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Effects of barium salt on the fixation of chloride ions in hardened mortars

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Abstract

The effects of barium sulfate on the fixation and permeability of chloride ions are discussed. It was found that greater amounts of chloride ion were fixed during the hydration of C_3A synthesized in the presence of $BaSO_4$. When C_3A and $CaSO_4{\cdot}2H_2O$ were mixed and hydrated in the pseudo-seawater, the long-term production of the Friedel salt, which was converted from monosulfate, increased with the amount of $BaSO_4$. The mechanisms of the Friedel salt formation associated with the anion exchange are discussed. We also studied the chloride ion permeability in hardened mortar specimens immersed in the pseudo-seawater under a constant electric current. Ordinary cement mortar containing $BaSO_4$ showed smaller chloride ion permeability. Because we found no difference in the pore structure of the cement mortars with or without $BaSO_4$, it is most likely that not only synthesized C_3A but also the ordinary cement mortar can fix greater amounts of chloride in the presence of $BaSO_4$.

Keywords: Hydration products; X-ray diffraction; Permeability; Chloride; Barium sulfate

1. Introduction

Prevention of the salt damage to reinforced concrete structures has now become a very important subject. Not only the direct reinforcement protection but also the concrete mixture design to have a durable structure must be introduced. In order to fix as much chloride ions as possible that ingress from the concrete surface, we have studied the effect of admixtures [1,2], and the difference in the chemical structure of superplasticizers [3] on the chloride ion fixation. In this study, we aimed to clarify the mechanism of cement hydration in the pseudo-seawater with particular emphasis on the chloride ion fixation. It was found that a higher amount of chloride ion was fixed during the hydration of C_3A synthesized in the presence of barium sulfate. We also determined the chloride ion permeability in hardened mortar specimens immerged in the pseudo-seawater under a constant electric current, and discussed the effects of barium sulfate on the fixation of chloride ions.

2. Experiment

2.1. Specimen

2.1.1. Synthesis of monosulfate

$CaCO_3$ and Al_2O_3 were mixed at a molar ratio of 3:1 and burnt for 4 h twice. The resulting C_3A, nearly a single phase, was screened to pass the 75-μm sieve. $CaSO_4{\cdot}2H_2O$ of 20 mass% was then mixed with the C_3A and hydrated at a solid–water ratio of 0.65 and cured in the mold for 7 days at a temperature of 20°C. Hydration of the specimen was interrupted by ethanol–acetone, dried in a desiccator and screened to pass the 105-μm sieve. $BaSO_4$ was added to the above mixture, together with the cement or $CaSO_4{\cdot}2H_2O$, for 2, 4 and 8 mass% to see

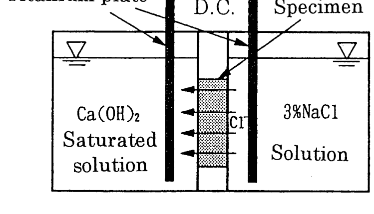

Fig. 1. Apparatus for rapid chloride ion penetration test.

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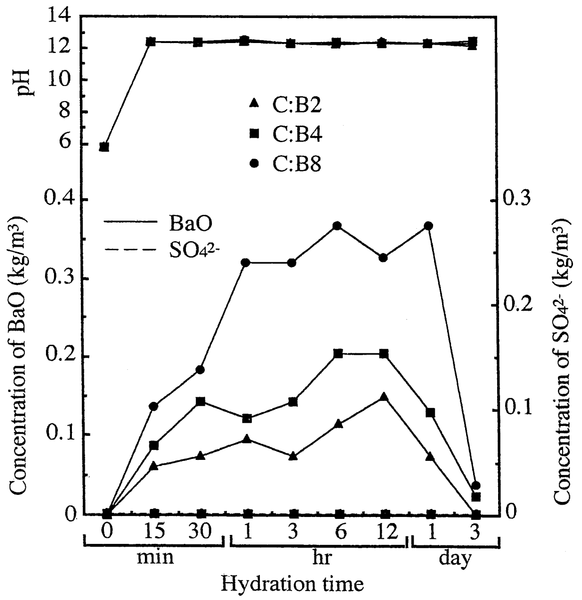
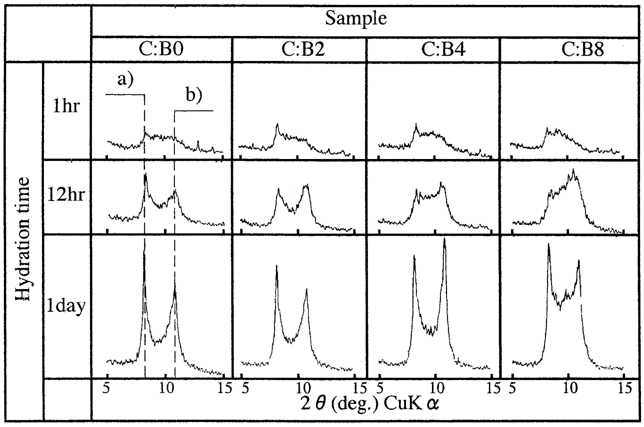


