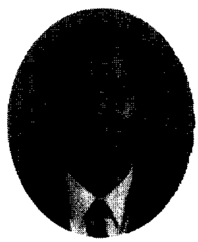
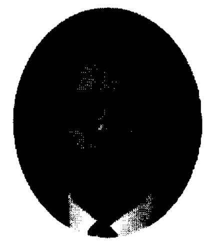
해수 및 염화 나트륨이 공급되는 환경에서 실리카 흄의 알칼리-실리카 반응에 대한 억제효과

Effectiveness of Silica Fume on Alkali-Silica Reaction in the Presence of Sodium Chloride and Sea Water





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요 약

본 연구에서는 海水 및 鹽化나트륨이 공급되는 환경에서 실리카 흄의 알칼리실리카반응에 대한 抑制效果를 구명한 것이다.

연구에 사용된 鹽化나트륨 濃度는 2.8%, 10%, 20%였으며, 反應性 骨材는 일본산 安山岩이었다. 실리카 흄은 노르웨이산으로 比表面積이 $20m^2/g$인 것을 사용했다. 실리카 흄의 置換率은 시멘트 重量에 대해 5%, 7%, 9%, 10%로 하였다.

연구결과, 20%의 鹽化나트륨이 공급되는 환경에서 알칼리실리카반응에 의한 유해한 膨脹의 抑制는 본 연구에서 사용된 실리카 흄의 경우, 置換率 9% 이상에서 달성되었다.

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• 본 논문에 대한 토의를 1999년 2월 28일까지 학회로 보내 주시면 1999년 4월호에 토의회답을 게재하겠습니다.

1. Introduction

Silica fume is a by-product of the manufacturing of elemental silicon and ferro silicon alloys. As silica fume has extreme fineness and high silica content, it is known as a highly effective pozzolanic material. The presence of the finely divided pozzolans in the concrete restricts the mobility of the alkalis and hydroxyl ions needed to cause the destructive expansive reaction.

A number of published data indicate that silica fume is effective in neutralizing harmful expansion due to alkali-silica reaction[1-6]. When silica fume is used as a partial substitute material for ordinary portland cement, it works as filler between capillary pore or aggregate and cement paste. Although silica fume addition does not reduce total porosity of the paste, it does reduce the size of the threshold pore diameter, leading to lower permeability[7, 8].

Silica fume dilutes alkali ions in the pore structure of concrete[9]. The nature of the CSH produced by the pozzolanic reaction has a lower $CaO-SiO_2$ ratio than that produced by the hydrating cement silicates, thus being able to incorporate large amounts of alkali ions in its structure, leading to a reduction in the amount available for the alkali-silica reaction[10]. The incorporation of silica fume in concrete also reduces the calcium hydroxide of concrete, thus also reducing the pH in pore solution[11, 12]. The above results indicate that suppression of the alkali-silica reaction by silica fume is attained with physical process by alkali dilution and compaction due to its extreme fineness, and with chemical one by its pozzolanic reaction.

But the physical and chemical process of silica fume on alkali-silica reaction would depend upon the type of cement and reactive aggregate, the silica fume used, and the water-to-cementitious materials ratio of the mixture. Also suppressing characteristics of silica fume to alkali-silica reaction may be different to the exposure condition such as Cl^- ions.

Cl^- ions permeating into concrete aggravates the leaching of calcium hydroxide from the CHS of cement hydrates. Such phenomenon is more conspicuous in the presence of sodium chloride than in the other salts containing Cl^- ion[13-15]. Calcium hydroxide when leached from the CSH either reacts with cement hydrates or exists as Ca^{2+} ion in the pore solution. Calcium hydroxide in concrete works not only as a source of alkali ions to ASR, but also as a buffer solution that keeps the level of pH high in the pore solution. Therefore the increase in Ca^{2+} ion in the pore causes the diffusion of alkali ions such as Na^+ and K^+ into the reactive aggregate, and results in an higher expansion due to ASR[16].

Under the environment where alkali-silica reaction is promoted by sodium chloride without alkali ions, harmful expansion may be suppressed by higher silica fume replacement than in tap water. However, there are few studies on the effectiveness of silica fume to alkali-silica reaction in saline water.

