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ALKALI-SILICA REACTIVITY OF ANDESITE IN NaCl SATURATED SOLUTION

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Abstract

This paper presents the alkali-silica reactivity of andesite and expansion behavior of mortar in NaCl saturated solution. Glassy andesite without silica minerals was non-expansive in a NaCl saturated solution, whereas mortar bars using cristobalite-bearing aggregate showed large expansions. Dissolution of glass and cristobalite depend on OH⁻ concentration of alkali solution. OH⁻ concentration of pore solution of mortar under NaCl saturated solution was low. Under this condition dissolved amount of glass is not enough to cause expansion whereas cristobalite dissolved enough. These results indicate one possibility of limited risk of glassy andesite without reactive silica minerals in specific conditions even if alkalis are supplied from environments, such as deicing salts or sea salt as long as the initial alkali content in concrete is controlled under certain amount. In NaCl saturated solution, expansion of mortar bars incorporating cristobalite-bearing aggregate was larger although OH⁻ concentration of its pore solution was lower. This result may be caused by the increment in dissolution of cristobalite because of high ionic strength.

Keywords: andesite, Danish test, pore solution, OH⁻ concentration, Ionic strength

1. INTRODUCTION

Andesite is a typical reactive aggregate and is common in Japan. Alkali-silica reactivity of andesite is complex because of its various mineral compositions related to alkali-silica reaction, ASR. The reactivity is considered to be attributed to its volcanic glass and reactive silica minerals such as tridymite and cristobalite.

Andesite and other volcanic rocks have been examined extensively in Japan but mainly by the chemical method and the mortar bar accelerating test in which alkali content of cement is

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controlled as 1.2 % by mass and cured at 40 °C according to JIS (Japanese Industrial Standards) A 1146. Actually, due to change in alumina source from clay to coal ash from middle 80's, alkali level of Japanese Portland cement was limited less than 0.65% by mass. This situation was quite effective to control ASR caused by the high initial alkali content. Therefore, it is thought that remained risks of ASR in Japan are due to an alkali release from aggregate, alkali supplied from deicing salt or seawater, and a pessimism.

It is well known that deicing salt or seawater accelerate alkali-silica reaction. A number of accelerated mortar bar tests reproducing NaCl penetration such as Danish test [1] in which mortar immerse NaCl saturated solution. It is reported that the Danish test give different result from JIS A 1146 [2]. However, the discussion on the difference in reactivity of andesite in different alkali conditions has been limited. In order to analyze the reason why andesite shows different reactivity, the correlation between phase composition of andesite and expansive behavior in various alkali conditions was examined.

In this study, alkali -silica reactivity of andesite in NaCl saturated solution was discussed from the view point of pore solution composition and dissolution behaviour at various alkali solution.

2. EXPERIMENTAL

2.1 Materials

Cement used was commercial Japanese Ordinary Portland cement having alkali content of 0.60 % by mass as $\text{Na}_2\text{O}_{\text{eq}}$. Aggregates examined were collected from different 5 places in all over Japan. All of them are volcanic rocks and called "andesite" in field. The chemical compositions of the aggregates were measured by X-ray fluorescence analysis, XRF, as presented in Table 1.

Table 1: Chemical compositions of aggregates by XRF (mass%)

name	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I.	Total
C1	60.75	0.70	16.80	6.37	0.14	2.47	6.99	2.88	1.50	0.12	1.16	99.88
C2	68.18	0.32	13.94	3.19	0.05	3.10	3.41	3.65	2.97	0.10	0.89	99.80
C3	64.76	0.84	14.45	5.66	0.06	2.12	5.16	3.52	1.89	0.16	1.12	99.74
C4	58.02	0.89	17.81	7.50	0.14	2.39	7.64	3.38	1.82	0.18	0.05	99.81
G1	57.71	1.12	16.33	7.8	0.16	2.88	7.6	3.01	1.64	0.21	1.34	99.8

Petrographic evaluation was carried out for polished thin section by using an optical microscope. Phase compositions including type of silica mineral were also evaluated by X-ray diffraction method, XRD. The condition of analysis was Cu K α , 40 kV, 26 mA, 2.0 °/min of scan speed, and 0.05 °/step. Peak height of the silica mineral such as cristobalite, tridymite, and quartz are used as an index to compare comparative content. It is reported the amount of glass phase can be quantified by the phase analysis based on mapping data by electron probe microanalysis, EPMA with five wavelength dispersive type spectrometers, WDS. [3] The amount of glass phase, in this study, quantified by the above mentioned method.

