

ALKALI-SILICA REACTIVITY AND EXPANSION OF MORTAR INCORPORATING GLASSY ANDESITE IN ALKALINE SOLUTION

Yuichiro Kawabata^{1,*}, Kazuo Yamada² and Hiromichi Matsushita³

¹Graduate School of Engineering, Kyushu University (JSPS Research Fellow),
744 Motooka, Nishi-ku, FUKUOKA, Japan

² R&D Center Taiheiyo Cement Corporation, 2-4-2, Osaku, Sakura-shi, CHIBA, Japan

³ Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, FUKUOKA, Japan

Abstract

This paper presents the alkali-silica reactivity of glassy andesite and expansion behavior of mortar in various accelerated mortar bar tests. The alkali-silica reactivities of glassy andesite are different depending on the types of the test. Glassy andesite without silica minerals was non-expansive in saturated NaCl solution whereas mortar bars using cristobalite-bearing aggregate showed large expansions. In order to clarify the mechanism of this phenomenon, detailed experiments were examined. The pH value of pore solution of mortar under saturated NaCl solution was lower than those in other conditions. In lower OH⁻ concentration, the dissolved amount of glass was considerably less than that of cristobalite. 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 as deicing salts or sea salt as long as the initial alkali content in concrete is controlled under certain amount.

Keywords: glass, accelerated mortar bar test, pore solution, pH-dependence of dissolution

1 INTRODUCTION

Andesite is a typical reactive aggregate and is common in Japan. One fourth of crushed aggregate is andesite [1]. However, the discussion on the difference in reactivity of andesite in different alkali conditions has been limited. 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 controlled as 1.2 % by mass and cured at 40 °C according to JIS (Japanese Industrial Standards) A 1146. However, because of the 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 alkali release from aggregate, alkali supplying from deicing salt or seawater, and pessimum. The condition of accelerated mortar bars test should correspond to remained risks of ASR. Though a number of test methods are supposed, sometimes different tests give different results [2]. 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 has been examined.

For glassy andesite without silica minerals, one interesting result has been reported. Previous work of this study showed that the andesite was innocuous in saturated NaCl solution whereas andesite incorporating reactive silica minerals showed high reactivity [3]. Further investigation is needed to clarify the alkali-silica reactivity of volcanic glass.

In this study, various accelerated mortar bar tests using 5 types of andesite with different phase composition were conducted. Alkali-silica reactivity of volcanic glass in various alkali conditions was discussed from the viewpoint of pH of pore solution and pH-dependence of volcanic glass.

2 MATERIALS AND METHODS

2.1 Materials

* Correspondence to: kawabata@civil.doc.kyushu-u.ac.jp

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 as andesite in field. The chemical compositions of the aggregates were measured by X-ray fluorescence analysis, XRF and which are presented in Table 1.

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 $\text{Cu K}\alpha$, 40 kV, 26 mA, 2.0 °/min of scan speed, and 0.05 °/step. Peak height of each silica mineral such as cristobalite, tridymite, and quartz are used as an index to compare comparative content. Of course, although direct diffraction strength is not proportional to the content because of many factors, only preliminary quantification was tried in this study. In this study, it is no necessity to have very accurate quantification of these mineral phases.

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. The same thin sections used for petrographic evaluation were used after carbon coating. Accelerating voltage was 15kV and the probe current was 50nA. The beam size was minimized at this condition. Vacuum condition was stable enough for quantification. Scanning of sample is not continuous but discrete and the dwell time was 40 ms/pixel. Exact detection limits for all elements have not established. However, at least for the discrimination, judging from the concentration difference between existing phases, adequate accuracy was thought to be obtained. In order to avoid the drift of sample during mapping to make elemental scatter diagram, important five elements e.g. Si, Al, Na, K and Fe, are measured simultaneously.