Fig. 2. Changes in pH and concentration of BaO and SO_4^{2-} in liquid phase of C_3A–$BaSO_4$ system vs. hydration times.



a) C_4AH_{19} (d=1.064nm)
b) C_4AH_{13} (d=0.792nm)

Fig. 3. XRD patterns of C_3A–$BaSO_4$ system hydrates at various hydration times. Sample C: C_3A, B0, B2, B4, B8: $BaSO_4$ 0–8 mass%.

the effect on the chloride ion fixation. The $BaSO_4$ was a first-grade reagent of Wako with a particle size distribution of over 74 μm — 30%, from 105 to 149 μm — 30%, below 149 μm — 30% and the rest was a fine powder distribution from 74 to 149 μm.

2.1.2. Hardened mortar

River sand fine aggregate was mixed with the ordinary Portland cement at a mass ratio of 2:1 and $BaSO_4$ was also added to the mixture. The mortar cylinder of 5 cm in diameter was cured for 28 days and then cut out to have a thickness of 1 cm for the diffusion cell.

2.2. Pseudo-seawater

A 27.40-g NaCl and a 10.81-g $MgCl_2 \cdot 6H_2O$ were mixed in 1000 ml of water.

2.3. Test methods

2.3.1. $BaSO_4$ content

A 0 to 8 mass% of $BaSO_4$ was added to C_3A and was hydrated with a solid–water ratio of 0.5. Solid–liquid separation was made at each prescribed hydration time and

Table 1
Hydration products of C_3A–$BaSO_4$ system vs. hydration times

	Hydration time							
Sample	15 min	30 min	1 h	3 h	6 h	12 h	1 day	3 days
C:B0	●C_3A	●C_3A	●C_3A	●C_3A △C_4AH_{13}	●C_3A ●C_3AH_6 ■C_4AH_{19} □C_4AH_{13}	■C_3A △C_3AH_6 △C_4AH_{19} △C_4AH_{13}	■C_4AH_{19} ■C_4AH_{13} △C_3A △C_3AH_6	●C_3AH_6
C:B2	●C_3A ○$BaSO_4$	●C_3A ○$BaSO_4$	●C_3A ○$BaSO_4$ □C_4AH_{19}	●C_3A ○$BaSO_4$ △C_4AH_{19} △C_4AH_{13} □C_3AH_6	●C_3A ○$BaSO_4$ ●C_4AH_{19} △C_4AH_{13} □C_3AH_6	■C_3A ○$BaSO_4$ ■C_3AH_6 △C_4AH_{19} △C_4AH_{13}	■C_4AH_{19} ■C_4AH_{13} △C_3A □C_3AH_6	●C_3AH_6 ○C_4AH_{19}
C:B4	●C_3A □$BaSO_4$	●C_3A □$BaSO_4$	■C_3A □$BaSO_4$ □C_4AH_{19}	●C_3A □$BaSO_4$ △C_4AH_{13} □C_4AH_{19}	●C_3A □$BaSO_4$ ●C_4AH_{19} ●C_3AH_6 ■C_4AH_{13}	■C_3A △C_4AH_{13} △C_4AH_{19} □C_3AH_6	■C_4AH_{19} ■C_4AH_{13} □C_3A ○C_3AH_6	■C_3AH_6 □C_4AH_{19} □C_4AH_{13}
C:B8	●C_3A □$BaSO_4$	●C_3A □$BaSO_4$	■C_3A □$BaSO_4$	●C_3A □$BaSO_4$ △C_4AH_{13} □C_4AH_{19}	■C_3A □$BaSO_4$ ●C_4AH_{19} ●C_3AH_6 □C_4AH_{13}	■C_3A △C_4AH_{19} △C_4AH_{13}	■C_4AH_{19} ■C_4AH_{13} □C_3A □C_3AH_6	●C_3AH_6

● Very strong, ■ strong, △ middle, □ weak, ○ very weak.