The rock type and major mineral composition of aggregates are summarized in Table 2. The rock type was determined by their micro-textures and the silica content. Aggregate, C2 is dacite. Other four kinds aggregate are andesite. In this study, 5 aggregates was classified into

the two series, the series C and the series G. Series C (C1-C4) is bearing cristobalite and its content in the C1 is highest, and that of the C4 is the smallest. Series G (G1) is glassy andesite without silica mineral.

Table 2: Mineral composition

name	Rock type	qz	cr	tr	pl	px	cl	gl
C1	Andesite	○	⊙		⊙	⊙	•	-
C2	Dacite	⊙	○		⊙	⊙	•	15
C3	Andesite	○	○		⊙	⊙		-
C4	Andesite	△	○		⊙	⊙		16
G1	Andesite				⊙	⊙		27

⊙:1000<, ○:1000-500, △:500-250, •:250> (cps)
 qz: quartz, cr: cristobalite, tr: trydimite, gl: glass, pl:plagioclase, pyz: pyroxene, cl: clay minerals

The result by chemical method according to JIS A 1145 is shown in Figure 1. In JIS A 1145, large size aggregate was crushed into powders having particle size distribution in the range of 150 - 300 μm and was kept in 1000mmol/l NaOH solution for 24 hours at 80°C. The amount of dissolved silica, Sc and the amount of reduction in alkalinity, Rc in the solution were measured. All samples were judged as “not innocuous”. C1 and C2, which contain clay minerals, were plotted high Rc area because of ion exchange of clay minerals. Rc of G1 which is glassy andesite, is lower than others containing cristobalite.

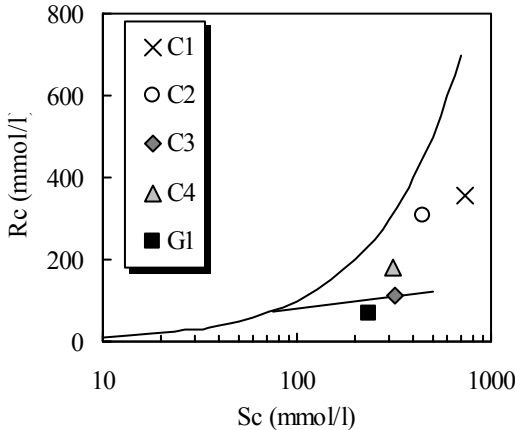


Figure 1 : Results of chemical test (JIS A 1145)

2.2 Evaluation of reactivity of aggregate in different alkali solution

For C1, C3 and G1, the amount of dissolved silica, Sc and the amount of reduction of in alkalinity, Rc at different OH⁻ concentration were measured. OH⁻ concentrations were 100, 200, 400, 1000mmol/l, respectively. Testing methods were same as JIS A 1145 except for OH⁻ concentration.

2.3 Mixture proportion

Mortar specimens (40×40×160mm) were prepared with water-to-cement ratio of 0.50 and sand to cement ratio of 2.25. Mortar bars were used for the length change test. In JIS A 1146, it is regulated that NaOH should be added into the mixture such that the $\text{Na}_2\text{O}_{\text{eq}}$ of the cement is 1.2% by mass. In addition, the mortar bars having the $\text{Na}_2\text{O}_{\text{eq}}$ of the cement of 1.8% and 2.4% were tested in this study.

2.4 Accelerated mortar bar test

Two different kinds of accelerated mortar bars tests were carried out in this study, Danish test [3] and JIS A 1146. Methods of each test are given as follows.

Danish test

In this method, specimens were cast without adding NaOH solution and immersed in NaCl saturated solution at 50°C for 3 months. Length change was measured at 20°C after pre-cooling at weekly intervals.

JIS A 1146

Mortar specimens were remained in the molds for 24hours. Then they were removed from the molds and their initial length was measured. They were placed in the fog container, controlled as the temperature of 40°C and the relative humidity (R.H.) of 100% for a period of 6 months.

2.5 Pore solution analysis

Pore solutions of mortar tested in each accelerated mortar bar test were extracted by the high pressure apparatus. Concentrations of Na^+ , K^+ , Ca^{2+} , and silicate anion were determined by induction coupled plasma mass-spectroscopy, ICP-MS. OH^- concentrations was measured by titration, and SO_4^{2-} and Cl^- concentration was measured by ion chromatography. In this study, limestone aggregate was used as non-reactive aggregate ($\text{Sc} = 3\text{mmol/l}$, $\text{Rc} = 23\text{mmol/l}$).

