LATE-EXPANSIVE ASR IN A 30-YEAR OLD PC STRUCTURE IN EASTERN JAPAN

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Abstract

RC foundation of a PC structure has undergone combined ASR of late-expansive sedimentary rocks (sandstone, mudstone, chert) and early-expansive volcanic rocks (andesite, dacite, rhyolite) in the sand and gravel aggregates. Despite the wide difference in the rock types, crack-filling ASR products presented a single compositional trend line on the [Ca/Si]-[Ca]/[Na+K] diagram, ranging from expansive ASR gel (1/4, 1) to non-expansive CSH gel (1.5, 100). The most alkali-rich products had crystallized into non-expansive rosettes, which apparently constitute a solid solution from mountainite (1/4, 2/3), but mainly from fedorite, (1/4, 4/5) to shlykovite (1/4, 1) by the cation ratio. Beside these, active gels with the highest alkali/(alkali+calcium) and silicon/(alkali+calcium) ratios formed a pop-out of glassy rhyolite, suggestive of the most viscous and expansive nature. Accelerated concrete core expansion test confirmed expansion potential of the concrete.

Keywords: ASR gel, fedorite, mountainite, rosette, shlykovite.

1 INTRODUCTION

An old PC wall structure in Eastern Japan, built in 1978 and subjected to seismic strengthening in 1996, exhibited continuous crack growth on its RC foundation (Figure 1a) where repair work was done by coating with urethane. Engineers in 2006-08 noticed that severely cracked areas (width >1mm) on the periphery of foundation contained fractured reinforcing steel bars with the bending radius (2.6-2.7D) that meets the specification (>2.5d for D=22mm) (Figures 1b,c). However, there was several inconsistencies: 1) coarse aggregate separated from concrete was identified without performing thin section petrography, 2) ASR gel was identified by EDS on the fracture surface without recording positions, 3) concrete cores gave negligible residual expansion (<0.02% at 6 months: criterion 0.1%) in the JCI-DD2 test (dia.10cm by L 25cm, 40°C, >95% RH), suggestive of ceased ASR, whereas 4) cracks showed a steady growth. Hence to clarify the nature of AAR, a detailed petrographic examination was made.

2 MATERIALS AND METHODS

Concrete core sample (dia.7.5cm x L30cm) taken from the RC foundation (NE corner) in late 2008, wrapped with a cling film to enhance exudation of ASR sol/gel (2 days), was subjected to core-scanning (360° lateral surface) for modal analysis of coarse aggregate (>5mm). Polished thin sections (25 x 35mm, thickness 15µm) were prepared for polarizing microscopy to identify the rock types, sites of reactions, the extent and the sequence of ASR in concrete, following the author's format (Table 2)(e.g.[1]). They underwent quantitative EDS analysis (JEOL JSM 5310LV/JED 2140, 15kV, 0.12nA, ZAF) (Figure 1d) of unhydrated cement particles to estimate the minimum content of cement alkali (Table 1)[1] and reaction products to compare compositions with natural minerals. An accelerated concrete core expansion test was done to confirm expansion potential of the concrete (dia.5cm x L13cm, 80°C, 1M NaOH: criterion >0.1% at 21 days) [1].

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3 RESULTS

3.1 Minimum alkali content of clinker

Cement particles had a fine-grained interstitial texture containing calcium aluminate crystals (Figures 3g,h). The estimated minimum alkali content of clinker based on the alkali content of the major Portland cement phases (alite, belite aluminate and ferrite) was Na₂Oeq 0.62% (Table1), which corresponds to 0.75% cement alkali (0.62x1.3x0.93=0.75%) assuming the ratio of water-soluble alkali from alkali-sulfate (30%) and of dilution by gypsum and additives (7%). Thus, the cement alkali in concrete was Na₂Oeq 2.3kg/m³ [0.75/100)x300], but additional water-soluble alkalis might have been supplied from illite and feldspars in the sedimentary aggregates in concrete.