This paper presents the result of the suppressing effectiveness of silica fume to alkali-silica reaction in the presence of sodium chloride. In order to both promote alkali-silica reaction and acquire the safety value to control of alkali-silica reaction, 20 percent of sodium chloride solution was used.

2. Experimental Test Program

2. 1 Materials

Cement used in the experiment was ordinary portland cement made by Japan. Silica fume made by Norway was used in the experiment and its specific surface area was $20m^2/g$. Table 1 shows the chemical composition of cement and silica fume. The reactive aggregate that was used was Japanese andesite. Table 2 shows the physical property of aggregate used in the experiment.

2. 2 Test Specimens

The experiment followed the method of the Japanese Industrial Standard: JIS A 5308(mortar bar expansion test). Three mortar prisms(40x40x160mm in size) with reactive aggregate, cement(cementitious material), water ratios of 4.5 : 2 : 1, using a cement with an enhanced alkali cement of 1.2±0.05 percent by mass of equivalent sodium oxide, were used. They were then demoulded after 24 hours. After measuring the length, the specimens were wrapped twice with moist paper, placed in a polythene zipper bag with 10cc of 20 percent sodium chloride solution and stored in containers at 38℃. Sodium chloride content ranges used in the experiment were 2.8, 10 and 20 percent. Some specimens were immersed in sea water for a comparison with the expansion rate of those in 2.8 percent sodium chloride solution. 2.8 percent of sodium chloride content means the amount of dissolved salt contained in the sea water used. Moist paper and sodium chloride solution were newly replaced after every measurement of the length of the specimen. The amount of sodium chloride solution replaced was 10cc for 13 weeks(3 months), and 20cc after that. The replacement proportions of portland cement by silica fume were 5, 7, 9, and 10 percent, respectively.

Table 1 The chemical composition of cement and silica fume

Materials(%)	Cement	Silica fume
CaO	64.40	
SiO_2	21.80	89.60
Al_2O_3	4.90	0.87
Fe_2O_3	3.00	1.30
MgO	1.40	2.22
Na_2O	0.38	0.48
K_2O	0.48	2.15
SO_3	1.90	0.62
C		1.92
ig. loss	1.40	3.50

Table 2 Physical property of aggregate used in experiment

Specific gravity	2.69
Absorption(%)	1.64
Fineness modulus	2.90
Weight per unit volume(kg/m^3)	1,750
T.M.F*(%)	3.10

T.M.F* : Test for materials finer than 0.074mm sieve.

2. 3 Measurement

Measurements of length were made at 2, 4, 8, 13 and 26 weeks(6 months). If the observed expansion did not exceed 0.10 percent after 6 months, the combinations of reactive aggregate and cement with silica fume were considered safe.

The chloride content of the specimens was measured after 6 months of immersion in different sodium chloride solutions. These values were calculated using an average of three specimens, and presented as total chloride and water soluble chloride content. The analysis of chloride content followed the chloride analysis method on the hardened concrete of the Japanese Concrete Institute.

3. Results and Discussion

3. 1 Pessimum of Reactive aggregate to Alkali-Silica Reaction

Although aggregate is reactive, the expansion of aggregate due to ASR is different from the replacement rate of the innocent aggregate by the reactive. Some aggregate shows its highest expansion in a certain replacement. This phenomenon is called pessimum. The information on pessimum of reactive aggregate is one of the important factors in judging precisely whether aggregate is reactive or not.

Figs. 1 and 2 indicate the expansion of the mortar bars containing different reactive aggregate replacements in both tap water and 20 percent sodium chloride solution. As shown in figs. 1 and 2, expansion increased with an increase in the reactive aggregate replacement. Some aggregate have different characteristics under the changed environments, such as those containing alkali and chloride ions. However the aggregate used in this study did not show any pessimum in both tap water and 20 percent sodium chloride solution.

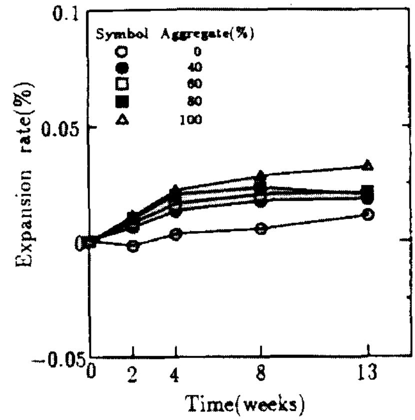

Fig. 1 Expansion of mortar bars with different reactive aggregate replacement in tap water.

