# OLDEST EXAMPLE OF ALKALI-SILICA REACTION IN JAPAN – TOKYO BAY SEA FORTS NO. 2 AND NO. 3, CONSTRUCTED 120-100 YEARS AGO

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#### Abstract

Concrete samples from Tokyo Bay sea forts, constructed over 100 years ago underwent lateexpansive ASR of crypto- to microcrystalline quartz in the sedimentary gravel used (sandstone, chert and tuff). The minimum alkali content of the cement estimated by EDS analysis of unhydrated cement particles (alite, belite, aluminate and ferrite) in the hardened concretes, ignoring water-soluble alkali from alkali sulfates, ranged Na<sub>2</sub>Oeq 0.6-1.0%, which was sufficient to promote ASR. Reaction products of ASR had textures in common with those of modern ASR-affected concretes. Alkali-rich rosette-shaped crystals were similar in composition to shlykovite and rhodesite, when water contents were ignored. Portland cement particles were very coarse-grained, retaining unhydrated clinker phases. This suggests that cement hydration and strength development of the concretes were very slow and that large air voids absorbed ASR gel, thus accommodating expansion pressure generated by the ASR gel within reacted aggregates.

Keywords: Alkali-silica reaction, petrographic examination, minimum cement alkali, shaft kiln, rotary kiln

### 1 INTRODUCTION

Sea Fort No. 2 (Daini Kaiho) and Sea Fort No. 3 (Daisan Kaiho) are artificial islands constructed at the entrance of Tokyo Bay for the purpose of defending the capital of Tokyo in the Meiji era (Figure 1 A). Construction of Sea Fort No. 2 (Figures 1B,C) started with mounding the foundation in 1889 (Meiji 22) and completed with the installation of cannons and upper structures in 1914 (Taisho 3) [1,2,3]. This was followed by the mounding of Sea Fort No. 3 (Figure 1D) in 1892 (Meiji 25) and completion of the installation of cannons in 1921(Taisho 10) (Table 1). However, they were substantially damaged by the Great Kanto Earthquake in 1923 and Sea Fort No. 3 turned to a reef. In order to ensure safe cruising of large vessels, concrete structures of Sea Fort No. 3 were dredged and demolished between 2000-2007. In the late period of 1903-1924, the production method of Portland cement in Japan started to switch from shaft kiln (a batch type) to rotary kiln, a prototype of the modern rotary kilns in Japan. Shaft kilns ceased to be used in Japan in 1924 [4,5].

At Sea Fort No. 2, non-RC mass concretes, a parapet wall of coastal revetment on the north side (construction 1889-1899), encircling wall of the battery cannon, and observatory (construction 1900-1907), presented external cracks due to ASR. These represent possibly the oldest concrete structures damaged both externally and internally by ASR in Japan. Other structures in this fort and the concrete wall of a warehouse at nearby demolished Sea Fort No. 3 (1909-1921) produced ASR gel without cracking on the concrete surfaces.

In this paper, concrete samples taken from these Tokyo Bay sea forts, constructed over 100 years ago and struck by the great Kanto Earthquake in 1923, were examined petrographically based on polarizing/reflecting microscopy, SEM observation, and quantitative EDS analysis to clarify the nature of ASR and classical cements as identified in them. These observations revealed long-term durability of concrete.

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### 2 MATERIALS AND METHODS

# 2.1 Materials

The concretes studied in this paper were collected from the parapet wall, the encircling wall, the observatory at Sea Fort No. 2, and the warehouse at Sea Fort No. 3 (Figures 2A,B,C,D).

# 2.2 Methods for assessment and analysis

# Polarizing/ reflecting microscopy

Polished thin sections of about 15 µm thickness were made from chips measuring 25 mm x 30 mm cut out from the specimens. These sections were observed by polarizing/reflecting microscopy, and the type, shape, characteristics, and structure of the materials used were checked.

