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Compatibility between ecocement produced from incinerator ash and reactive aggregates in ASR expansion of mortars

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Abstract

Recently, in Japan, two new-type hydraulic cements, high early strength type ecocement (HEC) and normal type ecocement (NEC), have been developed using incinerator ashes up to 50% of the raw materials. In this study, the compatibility of these ecocements with various types of reactive aggregates with respect to alkali–silica reaction (ASR) was studied. Ordinary Portland cement (OPC) and blast furnace slag cement (BFSC) were also used for a comparative study. Two types of the accelerated mortar bar expansion test, the JIS A1146 and the Danish methods, were used to clarify the expansion behavior of mortars made with the above cements. The influence of a combination of the chemical and mineralogical compositions of cement and the reactive components of aggregate on both the amount of ASR gel and the expansion rate of the mortar was also investigated. From the results, it was found that the expansion behaviors of mortars due to ASR varied significantly depending on a combination of both the mineralogical composition of cement and the reactive component of aggregate.

Keywords: Alkali–aggregate reaction; Cement; Hydration products; EDX; X-ray diffraction

1. Introduction

Recently, in Japan, two new types of ecocement made from incinerator ashes have been developed, high early strength type one (HEC) and normal cement type one (NEC) [1]. There are few studies concerning the combined effect of the mineral composition of cements and that of reactive aggregates on the amount of alkali–silica reaction (ASR) gel formation and the subsequent expansion of concrete. As a result, the expansion behavior of the reactive aggregate-bearing mortars using these ecocements cannot be deduced from their chemical and mineralogical compositions.

This study, therefore, aims at investigating such a relationship by using four types of cements, to prepare the mortar with each of four types of reactive aggregates. The reactive aggregates used were river gravel, crushed chert rock and two types of crushed andesite rocks. The accelerated mortar bar test methods, according to the Japanese and Danish specification, were employed to clarify the expansion behavior of reactive aggregate-bearing mortars due to ASR.

2. Experimental

2.1. Chemical and physical properties of cements

The chemical compositions and physical properties of four types of cements used in this study are presented in Tables 1 and 2. It is seen that the total alkali content of Na_2O_{eq} of ordinary Portland cement (OPC) and blast furnace slag cement (BFSC) is made up of both Na_2O and K_2O, whereas in the case of two types of ecocement, HEC and NEC, Na_2O mainly constitutes their alkali content since their K_2O content is quite small. Also, as the C_3S and β-C_2S content of HEC and NEC are lower, less amount of calcium hydroxide is expected to be produced in their hydration in comparison to that of OPC [1]. On the other hand, the amount of SO_3 content in relation to C_3A in the HEC and NEC is higher than that of OPC and BFSC. In particular, HEC contains $C_{11}A_7CaCl_2$ in place of C_3A in OPC and,

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Table 1
Chemical and mineral compositions of various types of cements (%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
OPC	20.46	5.21	2.75	64.47	1.34	1.90	0.35	0.41
BFSC	25.24	7.86	1.82	56.98	3.04	2.16	0.28	0.37
HEC	15.25	10.12	2.86	57.14	1.73	9.45	0.48	0.02
NEC	16.75	7.99	3.92	60.81	1.93	3.79	0.39	0.02
	C_3S	C_2S	C_3A	C_4AF	$C_{11}A_7CaCl_2$			
OPC	62.5	11.6	9.2	8.4	–			
BFSC	–	–	–	–	–			
HEC	41.5	12.5	–	8.7	16.8			
NEC	50.1	10.3	14.5	11.9	–			

hence during its hydration, Friedel's salt and ettringite would be the favored hydration products as opposed to the monosulfo-aluminate hydrate [2].

2.2. Mineral compositions and alkali–silica reactivity of aggregates

The mineral compositions and alkali–silica reactivity of the aggregates are presented in Table 3. Actually, the damages of concrete due to ASR have been found from previous studies in the concrete structures made with these aggregates.