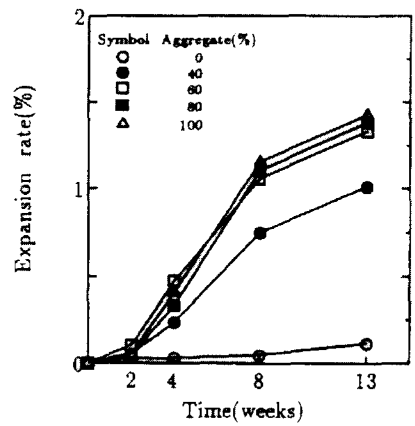

Fig. 2 Expansion of mortar bars with different reactive aggregate replacement in 20 percent sodium chloride solution.

3. 2 Comparison of Expansion Rate with Different Sodium Chloride Content

Fig. 3 shows the results of the expansion rates of the mortar bars immersed during six months in tap water, 10 percent, and 20 percent sodium chloride solution. The specimen in tap water was slow in the alkali-silica reaction, and showed a lower expansion rate. The specimens in sodium chloride solution on the other hand, were quick, and showed much higher expansion rates. Expansion rates also increased with an increase in sodium chloride content.

Na^+ ion reacts with silica from the aggregate to form alkali silica gel. Such a reaction is accelerated with an increase in Na^+ ion at the reaction site[17]. Also the increase in Cl^- ion facilitates the leaching of calcium hydroxide from the CHS of cement hydrates, and results in a higher expansion due to ASR.

In this study, the greater expansion in 20 percent sodium chloride solution might be attributed to an increase in Na^+ and Cl^- ion(fig.4).

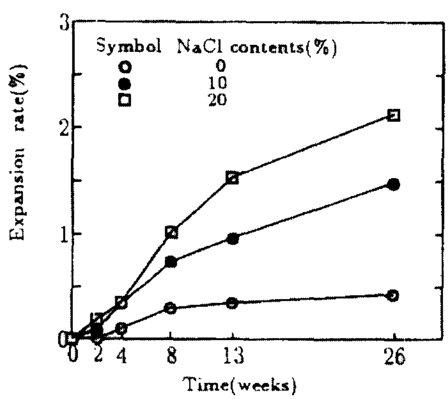

Fig. 3 Expansion of mortar bars due to alkali-silica reaction immersed in different percentage soution of NaCl.

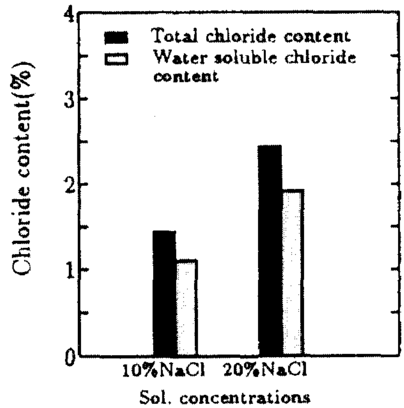

Fig. 4 Chloride ion concentration in mortar bars after 6 months in 10 percent and 20 percent NaCl solution.

3. 3 Effectiveness of Silica Fume on Alkali-Silica Reaction in 20 Percent Sodium Chloride Solution

Fig. 5 shows expansion plotted against age for the mortar bars containing silica fume in 20 percent sodium chloride solution, in which 5, 7, 9 and 10 percent by mass of cement were replaced by silica fume.

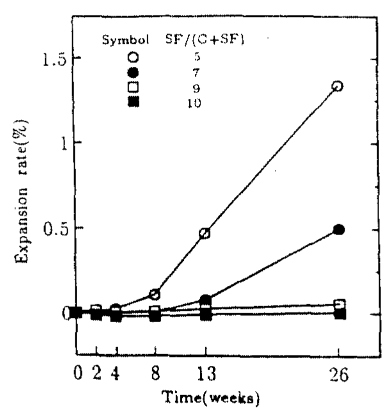

Fig. 5 Effectiveness of different silica fume replacements in preventing alkali silica reaction in 20% NaCl solution.

