), stir continuously at 20 ± 2 °C for required hydration duration, then filter with a vacuum filter.

3. Results and discussion

The yield value of cement paste is correspondent to the minimal stress to break the flocculent structure in the paste. If the yield value increases, the fluidity of cement paste will decrease. The faster the yield value increases, the faster the fluidity decreases. The influence of CL–SB on the yield value of fly ash cement paste is shown in Fig. 1. It remarkably enhances the yield value so that CL–SB consists 0.7% by weight of the cement. The effect of CL–SB on cement S with the calcined gypsum is larger than that on cement E with gypsum.

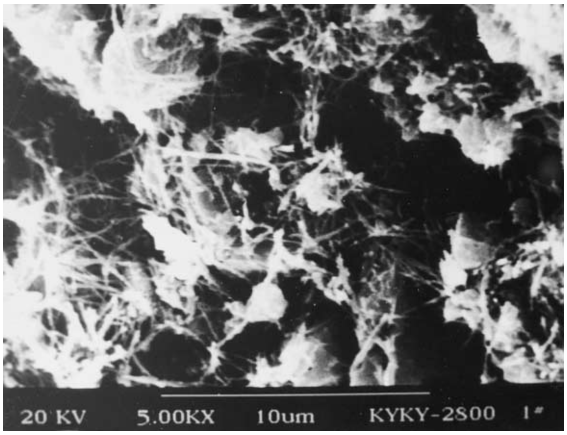


Fig. 2. SEM photograph of paste $E_{0.7}$ hydrated for 2 h.

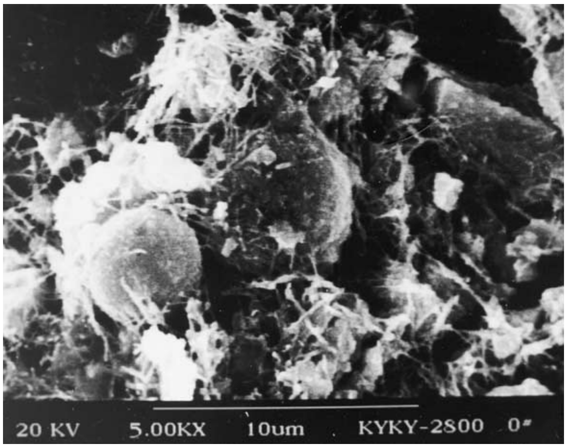


Fig. 3. SEM photograph of paste $S_{0.7}$ hydrated for 30 min.

It is well known that at the initial hydration stage of common silicate cement ettringite crystallizes out in the form of gelatinous hydrates, which surround the surface of C_3A contained in clinker particles. However, both the SEM pictures of $E_{0.7}$ hydrated for 2 h and that of $S_{0.7}$ hydrated for 30 min (Figs. 2 and 3) show that individual larger ettringite crystal particles crystallize in the shape of needles. These needle-like crystal particles are distributed in the solution at a certain distance from the surface of clinker particles. The occuring of above-mentioned phenomena is due to the adding of CL-SB into the cement no matter gypsum or the calcined gypsum in the cement is blended. The DTA curves of several samples are shown in Fig. 4. The appearance of the heat absorption peak at 128 °C is due to the dehydration of ettringite. The 128 °C peak area of $E_{0.7}$ hydrated for 2 h is greater than that of E hydrated for the same time limit, and the 128 °C peak of $S_{0.7}$ hydrated only for 30 min also reaches a certain size. This indicates that CL–SB causes the amount of ettringite formed at the initial hydration stage to increase, and that the rate of ettringite

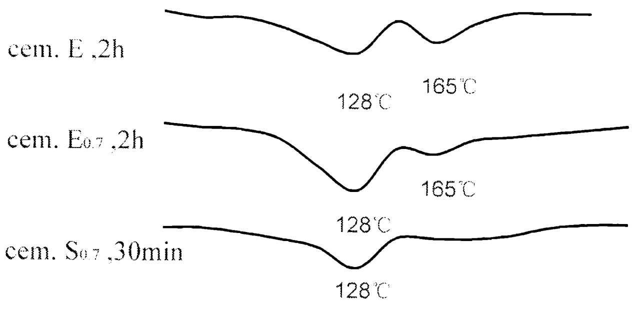


Fig. 4. DTA curves of cement pastes.