3. RESULTS

3.1 Expansion behaviour of mortar

Danish test

Figure 2 shows the expansion behavior of mortar bars tested according to the Danish test. In the Danish test, expansion behavior of different kinds of mortar bar is different according to their mineral compositions of aggregates. Mortar bars using cristobalite-bearing aggregate showed large expansions.

On the other hand, Mortar bars using G1, glassy andesites without silica minerals, was non-expansive in the Danish test. This result is accordance with reported Kawabata et. al. [4].

Kawabata et. al. also indicated that expansion in Danish test depend on its cristobalite content [4]. Figure 3 shows the relationship between peak intensity of cristobalite by XRD and expansion at 91days. In Danish test, there is a liner correlation between the expansion and cristobalite content of aggregate except for C3. The reason why C3 which contains moderate amount of cristobalite expanded larger will be subject of a further study.

JIS A 1146

Figure 4 shows the expansion behavior of mortar bars with different alkali contents for C1. The expansion increases with alkali content of cement. Figure 5 shows the relationship

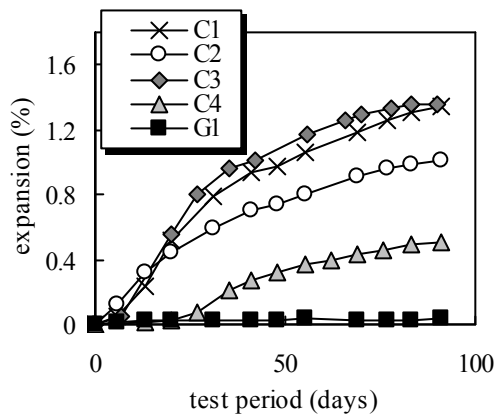


Figure 2: Danish test

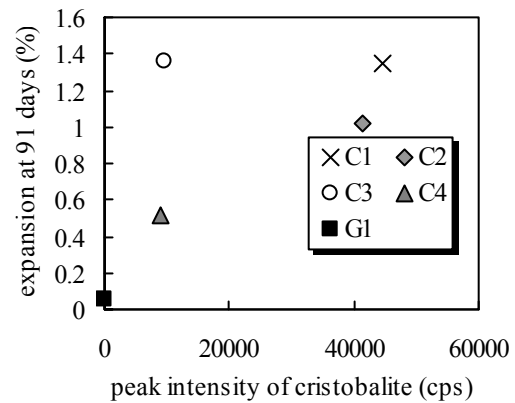


Figure 3: cristobalite content and expansion

between alkali content of cement and expansion at 182 days. In JIS A 1146, all samples expanded and were judged “not innocuous”. Glassy andesite without silica mineral expanded. An important finding is that no correlation between mineral composition of used aggregate and expansion is found, although the accuracy of quantification may affect the results in some degree. This result seems to be associated to pessimum effect. It is revealed that aggregates plotted in large Sc and Rc in chemical test give relatively low expansions in mortar or concrete even though they are extremely reactive with alkalis. This kind of aggregates can be estimated to show a pessimum effects. Sc and Rc of C2 and C1 are very large. The expansion of mortar using C2 and C1 seems to be affected by a pessimum effect. This is a subject of a further study.

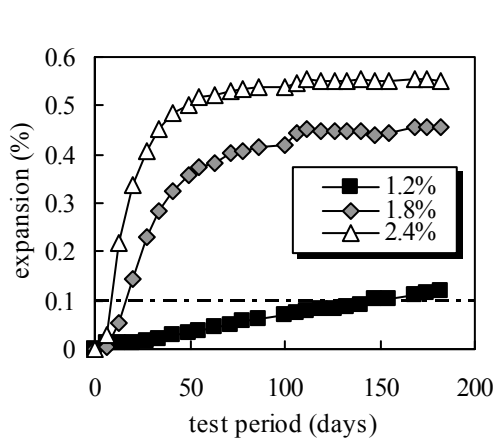


Figure 4: JIS A 1146

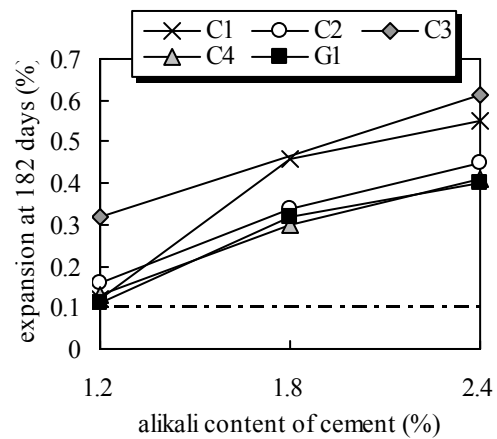


Figure 5: Alkali content of cement and expansion

4. DISCUSSION

4.1 Why glass phase showed no expansion in Danish test

Generally, reactivity of volcanic glass is thought to be very high and mortar using G1 expanded in JIS A 1146. In Danish test, however, glassy andesite without silica minerals, G1 showed no expansion. This phenomenon can be explained from the dissolution behaviour of volcanic glass in different OH⁻ concentration solution.

