

INVESTIGATION OF ALKALI-AGGREGATE REACTION IN AGGREGATES

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ABSTRACT

Alkali aggregate reaction (AAR) in aggregates is influenced by kind of alkali and alkali salt. Na ion is more significant on the AAR than K ion, and alkali hydroxide and alkali chloride influences much of the expansion at an early age and at later ages, respectively. There is a relationship between amount of dissolved silica and expansion of structure, and a limit of alkali content for aggregates. The AAR product contains very high amounts of Na and K ion.

Keywords : Alkali aggregate reaction, Alkali, Alkali chloride, Alkali hydroxide, Dissolved silica, Expansion, Mineral composition

INTRODUCTION

Alkali-aggregate reaction (hereinafter as AAR) is known a chemical reaction between reactive minerals of aggregate and alkali. The alkali-aggregate reaction occurs between the alkali metals in the pore water of a concrete and an unstable mineral of the aggregate. There are three types of alkali - aggregate reaction which causes deterioration of concrete, these are alkali - silicate reaction, alkali-carbonate reaction and alkali-silica reaction. Deterioration due to the alkali - silica reaction is more common than that due to either the alkali - silicate or alkali - carbonate reaction. (Hobbs 1988) The alkali - silica reaction is a reaction between the hydroxyl ions in the pore water of a concrete and silica which exists in significant quantities in the aggregate. (Hansen 1994)

The pore solution contains sodium ions Na^+ , potassium ions K^+ , calcium ions Ca^{++} , and hydroxyl ions, OH^- . The concentration of these alkali metals and hydroxyl ions are dependent on the quantities of alkali compounds in the cement used. The pH of the pore solution in a concrete made with a low alkali content cement ranges from 12.7 to 13.1 and in the case of high alkali content cement from 13.5 to 13.9. (Hobbs 1988, Jelenic-Bezjak 1983) Hydroxyl ions are imbibed into the silica particle and some of the silicon oxygen linkages are attacked, weakening the bonding locally. Sodium and potassium cations then diffuse and attract water to form a gelatinous metal alkali ion hydrous silicate, resulting in expanding the concrete.

In this paper, Alkali - aggregate reactions in various aggregates were investigated using chemical and physical tests, and microscope observation. In addition, the effects of the texture of aggregate, alkali metal and Cl ion concentrations added to the concrete on these reactions were studied. The mechanisms of the alkali-aggregate reaction are also discussed.

EXPERIMENTAL

Materials

The cement with total Na_2O eq. = 0.658% was used in this experiment (Table 1). Aggregates used in the study are shown their X-ray diffraction results in the Table 2.

Pyrex is composed of amorphous (sometimes called as glass) phase. Aggregates named as Yamakawa and Ishikawa (hereinafter as YM and IS) which are produced in Japan comprise of Feldspar as a primary mineral, Quartz as a secondary mineral and cristobalite as a minor mineral. Aggregates produced in Hiroshima and Dojiki in Japan and in California in America (hereinafter as HR, DJ and CA, respectively) show a quartz as a primary mineral, Feldspar as a secondary mineral as shown in Table 2. YM, IS and CA aggregates are Andesite. HR and DJ aggregates are Slate.

Experimental

Chemical test was applied to all aggregates for determination of soluble silica and reduction of alkalinity according to the ASTM method C289. Mortar bar test (ASTM C227) was also conducted for measuring linear expansions of mortar specimens made with various aggregates. Mortar specimens were made adding alkali to control specimens as sodium hydroxide or potassium hydroxide with Na₂O eq. base 1.20% and 1.75% in order to investigate the effects of alkali content and kinds of alkali on the AAR reaction. In addition, alkali chlorides (KCl and NaCl : 1.2 %) were also added for studying effects of Cl ion on the AAR in the mortar bars. Polarizing microscopic analysis was conducted for observing micro-structure of aggregate and studying the AAR reaction.

Table 1. Chemical composition of cement used in the study. (unit : wt.%)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	F-CaO	L.O.I	Na ₂ O eq.
19.7	6.0	3.4	62.7	3.3	2.1	0.10	0.84	1.1	1.8	0.658

Table 2. Mineral compositions of aggregates used in the study analyzed by XRD method.