No.	Hydrate	Constitutional formula	2θ (deg.)	d (nm)	(h k l)
①	**C_4AH_{19}**	**$[Ca_2Al(OH)_6]_2(OH)_2 \cdot 12H_2O$**	**8.8**	**1.064**	**(006)**
②	**C_4AH_{13}**	**$[Ca_2Al(OH)_6]_2(OH)_2 \cdot 6H_2O$**	**11.2**	**0.792**	**(001)**
③	$C_3A \cdot CaSO_4 \cdot 12H_2O$	$[Ca_2Al(OH)_6]_2SO_4 \cdot 6H_2O$	9.9	0.890	(003)
④	$C_3A \cdot CaSO_4 \cdot 11H_2O$	$[Ca_2Al(OH)_6]_2SO_4 \cdot 5H_2O$	10.3	0.855	(006)
⑤	$C_3A \cdot CaSO_4 \cdot 14H_2O$	$[Ca_2Al(OH)_6]_2SO_4 \cdot 8H_2O$	9.3	0.955	(003)
⑥	$C_3A \cdot CaSO_4 \cdot 16H_2O$	$[Ca_2Al(OH)_6]_2SO_4 \cdot 10H_2O$	8.6	1.023	(003)

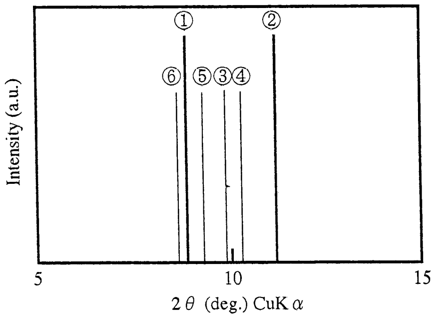


Fig. 4. XRD data of C_4AH_x and AFm phases.

the $BaSO_4$ dissolved in the liquid phase was determined by the atomic absorption and ion chromatography techniques.

2.3.2. Chloride ion fixation

Two grams of the synthesized monosulfate were dispersed in 100 ml of pseudo-seawater and stirred for a prescribed duration at a temperature of 20°C. Then the solid and liquid phases in the solution was separated by filtration. Chlorides in the solid phase were determined by XRD, scanning electron microscope (SEM), TG-DTA and EPMA while that in the liquid phase by atomic absorption and liquid chromatography.

2.3.3. Chloride ion permeability

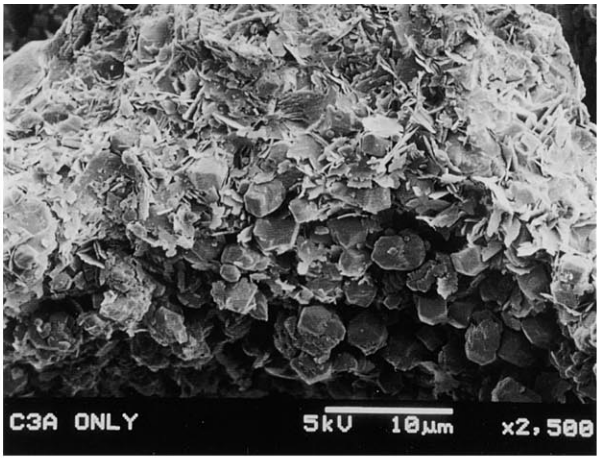
A diffusion cell as shown in Fig. 1 was set up and operated under following conditions; a voltage ranging from 2 to 10 mV, a constant current of 1.96 mA, a temperature of 20°C and the weld time of 25 days at a constant current. The chloride ions that passed the mortar specimen from the NaCl solution of 3 mass% was determined.

2.3.4. Pore size distribution and total porosity

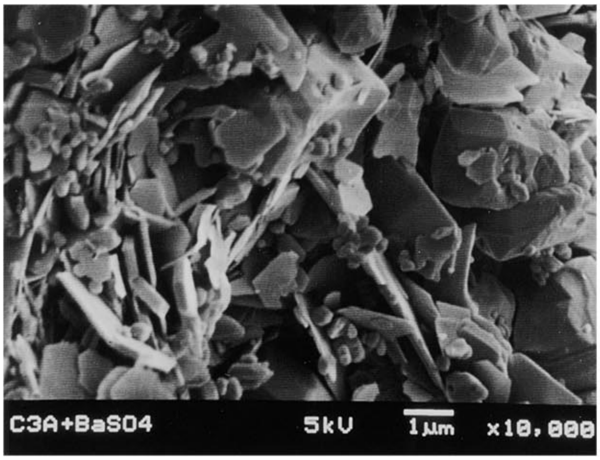
The pore size distribution and the total porosity of the mortar specimen with $BaSO_4$ were determined by mercury porosimeter.