#### Scanning electron microscopy

Using the same polished thin sections that were used for the polarizing microscopy, clinker minerals, cement paste, hydrates, and precipitates were observed using back-scattered electron detector (BSE) with a scanning electron microscope (SEM) (JEOL JSM-7001F). Carbon coating was used on the surface of the polished thin sections as electrical conduction treatment. Quantitative EDS analysis of the chemical composition of ASR gel and clinker minerals was done after completing polarizing and scanning microscopy. Quantification of the major elements (SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, SO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>) was performed using an energy dispersive X-ray detector (EDS: Oxford INCA Penta FET x3) equipped on a SEM (JEOL JSM-7001F). The measurement conditions were: acceleration voltage 15 kV, beam current 0.30 nA, measurement time 60 s, and dead time 25%, using XPP correction (modified  $\varphi qz$ ).

### 3 RESULT

### 3.1 Petrography

The characteristics observed for each of the aggregate, cement and clinker minerals, and cement paste are described below.

#### Aggregate

The type, grain size, rock and minerals of the aggregate examined are given in Table 2. Progress of ASR is shown in Table 3. Coarse aggregates in the parapet wall, the encircling wall and the observatory at Sea Fort No. 2 were well-rounded coarse gravel of sedimentary rocks consisting of sandstone, chert and shale with small amount of volcanic rocks. Coarse aggregates in the warehouse at Sea Fort No. 3 were well-rounded coarse gravel of sedimentary rocks dominated by sandstone chert and shale. The grain size of the fine aggregate is larger in the parapet wall than in others. Large amounts of shells were observed in the parapet wall. Fine aggregates were mainly fragments of quartz, feldspar, and volcanic rocks of andesite and rhyolite, along with small amounts of shells.

### Alkali-silica reaction

There were large irregular air-voids around the aggregates and in the cement paste of the concretes from Sea Fort No. 2 (parapet wall, encircling wall and observatory). Exudation of ASR gel was recognized around reactive aggregates including sandstone, chert, shale, andesite and rhyolite (Figures 3A, B, C). Reaction rim caused by ASR was also observed. In the encircling wall, rosette crystals were present in a large air-void around a chert pebble and were surrounded by amorphous ASR gel (Figure 3B). In the observatory concrete, a small crack was visible in aggregates by SEM observation on the polished thin section. By contrast in the warehouse concrete, there were few air-voids and dense cement paste. Crack-filling ASR gel was observed in the sandstone pebble having crystallized into rosette inside the aggregate (Figure 3D). Therefore the grade of ASR in all samples was weak. Crypto- to microcrystalline quartz was present in the sedimentary rocks, whereas glass and cristobalite were present in some volcanic rocks.

#### Cement and clinker minerals

The features of cement particles used in the concretes from Sea Fort No. 2 and Sea Fort No. 3 are given in Table 4. Compositions of unhydrated cement minerals are shown in Table 5.

Cement particles in the concretes taken from Sea Fort No. 2 (parapet wall, encircling wall and observatory) were characterized by larger size (maximum size  $>200\mu$ m) compared to that of the fine aggregate, as well as by a less homogeneous texture than those of modern Portland cements with relict unhydrated clinker phases. Coarse clusters of boat-shaped belite (Figure 4B,C) and light brownish

round belite (Figure 4A), featuring cross lamellae and dotted precipitation, were also observed. The interstitial aluminate and ferrite phases were coarsely crystallized materials (Figure 4A), compared with those found in modern Portland cement. Alkali-aluminate with a birefringence, occurring as a large prisms and blades between interstices of belite was identified by polarizing microscopy (Figure 4D). It had highly Na-rich compositions in both the encircling wall and the observatory, while it was low in alkali in the parapet wall according to EDS analysis. In the warehouse, cement particles were characterized by large size (maximum size  $>200\mu$ m), retaining unhydrated clinker phases, and by coarse clusters of clearly, small and round belite. Elongated alkali-aluminate occurred interstitially between belite. It was highly Na and K-rich compositions as revealed by EDS analysis.