3.2 Petrography

Scanned core image (Figure1e) afforded modal analysis of coarse aggregate, by simplifying similar rock types (Figures 1f.g): dacite (rhyolite), silicified tuff (meta-rhyolite, meta-welded tuff resembling porphyry), porphyrite (meta-andesite), siltstone (fine-grained sandstone). About 30% of gravel particles exuded ASR sol/gel, including andesite (55%), dacite (50%), silicified tuff (37%), porphyrite (20%), tuff (11%), sandstone (49%), chert (40%), mudstone (37%) and siltstone (23%). Volcaniclastic rocks came from Neogene Green Tuff formations, and chert from Mesozoic formations.

In thin section, ASR proceeded in the following sequence (Table 2): 1) rim formation in aggregate, 2) sol/gel rimming of aggregate, 3) internal cracking of aggregate, 4) crack extension from aggregate into cement paste, and 5) precipitation of ASR gel into air voids along cracks. Early-expansive volcanic rocks with cristobalite (Figure 3a) were present in a small quantity (7%), i.e. andesite (Figure 2a), dacite (Figures 2b, 3a) and glassy rhyolite (Figure 2c), the latter in the sand fraction producing pop-out one week after coring. The majority of the aggregate was late-expansive sedimentary rocks containing crypto- to microcrystalline quartz and illite: sandstone (Figures 2e, 3b), mudstone (Figures 2f, 3d,e), radiolarian mudstone (Figure 2g) and chert (Figure 2h, 3f). This quartz occurred in altered volcanic rocks and silicified tuff (Figure 2d), being also late-expansive, which had been recrystallized during diagenesis, hydrothermal alteration or metamorphism. Crack-filling ASR gel formed a plug just inside the aggregate-paste interface, grading into anisotropic rosettes inside the aggregate (Figure 2h). The overall grade of ASR in concrete evaluated by petrography was intense.

3.3 Compositions of reaction products

ASR gel on the [Ca/Si]-[Ca]/[Na+K] diagram

ASR products in the gravel aggregate from the same concrete core sample presented a single compositional trend line (Figure 4a), representing the *type I evolution* as defined by Katayama [2], despite the wide difference in the rock types (dacite, sandstone, mudstone and chert). Crack-filling ASR gels within the aggregate are typical alkali silica gel, rich in alkali occupying the lower left of the diagram, with [Ca/Si]=1/4-1, [Ca]/[Na+K]=1-10. ASR gels that had exuded into cracks within the cement paste are characterized by enriched Ca and decreased alkali, representing the middle portion of the diagram with [Ca/Si]=1-1.5, [Ca]/[Na+K]=10-100. ASR gels within air voids are most enriched in Ca but depleted in alkali, located around the "convergent point" at around [Ca/Si]=1.5, [Ca]/[Na+K]=100. At this point, an apparent chemical equilibrium is attained between ASR gels and CSH gels that had originated from the hydrating cement minerals alite and belite in concrete. On the other hand, ASR products on the most alkali-rich corner of this compositional line, around [Ca/Si]=1/4, [Ca]/[Na+K]=2/3 to 1, appeared as rosette crystals. They apparently constitute a solid solution starting by the cation ratio from mountainite (1/4, 2/3)=Na₂O 0.5K₂O 2Na₂O · 3CaO 16SiO₂Ca(F,Cl,OH)₂7H₂O, to shlykovite (1/4, 1)=(K, Na)₂O · 2CaO · 8SiO₂ · 7H₂O [3].

