

# EFFECTS OF ALKALI SUBSTITUTION ON SUPPRESSION OF AAR

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## SUMMARY

This paper presents the results of the study to suppress AAR in an existing concrete structure by a catalyst with chelate function. The experiments were conducted with a mortar bar specimen artificially affected by AAR. The results show that alkaline metallic elements were discharged from a mortar bar specimen that has been affected by AAR, and alkali density was reduced. Also, expansion test on the mortar bar specimen with this catalyst was conducted, and suppression effect on AAR was verified.

*Keywords: AAR, catalyst, discharge of alkali, existing concrete structure, suppression of AAR*

## INTRODUCTION

Many years have passed since the identification of phenomenon of deterioration of concrete structures due to the damage of cracking by AAR. Various measures and test methods as countermeasures against AAR have been researched and inspected by laboratory test and on-site application. However, most of the measures and the test methods are effective basically for structures under construction.

The countermeasures for existing concrete structures which are suffering from AAR are required to suppress it without destroying the structures, although this is very difficult. Therefore ordinary methods conventionally used so far are mainly designed to prevent water infiltration into the concrete by applying coating materials on the surface and injecting the material in cracks of the structures. However, these methods could not always be permanent countermeasures for AAR because of deterioration of the coating materials etc. In addition, the coating on concrete surface encourages heating effect of the structures, which might accelerate AAR.

Kuramoto et al. (1992) reported that a catalyst with metallic carrier function is effective in suppressing AAR in an existing concrete structure. This study is to verify effect of the catalyst applied to structures with AAR on suppression of AAR by laboratory experiments.

## EXPERIMENTS ON AAR SUPPRESSION FUNCTION ON SPECIMENS

### Procedure of the experiments

Experiments on mortar specimens were conducted to verify the efficiency of application of alkali substitution by the catalyst as a countermeasures against AAR in an existing concrete structure. This has the basis that a metal carrying catalyst with chelate function accelerates the same as the cement hydration reaction producing CSH in concrete. The following are the procedure of the experiments.

- Verify the macroscopic suppressing effects on reactive aggregates by the catalyst, under ambient conditions where AAR is artificially developed.
- Verify the effects of the discharge of alkali metal from the specimens with artificial AAR by the catalyst.
- Verify AAR suppressing effects of the catalyst by measuring expansion rate of mortar bar specimens which are acceleratedly cured.
- Verify the difference of AAR suppressing effects by the difference of age of specimens through long termed expansion experiment.
- Verify the difference of AAR suppressing effects under different conditions of curing.

### Materials used for the experiments

Specimens were mixed with high alkaline contents to induce AAR artificially. Standard sands and Pyrex glass particles(PG) were used as the reactive aggregates.

Table 1 Mix proportion on the specimens (by weight)

mix proportion	portland cement	aggregate		water W/C	Na <sub>2</sub> O equivalent
		sand	PG		
A	1	2	—	0.6	0.020
B	1	—	2.25	0.6	0.012
C-1	1	—	2.25	0.6	0.0085
C-2	1	—	2.25	0.6	0.011
D	1	—	2.26	0.6	0.011

Carboxylic acid consisting of more than 2 carboxyl groups, for example, was used as metal carrying catalyst with chelate function. Gypsum (CaSO<sub>4</sub>) was used to help substitution reaction of the catalyst. Table 1 shows the mix proportion of each specimen.

## TEST RESULTS

### Macroscopic verification experiments of AAR suppression effect.

Specimens with Pyrex glass particles(mean particle size of 0.65mm) as aggregates were prepared. The specimens were placed under ambient atmospheric conditions where AAR was artificially developed, and the effect of this added catalyst on AAR suppression was observed. The specimens were prepared using high alkline mortar mixed with standard sand in the mix proportion(A) and cast as in Fig.1. Four holes in the specimen(a) were filled with Pyrex glass particles, gypsum and the catalyst, and the holes in the specimen(b) were filled with Pyrex glass particles,

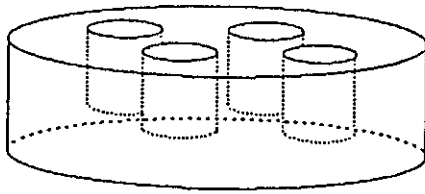


Fig.1 Shape of the specimens

gypsum and ordinary mortar, as seen in Fig.2. These 2 specimens were placed in a sealed container and acceleratedly cured for 9 weeks under ambient conditions of 40 °C and R.H.100%. Then the specimens were kept cured for 9 more weeks under ambient conditions of 20 °C and R.H. 100%. After that, the portion filled with Pyrex glass particles in each specimen was cut off with a diamond cutter and any change was observed. The sections of the specimens are shown in Fig.3. The Pyrex glass particles embedded in the specimen(a) filled with the catalyst hardly indicated any change; however, those in the specimen not treated with any catalyst were liquefied by AAR, demonstrating that none of the particles retained their original shapes.