The mortar bar containing 5 percent replacement of cement by silica fume showed expansion in excess of 0.05 percent at four weeks after commencement of the test, which is judgement criterion for distinguishing between deleterious and innocuous expansion at three months. Also, in the case of the mortar bar containing 7 percent silica fume, expansion exceeded 0.05 percent of three months at eight weeks. However, mortar bar with 9 percent silica fume showed 0.06 percent of expansion at six months. Its value was much lower than 0.1 percent of expansion, which is judgement criterion for distinguishing between deleterious and innocuous expansion at six months. On the other hand, at the level of 10 percent replacement, expansion showed 0.005 percent at six months.

Alkali-silica reaction is a reaction between the alkali ions from cement and certain forms of silica which occasionally appear in significant quantities in the aggregate. If moisture is available around aggregates, the charge on the surface of silica bring about surface hydration. Therefore, the surface of a silica particle is weakly acidic. However, when a dilute solution of sodium hydroxide is used, silica can be peptized by alkalis. If the sodium hydroxide concentration is higher, the sodium hydroxide not only removes and neutralizes the surface of hydrogen ions, but also serves as silicon-oxygen-silicon linkages that hold the whole mass together[17]. An alkali-silica complex which is formed through the reaction causes expansion and cracking by taking up water. Water, alkalis and reactive silica are a dispensible condition inducing alkali-silica reaction. Therefore, in order to prevent alkali-silica reaction, one of these essential conditions should be eliminated.

The fine particle of silica fume not only acts as filler between aggregate and cement pastes, but also works as a dilutor of alkali ions in the pore solution of concrete. Silica fume also reacts with calcium hydroxide which is liberated during hydration of portland cement. Alkali dilution and filling actions of silica fume(physical process), and its pozzolanic reaction(chemical process) play important roles in reducing destructive expansion due to alkali-silica reaction. However, physical and chemical effects of silica fume on alkali-silica reaction differ according to replacement levels, and the exposure condition such as Cl^- ions

In this study less than 7 percent silica fume replacement failed to control destructive expansion due to alkali-silica reaction. But 9 percent silica fume did not show any destructive expansion in six months. This means that physical and chemical effects of silica fume on alkali-silica reaction in 20 percent sodium chloride solution is attained with at least a level of 9 percent replacement.

Alkali-silica reaction is promoted by chloride ion. According to Kim et al.[18], expansion due to alkali-silica reaction in the presence of sodium chloride solution increases with an increase in sodium content. Therefore, in order to control destructive expansion in brine water, permeability of chloride ions to concrete from the outside should be prohibited as low as possible.

Fig. 6 indicates the results of chloride ion concentration in the mortar bars containing 0, 5, 7, and 9 percent silica fume after six month immersion in 20 percent sodium chloride solution. As shown in fig. 2, the amount of chloride content in the specimen decreased with an increase in the amount of silica fume used. Alkali-silica reaction depends upon various conditions such as humidity, temperature, type of aggregate or cement used, and the size of aggregate particle. The threshold of chloride content causing destructive expansion is not clear.

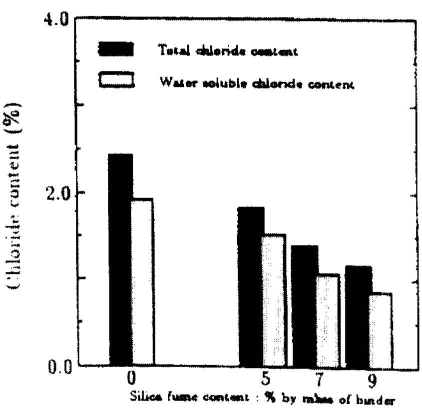

Fig. 6 Chloride ion concentration in mortar bars containing different silica fume replacements after 6 months in 20% NaCl solution.

However, the result from fig. 6 indicates that more than 9 percent silica fume is enough replacement for neutralizing destructive expansion inducing chloride ions.

3.4 Effectiveness of Silica Fume on Alkali-Silica Reaction in Sea Water

Fig. 7 gives the result of expansion in the mortar bars containing 7 percent silica fume replacement immersed in sea water and different sodium chloride solution. 2.8 percent of sodium chloride content means the amount of dissolved salt which contains in the used sea water. As shown in fig. 7, in the case of the specimen immersed in sodium chloride solution, expansion showed greater value in 20 percent sodium chloride solution than the 2.8 percent specimen. However, any difference in expansion between sea water and 2.8 percent sodium chloride solution was not made.