Rosette crystals and their cation site diagram

Na-K-Ca silicate hydrate minerals, which occur as veins and alteration products in the hyper-alkaline pegmatites and intrusions, are thought to be natural counterparts to the ASR rosettes in concrete [3, 21]. On the cation site diagram (Figure 4b), their published compositions were recalculated at O=20 and plotted assigning to the tetrahedral (Si, Al, S) and octahedral sites (Ca, Mg, Fe, Ti, Mn), the latter including the interlayer/void- filling cations (Ca, Na, K). They include cryptophyllite (K,Na)₄Ca₂Si₈O₂₀ 10H₂O, mountainite Ca₂Na₂KSi₈O_{19.5} 6.5H₂O, fedorite K_{0.5}Na₂Ca₂Si₈ O_{19.25} 4H₂O (OH=0.5O+0.5 H₂O), shlykovite (K,Na)₂Ca₂Si₈ O₁₉₇H₂O, rhodesite KCa₂ Si₈O_{18.5} 6.5H₂O [3], apophyllite KCa₄ Si₈O_{20.5} 8.5 H₂O and reverite (K,Na)_{0.67}Ca_{4.67} Al_{0.67}Si_{7.33}O_{20.67}3.33H₂O. With these minerals, ideal numbers of (a) oxygen and (b) total octahedral cations (plus interlayer/void-filling cations), calculated keeping the constant tetrahedral cation number=8.0, decrease in regular stepwise: cryptophyllite (20.0, 6.0), mountainite (19.5, 5.0), ferodite (19.25, 4.5), shlykovite (19.0, 4.0) and rhodesite (18.5, 3.0)[21]. In other word, a new mineral has been registered on this arithmetic progression.

The actual compositions of these minerals, recalculated in this way from the published analytical data, differentiate them with only small difference in the above parameters (a,b), when their structural aspects are ignored (Table 3). This means that there is a strong possibility to discover unknown mineral phases in this series, if a concept of solid solution with intermediate parameters is discarded. Recalculated compositions of ASR products range from cryptophyllite to fedorite for the published data, while the selected rosettes in this study range from mountainite to shlykovite, mostly between fedorite and shltkovite (Table 3), lying on the trend line from mountainite to shlykovite within the cryptophyllite-reverite-rhodesite triangle (Figure 4b). The analytical sum totals of the rosettes (Table 3) were up to 30% shorter than their counterpart minerals, due to thin flaky crystals (thickness <0.1-0.5µm) (Figures 3a,c,d,f) which allowed transmission of electron beam and dispersion on crystal edges.

$[CaO]/[Na_2O+K_2O+CaO]-[SiO_2]/[Na_2O+K_2O+CaO]$ diagram

Composition of the primary ASR gel (virgin gel) before contaminated by Ca ions from the cement paste was estimated, assuming the equivalent replacement (Na,K)₂O=CaO [3, 21]. For the ASR gel in the gravel aggregate (dacite, sandstone, mudstone and chert), the ratio [SiO₂]/[Na₂O+K₂O] of this hypothetical virgin gel (intercept at CaO=0 on the abscissa) (Figure 4c) was 5.8, which resembles the reported ratios for andesite aggregates in Japan [3]. Rosette crystals had compositions similar to mountainite ([CaO]/[Na₂O+K₂O+CaO] =4/7=0.57, [SiO₂]/[Na₂O+K₂O+CaO]=16/7=2.29), fedorite (4/6.5=0.62, 16/6.5=2.46) and shlykovite (2/3 =0.67, 8/3=2.67), of which fedorite-shlykovite (>0.6) seems to be more likely. With the glassy rhyolite that had popped out (Figure 2d), two gel veins (A,B) were analyzed, cleaning up the polished thin section with a tissue wiper (Kimwipe) after one year of the vacuum storage after thin sectioning. The estimated ratio of the virgin gel was [SiO₂]/[Na₂O+K₂O]=8.2 (Figure 4d), similar to the case of pop-out glassy rhyolite in Japan [3]. ASR gels in the interior of the aggregate (vein A, depth >200 µm) were alkali-rich with [Na₂O+K₂O]/[Na₂O+K₂O+CaO] =0.4-0.7 (Figure 4e), i.e. [CaO]/[Na₂O+K₂O+CaO]= 0.3-0.6, and closer to the virgin gel.