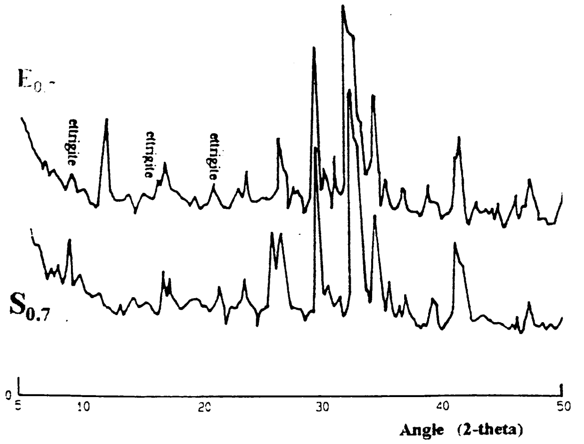


Fig. 5. XRD patterns of pastes $E_{0.7}$ and $S_{0.7}$ hydrated for 30 min.

crystallization is faster in cement with the calcined gypsum. As shown in Fig. 5, the ettringite diffraction peak of $S_{0.7}$ hydrated for 30 min is higher than that of $E_{0.7}$ hydrated for the same time limit. Obviously, it is the variation of the status of ettringite crystallization that brings about the rapid lowering of the fluidity of the cement paste with added CL–SB.

So why will CL–SB change the status of ettringite crystallization?

The following equation describes the crystallization of ettringite from the solution of cement paste:

$$6Ca^{2+} + 2AlO_2^- + 3SO_4^{2-} + 4OH^- + 29H_2O$$
$$= 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O$$

Because ettringite crystals are born out of the solution, the change of the liquid-phase composition will undoubtedly change the status of ettringite crystallization. As shown in Fig. 6, the concentration of CaO is smaller and both the concentrations of Al_2O_3 and of SO_3 are greater in the solution of paste $E_{0.7}$, compared to those in the solution of paste E. At the initial hydration stage of cement E without CL–SB, ettringite can only crystallize out on the surface of C_3A contained in clinker particles in which AlO_2^- ions can be supplied. This is because the concentration of Al_2O_3 in the solution of paste E is almost zero. In paste $E_{0.7}$, ettringite can crystallize from the solution at a certain distance from the surface of clinker particles. This is because the liquid-phase composition has been changed; the concentration of