Fig. 1 shows the X-ray diffraction (XRD) patterns of the aggregates. The river gravel is composed of two types of stone particles, brown particles that originate from andesite and grey-black particles that originate from sandstone. The XRD pattern shows that the brown andesite particles, constituting about 20% of total particles in the river gravel, contain the cristobalite and volcanic glass as reactive components. The crushed chert aggregates contain the microcrystalline quartz. Also, the andesite A aggregates contain the cristobalite and volcanic glass, while the andesite B aggregates contain the clay mineral of montmorilonite produced in the process of weathering of volcanic glass in addition to the cristobalite and volcanic glass.

From the result of the chemical test method according to JIS A 1145, the river gravel was judged to be innocuous probably because reactive particles are only 20% of total ones. On the other hand, the crushed chert and andesite A and B aggregates were judged to be deleterious. Fig. 2 shows the results of the accelerated mortar bar test method according to ASTM C1260. According to this test, the chert is judged to be innocuous, however, the river gravel and andesites A and B aggregates are judged to be deleterious. The graph also shows that the expansion curves of both andesite A and B aggregates vary linearly with the time of exposure, while that of the river gravel shows the nonlinear behavior. This may be because the reactive mineral component content in the river gravel is small and limited compared with that of the andesite aggregates. On the other hand, the expansion in the mortar bar made with the crushed chert aggregate is almost at the limiting value, but judged to be innocuous according to this test. This chert aggregate may be judged to be deleterious if its pessimum content is taken into consideration [3].

2.3. Test methods

2.3.1. Mortar bar test method (JIS A1146)

The mixture proportion of the mortar is water:cement:aggregate = 0.5:1:2. Depending on the Na_2O_{eq} of the cement, the extra amount of NaOH solution was added into the mixture such that the Na_2O_{eq} of the cement is 1.2% of the mixture by weight. Three mortar bar specimens were cast for each cement–aggregate combination. The initial lengths of the mortar bars were measured immediately after removing the mould. They were then placed in the fog container, which is maintained at temperature of 40 °C and relative humidity (RH) of 100% for a period of 6 months. The lengths of the mortar bars were measured at weekly intervals.

2.3.2. Mortar bar test method (Danish method)

In this method, the same mixture proportion is adopted as that of the JIS A 1146 method; however, the Na_2O_{eq} of the cement is not adjusted. Three mortar bar specimens were made for each cement–aggregate combination. After demoulding, the initial length of each specimen was measured, and then the mortar bars immersed in saturated NaCl solution at 50 °C for 6 months [4]. Measurements were taken at weekly intervals as above.

2.3.3. XRD analysis and differential scanning calorimetry (DSC)

Samples were taken from the middle portion of the mortars, grounded into fine powder passing the 150-μm sieve size, which was used for XRD and DSC analysis. In particular, the DSC curves were analyzed quantitatively for

Table 2
Physical properties of various types of cements

	Density (kg/m^3)	Blaine fineness (m^2/kg)	Setting time		Stability of cement	Compressive strength (N/mm^2)		
			Min (h–min)	Max (h–min)		3 days	7 days	28 days
OPC	3160	327	2–25	3–30	Good	25.6	42.8	61.7
BFSC	3040	377	2–45	4–10	Good	21.0	33.9	60.2
HEC	3130	530	0–08	0–20	Good	32.0	35.0	48.0
NEC	3170	425	2–30	4–00	Good	25.0	35.0	51.0

Table 3
Reactive mineral components in aggregates and alkali–silica reactivity of aggregates

Type of aggregate	Reactive mineral	Chemical method (mmol/l)			ASTM C1260 mortar bar method*	
		Rc	Sc	Result	Expansion (%)	Result
River gravel	Volcanic glass cristobalite	92	22	Innocuous	0.42	Deleterious
Crushed chert	Crystalline silica amorphous silica	88	391	Deleterious	0.09	Innocuous
Andesite A	Volcanic glass cristobalite	109	289	Deleterious	0.70	Deleterious
Andesite B	Volcanic glass cristobalite montmorilonite	223	609	Deleterious	0.50	Deleterious

* Interpretation of ASTM C 1260 test result: 14 days expansion below 0.1%—innocuous 0.1–0.2%—uncertain; above 0.2%—deleterious.

the Friedel’s salt content, which appears as an endothermic peak at 320 °C, and also for calcium hydroxide content, which also appears as an endothermic peak at 460 °C.