Because of thin section (around 20 μm) for optical microscope observation and the overlapping of glass phase and others, it is not always easy to distinguish glass phase from others. However, the obtained information by EPMA is limited to one to a few μm size volume and the detailed phase analysis is possible under this spatial resolution. Another merit of EPMA is the number of counting. Usual point counting by optical microscope takes long time because it needs to count at 3000 points at least. By using EPMA, ten thousands points are obtained automatically. The procedure to estimate glass phase content is explained in the next chapter.

The rock type and major mineral composition of aggregates are summarized in Table 2. For X-ray fluorescence analysis by WDS, a typical measurement condition used constantly in the geological department in Kyushu University was applied under their collaboration [4]. The rock type was determined by their micro-textures and the silica content. One aggregate, Da (D) is dacite. Other four kinds aggregate are andesite. An(A) and An(B) contain no silica minerals. Cristobalite content of An(E) is the highest and Da(D) follows.

2.2 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 cast 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 cast so as the $\text{Na}_2\text{O}_{\text{eq}}$ of the cement was 1.8 and 2.4% were tested in this study.

2.3 Chemical test (JIS A 1145)

Reactivity of aggregate in alkali solution was evaluated by the chemical method according to JIS A 1145. The 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 were measured. Sc and Rc of An(A) and An(E) were also measured at different OH^- concentration, 100, 200, 400 and 1000mmol/l.

2.4 Accelerated mortar bars test

Three accelerated mortar bars tests were adopted in this study. Figure 1 summarizes the flow chart of accelerated mortar bar tests. Table 3 lists the combination of samples and accelerated mortar bar tests.

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. After precuring, they were placed in the fog container, which is maintained at temperature of 40°C and relative humidity (R.H.) of 100% for a period of 6 months.

ASTM C 1260

In this method, specimens were cast without adding NaOH solution. After demolding, the specimens were stored in water at 80°C for 24 hours. After precuring process, specimens were immersed in a 1000mmol/l NaOH solution at 80°C for 4 weeks.

Danish test [4]

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

2.5 Pore solution analysis

Pore solutions of mortar tested in each accelerated mortar bar test were expressed by the high pressure apparatus. Concentrations of Na⁺, K⁺, Ca²⁺, and Silicate anion were determined by induction coupled plasma mass-spectroscopy, ICP-MS. OH⁻ concentrations was measured by titration, and SO₄²⁻ and Cl⁻ concentration was measured by ion chromatography. In this study, limestone aggregate was used as non-reactive aggregate (Sc = 3mmol/l, Rc = 23mmol/l).

3 RESULTS

3.1 Phase composition of andesite

Images of optical microscope and EPMA mapping of An(B) and An(C) are shown in Figures 2 and 3 respectively. Scatter diagram of silica and alumina for measurement points are useful to identify the phases such as plagioclase and pyroxene. Of course, by optical microscope these phases can be identified very easily but the spatial resolution is completely different. As mentioned before, thickness of thin section and overlapping of phases limits the quantification of glass phase. By using scatter diagram reproduced from the measurement results by EPMA mapping, composing phases can be distinguished and the content (area %, which is the same as volumetric % in this case) can be estimated [5].

Judging from EPMA data, optical microscope image, scatter diagram of silica-alumina in Figures 2 and 3, different places of chemical composition shown in the scatter diagram are able to identify their phases. By counting number of area estimated as glass phase, the area % can be estimated.

In An(B) shown in Figure 2, clear phenocrysts and matrix of glass phase are observed without alteration. K locates in matrix glass phase mainly because K is not contained so much in phenocrysts such as plagioclase and pyroxene and it remained in liquid phase that was consolidated as glass phase in this case. Silica mineral does not exist in An(B).

In An(C), the texture is more complex because of alteration. The areas of high K concentration seem to be slightly altered glass phase. Figure 3 shows the existence of silica mineral. This silica mineral is identified as cristobalite by XRD.

By the same procedure, glass contents of other samples were estimated.

An important point of phase composition, An(A) and An(B) do not contain any reactive silica mineral but contains plenty of glass phase. Other An(C), Da(D), and An(E) contain glass phase in some degree but they contain the significant amount of reactive cristobalite.