#### 3.2 Composition of reaction products

# [Ca/Si]-[Ca]/[Na+K]diagram of ASR gel and CSH gel

In order to evaluate the progress of ASR in concrete in terms of composition of ASR gel, EDS compositions of ASR gel were given in Figure 5, plotted on the [Ca/Si]-[Ca]/[Na+K] diagram. ASR products in the aggregate from the same concrete core sample presented a single compositional trend line. In the parapet wall, the compositional range of ASR gels filling air-void near the shale in concrete was narrow, falling near a "convergent point" at around [Ca/Si]=1.5, [Ca]/[Na+K]=200-300 (Figure 5A). In the encircling wall, the compositional trend line of ASR gels (rosette crystals and amorphous ASR gels) in voids near chert was intermediate in length, spanning from the left side in figure (alkali rich) to the midway near about [Ca/Si]=0.7, [Ca]/[Na+K]=5, to the "convergent point" at around [Ca/Si]=1.4, [Ca]/[Na+K]=300-400 (Figure 5B). Composition of rosette crystals was at around [Ca/Si]=0.25, [Ca]/[Na+K]=1. In the observatory concrete, the compositional trend line of ASR gels was the longest, ranging from the typical ASR gels to a Ca-rich ASR gel around [Ca/Si]=1.0, [Ca]/[Na+K]=40, although not reaching the "convergent point" at around [Ca/Si]=1.5, [Ca]/[Na+K] = 400 (Figure 5C). In the warehouse, the compositional trend line of ASR gels filling the crack in the sandstone is intermediate in length, it extended from rosette crystals at around [Ca/Si]=0.25, [Ca]/[Na+K]=1 to [Ca/Si]=0.7, [Ca]/[Na+K]=5, and did not reach the "convergent point" at around [Ca/Si]=1.4, [Ca]/[Na+K]=300-400 (Figure 5D).

### 4 **DISCUSSION**

#### 4.1 Aggregate

Coarse aggregates in all samples were mainly coarse gravel of sedimentary rocks consisting of sandstone, chert and shale. Their source was assumed to be the Tama River on the western border of Tokyo prefecture. Paleo-Mesozoic sedimentary rocks are distributed along the shores of Tama River. Large amounts of sea shells were contained in the fine aggregate of the parapet wall, this indicates that sea-sand was used for the parapet wall.

#### 4.2 Cement and clinker minerals

#### Method of cement production

Cement particles were characterized by large size (maximum size  $>200\mu$ m), retaining unhydrated clinker phases and were less homogeneous than those of modern Portland cements. This is characteristic of old cements, because crushing methods for cements were not developed at the time of construction of the sea forts in Japan. This grain size was nearly comparable to that in Otaru [6] and Sea Fort No. 3 [7] and Yokohama Training Dyke [8], but was finer than that from Nobiru [9]. Coarse clusters of boat-shaped belite and light brownish round belite, featuring cross lamellae and dotted precipitation and coarse crystallized interstitial phases, suggest a very slow cooling of burning in cements from three concrete structures in the Sea Fort No. 2. This is a texture typical of cement from a shaft kiln. On the other hand, coarse clusters of defined, small and round belite and a fine grained interstitial phases (slender) alkali-aluminate in concrete of the warehouse indicate a typical texture of cement from early rotary kiln. This texture indicates that the clinker was burned and cooled in a short time.

#### Clinker raw mix

In the Meiji era (1875-), cement clinker was produced by burning a layered mix of coal and raw material composed of slaked lime and clay material taken from the river bed. Generally the sand fraction included feldspar (albite) rich in Na, a clay fraction contained clay minerals (illite) rich in K, and weathering residue rich in Ti. Thus the formation of alkali-aluminate suggests that this sand was used for the clinker raw mix. Alkali-aluminates were rich in Na except for that of the parapet wall, which was assumed to be leached. Clinker in the observatory was poor in K and Ti, which means that

the "clay material" was sand. On the other hand, clinker in the warehouse produced by rotary kiln was rich in K and Ti, which means that the "clay material" was both sand and clay. This trend suggests that the production methods were switching from shaft kiln to rotary kiln late in the Meiji era (1905-), however "clay material" with similar composition was used for cement clinker at the early stage of produced by rotary kiln.