2.3.4. Acetic acid–uranium fluorescence method

After the mortar bar test method, the amount and distribution of the ASR-gel formed during the exposure period were inspected visually. Each mortar bar was split into two halves and then the fresh surface sprayed with the acetic acid–uranium solution. The ASR-gel was inspected visually with the aid of a UV light [5].

2.3.5. SEM-EDX

The chemical compositions of the ASR gel formed around reactive aggregates after the mortar bar test method according to the JIS A 1146 and Danish method were also analyzed by the energy dispersive X-ray analysis.

2.3.6. Chloride penetration into mortar

The chloride penetration depth in the specimens after the mortar bar test method according to the Danish specification was measured. In the measurement procedure, each specimen was split longitudinally into two halves and then the fresh surfaces sprayed with a 0.1-N solution of $AgNO_3$ reagent. The depth of chloride penetration was obtained by measuring the depth of the whitish coloration, which indicates the formation of AgCl from the reaction between the reagent and the chloride ions on the fresh surface of the mortar bars [6].

3. Results and discussion

3.1. Expansion behavior of mortars in moist fog chamber

Fig. 3 shows the result of the mortar bar test method according to JIS A 1146. The broken lines show the limits of expansion according to the JIS A 5308. For 3- and 6-month exposure periods, specimens that expand more than 0.05% and 0.1%, respectively, are considered to be deleterious. It can be seen that in the case of the BFSC specimens, the expansion of the mortars made with four reactive

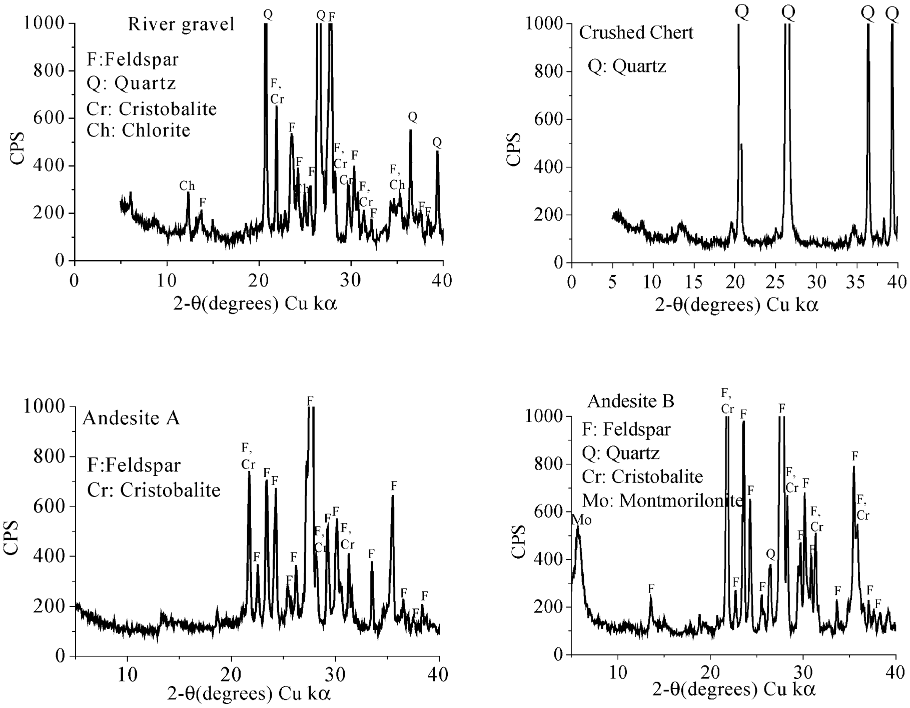

Fig. 1. X-ray diffractograms of aggregates used.