3. Results and discussion

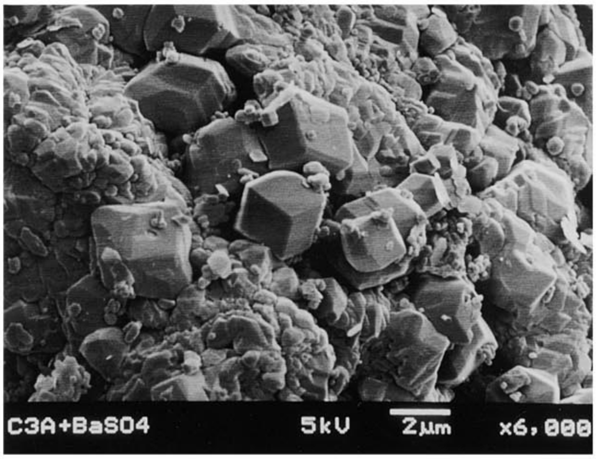
3.1. Solubility of $BaSO_4$



C_3A-H_2O system hydrates



C_3A-$BaSO_4$-H_2O system hydrates



C_3A-$BaSO_4$-H_2O system hydrates

Fig. 5. SEM of C_3A–$BaSO_4$ system hydrates at 4 weeks.

$BaSO_4$ additions were intended to fix as much as chloride ions as possible in the cement hydration products and to give an appropriate structure to the hardened body. Similarly, Lee et al. [4] studied the effects of Na_2SO_4 on the C_3A hydration in the presence of $CaSO_4 \cdot 2H_2O$ and carbon

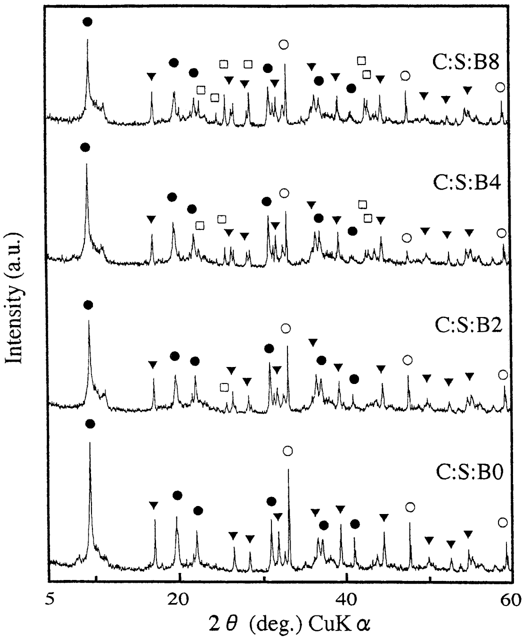


Fig. 6. XRD patterns of $C_3A-CaSO_4{\cdot}2H_2O-BaSO_4$ system hydrates at 1 week curing. ● Monosulfate, ○ C_3A, ▼ C_3AH_6, □ $BaSO_4$.

dioxide. But we expected that $BaSO_4$ might provide a better chloride ion fixation capability.

Changes in concentrations of Ba^{2+} and SO_4^{2-}, determined by the procedure described in Section 2.3.1, are shown in Fig. 2. Results are expressed in terms of BaO and SO_3.

$BaSO_4$ is a very insoluble matter with the solubility product constant K_{sp} of 1.3×10^{-10}, hence it was supposed that it has nothing to do with the hydration reaction.

However, in the presence of C_3A, the Ba^{2+} in the liquid phase showed considerable dissolution according to the dosage; 0.38 kg/m^3 of BaO dissolved when $BaSO_4$ of 8 mass% was added. On the other hand, the solubility of SO_3 was supposed to be quite low from the solubility product constant and very few dissolved amounts was actually found in the experiment. The XRD results for the solid phase are shown in Table 1. The diffraction peaks of $BaSO_4$ almost disappeared after 12 h of hydration.

The possible reasons for the dissolution of $BaSO_4$ during hydration are as follows.

During C_3A hydration to the final product of C_3AH_6, intermediate products of C_4AH_{19} and C_4AH_{13} are found.The intermediate products, expressed as $[Ca_2Al{\cdot}(OH)_6]_2{\cdot}xH_2O$, have a layered structure of the hexagonal system, like monosulfate, incorporating water molecules and OH^- between layers. These hydrates form a double salt by exchanging OH^- with other anions. When $BaSO_4$ is present in these processes, Ba^{2+} can be dissolved into the liquid phase and SO_4^{2-} may be incorporated to the layered structure in exchange for OH^-, resulting in the formation of the monosulfate type AFm phases. The hydration products C_4AH_{19} and C_4AH_{13} are coexisting during the exchange and finally converted to C_3AH_6, which further deposits $Ca_3[Al(OH)_6]_2$ ionic lattice structure as a stable phase and alumina gel, $Al(OH)_3$. The AFm phase obtained in our experiment was very poor in crystallinity and was amorphous.