#### 4.3 Estimation of minimum alkali content of clinker

The minimum alkali content of the unhydrated clinker existing in the concrete was estimated by EDS quantitative analysis of the major Portland phases (alite, belite, aluminate, ferrite) [10], by assuming the content of four major cement minerals (alite 40%, belite 35%, aluminate 13%, ferrite 9%, Table 5) from average chemical composition of Portland cement around 1905-1920 in Japan [11], as well as by ignoring water-soluble alkali sulfates dissolved in water. It ranged from Na<sub>2</sub>Oeq 0.23% in the parapet wall, through 0.62% in encircling wall and 0.73% in the observatory, to 0.96% in the warehouse. When the contribution of soluble alkali from alkali sulfate is assumed to be 20% (e.g.[12]), total alkali content of the original cement would then be Na<sub>2</sub>Oeq 0.28% in the parapet wall, 0.74% in the encircling wall, 0.88% in the observatory, 1.15% in the warehouse. The cements used for three structures were high-alkali cement (Na<sub>2</sub>Oeq>0.6%) except for the parapet wall.

### 4.4 Composition of reaction products

# [Ca/Si]-[Ca]/[Na+K]diagram of ASR gel and CSH gel

ASR products in the aggregate from the same concrete core sample presented a single composition trend line. According to Katayama, chemical equilibrium occurs between ASR gels and CSH gels in which alite and belite have hydrated, hence a "convergent point" exists at around [Ca/Si]=1.5, [Ca]/[Na+K]=100-500 [12]. Generally, alkali rich ASR gels located on the left side in the diagram are expansive, but as ASR gels become increasingly Ca rich to the right side, expansibility decreases. When composition of ASR gel reaches a "convergent point", expansibility is lost.

In the parapet wall, the composition trend line of ASR gels reached a "convergent point", that is, ASR came to an end. The parapet wall located on the north side at Sea Fort No. 2, has a small section which directly received wind and rain and sea spray. Thus it would be that intense weathering had leached alkali from concrete, which explains the absence of ASR gels in concrete.

In the encircling wall, the observatory, and warehouse, ASR gels did not reach a "convergent point", that is, ASR is still developing. In the encircling wall, there are points of more alkali-rich composition of amorphous ASR gels, as on the left side of Figure 5B. This suggests that primary ASR gels had crystallized into rosettes, and since then new ASR gels had been produced.

Composition of rosette crystals resembles shlykovite  $(K,Na)_2Ca_2Si_8O_{19}7H_2O$  [12] at around [Ca/Si]=0.25, [Ca]/[Na+K]=1 in the encircling wall and resembles rhodesite  $KCa_2Si_8O_{18.5}$  6.5H<sub>2</sub>O at around [Ca/Si]=0.25, [Ca]/[Na+K]=1 in the warehouse (Table 6). These substances have been reported from many structures undergoing ASR [13].

#### 4.5 The reason for undeveloped ASR

All of these concretes underwent ASR of the sedimentary gravel used (sandstone, chert and tuff), though the structures in the field looked generally sound. ASR reactive mineral is crypto- to microcrystalline quartz, indicating late-expansive ASR and cement particles in these old concretes were much coarser (maximum size  $>200\mu$ m) and less homogeneous than those of modern Portland cements, retaining unhydrated clinker phases. This suggests that cement hydration and elution of alkali from cement were very slow. Therefore it would take a long time to produce expansive ASR gel, and large air-voids would have adsorbed ASR gel, thus accommodating expansion pressure generated by the ASR gel within reacted aggregates. In the warehouse, the concrete texture was characterized by dense cement paste, with abundant large clusters of small rounded belite, which hydrated slower than alite. Therefore, strength development of the concretes was also slow and crack-filling ASR gel in reactive aggregate had not extended to cement paste.