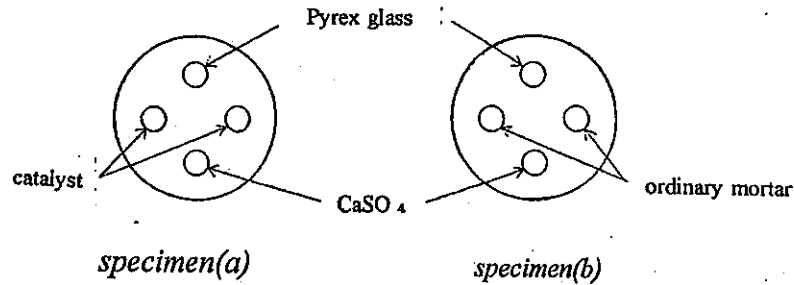
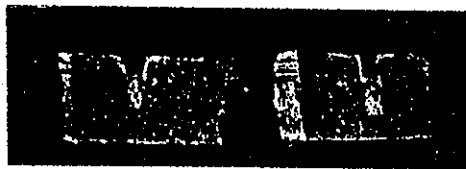


Fig.2 Location of holes filled with Pyrex glass, gypsum and catalyst



specimen(a)

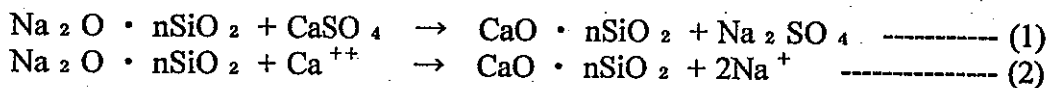


specimen(b)

Fig.3 State of Pyrex glass particles after accelerated curing

### Analytic experiment on solution where specimens were immersed

This is an experimental report on mixing of 'slag' powder and gypsum for suppressing AAR. As can be imagined from the observations of efflorescence, where alkali metal sulfates constitute the main component of efflorescence, it may be expected that the alkali metal as the main cause of AAR will be combined with  $SO_4^{--}$  of gypsum according to reaction(1) as shown below and its natural byproduct, efflorescence will be discharged outside of the concrete body. Reaction (2), which shows that the catalyst accelerates the production of hydrates in concrete to breed calcium silicate hydrates, is extremely close to the reaction(1).



The experiments were conducted to verify that alkali metal combines with  $\text{SO}_4^{--}$  and are discharged outside the concrete body. To verify the effect of alkali metal discharge, the experiment was conducted by analyzing the solution where part of specimens affected by artificial AAR was immersed for accelerated curing. Four series of mortar specimens  $\phi 50\text{mm} \times 40\text{mm}$  in size in mix proportion(B) for artificial AAR were prepared and dry cured for 3 weeks at room temperature. After the curing period, bore holes 30mm in depth were driven by  $\phi 7\text{mm}$  drill in specimens. Four series are set as: ① untreated, ② one bore hole filled with 1g of gypsum, ③, ④ 2 bore holes, one filled with 1g of the catalyst, the other filled with 1g of gypsum. Fig.4 shows rough sketch of the specimens for analytic experiment on solution where the specimens were immersed.

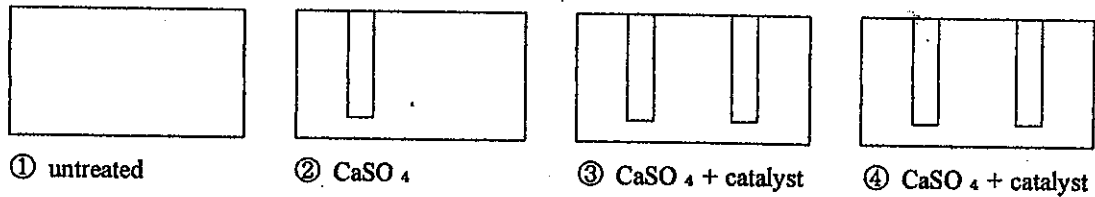


Fig.4 Specimens for analytic experiment on solution where the specimens were immersed