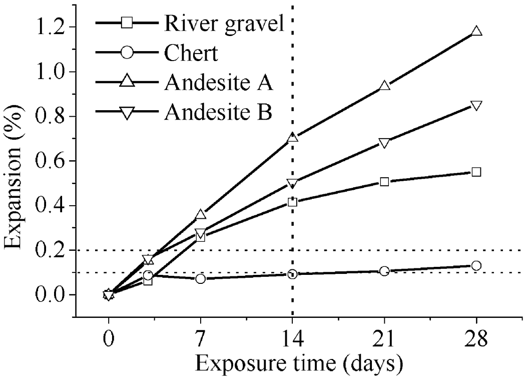

Fig. 2. Expansion behaviors of mortar bars by ASTM C 1260.

Table 4
Result of visual inspection of ASR-gel formation (JIS A 1146 method)[a]

	OPC	BFS	HEC	NEC
River gravel	II	I	II	II
Crushed chert	III	I	III	III
Andesite A	III	I	III	III
Andesite B	II	I	II	II

I (no ASR-gel) → IV (high amount of ASR-gel).

[a] Interpretation of result of visual inspection by acetic acid–uranium fluorescence method.

aggregates is about 0.05% even at maximum value. Thus, BFSC is capable of restraining ASR expansion for a long-term period even with very reactive aggregates. This may be because in the hydration of BFSC, the alkalis within the cement as well as that mixed with the cement are taken into the hydrates and hence unavailable for the reaction with the reactive aggregate. Also, a dense microstructure of BFSC reduces the mobility of moisture and alkali ions, which is absorbed by the ASR-gel to cause expansion.

In OPC mortars the expansion mainly depends on the alkali–silica reactivity of aggregate used. In the JIS A 1146 method, the mortars made with a combination of HEC and crushed chert caused the largest expansion. This is because HEC contains about 17% of $C_{11}A_7CaCl_2$. In the hydration of HEC, both Friedel's salt and sodium hydroxide are formed, which leads to an increase in the OH^- concentration in the pore solution of mortar.

Table 4 shows the result of visual inspection of the amount of ASR-gel using acetic acid–uranium fluorescence method after the mortar bar test according to JIS A 1146. In the case of the river gravel, the fluorescence area was very small only around the brown andesite particles. In the case of the chert aggregate, ASR-gel was uniformly formed in the mortar to a greater extent that is the proportion of the area within which ASR-gel was observed. On the other hand, in the case of the andesite aggregates, the extent of ASR-gel was also large but a little bit smaller than that of the chert aggregate. Comparing two types of andesite aggregates, a higher amount of ASR-gel was formed in andesite A aggregate than in andesite B aggregate. However, the amount of ASR-gel formed in the mortars made with BFSC was very little for all the reactive aggregates.