3.2 Chemical test

The results by chemical method are shown in Figure 4. The judgment line whether reactive or innocuous is Rc: Sc = 1:1 according to JIS A 1145 and this is not the same as the original ASTM C 289. All samples were judged as reactive. Da(D) and An(E), which contain clay minerals, are plotted in high Rc area. Ion exchange of clay minerals causes high Rc. Rc of An(A) and An(B), which are glassy andesite, is lower than other andesite containing cristobalite. The reason is estimated as that the alkali releases from glass phase. K and a part of sodium exist in glass phase and dissolve out with glass dissolution.

3.3 Expansion behaviour of mortar

JIS A 1146

Figure 5 shows the expansion behavior of mortar for An(E). Expansion increases with alkali content of cement. Figure 6 shows the relationship between alkali content of cement and expansion at 182 days. In JIS A 1146, all samples expanded and were judged “not innocuous”. Expansion of

mortar, however, is almost the same in all samples. An important finding here is that there is no correlation between mineral composition of used aggregate and expansion, although the accuracy of quantification may affect the results in some degree. This result seems to be associated to a 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 pessimum effects. Sc and Rc of Da(D) and An(E) are very large. The expansions of mortar using Da(D) and An(E) seem to be affected by pessimum effect. This will be the subject of a further study.

ASTM C 1260

Figure 7 shows the expansion behavior of mortar bars tested according to ASTM C 1260. Mortar bars using cristobalite-bearing aggregate expanded larger than those using glassy andesite. Expansion, however, is not dependent on the cristobalite content. In ASTM C 1260, volcanic glass is expected to affect the reactivity of aggregate.

Danish test

Figure 8 shows the expansion behavior of mortar bars tested according to the Danish test. In the Danish test, expansion behaviors are completely different according to mineral composition of used aggregates. Mortar bars using cristobalite-bearing aggregate showed large expansions. Expansions of mortar bars are strongly dependent on cristobalite content of aggregate.

The most striking feature is that mortar bars using An(A) and An(B), in other words, glassy andesites without reactive silica minerals, were non-expansive in the Danish test while they showed expansion in JIS A 1146 and ASTM C 1260. Thus, volcanic glass is judged “non-reactive” in the Danish test. This result is accordance with our previous work [3].

4 DISCUSSION

4.1 Dissolution behaviour of volcanic glass

In a general chemical method, the dissolution of glass phase is difficult to separate from the dissolution of other silica phases. Therefore, K that is mainly included in glass phase in most samples in this case examined was selected as an indicator of glass dissolution.

The relationships between OH⁻ concentration and Sc are shown in Figure 9 for An(A) of glassy andesite without silica phase and An(E) of andesite with plenty amount of cristobalite. Sc is very sensitive to OH⁻ concentration that corresponds to pH for both cases. An(A) showed 242 mmol/l of Sc at [OH⁻] = 1000 mmol/l. This value is usually judged high enough as reactive aggregate. However, at [OH⁻] = 400 mmol/l, Sc of An(A) decreased to only 39 mmol/l.

The relationships between Sc and the increase in K concentration in solution after the test are shown in Figure 10. An(A) 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 An(E) is limited, the high Sc is expected to come from cristobalite mainly. Sc at [OH⁻] = 400 mmol/l is 130 mmol/l and still high enough to show high reactivity in Danish test.

4.2 Pore solution composition

Table 4 lists the compositions of pore solution of mortar bars tested in each accelerated mortar bar test. In JIS A 1146, OH⁻ concentrations of pore solution were dependent on alkali content of cement. In Danish test, OH⁻ concentration increased 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 lower than that in JIS-1.2 test. Ionic strength of pore solution in Danish test was the largest. Chatterji [6] has indicated the importance of ionic strength of pore solution on the expanding behaviors. Ionic strength of solution increases surface charge density of aggregate particle. One possible explanation of the larger expansion of mortar bars in Danish test is the effect of the higher ionic strength of pore solution.