The specimens were immersed in distilled water and stored for 16 weeks at  $40^\circ\text{C}$  for accelerated curing. After 16 weeks of the curing period, the solution was collected from each series and quantitative analysis of Na, K, Ca and  $\text{SO}_4$  was conducted by flame analysis and ion chromatography. The results of the analysis are shown on Table 2. There are little difference in quantities of discharged ions between series

Table 2 Results of the analytic expermen (PPM)

specimen	$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{++}$	$\text{SO}_4^{--}$
① untreated	1480	1520	6.1	700
② $\text{CaSO}_4$	1470	1600	8.6	640
③ $\text{CaSO}_4$ + catalyst	3550	2060	5.7	3080
④ $\text{CaSO}_4$ + catalyst	3600	2250	7.1	2920

① and ②. However, in ③ quantity of discharged  $\text{Na}^+$  is 2.4 times greater than series ①,  $\text{K}^+$  1.4 times, Ca 0.9 times,  $\text{SO}_4^{--}$  4.4 times. There are evident differences between series ①② and series ③④. Notably there are remarkable differences in concentration of  $\text{Na}^+$  and  $\text{SO}_4^{--}$ , which verifies the discharge of  $\text{Na}_2\text{SO}_4$ .

### Verification experiment on suppression of expansion

As the effect of alkali substitution and discharge by the catalyst has been verified by the experiments, suppression of expansion by the catalyst was verified. Method of the experiments: mortar bars affected by artificial AAR were filled with catalyst and gypsum in center, then accelerated cured and expansion rate was measured. Mortar bar specimens ( $40 \times 40 \times 160\text{mm}$ ) in 2 kinds of mix proportion (C-1, C-2) having different equivalent of  $\text{Na}_2\text{O}$  were prepared. After 2 weeks of dry curing at room temperature, a bore hole was driven horizontally in the center of the specimen by

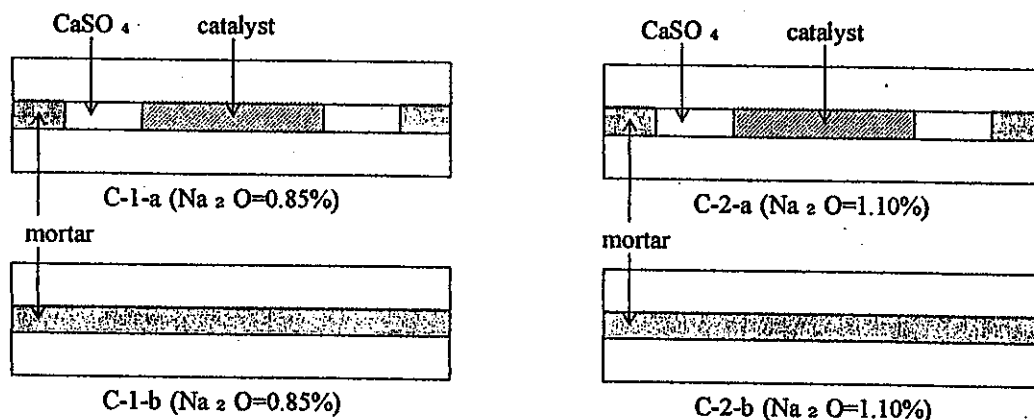
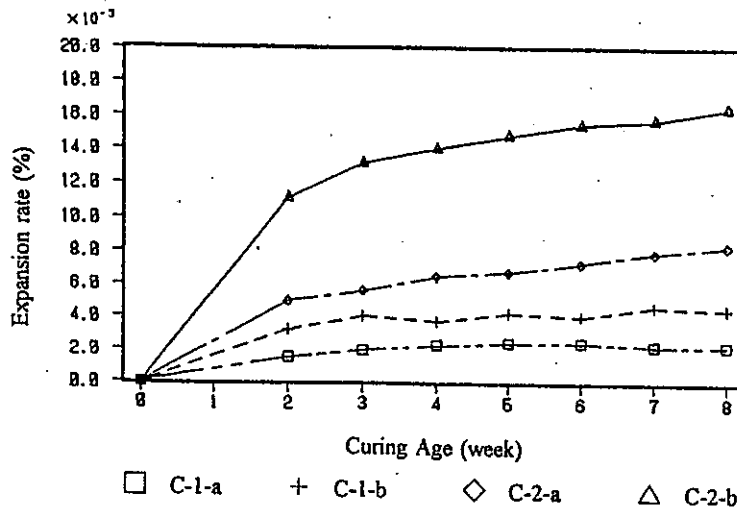