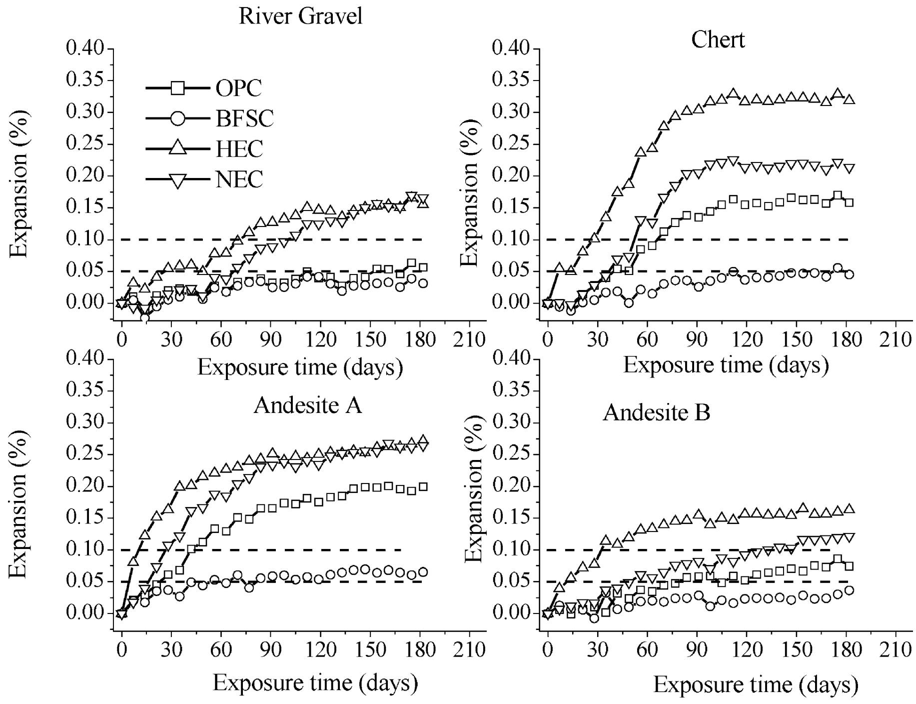

Fig. 3. Expansion behaviors of mortar bars by JIS A 1146.

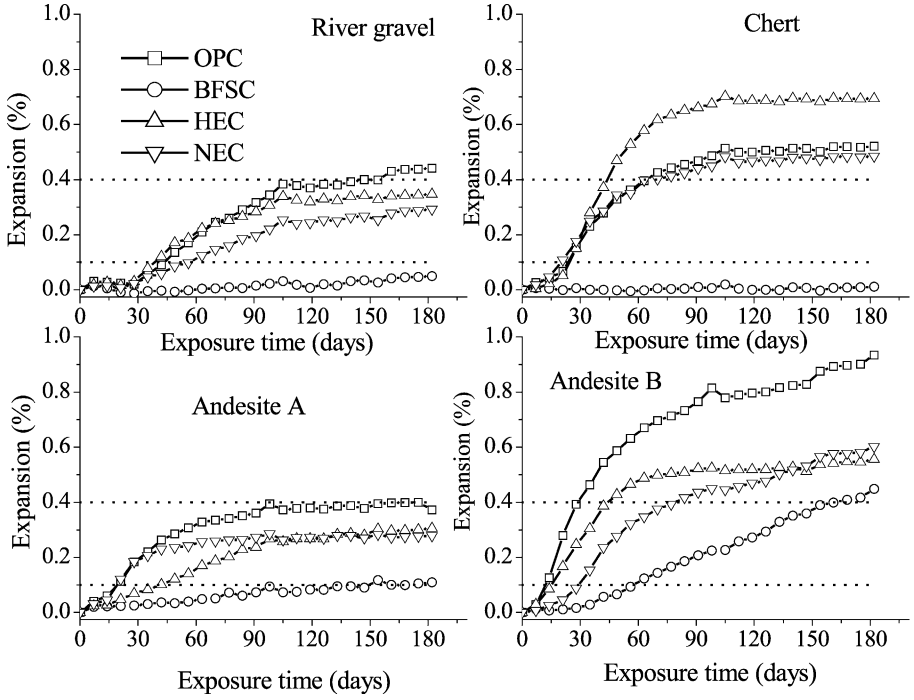

Fig. 4. Expansion behavior of mortar bars by Danish method.

3.2. Expansion behavior of mortars in saturated NaCl solution

Fig. 4 shows the results obtained from the mortar bar test method according to the Danish specification. In this method, the expansion of mortars gradually occurs as sodium chloride penetrates into the mortar bars. Similarly, the extent of expansion of mortars also depends on the alkali–silica reactivity of aggregates. It can be seen that the expansion in all the mortar bars is significantly higher at the later period than that in the JIS A 1146 method. Also, in the case of the JIS A 1146 method, the expansion of mortars approaches to a limiting value, whereas in the case of the Danish method immersed in the saturated NaCl solution, the expansion continues to increase with the immersion period, although its rate decreases as the immersion period increases.