Specimens (Symbol)	Minerals					
	Feldspar	Quartz	Cristobalite	Mica	Chlorite	Pyroxene
Yamakawa (YM)	+++++	+++	+	+		
Ishikawa (IS)	+++++	+++	+			
Hiroshima (HR)	+++	+++++		+++	+	
Dojiki (DJ)	+++	+++++			+	
California (CA)	+++++	+++++	+			
Pyrex (Py)	Amorphous phase					

+++++ : major amount, +++ : medium amount, + : minor amount, - : trace

RESULTS AND DISCUSSION

Microscopic observation

Figure 1 shows the results of microscopic observation for aggregates using powder method. The amorphous phase is observed in YM, IS, DJ and HR aggregates. The HR and YM aggregates show large amounts of amorphous phase, which is responsible for AAR and expansion of mortar. Figure 2 shows the results of microscopic observation for the YM aggregate. The YM aggregate was observed to be composed of Plagioclase,

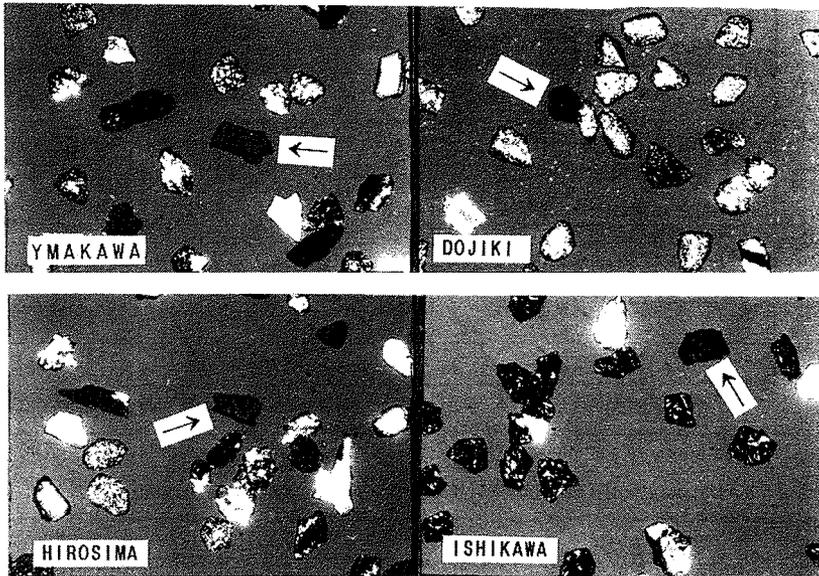


Figure 1. Polarized microscopic micrographs for aggregates used in the study. (Arrow indicates amorphous)

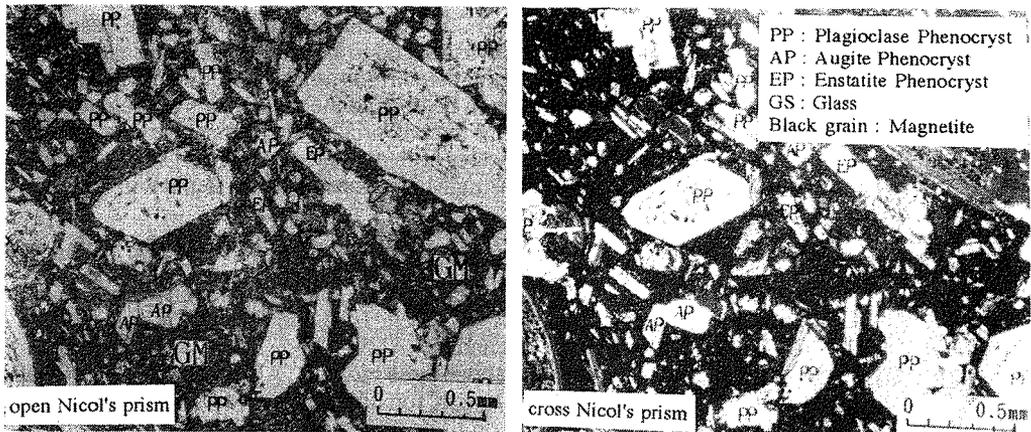


Figure 2. Polarized microscopic micrographs for the YM aggregate.