Fig.5 Mortar bar specimen

drill  $\phi$  7mm in diameter. The specimens were classified in to two series(A,B) by equivalent of  $\text{Na}_2\text{O}$ . A specimen of each series was filled with 4g of the catalyst in the center of the hole, and on its sides 4g of gypsum was filled, then ordinary mortar was filled to seal the hole. Other specimen of each series was filled and sealed with ordinary mortar only. Fig.5 shows a rough sketch of the specimens. The specimens were dry cured for 3 weeks at room temperature, then sealed in a container in humid state and kept cured for 7 more weeks at room temperature. After the curing period at room temperature, the specimens were cured 8 more weeks under ambient conditions of  $40^\circ\text{C}$  and R.H.100% for accelerated curing. During the period of the accelerated curing, at intervals of one week, the specimens were put under conditions of  $20^\circ\text{C}$  and R.H.60% for 24 hours and its length were measured by dialgauge. Table 3 shows the results. Fig.6 is the graph of expansion rate of mortar bar specimens. Both catalyst treated and untreated mortar bars of  $\text{Na}_2\text{O} = 0.85\%$ (C-1-a,b) showed tendency to expand until 3rd week then expansion stopped. Mortar bars of  $\text{Na}_2\text{O} = 1.10\%$ (C-2-a,b) also showed tendency

Table 3 Mortar bar expansion measurements

week	$\text{Na}_2\text{O}=0.85\%$				$\text{Na}_2\text{O}=1.10\%$			
	C-1-a		C-1-b		C-2-a		C-2-b	
	expansion amount (mm)	expansion rate (%)	expansion amount (mm)	expansion rate (%)	expansion amount (mm)	expansion rate (%)	expansion amount (mm)	expansion rate (%)
standard	160.307		160.080		160.690		160.052	
2	0.024	0.015	0.051	0.032	0.079	0.049	0.179	0.112
3	0.030	0.019	0.064	0.040	0.088	0.055	0.213	0.133
4	0.037	0.023	0.060	0.037	0.103	0.064	0.227	0.142
5	0.039	0.024	0.067	0.042	0.107	0.067	0.240	0.150
6	0.038	0.024	0.064	0.040	0.116	0.072	0.249	0.156
7	0.036	0.022	0.073	0.046	0.125	0.078	0.255	0.159
8	0.035	0.022	0.070	0.044	0.133	0.083	0.266	0.166



to expand rapidly for first 2 to 3 weeks and after that the mortar bars kept expanding slowly. In both series, expansion rates of specimens filled with the catalyst were reduced to 50% compared with those of specimens filled with ordinary mortar.

Fig.6 Mortar bar expansion rate

### Long term expansion test

Long term expansion test at room temperature was conducted to verify long term effect of AAR borne in existing concrete structures. Mortar bar specimens (40 X 40 X 160mm) with high alkaline mortar in mix proportion (B) were prepared. After 1 week of dry curing, a 7mm bore hole was drilled horizontally in the center of each specimen which was then filled with catalyst etc. Table 4 shows specifications of the specimens. The specimens were cured for 1 week and amount of expansion was measured. In this experiment accelerating test under conditions of high temperature and high humidity and the test at room temperature were conducted to investigate the tendencies of their expansions and the difference. Table 5 shows the results.

Table 4 Specifications of specimens for long term expansion test

No.	mark	mix proportion	curing condition	catalyst	gypsum	ordinary mortar	note
①	D-M-1	D	room temp	—	—	○	
②	D-M-2	D	room temp	○	○	○	
③	D-M-3	D	room temp	○	—	○	
④	D-H-1	D	accelerated → room temp	—	—	○	acceleration until 41st wk
⑤	D-H-2	D	accelerated → room temp	○	○	○	acceleration until 41st wk

○ : material filled in the mortar bar specimen

Fig.7 is the graph of the results shown in table 5. Fig.8 is the graph of expansion amount of untreated mortar bar specimens to observe the effects depending upon differences of curing conditions. The mortar bars tested in the accelerating test