Table 5 shows the result of the chloride penetration depth measured after the immersion period. It can be seen that, in all specimens except for the BFSC ones, the chloride penetrates completely into the center of the mortar bar. Comparing this result to that of the expansion, it is considered that the difference in expansion among the specimens of OPC, NEC and HEC is due to the difference in their mineral compositions, and also the amount of calcium hydroxide in the mortar since the chlorides that may influence ASR-gel formation penetrated to the same extent into their mortars.

Table 6 shows the result of the visual inspection of the amount of ASR-gel using the acetic acid–uranium fluorescence method after the mortar bar test method according to the Danish specification. It can be seen that, in the case of BFSC, the amount of ASR-gel is smaller in the mortars made with crushed chert and river gravel aggregates but higher in the mortars made with andesites A and B aggregates. The ASR-gel formed in BFSC mortars was observed only within the surface regions penetrated by chlorides. In the case of OPC, HEC and NEC, relatively large amounts of ASR-gel were observed due to chlorides penetrating deeply into the center portion of the mortar bar made with all the aggregates. This result validates the fact that the sodium

Table 5
Chloride penetration depth of mortar bar by Danish method (mm)

	OPC	BFS	HEC	NEC
River gravel	*	5.6	*	*
Crushed chert	*	6.7	*	*
Andesite A	*	14.3	*	*
Andesite B	*	*	*	*

* Chloride penetrated up to the center of section (40 × 40 mm).

Table 6
Result of visual inspection of ASR-gel formation (Danish method)[a]

	OPC	BFS	HEC	NEC
River gravel	III	I	III	III
Crushed chert	IV	I	IV	IV
Andesite A	III	III	III	III
Andesite B	IV	IV	IV	IV

I (no ASR-gel) → IV (high amount of ASR-gel).

[a] Interpretation of result of visual inspection by acetic acid–uranium fluorescence method.

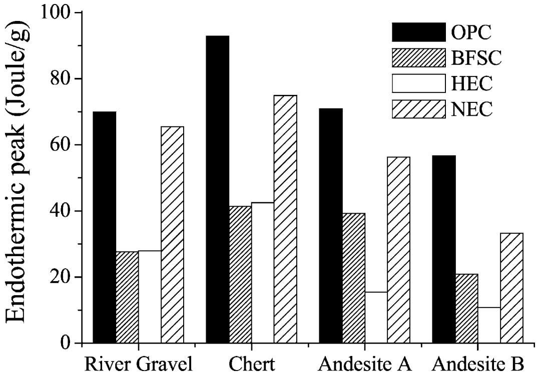

Fig. 5. Calcium hydroxide content obtained from DSC analysis of mortars used for the JIS A 1146 method.

chloride supplying from external sources has a positive influence on ASR expansion of concrete [7,8].

3.3. Compatibility between cement and reactive aggregate in two-types of mortar bay test

For the same combination of cement and aggregate, the JIS A 1146 and the Danish method gave the same result in some cases, but the different result in other cases on the determination of alkali–silica reactivity of aggregate. For example, in the case of the river gravel, the JIS A 1146 method showed that the mortar made with NEC and HEC was deleterious while that of OPC was innocuous. On the other hand, in the Danish method, in all cases except for BFSC, the degree of expansion was more than that obtained from the JIS A 1146 method, especially in the mortars made with the river gravel. A closer look at all the results seems to indicate that the Danish method gives a strict result than the JIS A 1146 method.

Figs. 5 and 6 show the results of the DSC test performed on samples taken from the center of the specimens used for the JIS A 1146 method. It is found that the amount of calcium hydroxide formed changes with the cement–aggregate combination, and that Friedel's salt content is very small in all combinations. In particular, in the case of HEC and BFSC, the amount of calcium hydroxide formed is less than that in OPC in the mortars of all the aggregates. Also, for the same cement, the amount of calcium hydroxide formed in the case of andesite B is lower than that in the mortars of the other aggregates. This is because andesite B contains the clay mineral of montmorilonite that adsorbs the cations of K^+ and Na^+ between the sheets of its structure in an ion substitution reaction [9], reducing the OH^- ion concentration in the pore solution of mortar. Thus, in the JIS A 1146 method, the part of the NaOH added into the mixture to accelerate ASR is also immobilized by the montmorilonite contained in andesite B, hence, the lower amount of ASR gel formation and expansion in the mortars made with andesite B.