3.2. Fixation of Ba^{2+}

Hydration products of C_3A coexistent with $BaSO_4$ were analyzed by XRD in a range from 2θ (deg) 5 to 15 as shown in Fig. 3. With the addition of $BaSO_4$, a slight difference in the diffraction angle and in the peak intensity can be seen. This may be attributed to the substitution of trace Ba^{2+} with C_4AH_{19}, C_4AH_{13} and their conversion product C_3AH_6. The ionic radii of Ca^{2+} and Ba^{2+} are 1.00 (six-coordination) and 1.35 μm, respectively. Ba^{2+} may also be involved in AFm phases though the diffraction peaks attributed to AFm phases are shifted depending on their crystal waters as shown in Fig. 4. The influences of Ba^{2+} can be supported by an SEM image of hydration products of C_3A in the presence of $BaSO_4$ as shown in Fig. 5, where C_3AH_6 crystals are shown as a cubic system though it normally exhibits an icositetrahedron granular structure.

3.3. Effects of $BaSO_4$ on the formation of Friedel salt

Fixation processes of chloride ions during the hydration of cement is a very important subject in the study of the durability of concrete. One of the reactions during the fixation is the conversion reaction of C_3A.

XRD results of the specimen hydrated for 7 days in the presence of 20 mass% of $CaSO_4{\cdot}2H_2O$ and 0 to 8 mass% of $BaSO_4$ are shown in Fig. 6. In these hydration processes, not only monosulfate but also unhydrated C_3A and C_3AH_6 are produced. Two grams of the specimen was mixed with 100 ml of the pseudo-seawater and the conversion process to the Friedel salt was traced by XRD analysis as shown in Fig. 7. In the presence of $BaSO_4$, the XRD intensity peaks showed

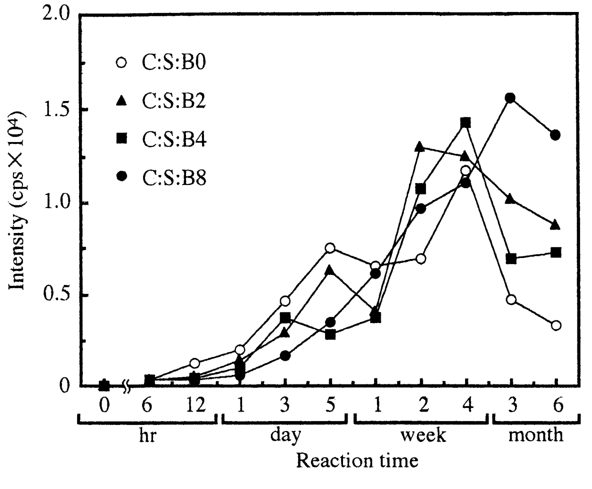


Fig. 7. Changes in XRD intensity of Friedel salt (d = 0.781 nm) vs. reaction times in the pseudo-seawater.

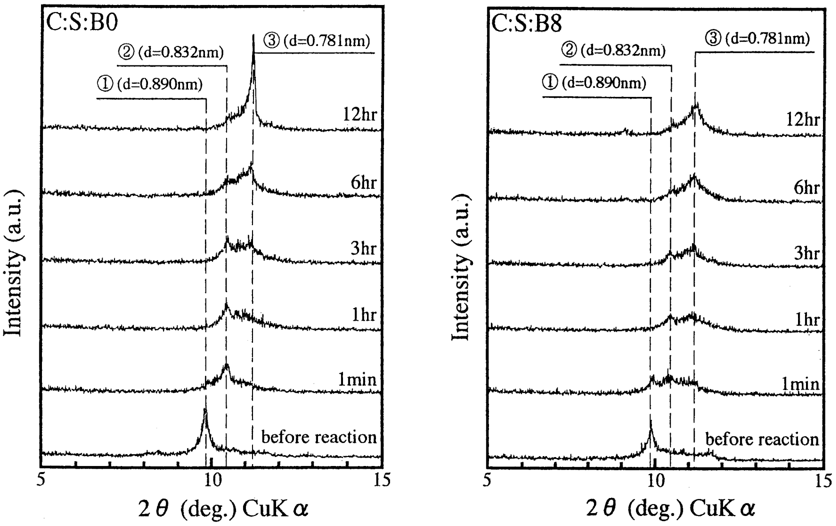


Fig. 8. XRD patterns of the transition from monosulfate to Friedel salts at various reaction times in the pseudo-seawater. (1) Monosulfate ($C_3A{\cdot}CaSO_4{\cdot}12H_2O$). (2) $6CaO{\cdot}2Al_2O_3$ ($CaSO_4{\cdot}CaCl_2$)$\cdot 24H_2O$. (3) Friedel salt ($C_3A{\cdot}CaCl_2{\cdot}10H_2O$).

considerable variation with the hydration time implying the difference in the amount of Friedel salt production. When the $BaSO_4$ addition was 8 mass%, the formation of Friedel salt was most remarkable after 2 weeks of hydration. The process of the Friedel salt formation, a reaction of monosulfate with chloride ion with an intermediate product of $C_3A{\cdot}1/2(CaSO_4{\cdot}CaCl_2){\cdot}12H_2O$ [1,2], is shown in Fig. 8.