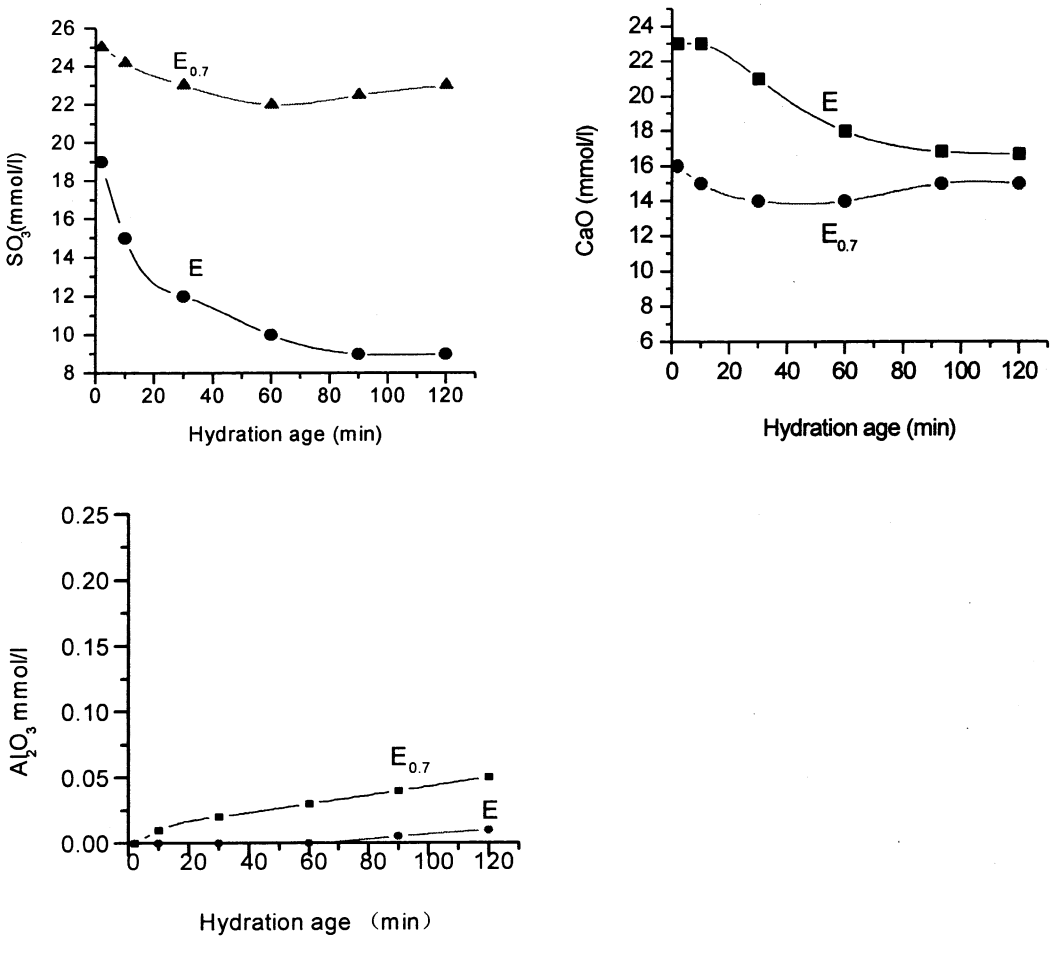


Fig. 6. Variation of liquid-phase compositions in pastes E and $E_{0.7}$.

AlO_2^- ions in the solution of paste $E_{0.7}$ at the initial hydration stage can meet the demand for forming ettringite.

According to theories of crystallization, the rate of nucleation depends on the supersaturation level of the solution. The greater the supersaturation level of solution, the greater the rate of nucleation. On the surface of C_3A contained in clinker particles, both the concentrations of AlO_2^- ions and of Ca^{2+} ions are greater and the rate of nucleation is greater as long as the concentration of SO_4^{2-} ions is ensured to a certain extent. If a large number of nuclei grow at the same time, a large number of tiny crystal particles will be produced. However, for paste $E_{0.7}$, even though the rate of nucleation on the surface of C_3A contained in clinker particles is still greater than that in the liquid phase at a certain distance from the surface of clinker particles, these nuclei do not grow into crystals easily. The growth of nuclei in the liquid phase has priority over that on the surface of C_3A contained in clinker particles because it is easier for SO_4^{2-} ions from gypsum to diffuse to the liquid phase between clinker particles. Because the rate of ettringite nucleation in the liquid phase is slower, the number of formed crystal particles decreases and the larger ettringite crystal particles can be produced as long as there is enough room for crystal growth. Since the entropy of the crystallization in the dilute solution is large, the rates of crystal growth in different directions are different from each other significantly; thus, the needle-like crystal particles can be produced. It is obvious that in the paste $E_{0.7}$ with CL–SB, the ettringite crystals produced do not cover tightly over the surface of C_3A contained in clinker particles to inhibit the hydration of C_3A. Although lignosulphonate anion may be absorbed on the surface of cement particles to form the screen, the amount of CL is so little that the hydration of C_3A will still be in slow progress. Consequently, the rate of formation of ettringite in paste $E_{0.7}$ with CL–SB is greater than that in paste E without CL–SB.

Fig. 7 illustrates the difference between the liquid-phase compositions of pastes $E_{0.7}$ and $S_{0.7}$ at the initial hydration stage. Apparently, the liquid-phase composition of cement paste with CL–SB is affected by the type of gypsum blended in the cement. As in Fig. 8, the solubilities of gypsum in the saturated calcareous water with and without CL–SB are quite different. It is the same with the solubility of the 1050 °C calcined gypsum. The concentration of SO_3 in saturated calcareous water with CL–SB is higher than that in saturated calcareous water without CL–SB and