4.3 Reactivity of glass phase

Generally, reactivity of volcanic glass is thought to be very high. In Danish test, however, glassy andesite without silica minerals showed no expansion. The reason for this phenomenon can be explained as follows:

Solubility of volcanic glass is strongly dependent on pH of solution. At $[\text{OH}^-] = 400 \text{ mmol/l}$, volcanic glass cannot dissolve enough to expand. OH^- concentration of pore solution decreases while ASR proceeds because of adsorption of alkali by silicate anion. In Danish test, OH^- concentration of pore solution is 508 mmol/l . At $[\text{OH}^-] = 508 \text{ mmol/l}$, dissolution of volcanic glass stops at beginning of reaction.

OH^- concentration of pore solution in JIS-1.2, 602.8 mmol/l is higher than that in Danish test. Pore solution analysis of mortar tested in ASTM test was not conducted. It is expected that OH^- concentration in ASTM C 1260 is close to 1000 mmol/l . In JIS and ASTM tests, glass dissolution continues because of high pH condition of pore solution. This causes the discrepancy between each accelerated mortar bar test.

These results indicate 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. Most of the previous studies on reactivity of volcanic glass investigated at the condition of high alkaline solution. Dissolution of glass, however, is dependent on its chemical composition and that of surrounding solution. High alkali containing glass like wasted glass dissolves at low pH solution. More detailed work is required to elucidate the relationship between chemical composition of glass phase and alkali-silica reactivity.

5 CONCLUSIONS

Reactivity of volcanic glass was evaluated in various tests with different types of alkali condition. 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 and ASTM C 1260, 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 of pH, the reactivity of glass decreased drastically. At 13.6 of pH, glass phase could not dissolve 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) Expansion is correlated to cristobalite content in the Danish test although the other tests could not show no correlation between expansion and cristobalite content. The reason is the additional role of glass phase at high OH^- concentration to expansion.

6 REFERENCES

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

	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	LOI	Total
An(A)	57.71	1.12	16.33	7.80	0.16	2.88	7.60	3.01	1.64	0.21	1.34	99.80
An(B)	62.74	0.93	14.72	5.73	0.16	1.67	6.01	2.94	2.30	0.25	2.30	99.75
An(C)	58.02	0.89	17.81	7.50	0.14	2.39	7.64	3.38	1.82	0.18	0.05	99.81
Da(D)	68.18	0.32	13.94	3.19	0.05	3.10	3.41	3.65	2.97	0.10	0.89	99.80
An(E)	60.75	0.7	16.8	6.37	0.14	2.47	6.99	2.88	1.5	0.12	1.16	99.88

TABLE 2: Assemblages of major phases of aggregates by XRD.
Glass contents (volume %) are estimated by EPMA. cps: counts per second.

	Rock type	qz	cr	tr	pl	px	cl	gl
An(A)	Andesite				⊙	⊙		27
An(B)	Andesite				⊙	⊙		55
An(C)	Andesite	△	○		⊙	⊙		16
Da(D)	Dacite	⊙	○		⊙	⊙	·	15
An(E)	Andesite	○	⊙		⊙	⊙	·	-

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

TABLE 3: Combinations of aggregate samples and accelerated mortar bar tests.

test method	alkali content	sample					
		An(A)	An(B)	An(C)	Da(D)	An(E)	
JIS-1.2	JIS A 1146	1.2	○		○	○	○
JIS-1.8		1.8	○		○	○	○
JIS-2.4		2.4	○		○	○	○
Danish test	0.62	○	○	○	○	○	○
ASTM C 1260	0.62	○		○	○	○	○

TABLE 4: 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

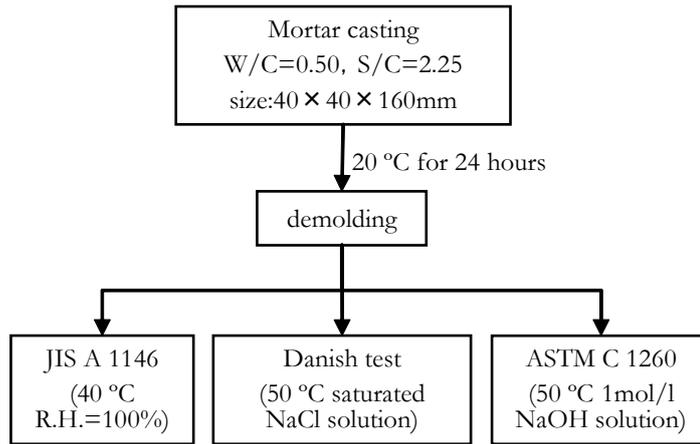


Figure 1: Flow chart of accelerated mortar bar tests.