In the parapet wall, estimated minimum alkali content of clinker was low, although ASR had occurred. The parapet wall facing north at Sea Fort No. 2 is a substructure that directly received wind and rain and sea spray and the section was small. Thus it would be that a significant amount of alkali had leached from unhydrated cement particles. On the other hand, the other 3 samples were from the superstructure with large sections, at which effects of weathering were limited.

### 5 CONCLUSIONS

- All these concretes taken from Sea Fort No. 2 and No. 3 underwent late-expansive ASR of crypto- to microcrystalline quartz in the sedimentary gravel used (sandstone, chert and tuff).
- The minimum alkali content of the cement was estimated by EDS analysis of unhydrated cement particles (alite, belite, aluminate and ferrite) in the hardened concretes.
- This was based on the assumption that the content of four major cement minerals (alite 40%, belite 35%, aluminate 13%, ferrite 9%, Table 5) from average chemical composition of Portland cement around 1905-1920 in Japan and ignoring water-soluble alkali from alkali sulfates, ranged Na<sub>2</sub>Oeq 0.6-1.0%, which was sufficient to promote ASR.
- The concrete of the parapet wall had a small section, hence the leaching of alkali from alkalialuminate was intense. Reaction products of ASR had textures in common with those of modern ASR-affected concretes. Alkali-rich rosette crystals were similar in composition to shlykovite and rhodesite.
- Cement particles in these old concretes were much coarser (maximum size >200µm) and less homogeneous than those of modern Portland cements, retaining unhydrated clinker phases. This suggests that cement hydration and strength development of the concretes were very slow and that abundant large air voids absorbed ASR gel, thus accommodating expansion pressure generated by the ASR gel within reacted aggregates.

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year	1881		1885	85 1889 1893 1897 1901 1905 1909 1913 1917 1								1921								
	M14		M 18		M 22 M 26 M 30						M 34		M 38		M 42	Т2	Г6		Г10	
Sea Fort No. 1	sub	struc	ture	upe	erstruct	ture														
Sea Fort No. 2		substructure uperstructure																		
Sea Fort No. 3				substructure uperstructure																
Shaft kiln	*																			
Rotary kiln																				
M : Meiji Era, T	M : Meiji Era, T : Taisho Era																			

TABLE 1: Transition of Tokyo Bay Sea Fort and domestic cement plants.

\* Shaft kiln of Asano Cement Plant, major cement source in the Tokyo area, was abandoned.

Timbili al figgregate abea ni bea i orto i tol a ana i tol bi	TABLE 2:	Aggregate used	in Sea	Forts	No.	2 and	No.	3.
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	] .		Sea Fort No. 2								
san	npie	parapet wall	encircling wall	observatory	warehouse						
	Туре	Gravel	Gravel	Gravel	Gravel						
Carrier	Particle size	Max 40 mm	Max 40 mm	Max 40 mm	Max 50 mm						
aggregate	Rock type	Sandstone, Shale, Chert, Rhyolite	Sandstone, Shale, Chert, Andesite	Sandstone, Shale, Chert, Andesite	Sandstone, Chert , Shale						
Fine aggregate	Туре	Sand	Sand	Sand	Sand						
	Particle size	0.5 -2 mm	0.2- 0.5 mm	0.2 -0.5 mm	0.2 -0.5 mm						
	Pieces of crystal	quartz , feldspar	quartz , feldspar	quartz , feldspar	quartz , feldspar						
	fragments of	Chart and volcanic rock	Volcanic rock such as	Volcanic rock such as	volcanic rock such as						
	rock	such as andesite	andesite and rhyolite	andesite and rhyolite	basalt and andesite						
	other	Large amount of shell	small amount of shell	small amount of shell							