In a general, in the chemical method, the dissolution of glass phase is difficult to be separated from the dissolution of other silica phases. Therefore, potassium that is mainly included in glass phase in most samples was selected as an indicator of glass dissolution.

The relationships between OH⁻ concentration and Sc are shown in Figure 6 for C1 and C3 of andesite with cristobalite and G1 of glassy andesite without silica mineral. Sc is very sensitive to OH⁻ concentration for both cases. The relationships between Sc and the increase in potassium concentration in solution after the test are shown in Figure 7. G1 showed a linear correlation between Sc and K concentration which indicates dissolved silica is from glass phase because K exists only in the glass phase. Because the increase in K concentration of C1 is limited, the high Sc is expected to come from cristobalite mainly. The dissolution behavior of C1 and G1 is regarded as the dissolution behavior of cristobalite and glass phase. Thus, Sc of glass phase at [OH⁻]=400mmol/l is only 39mmol/l.

Table 3 presents the compositions of pore solution of mortar bars tested in each accelerated mortar bar test. In JIS A 1146, OH⁻ concentrations of pore solution is dependent on alkali content of cement. In Danish test, OH⁻ concentration is higher than JIS-0.6 because of ion exchange of Cl⁻ and OH⁻ in monosulfate. It is noted that OH⁻ concentration of pore solution of mortar bar tested in Danish test was 508mmol/l which is lower than that in JIS-1.2 test.

At [OH⁻] =508mmol/l, the concentration of pore solution in Danish test, dissolution of volcanic glass may be not enough to expand the mortar bars. Therefore, G1, grassy andesite without silica mineral showed no expansion.

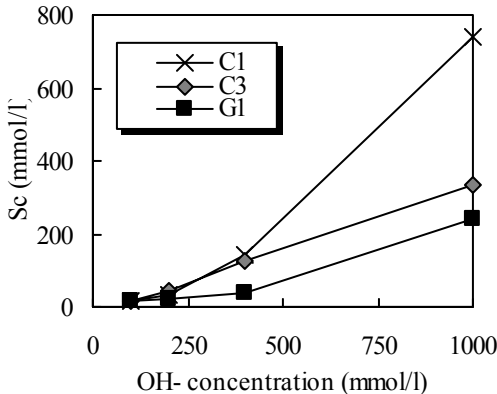


Figure 6 : OH⁻ concentration and Sc

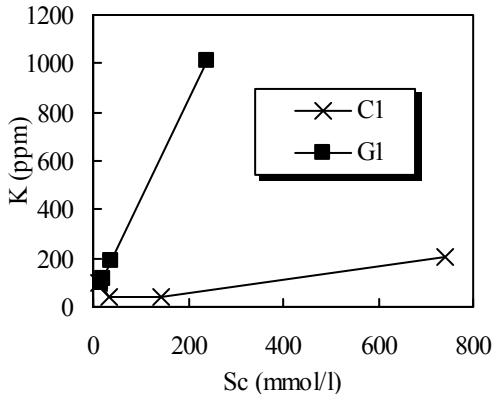


Figure 7 : Sc and K concentration

Table 3 : Chemical compositions of extracted pore solutions from mortars

	concentration (mmol/l)							ionic strength (mol/l)
	Ca ²⁺	Si ⁴⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	OH ⁻	
JIS-0.6	2.8	0.5	213.3	244.2	-	6.8	387.3	0.44
JIS-1.2	1.8	1.1	662.3	275.2	-	22.1	692.8	0.86
JIS-2.4	1.0	1.8	1089.9	189.9	-	80.8	1528.3	1.57
Danish	4.0	0.6	3353.4	351.3	2582.7	192.0	508.0	3.79

In addition, OH⁻ concentration of pore solution in JIS-1.2, 602.8mmol/l is higher than that in Danish test. In JIS test, glass phase dissolution continues because of high pH condition of pore solution. Therefore, glassy andesite without silica mineral, G1 expanded in JIS A 1146.