3.4. Ion exchange in monosulfate

The residual chloride ion concentration in the pseudo-seawater that was not fixed in the monosulfate was determined, and at the same time, concentration of SO_4^{2-} that dissolved from the monosulfate was also determined. These results are shown in Fig. 9.

A part of the fixed chloride ions dissolved with the evolution of hydration and then fixed once again in the solid phase while SO_4^{2-} dissolved in exchange for the chloride ions. This exchange is not always synchronized but showed a tendency to shift slightly.

It was shown that the SO_4^{2-} originated from the added, insoluble $BaSO_4$ affected the formation of monosulfate. The behavior of Ba^{2+} was also studied by EPMA mapping as shown in Fig. 10 where a portion of Ba coexists in the vicinity of Ca^{2+}. The EPMA 10-point line analysis is shown in Fig. 11. While the dissolution of insoluble $BaSO_4$ was confirmed as shown in Fig. 2, the EPMA study showed that the Ca^{2+} may be partly substituted by Ba^{2+}.

3.5. Effects of $BaSO_4$ on the pore structure and chloride ion permeability

Mortar specimens incorporating $BaSO_4$ was subjected to the chloride diffusion test at the age of 28 days. The chloride ion that migrated from the NaCl solution through the mortar was determined according to the procedure described in Section 2.3.2, and is shown in Fig. 12. Chloride ions electrically driven into the mortar specimen were partly fixed as the Friedel salt and partly transmitted to the $Ca(OH)_2$ solution. From the difference in the amount of transmittance between normal mortar and the mortar with

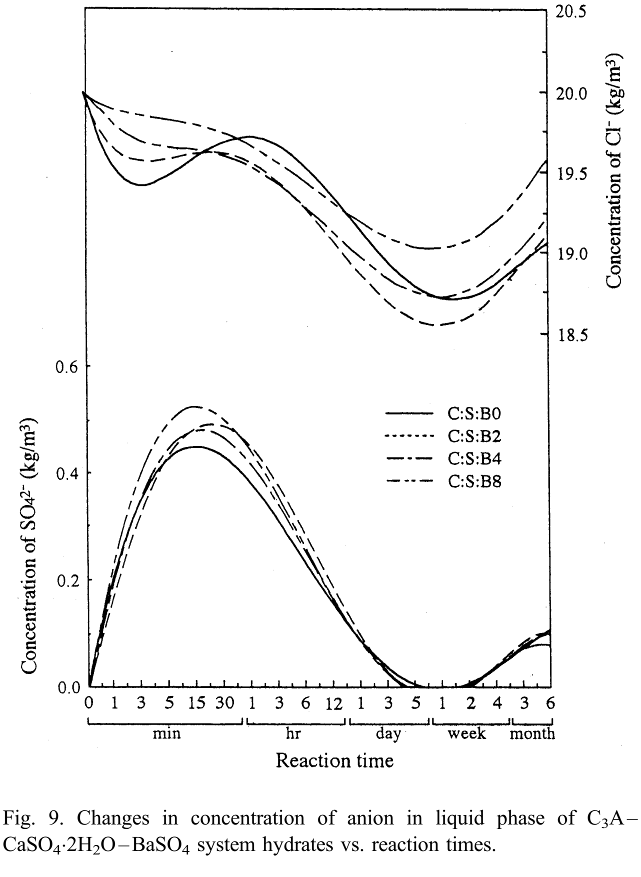
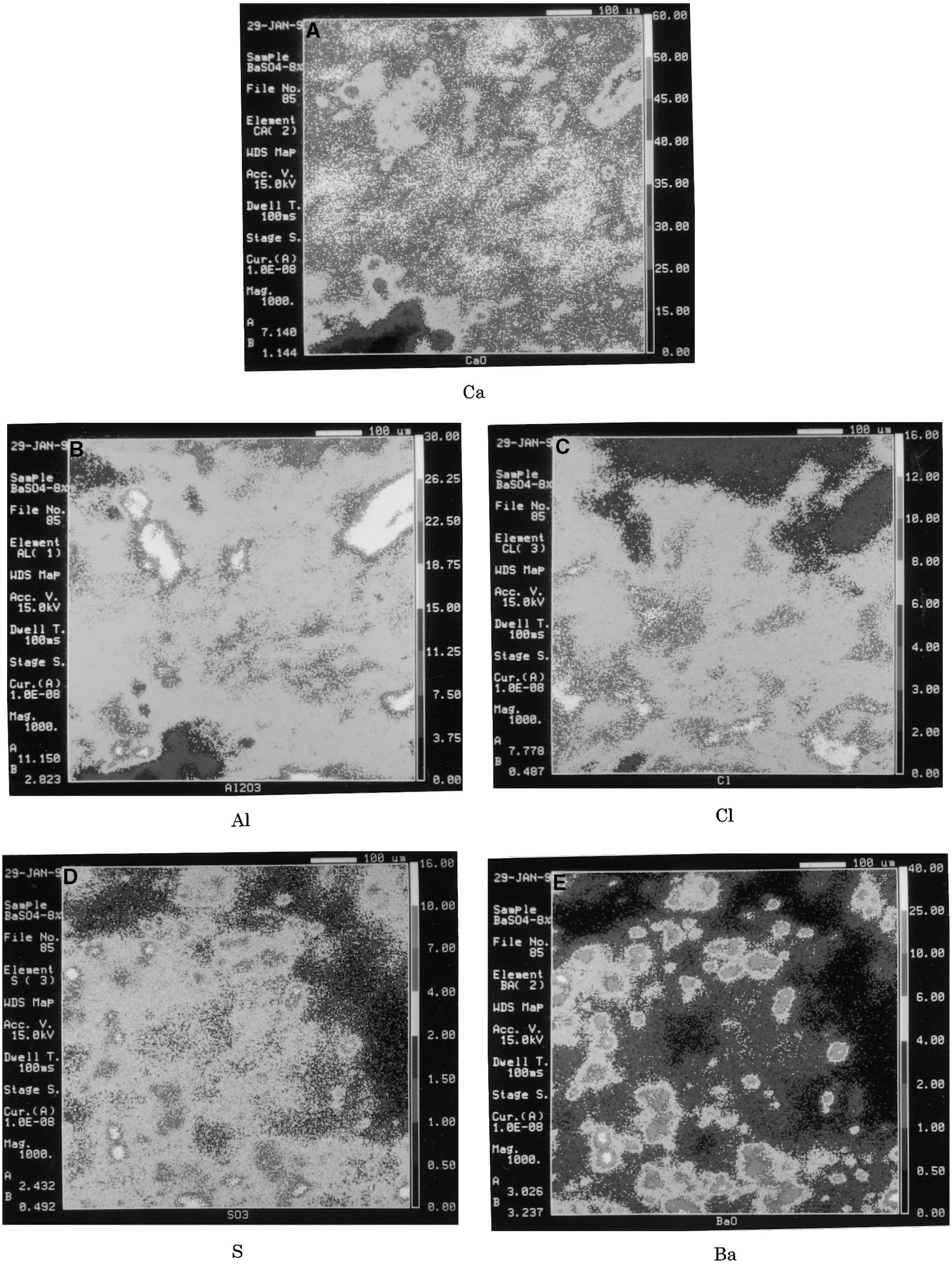