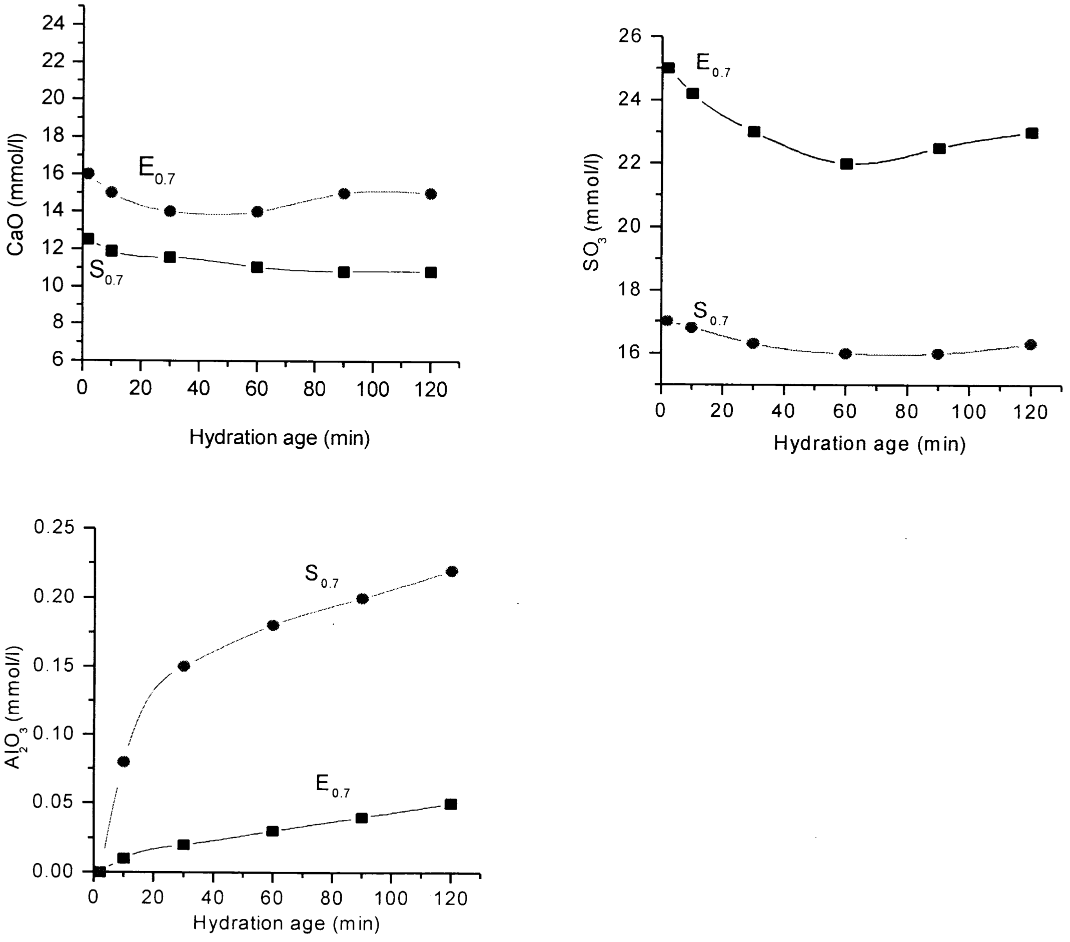
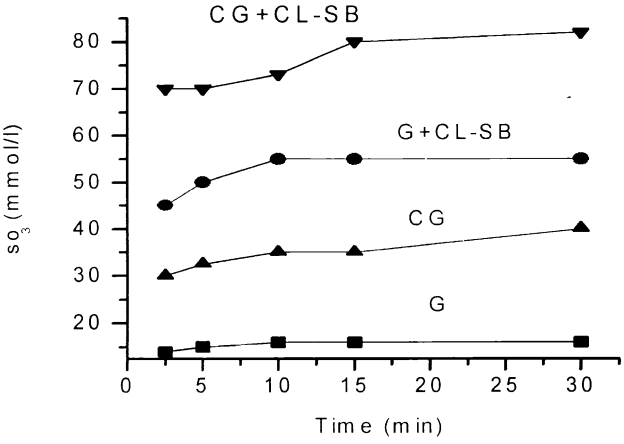


Fig. 7. Variation of liquid-phase compositions in pastes $E_{0.7}$ and $S_{0.7}$.



G=gypsum; CG=the 1050℃ calcined gypsum

Fig. 8. Influence of CL–SB on solubility of G&CG in the saturated calcareous water.

the concentration of SO_3 of the 1050 °C calcined gypsum is higher than that of gypsum even more. The reason that the concentration of SO_3 is lower in the solution of paste $S_{0.7}$ than in the solution of paste $E_{0.7}$ may be that ettringite crystallizes so fast from the solution of paste $S_{0.7}$ so that the concentration of SO_3 in the solution is reduced. Meanwhile, the concentration of Al_2O_3 in the solution of paste $S_{0.7}$ is higher than in the solution of paste $E_{0.7}$; thus, it can well be imagined that ettringite crystal particles will be even more distributed in the solution at a certain distance from the surface of clinker particles in paste $S_{0.7}$. Therefore, the ettringite crystals produced in paste $S_{0.7}$ do not cover the surface of C_3A contained in clinker particles to inhibit the hydration of C_3A more, and the amount of ettringite produced in paste $S_{0.7}$ is more than that in paste $E_{0.7}$.