Above mentioned result shows one possibility of limited risk of ASR expansion for glassy andesite in specific environments where alkalis are supplied from environments such as deicing salts when no silica minerals are included in the andesite and initial alkali content is controlled under certain value. The reason why volcanic glass is thought to be “reactive” is that the most of the previous studies on reactivity of volcanic glass was investigated under the condition of high alkali solution.

4.2 Why cristobalite-bearing andesite showed large expansion in Danish test

Above mentioned result shows that volcanic glass makes little contribution toward the expansion and the expansion level of mortars correlated with its cristobalite content in Danish test. OH⁻ concentration of pore solution is lower in Danish test than JIS-1.2 (Table 3). Figure 6 and 7 indicated that the dissolution of cristobalite depends on OH⁻ concentration. However, mortar used cristobalite-bearing aggregates showed the larger expansion in Danish test than JIS-1.2 even though OH⁻ concentration is lower. Therefore, it is thought that the alkali supplied from external source, NaCl affect the reactivity of cristobalite. It is observed characteristically in Danish test that ionic strength of pore solution is the largest. Chatterji [1] also has indicated the importance of ionic strength of pore solution on the expanding behaviors. Figure 8 shows the relationship between ionic strength of pore solution and expansion of mortar used, in C1. There is good correlation between ionic strength and expansion.

In order to clarify the effect of ionic strength to the reactivity of cristobalite, the amount of dissolved silica, Sc of C3 was measured when it immersed 400mmol/l NaOH solution which ionic strength was increased by addition of NaCl. Meanwhile, the temperature of solution, testing time and particle size distribution of aggregate were according to JIS A 1145. NaCl concentration was varied at 3 levels as 0 (non-additive), 3, 5mol/l, respectively. The relationship between NaCl concentration and Sc is shown in Figure 9. As NaCl concentration increased, that leads to the increasing ionic strength, Sc tend to be higher. At 5mol/l of NaCl concentration, Sc increases by 40% compared to the non-additive. This result indicates that the dissolution of cristobalite is affected by not only OH⁻ concentration but ionic strength in pore solution. Therefore, larger expansion of mortar in Danish test used cristobalite bearing andesite is attributed to an acceleration in the dissolution of cristobalite because of high ionic strength.

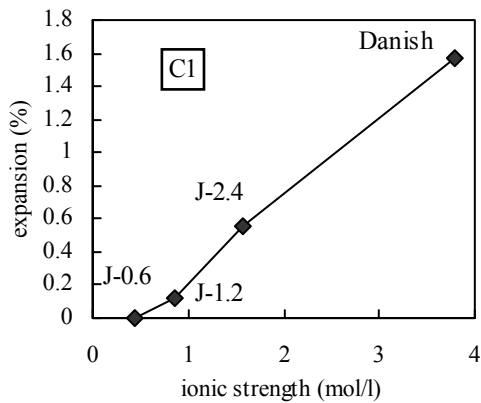


Figure 8: ionic strength and expansion

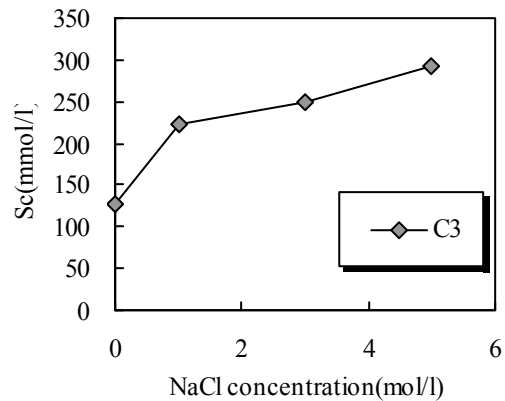


Figure 9: NaCl concentration and Sc

5. CONCLUSIONS

Alkali-silica reactivity of andesite in NaCl saturated solution was evaluated. The following conclusions were obtained.

- (1) Although glassy andesite without reactive silica minerals was judged as reactive by chemical test and mortar bars tests according to JIS A 1146, it was innocuous by Danish test reproducing the environments of deicing salt and sea water.
- (2) Glass phase was reactive at high OH^- concentration. With the decrease in OH^- concentration, the reactivity of glass was decreased drastically. At 400mmol/l of OH^- concentration, glass phase could not be dissolved even while cristobalite shows high reactivity.
- (3) OH^- concentration of mortar tested in the Danish test was lower than other accelerated mortar bar tests and this may be the reason of non-expansion of glassy andesite without reactive silica minerals.
- (4) Increment in the ionic strength of pore solution accelerated the dissolution of cristobalite and this may cause the large expansion in Danish test

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