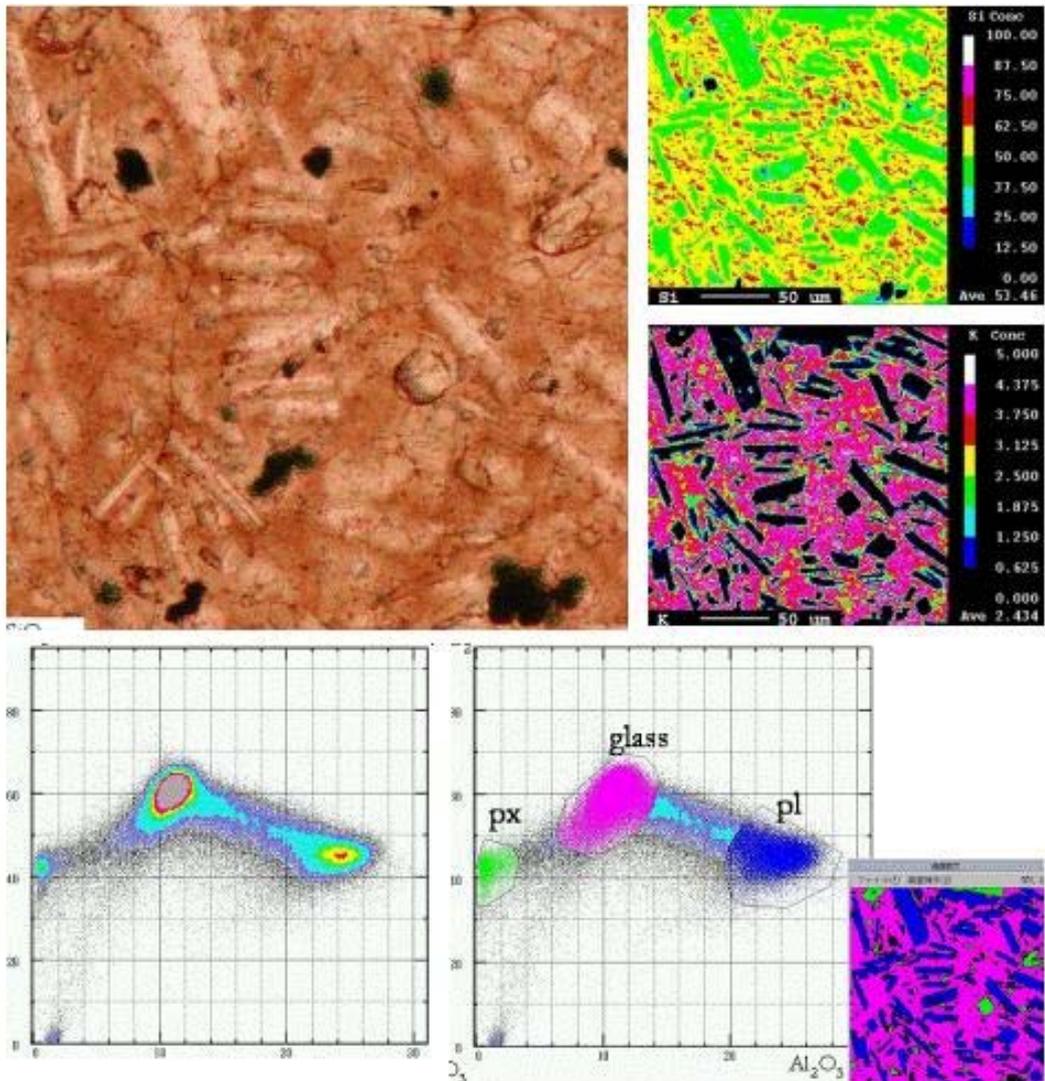


Figure 2: Optical microscope observation (upper left) and EPMA mapping of An(B) for Si and K (upper right). Both images indicate the same area. Scatter diagram of SiO₂ vs Al₂O₃ (lower left) and phase analysis indicating the distribution of pyroxene, plagioclase and glass phases.