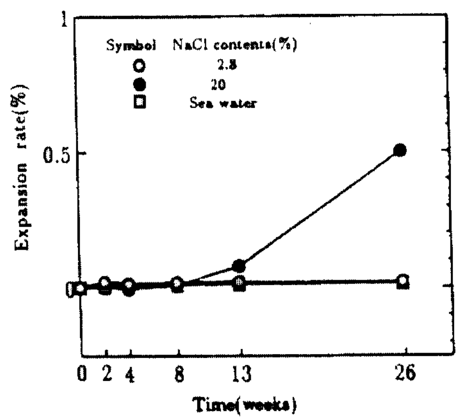

Fig. 7 Effectiveness of 7 percent silica fume replacement in preventing alkali silica reaction in different NaCl solution and sea water.

Fig. 8 indicates the result of chloride ion concentration in the mortar bars containing 7 percent silica fume after six month immersion in sea water, 2.8 and 20 percent sodium chloride solution. The chloride ion concentration of mortar bar immersed in 20 percent sodium chloride solution is about five times higher than the 2.8 percent sodium chloride specimen. These differences in chloride ion concentration of the mortar bars might cause a difference in their expansion. However any difference in chloride ion concentration between the specimens in sea water and 2.8 percent sodium chloride solution was not made. The result shows that promotion of alkali-silica reaction in sea water is attributed to sodium chloride. Also it indicates that the experiment data in sodium chloride solution provide good information for the estimation of alkali-silica reaction in sea water.

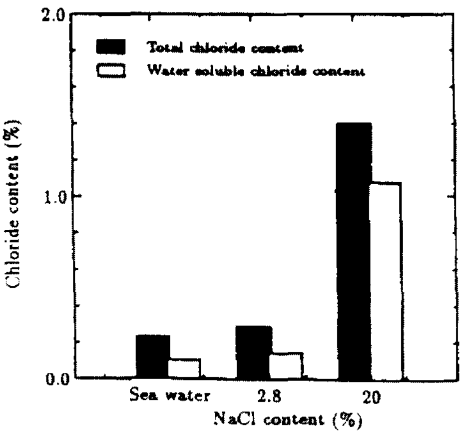

Fig. 8 Chloride ion concentration in mortar bars containing 7 percent silica fume replacement after 6 months in different NaCl solution and sea water.

4. CONCLUSIONS

In order to establish a suitable method in reducing destructive expansion due to alkali-silica reaction in the presence of sodium chloride solution and sea water, the effectiveness of partial replacement of silica fume was investigated.

The surface area of silica fume used in the experiment was about $20m^2/g$. The replacement proportions of portland cement by silica fume were 5, 7, 9, and 10 percent, respectively. Sodium chloride content ranges used in the experiment were 2.8, 10 and 20 percent. The use of 20 percent sodium chloride solution was not only to promote alkali-silica reaction, but also to acquire the safety value in suppressing alkali-silica reaction.

Effectiveness of silica fume on alkali-silica reaction in the presence of sodium chloride solution and sea water can be drawn from this study herein ;

1) More than 9 percent replacement of portland cement by silica fume stops deleterious expansion due to alkali-silica reaction in 20 percent sodium chloride solution.

2) Any difference in chloride ion concentration between the specimens in sea water and in 2.8 percent sodium chloride solution was not made. Promotion of alkali-silica reaction in sea water is attributed to sodium chloride. The experimental data in sodium chloride solution provide good information for the estimation of alkali-silica reaction in sea water.

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ABSTRACT

This study deals with the effectiveness of silica fume on alkali-silica reaction in the presence of sodium chloride and sea water.

The sodium chloride content ranges used in the experiment were 2.8, 10 and 20 percent. The reactive aggregate that was used was Japanese andesite. Also, silica fume of about 20m^2/g was used in the experiment. The replacement proportions of portland cement by silica fume were 5, 7, 9, and 10 percent, respectively.

The results indicate that more than 9 percent replacement of portland cement by silica fume stops deleterious expansion due to the alkali-silica reaction in 20 percent sodium chloride solution.

Keywords : alkali-silica reaction, silica fume, sodium chloride solution, replacement proportions.

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