Table 3. Mineral composition of the YM aggregate analyzed by polarized microscope method. (unit : %)

Plagioclase	Augite	Enstatite	Magnetite	Goethite	Amorphous
40	19	6	4	1	30

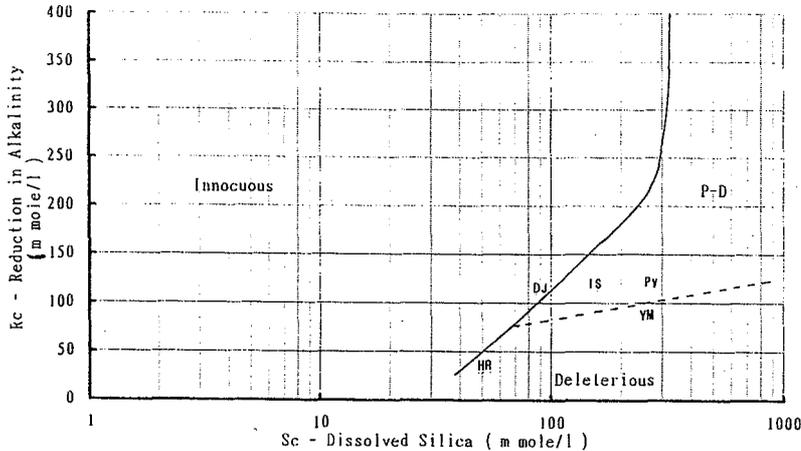


Figure 3. Schematic diagram of the potential reactivity of aggregate using a chemical method.

Pyroxene (Augite, Enstatite), amorphous phase etc. (Maru 1993) The mineral composition of the YM aggregate observed by polarized microscopic method is given in the Table 3. The cristobalite analyzed by XRD method is too little amount and very small size to observe this mineral by microscope.

Chemical method and mortar bar test

Reactivity of aggregates was tested using ASTM C289 (chemical method) and the results are shown in Figure 3. Only the DJ aggregate was judged to be innocuous aggregate. The IS and CA aggregates were judged to be potential deleterious aggregates, and YM, HR, and Pyrex deleterious aggregates. The YM which belongs to the deleterious aggregate area shows high content of reduction in alkali (toward the potential deleterious aggregate area), and the Pyrex (deleterious aggregate area) indicates high content of dissolved silica. These two aggregates were observed AAR reaction using Microscope and the results will be mentioned in the part of observation of AAR.

The mortar bar test was conducted using ASTM C227 for all aggregates. The results were given in the Table 4. All aggregates except Pyrex show less than 0.1% in linear expansion, considered as a harmful expansion level. But the linear expansion of mortar bar increases as the amount of alkali increases. At Na₂O eq. 1.2% the Pyrex, CA and YM show greater than 1.0% in expansion (Table 4 and 5). At Na₂O eq. 1.75% all aggregates indicate greater than 1.0% in expansion since about three months. All aggregates show that specimens Na ion added expand greater than those K ion added. This result may be explained by the diffusion rate of alkali metal ion. The diffusion rate of alkali ion is dependent on the radius, potential of ion. (Kasewa 1981) The radius of Na ion (0.97 Å) is smaller than that of K ion (1.33 Å), and the potential of Na ion (5.138 eV) is greater than K ion (4.339 eV). Therefore, Na ion is more active and easy to move than K ion in the structure. On the other hand the mineral composition of aggregate is very important factor for AAR. Aggregate containing silica compounds, cristobalite, amorphous phase etc. generally show harmful AAR. For the DJ aggregate, mortar bar test shows greater than 1.0% in expansion at Na₂O eq. 1.75% since two months and three months for NaOH and KOH, respectively, even though chemical test judges innocuous aggregate. This result

Table 4. Results of mortar bar test for the control aggregates and the alkali added aggregates.