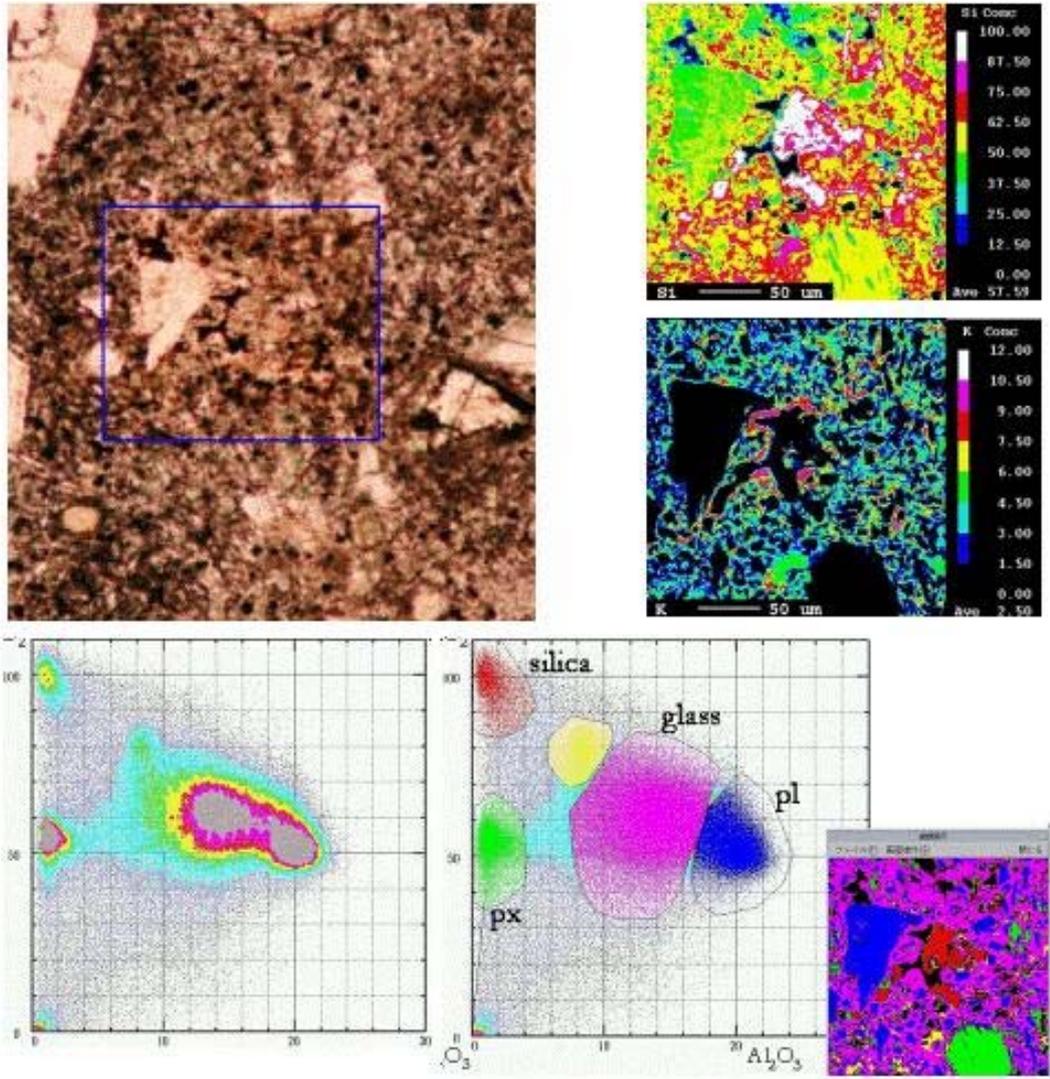


Figure 3: Optical microscope observation (upper left) and EPMA mapping of An(C) for Si and K (upper right). Indicated area in the optical microscope image was evaluated by EPMA. Scatter diagram of SiO₂ vs Al₂O₃ (lower left) and phase analysis (lower right).