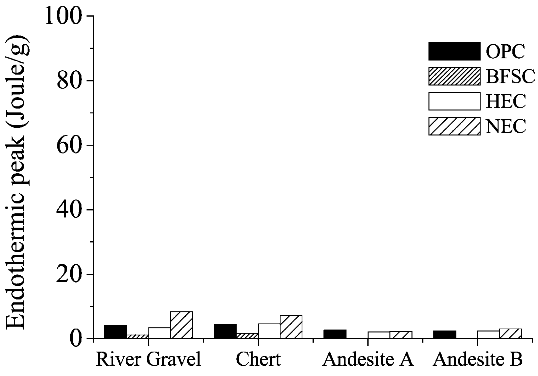

Fig. 6. Friedel's salt content obtained from DSC analysis of mortars used for the JIS A 1146 method.

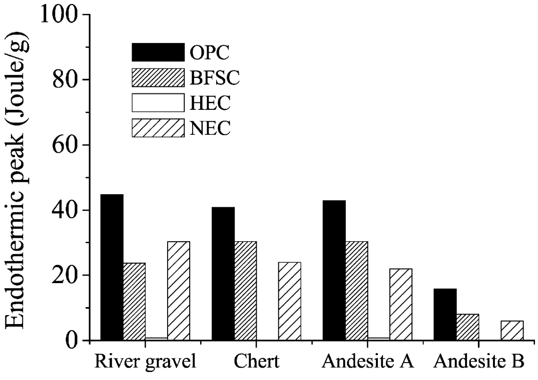

Fig. 7. Calcium hydroxide content obtained from DSC analysis of mortars used for the Danish method.

Figs. 7 and 8 show the results of the DSC test performed on samples taken from the center of the mortars used for the Danish method. It is found that, in the case of mortars made with HEC, there is little or no calcium hydroxide. Fig. 8 suggests that the amount of Friedel's salt formed in the mortars made with the river gravel, crushed chert, andesites A and B reduce in that order. In the Danish method, sodium chloride that penetrates into the mortar bars reacts with the aluminate phases to form Friedel's salt and also decomposes the calcium hydroxide phases, which releases hydroxide ions into the pore solution, thereby increasing ASR expansion [8]. On the other hand, the mortar made with BFSC and

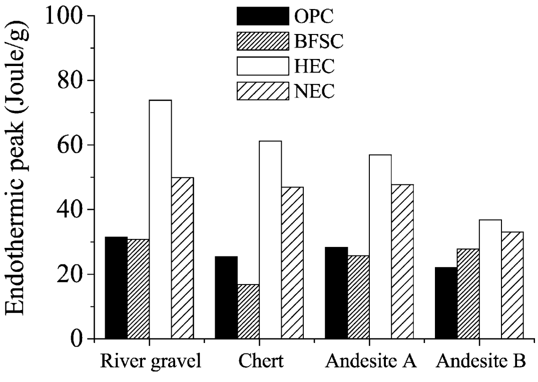

Fig. 8. Friedel's salt content obtained from DSC analysis of mortars used for Danish method.

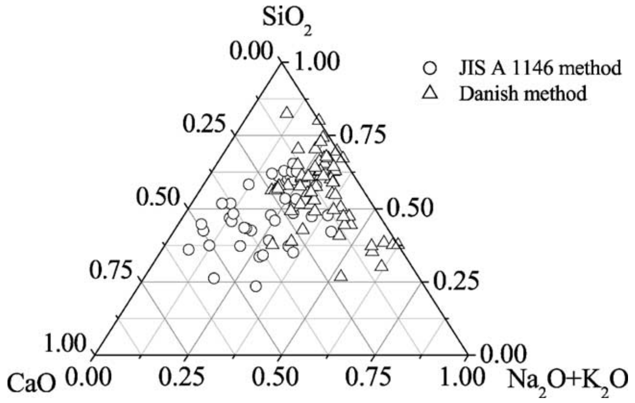

Fig. 9. Chemical compositions of ASR gel formed after the accelerated mortar bar test.

andesite B causes a long-term expansion because, in addition to ASR expansion due to the above mechanism, the adsorption of water molecules of montmorilonite itself also causes some part of expansion.