Aggregates		Mortar bar expansion (%)						
		1 mon.	2 mon.	3 mon.	4 mon.	6 mon.	9 mon.	12 mon.
Pyrex	Control	0.086	0.115	0.126	0.103	0.0948	0.141	0.143
	1.2 NH*	0.216	0.409	0.416	0.420	0.420	0.445	0.420
	1.75 NH	0.214	0.463	0.480	0.489	0.484	0.495	0.490
CA	Control	-0.020	-0.010	-0.020	-0.030	-0.040	-0.030	-0.030
	1.2 NH	0.079	0.141	0.163	0.172	0.210	0.255	0.250
	1.75 NH	0.170	0.243	0.257	0.248	0.289	0.342	0.345
IS	Control	0.026	0.027	0.028	0.024	0.017	0.008	0
	1.2 NH	0.031	0.033	0.045	0.026	0.031	0.022	0.029
	1.75 NH	0.057	0.129	0.254	0.260	0.282	0.262	0.278
	1.2 KH ⁺	0.026	0.035	0.036	0.032	0.038	-0.020	0.007
	1.75 KH	0.057	0.085	0.139	0.208	0.281	0.185	0.161
HR	Control	0.005	0.015	0.007	0.012	-0.010	-0.020	-0.020
	1.2 NH	0.002	0.008	0.017	-0.01	0.018	0.003	0.006
	1.75 NH	0.022	0.156	0.451	0.665	0.488	0.609	0.448
	1.2 KH	0.010	0.012	0.008	0.002	0.006	-0.010	0.006
	1.75 KH	0.018	0.111	0.311	0.418	0.462	0.500	0.500
DJ	Control	0.007	0.005	0.005	0.002	-0.010	-0.010	-0.020
	1.2 NH	0.001	0.005	0.006	-0.010	-0.010	0.006	0.016
	1.75 NH	0.025	0.059	0.085	0.095	0.131	0.158	0.258
	1.2 KH	0.007	0.008	0.004	0.009	0.006	-0.030	0.008
	1.75 KH	0.057	0.080	0.128	0.198	0.261	0.275	0.260

* : NaOH (Na₂O equivalent), + : KOH (Na₂O equivalent)

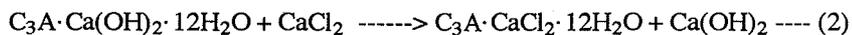
means that certain amount of alkali accelerates AAR, and dissolves silica from more active cristobalite and amorphous phase. The main mineral is also very important factor. The YM and IS, consisting of main mineral Feldspar and cristobalite, expanded much more than other aggregates. The same result of this study was also reported by Gillott et al. (Gillott et al. 1973)

For the YM aggregate (in the Table 5) mortar bar test shows expansion greater than 0.1% at alkali salt of Na₂O eq. 1.2% since four months regardless of kinds of alkali. Na ion also influences linear expansion much more than K ion. For chloride salts sodium chloride makes a mortar bar expand more than potassium chloride. These chlorides make a mortar bar expand less than alkali hydroxides at an early curing age (until four weeks), but as the curing age increases the specimens added alkali chlorides expanded more than those added alkali hydroxide. This result means that OH ion is much abundant in the specimens containing alkali hydroxide than alkali chloride at an early curing age. But at a long age Cl ion reacts with portlandite, 20 -30 % of cement hydrate in the structure (Park 1995), and produces Friedel salt, resulting in increasing volume change of structure. (Nison et al. 1990) The formation reaction of Friedel salt is as follows :

Table 5. Results of a mortar bar test for the control YM aggregates and the alkali added aggregates.

Alkali	Mortar bar expansion (%)						
	1 mon.	2 mon.	3 mon.	4 mon.	6 mon.	9 mon.	12 mon.
Control	0.019	0.022	0.019	0.005	0.013	-0.010	-0.030
NaOH	1.2*	0.013	0.029	0.063	0.122	0.113	0.108
	1.75	0.087	0.296	0.493	0.518	0.543	0.515
KOH	1.2	0.014	0.029	0.055	0.107	0.113	0.145
	1.75	0.041	0.233	0.453	0.538	0.511	0.515
NaCl	1.2	0.011	0.021	0.085	0.260	0.332	0.295
KCl	1.2	0.011	0.023	0.100	0.157	0.245	0.216

* Na₂O equivalent



From the results of chemical method and mortar bar test, a close relationship between Sc (amount of dissolved silica) and a linear expansion of mortar was found. For example, the aggregates of high value of dissolved silica, such as the Pyrex, YM and CA aggregates, show high linear expansion greater than 0.1% of mortar bar even though little amount of alkali (Na₂O eq. 1.2%) was added to mortar specimens.