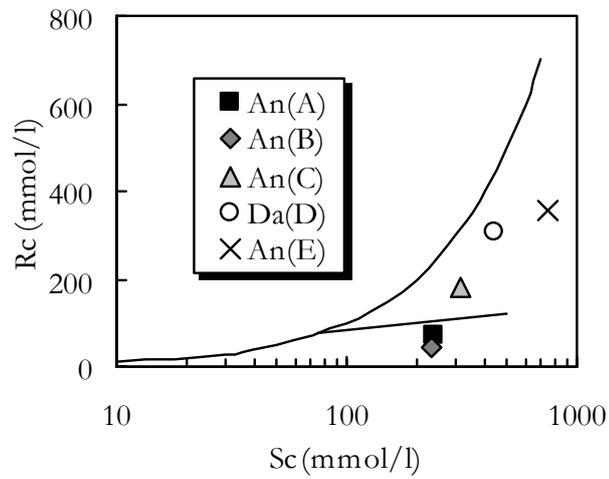


Figure 4: Results of chemical test (JIS A 1145).

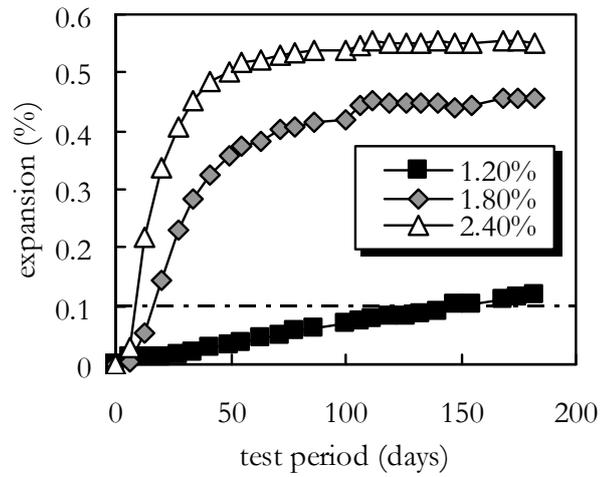


Figure 5: Expansion behavior of mortar containing An(E) (JIS A 1146).

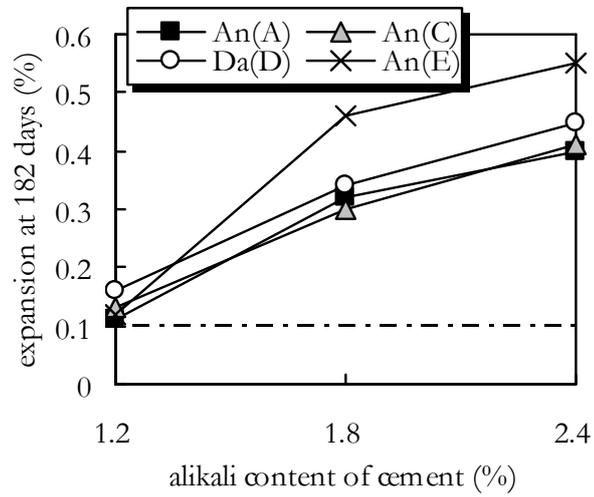


Figure 6: Alkali content of cement vs expansion at 182days.