# TABLE 3: Petrographic evaluation of the progress of ASR of concrete in thin section.

				Progr	Carde of ASP						
sample	agg	regate	A	Aggregate		Cem	ient paste	Grade	of ASK	General	
*	type	Rock type	rim Gel Crack-fil gel		-filling el	Void-filling gel	Petro graphy	Field	evaluation		
parapet wall	gravel	shale		xx				1	1-2	1	
	gravel	chert	х	+				1			
encircling wall	and	andesite	х	х				1	1-2	1	
	sand	tuff	(x)	(x)				1	1		
	araval	shale		х				1			
	graver	tuff	(x)	x				1	1.2	1	
observatory	and	andesite	XX	XX				1		1	
	sand	rhyolite	х	х				1			
	gravel	Sandstone			(x)			1			
warehouse	aand	andesite	XX					1	1	1	
	sand	rhyolite	x					1			
Occurrence o Grade of ASE	f ASR: xx o R: 3 intense	conspicuous, x , 2 moderate, 1	common, weak	(x) rare,							

	<u> </u>			
sample	parapet wall	encircling wall	observatory	warehouse
Construction age	1889-99	1900-07	1900-07	1909-1921
Туре	Shaft kiln	Shaft kiln	Shaft kiln	rotary kiln
Particle size	100-200 Max 250	50-150 Max 200	50-100 Max 200	100-150 Max 250
Feature of clinker minerals	Boat-shape belite Small round belite Cubic aluminate	Boat-shape belite Small round belite alkali-aluminate	Boat-shape belite Small round belite alkali-aluminate	Small round belite elongated alkali- aluminate

TABLE 4: Cement particles used in the concretes from Sea Forts No. 2 and No. 3.