Fig. 9 shows the chemical compositions of ASR gel analysed by SEM-EDX after the accelerated mortar bar test. It can be seen that the chemical compositions of ASR gel obtained by the Danish test method is quite different from those obtained by the JIS A 1146 method, which shows a lower calcium content (CaO) and higher alkali content ($Na_2O + K_2O$). Thus, in the Danish method, it is suggested that the chemical compositions of ASR gel formed also influenced the long-term expansion behavior of mortars to a significant extent [10]. It can be concluded that ASR expansion depends on a combination of the mineralogical compositions of cement and reactive aggregate used to a significant extent.

4. Conclusion

From the experimental results, it is concluded that:

(1) The expansion behavior of mortars due to ASR varies significantly depending on a combination of both the mineralogical composition of cement and the reactive component of aggregate because for a given reactive aggregate, the degree of ASR is influenced by hydration characteristics of cement used.
(2) In the JIS A 1146 and Danish method, a combination of cement and reactive aggregate gives different results of expansion behavior of mortars, which may be due to the difference in both amounts and chemical compositions of ASR gel formed in the two test methods.
(3) Ecocement contains much calcium chloro-aluminate phase in place of C_3A phase, which may be responsible for being susceptible to ASR compared with other cement in a saline environment.
(4) The Danish method gives a strict result in screening Japanese reactive aggregates independently of a combination of cement and reactive aggregate compared with the JIS A 1146 method.

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References

[1] T. Shimoda, S. Yokoyama, Ecocement—a new Portland cement to solve municipal and industrial waste problems, Proc. of International Congress on Creating with Concrete, Dundee, 1999, pp. 17–30.
[2] K.O. Ampadu, K. Torii, Characterization of ecocement pastes and mortars produced from incinerated ashes, Cem. Concr. Res. 31 (2001) 431–436.
[3] R.D. Hooton, C.A. Rogers, Development of the NBRI rapid mortar bar test leading to its use in North America, Constr. Build. Mater. 7 (1993) 145–148.
[4] S. Chatterji, An accelerated method for the detection of alkali–aggregate reactivities of aggregates, Cem. Concr. Res. 8 (1978) 647–650.
[5] K. Natesaiyer, Some application of the gel fluorescence test for alkali–aggregate reaction in concrete, Cem. Compos. 15 (1993) 3–6.
[6] N. Otsuki, S. Nagataki, K. Nakashita, Evaluation of $AgNO_3$ spray method for measurement of chloride penetration into hardened cementitious matrix materials, ACI Mater. J. 89–74 (1992) 587–592.
[7] P.E. Grattan-Bellew, A critical review of accelerated ASR tests, alkali–aggregate reaction in concrete, Proceedings of the 10th International Conference on Alkali–Aggregate Reaction in Concrete, 1996, pp. 27–37.
[8] M. Kawamura, N. Arano, K. Katafuta, ASR gel composition, secondary ettringite formation and expansion in mortars immersed in NaCl solution, J. Mater., Concr. Struct. Pavement, Jpn. Soc. Civil Eng. 641 (2000) 179–185 (in Japanese).
[9] F.A. Rodrigues, The alkali–silica reaction, the effect of monovalent and bivalent cations on the surface charge of opal, Cem. Concr. Res. 31 (2001) 1549–1552.
[10] S. Diamond, Chemistry and other characteristics of ASR gels, Proceedings of the 11th International Conference on Alkali–Aggregate Reaction in Concrete, 2000, pp. 31–40.