Fig. 9. Changes in concentration of anion in liquid phase of C_3A–$CaSO_4{\cdot}2H_2O$–$BaSO_4$ system hydrates vs. reaction times.



Ca

Al

Cl

S

Ba

Fig. 10. EPMA photographs of $C_3A-CaSO_4{\cdot}2H_2O-BaSO_4$ system hydrates at 4 weeks curing in the pseudo-seawater.

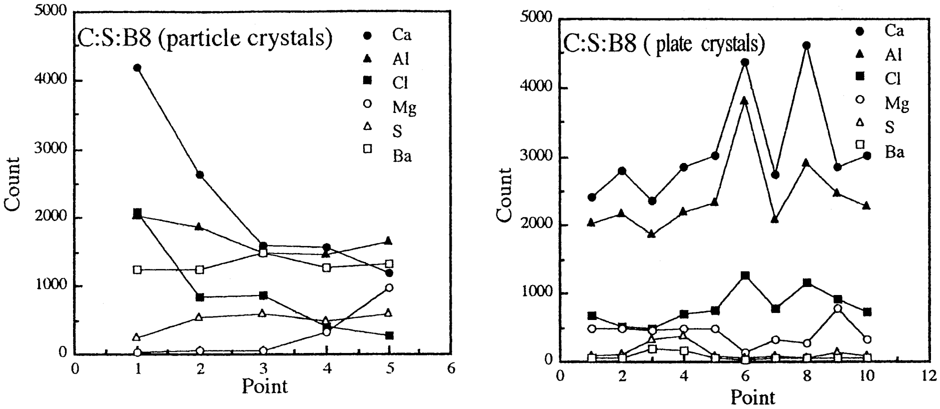


Fig. 11. Changes in numbers of X-ray counts by EPMA on $C_3A-CaSO_4{\cdot}2H_2O-BaSO_4$ system hydrates at 4 weeks curing in the pseudo-seawater.