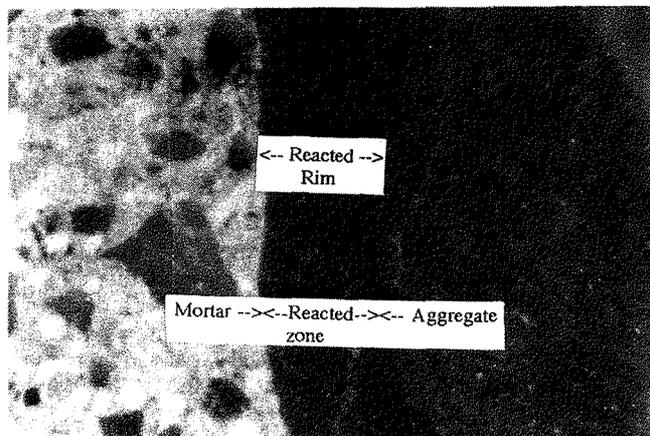


Figure 4. Metallic microscopic micrograph of AAR for the specimen made with the YM aggregate. This specimen contains alkali Na₂O eq. 1.75%.

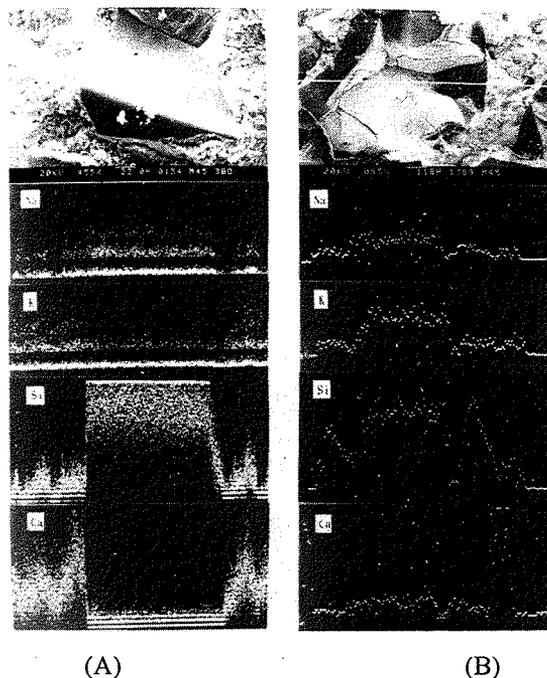


Figure 5. SEM micrographs and EDX results of the specimens made with the Pyrex.
 (A) Specimens cured for 30 days, (B) Specimens cured for nine months

Observation of AAR

Figure 4 shows the AAR for the specimen made with the YM aggregate at Na_2O eq. 1.75%. A black rim was observed at the boundary between cement paste and aggregate. AAR reaction proceeds from the surface to inner part of aggregate with absorbing water, resulting in expansion. (Powers et al. 1955, Struble et al. 1981)

Figure 5 shows the micrographs of mortar bar specimen made with Pyrex. This is the specimen containing alkali Na_2O eq. 1.2%. The specimen cured at 30 days does not show any product of AAR around aggregate, even though a mortar bar expands 0.214%. (in the Table 4) But the specimen cured at nine months shows the product of AAR (mortar bar test shows 0.495% in expansion). The product of AAR indicates different concentrations of cations compared with normal specimen. For example, Si ion concentration is low and alkali ions, both Na and K ion, are distributed much in the product of AAR. The K ion is also considered to play a big role for the AAR at a long age.

CONCLUSIONS

AAR is influenced by kind of alkali and alkali salt. For example Na ion is more significant on the AAR than K ion, and alkali hydroxide and alkali chloride influence much in expansion for an early age and for a long age, respectively.

There is a relationship between amount of dissolved silica and linear expansion of structure, and a limit of alkali amount for aggregates. AAR proceeds toward inner part of an aggregate with absorbing water, resulting in expansion. The AAR product contains very high amount of Na and K ion, which are considered to be significant on AAR in a specimen cured long time.

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