Fly ash and blast furnace slag are contained in cements $E_{0.7}$ and $S_{0.7}$. Cements $PE_{0.7}$ and $PS_{0.7}$ are respectively obtained from cements $E_{0.7}$ and $S_{0.7}$ by replacing all fly ash and blast furnace slag with clinker. The SEM pictures of $PE_{0.7}$ hydrated for 2 h and that of $PS_{0.7}$ hydrated for 30 min (Figs. 9 and 10) show that the status of ettringite crystallization in these samples without fly ash and blast furnace slag is basically similar to that of cement $E_{0.7}$ and $S_{0.7}$ (Figs. 2 and 3). Thus, it can be seen that the change in ettringite crystallization in cements $E_{0.7}$ and $S_{0.7}$ is mainly due to the effect of CL–SB, although the liquid-phase composition of cement is also affected by fly ash and blast furnace slag.

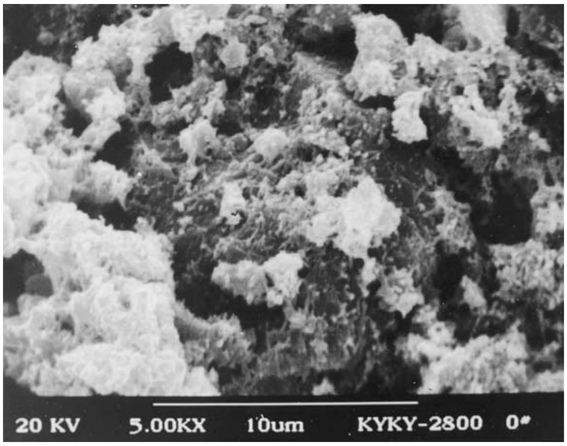


Fig. 9. SEM photograph of paste $PE_{0.7}$ hydrated for 2 h.

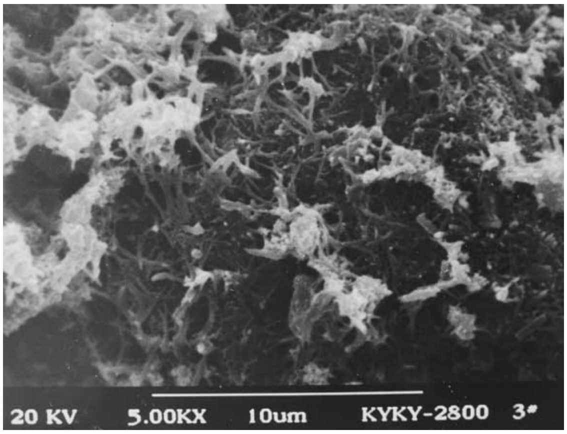


Fig. 10. SEM photograph of paste $PS_{0.7}$ hydrated for 30 min.

4. Conclusions

CL–SB (total of 0.7% by weight of cement and CL to SB ratio of 1:1.8) affects the liquid-phase composition of fly cement paste remarkably. As a result, the location where ettringite crystallizes is transferred from the surface of C_3A contained in clinker particles to the solution at a certain distance from the surface of clinker particles; the state of formed ettringite crystals is changed from a large number of tiny crystal particles into a limited number of larger needle-like crystal particles; and the amount of formed ettringite is increased. The variation of the status of ettringite crystallization causes the fluidity of fly ash cement paste to decrease rapidly. The effect of CL–SB on ettringite crystallization is stronger in fly ash cement with the calcined gypsum than it is in fly ash cement with gypsum.

Acknowledgments

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References

[1] O.I. Lukjanova, P.A. Renbinder, The influence of hydrophilic plasticizer, additions on the properties of concentrated cement suspension, Kolloidn. Zh. 19 (1957) 82–85.

[2] S. Brunauer, Portland cement composition and method, US Pat 3,689,294.

[3] I. Odler, J. Skalny, S. Brunauer, Properties of the system clinker–lignosulfonate–carbonate, Proceedings of the 6th International Congress on the Chemistry of Cement, Moscow, (1974) (suppl. paper).

[4] I. Jawed, Hydration of cement–lignosulfonate–alkali carbonate system, J. Am. Ceram. Soc. 62 (1979) 9–10.

[5] F. Škvára, V. Ševčík, Influence of high temperature on gypsum-free Portland cement materials, Cem. Concr. Res. 29 (1999) 713–717.