TABLE 5. Compositions of uninvariated cement initierals in concrete from sea ports no. 2 and no. 5 (w	TABLE 5:	Compositions of	of unhydrated	cement minerals in	concrete from	Sea Forts No.	2 and No. 3 (	(wt%	).
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														The a	verage
		SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	SO3	P <sub>2</sub> O <sub>5</sub>	Total	content i	n cement
							0							Na <sub>2</sub> O	K2O
	A.1'.	23.10	0.30	1.53	0.53	0.02	0.61	70.54	0.05	0.00	0.27	0.08	97.04	0.03	0.03
	Alite	23.83	0.12	0.96	0.47	0.07	0.59	71.72	0.09	0.13	0.09	0.12	98.19		
	Bolito	33.68	0.00	0.15	0.24	0.00	0.10	63.02	0.14	0.30	0.26	0.18	98.08	0.08	0.10
all	Dente	33.94	0.01	0.22	0.06	0.12	0.08	63.29	0.32	0.27	0.13	0.05	98.48		
t w:	Aluminate	3.63	0.23	31.31	3.52	0.00	0.57	59.26	0.17	0.03	0.00	0.00	98.73	0.02	0.01
ape	mannate	3.33	0.00	30.34	3.82	0.00	0.53	59.53	0.13	0.09	0.02	0.03	97.80		
Par	Ferrite	2.14	2.78	20.09	20.89	0.40	2.94	47.88	0.00	0.17	0.00	0.01	97.31	0.00	0.01
	renne	1.79	2.04	21.54	19.91	0.28	2.73	47.62	0.06	0.08	0.03	0.04	96.12		
	Na	12O*=0.0	7×0.4+0.	.23×0.35-	+0.15×0.1	13+0.03×	0.09=0.1	3, K <sub>2</sub> O*	=0.07×0.4	4+0.29×0	0.35+0.00	5×0.13	+0.13×	0.0.9=0.1	4
					Alkali	of minim	um (%) =	=Na <sub>2</sub> O*+	-0.658×K	$L_2O^* = 0.2$	23				
	A.1".	24.65	0.11	0.71	0.30	0.08	0.51	70.22	0.14	0.06	0.06	0.00	96.86	0.04	0.02
	Alite	24.88	0.15	0.68	0.50	0.06	0.57	70.94	0.05	0.04	0.07	0.00	97.94		
	BB	33.14	0.25	0.81	0.27	0.30	0.05	64.30	0.27	0.55	0.98	0.05	101.0	0.08	0.14
zall	Belite	31.34	0.42	0.91	0.34	0.00	0.10	63.08	0.18	0.23	0.14	0.00	96.74		
50 50	Alkali	3.68	0.09	29.95	3.47	0.06	0.22	55.39	2.53	0.69	0.16	0.00	99.52	0.33	0.01
clin	aluminate	2.93	2.42	19.74	20.73	1.36	3.14	47.90	0.00	0.04	0.00	0.00	98.26		
lcir	Forrito	2.47	0.71	24.01	20.61	0.15	2.01	48.72	0.17	0.14	0.00	0.00	98.99	0.01	0.01
Er	renne	24.65	0.11	0.71	0.30	0.08	0.51	70.22	0.14	0.06	0.06	0.00	96.86		
	Na	2O*=0.10	)×0.4+0.	23×0.35-	+1.27×0.1	3+0.16×	0.09=0.3	0, K <sub>2</sub> O*	=0.05×0	.4+0.39×	0.35+0.3	7×0.13	\$+0.10>	<0.09=0.2	21
					Alkali o	of minim	um (%) =	Na <sub>2</sub> O*+	0.658×K	$_{2}O^{*}=0.4$	4				
		24.37			0.76	0.01	0.76	69.22	0.14	0.07	0.09	0.00	96.05	0.05	0.04
	Alite	24 45	0.09	0.34	0.21	0.00	0.93	68.81	0.12	0.11	0.00	0.00	95.06		
	BB	33.10	0.26	0.78	0.56	0.02	0.08	63.96	0.47	0.00	0.45	0.36	100.0	0.15	0.03
ry	Belite	30.93	0.39	0.53	0.30	0.01	0.11	62.16	0.37	0.16	0.48	0.05	95.47		0.000
ato	Alkali	3.98	0.12	31.79	3.89	0.08	0.24	55.49	3.62	0.02	0.06	0.03	99.34	0.47	0.00
erv	aluminate	3.83	0.08	32.16	3.86	0.00	0.22	55.72	3.60	0.04	0.00	0.05	99.58		
SdC	р. 5	2.93	0.90	5.33	36.47	0.37	1.27	44.68	0.07	0.00	0.12	0.00	92.13	0.01	0.01
0	Ferrite	2.39	0.81	5.97	37.57	0.08	1.45	44.33	0.16	0.13	0.14	0.00	93.03		
	Na	2O*=0.13	3×0.4+0.	42×0.35-	+3.61×0.1	3+0.12×	0.09=0.6	8, K <sub>2</sub> O*	=0.09×0	.4+0.08×	0.35+0.0	3×0.13	\$+0.07>	<0.09=0.0	)7
					Alkali o	of minim	um (%) =	:Na <sub>2</sub> O*+	0.658×K	$_{2}O^{*}=0.7$	3				
		25.04	0.14	0.40	0.34	0.21	0.72	71.29	0.18	0.09	0.00	0.00	98.41	0.09	0.02
	Alite	24.56	0.30	0.51	0.50	0.00	0.77	72.10	0.25	0.03	0.25	0.00	99.28		
		32.14	0.15	0.72	1.13	0.00	0.21	63.58	0.48	0.64	0.11	0.01	99.18	0.20	0.20
	Belite	30.86	0.35	0.97	0.90	0.00	0.27	63.32	0.67	0.48	0.39	0.00	98.22		
use	Alkali	5.41	0.18	27.04	5.43	0.00	0.83	54.47	2.98	0.91	0.00	0.00	97.25	0.39	0.13
cho	aluminate	5.62	0.25	27.88	5.39	0.21	1.46	53.74	3.09	1.10	0.11	0.00	98.85		
varu	- ·	5.64	1.59	19.60	18.91	0.22	3.00	48.74	0.15	0.25	0.06	0.03	100.4	0.03	0.00
-	Ferrite	5.11	0.88	21.46	17.20	0.05	3.26	48.76	0.41	0.30	0.00	0.02	97.45		
	Na	20*=0.22	$2 \times 0.4 \pm 0.$	58×0.35-	+3.04×0.1	3+0.28×	0.09 = 0.7	1. K <sub>2</sub> O*	$=0.06 \times 0$	.4+0.56×	$0.35 \pm 1.0$	$1 \times 0.13$	s+0.28>	<0.09=0.3	38
	2.14				Alkali	of minim	um (%) =	$=Na_2O^* +$	-0.658xK	$_{2}O^{*}=0.9$	6				-
Na2O	* and K20	)* were	assumed	from the	content o	f four m	aior ceme	nt miner	uls (alite 4	0%. belit	e 35%, al	uminat	e 13%	ferrite 9º	%) from
avera	e chemico	l compos	ition of I	Portland	rement or	ound 101	0-1920 -	Janan		, sent					,
averag	se enemica	r compos		oruand	cincin al	04114 191	0-1720 11	i japan.							