Table 5 Measurements of mortar bar long term expansion test

week	room temperature						accelerated			
	D-M-1		D-M-2		D-M-3		D-H-1		D-H-2	
	expansion amount (mm)	expansion rate (%)	expansion amount (mm)	expansion rate (%)	expansion amount (mm)	expansion rate (%)	expansion amount (mm)	expansion rate (%)	expansion amount (mm)	expansion rate (%)
standard	161.318		160.867		160.857		159.726		160.554	
5	0.036	0.022	0.013	0.008	0.026	0.016	0.306	0.192	0.088	0.055
8	0.059	0.037	0.016	0.010	0.026	0.016	0.488	0.305	0.185	0.115
9	0.082	0.051	0.028	0.017	0.036	0.022	0.578	0.361	0.288	0.142
11	0.114	0.071	0.046	0.029	0.046	0.029	0.596	0.373	0.293	0.182
14	0.141	0.087	0.055	0.034	0.052	0.032	0.559	0.350	0.218	0.175
17	0.211	0.131	0.100	0.062	0.100	0.062	0.617	0.386	0.301	0.187
25	0.315	0.195	0.146	0.091	0.146	0.091	0.597	0.373	0.284	0.177
35	0.568	0.352	0.192	0.119	0.172	0.107	0.611	0.383	0.336	0.209
41	0.632	0.392	0.246	0.153	0.216	0.134	0.642	0.402	0.353	0.220
46	0.658	0.408	0.273	0.170	0.253	0.157	0.664	0.416	0.345	0.215
53	0.678	0.420	0.291	0.181	0.285	0.177	0.684	0.428	0.371	0.231
57	0.694	0.430	0.299	0.186	0.272	0.169	0.706	0.442	0.364	0.227

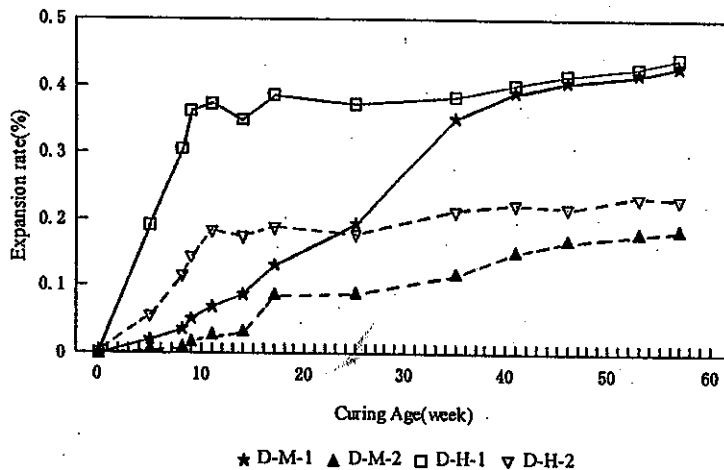


Fig.7 Results of long term expansion test

expanded rapidly until about 11th week. After that the expansion abruptly stopped and kept stable until 35th week when accelerated curing was ceased. The mortar bars cured at room temperature expanded gradually for 8 weeks and then began to show a steep expansion until near by 45th week. After that, they still showed expanding tendency, yet it became moderate. The expansion amount of mortar bar treated with the catalyst was reduced to 50% of that of the untreated. These results

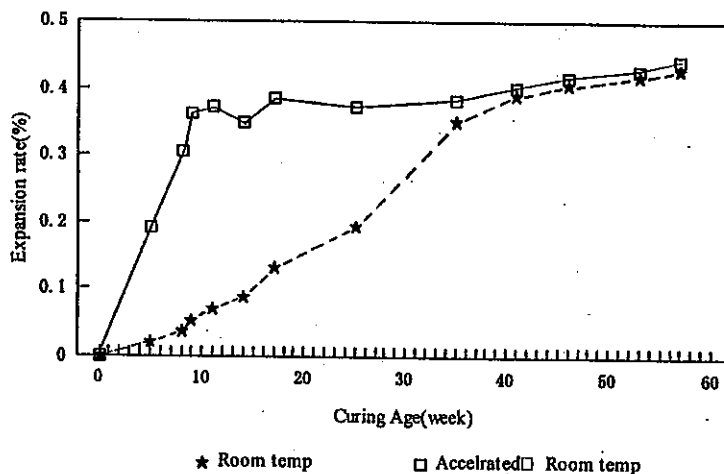


Fig.8 Influence of the difference of curing condition

coincide with the results of the experiment 3.3. The acceleration test was ceased at 41st week in this experiment and thereafter the test at room temperature has been continued. The results show that mortar bars which have been balanced to expand by accelerating test started expanding again and showed the same tendency as the mortar bars in curing at the room temperature.

## CONCLUSION

- It was verified that the addition of metal carrying catalyst with chelate function is effective for the on suppression of AAR.
- It was verified that carrier function of the catalyst is effective in the discharge of Na out of the specimens.
- It was verified that adding of the catalyst reduces expansion by AAR to 50%.
- It was observed that the specimen cured at room temperature tend to be expanding for a long time.

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