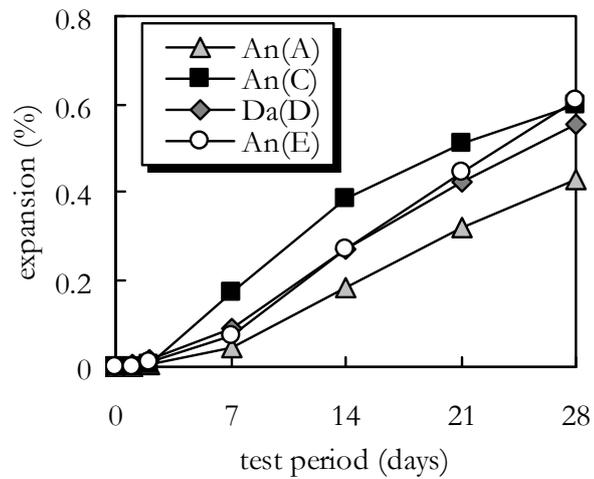


Figure 7: Expansion behavior of mortar (ASTM C 1260).

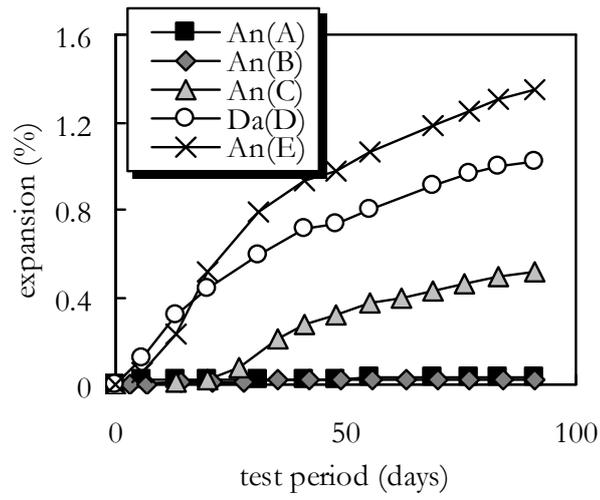


Figure 8: Expansion behavior of mortar (Danish test).

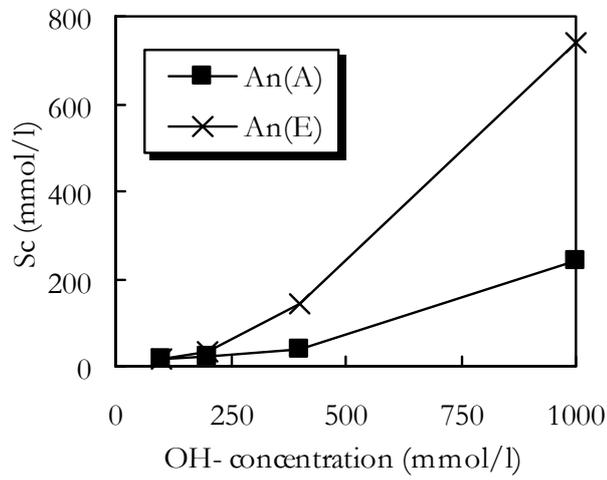


Figure 9: OH- concentration vs Sc.

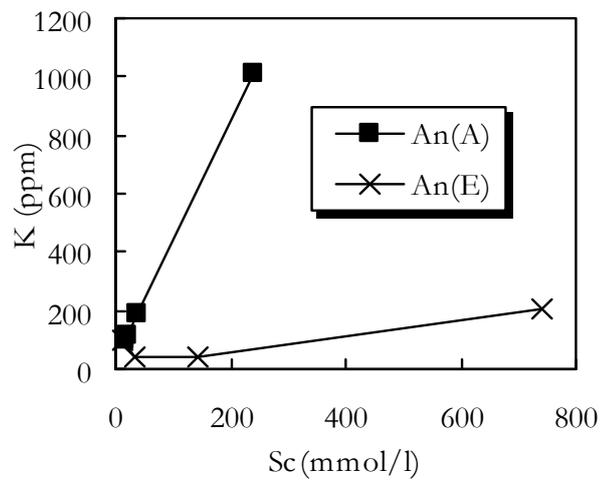


Figure 10: Sc vs K concentration.