BB: boat-shape belite.

Compositions (wt%)	SiOa	TiO	AlaOa	FeO*	MnO	MgO	CaO	NacO	K <sub>2</sub> O	SO <sub>2</sub>	P2OF	Total
Compositions (wr/o)	5102	1102	111203	nto	MillO	MgO	CaO	11420	K20	503	1205	TOTAL
Encircling wall	55.36	0	0.08	0.14	0	0.03	13.59	6.53	2.54	0	55.36	78.27
warehouse	65.13	0	0.1	0.03	0.06	0.05	14.53	3.14	0.9	0.18	65.13	84.12
A	t	etrahedra	ıl		(	octahedra	ıl		Int	terlayer*	k	
Atomic ratio (%)	Si	Al	S	Ca	Mg	Fe	Ti	Mn	Ca	Na	Κ	0
Encircling wall	8.00	0.01	0.00	2.00	0.01	0.02	0.00	0.00	0.11	1.21	0.47	<u>19.00</u>
Shlykovite		8.02				2.02				1.79		
warehouse	8.10	0.01	0.02	1.94	0.01	0.00	0.00	0.01		0.50	0.14	<u>18.5</u>
Rhodesite		8.13										

TABLE 6: Compositions of rosette crystals in concrete undergoing ASR and atomic ratio assumed as the natural minerals.

\*Total ion as FeO \*\*includes cations of void-filling within tetrahedral and octahedral sites.



FIGURE1: (A) Location of Sea Fort No. 2 and Sea Fort No. 3, (B) Sea Fort No. 2. Plain view: (C) Sea Fort No. 2, (D) Sea Fort No. 3.



FIGURE 2: Concrete samples for petrographic examination: (A) parapet wall, (B) encircling wall of the battery cannons, (C) observatory, (D) wall of warehouse.



FIGURE 3: Polarizing microscopy and BSE images of ASR gel: (A) air void-entering ASR gel of the parapet wall, (B) large air void -filling Na-rich rosette and Ca-rich ASR gel, (C) air void-entering ASR gel from the observatory, (D) Na and K-rich rosette from the warehouse.



FIGURE 4: Polarizing microscopy of cement particles: (A) brown, round belite with alkali-aluminate in parapet wall, (B) boat-shaped belite in encircling wall, (C) boat-shaped belite from observatory, (D) Belite cluster from warehouse.



FIGURE 5: EDS compositions of ASR gel and CSH gel in the concrete from Sea Forts No. 2 and No. 3: (A) parapet wall, (B) encircling wall of the battery cannons, (C) observatory, (D) warehouse.