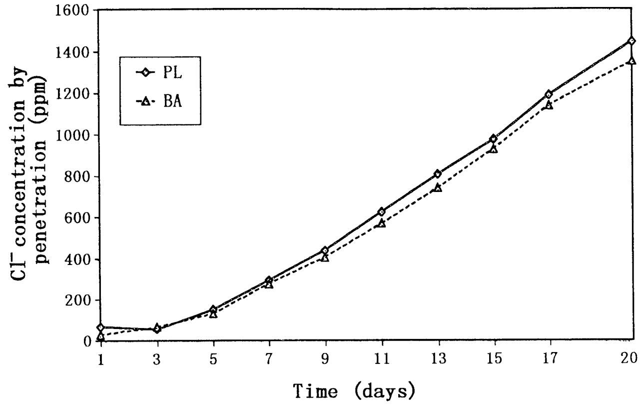


Fig. 12. Cl^- concentration by rapid penetration test vs. times.

$BaSO_4$, the chloride ion preventive capability of $BaSO_4$-added mortar was confirmed.

The pore size distributions of the mortar specimens were determined. It was shown that the difference between normal mortar and the $BaSO_4$-added mortar was very slight as shown in Fig. 13. Therefore, the difference in the chloride ion permeability can be attributed to the greater chloride ion fixation capability of the $BaSO_4$-added mortar than that of normal mortar.

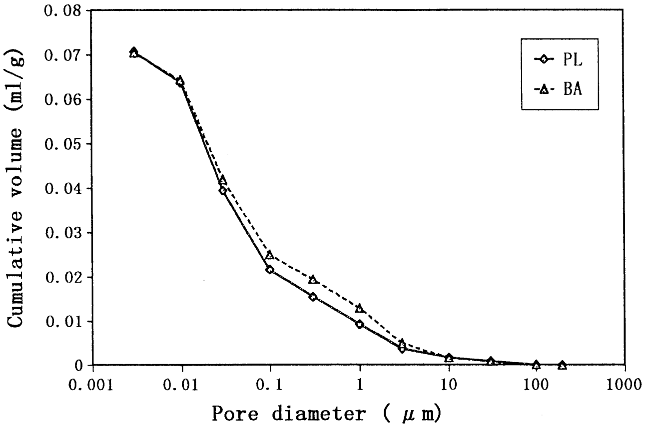


Fig. 13. Cumulative volume of hardened mortar vs. pore diameter (PL: OPC mortar, BA: OPC with 8 mass% $BaSO_4$).

4. Conclusions

By adding $BaSO_4$ during hydration of C_3A and evaluating the chloride permeability of hardened mortar with $BaSO_4$, we found that larger amounts of chloride ions can be fixed and higher diffusion resistance can be attained. Major findings are as follows.

1. When $BaSO_4$ was added during hydration of C_3A, the insoluble $BaSO_4$ was even dissolved to a certain extent. The Ba^{2+} concentration in the liquid phase increased according to the amount of $BaSO_4$ addition, while SO_4^{2-} adsorbed by the solid phase immediately.
2. When C_3A and $CaSO_4{\cdot}2H_2O$ were mixed and hydrated in the pseudo-seawater for 7 days, the long-term production of the Friedel salt, which was converted from monosulfate, became greater in the presence of $BaSO_4$.
3. When SO_4^{2-} and chloride ions were coexisting, the formation of the Friedel salt has an intermediate product of $C_3A{\cdot}1/2(CaSO_4{\cdot}CaCl_2){\cdot}12H_2O$.
4. Ordinary cement mortar with $BaSO_4$ was also able to fix chloride ions and showed smaller chloride ion permeability.

Acknowledgments

We extend our special thanks to Dr. S. Tada of Texte for the helpful discussions.

References

[1] Y. Umemura, N. Tsuyuki, H. Harada, Effect of admixture on the chloride ion permeability to hardened mortars, Annu Rep Jpn Concr Inst 19 (1) (1997) 991–996.

[2] Y. Umemura, N. Tsuyuki, H. Harada, Effect of admixture on the chloride ion fixation and permeability to hardened mortars, Concr Res Technol 9 (1) (1998) 143–152.

[3] Y. Umemura, N. Tsuyuki, H. Harada, Effect of WE water-reducing agents on the chloride ion fixation and permeability to hardened mortars, Concr Res Technol 9 (2) (1998) 115–125.

[4] H. Lee, Y. Ohba, E. Sakai, M. Daimon, Synthesis of hydration products of $3CaO{\cdot}Al_2O_3-CaSO_4{\cdot}2H_2O-CaCO_3-Na_2SO_4-H_2O$ system, Inorg Mater 4 (5) (1997) 196–204.