3.4 Accelerated concrete core expansion test

Unlike the JCI-DD2 test, this alkali-immersion test successfully detected deleterious reactivity of the aggregate in concrete, a mixture of early- and late-expansive rock types. Expansion of 0.23-0.24% at 3 weeks, exceeding the criterion for deleterious reactivity (>0.1% at 3 weeks) [1], was obtained (Figure 4f) which explains the swelling of the RC foundation of the structure at the time of investigation.

4 DISCUSSION

4.1 ASR gel

In the process of migration of ASR gel along cracks from the reacted aggregate into cement paste, diffusion takes place between alkali ions (Na, K) in the ASR sol/gel and Ca ions in the cement paste. That is, ASR

sol/gel liberates alkalis into CSH gel and absorbs Ca from cement paste, losing the expansionary nature. For this reason, ASR gel in the crack presents continuous compositions. The most alkali-rich ASR gels in concrete have been crystallized into non-expansive rosettes, but there are still expansive alkali-rich ASR gels in the cracks of the aggregate. Of the early-expansive rock types, glassy rhyolite formed more siliceous gels than that of the andesite aggregate, suggestive of larger expansive force. This rhyolite had a milky white tint, resembling glassy Whakamaru rhyolite in New Zealand rich in cryptocrystalline cristobalite with a marked pessimum proportion (10%). The presence of cristobalite in the volcanic rocks (7%) in the gravel probably enhanced the expansion of concrete due to pessimum phenomenon, even the alkali-level of the cement was not particularly high. Because additional alkali is possibly supplied from dominating sedimentary aggregate, and groundwater is accessible, it is likely that late-expansive ASR continues in the basement concrete.

4.2 Crystalline rosettes and natural counterparts

As regards the natural counterparts to the rosette crystals in concrete, okenite was first assumed a candidate for the rosettes with 10.5Å spacing [4,5], and an excellent analysis from Quebec [6] could derive a simple formula of this mineral 2CaO4SiO₂4H₂O by the replacement (K, Na)₂O=(Ca, Fe)O [7]. However, this is now attributed to cryptophyllite (K, Na)₂O-CaO 4SiO₂5H₂O (Table2) [2]. In early times, sodium was poorly detected by EDS and hence Na-free rhodesite was suggested [8], based on the average composition of the rosettes from Canada [5], Belgium [8], Australia [9] and South Africa [10], but this more resembles fedorite (Table3).

Rosette-forming minerals mountainite [7] and gyrolite [11] were also thought akin to the ASR rosettes, but they often needed a partial substitution of $(K, Na)_2O=CaO$ [7]. Recently, Katayama [7] predicted the missing links of the rosette crystals with [Ca/Si]=1/4, [Ca]/[Na+K]=1, and one of them was described as shlykovite by Pekov et al. [12], along with a refined crystal chemistry of mountainite [13]. These Na-K-Ca-silicate hydrate minerals are now considered to form a solid solution, at least, between mountainite and shlykovite (Figure 4b) [3, 21] due to the similarity of compositions and basal spacing (13.2-13.3Å) [12,13]. In terms of the cation ratio, fedorite is intermediate between these (Figure 4b), but its water content and basal spacing (11.7Å) are shorter [14], suggestive of a slightly dehydrated form. Under SEM, all the rosettes present a similar morphology (Figures 3a,f), but XRD identified mountainite from fedorite in ASR products [10,15].

ASR rosettes present the basal spacing of 12.0-12.5Å [5,8-10,15-18], 10.4-10.7Å [5,10] or 8.3-8.8Å [5,10,16], of which 12Å peak is highly moisture-sensitive and reversible up to 110°C: it contracts to 9.4-9.5Å at 40-50°C [17,18], shifts on further heating to 8.3Å at 80°C [10] and disappears at >200°C [10,17]. Upon partial dehydration at 40°C, the spacing of 3.56-3.59Å of the 12Å phase (absent in mountainite) contracts to 3.51-3.55Å [10], corresponding to fedorite (3.56Å), shlykovite (3.53Å) and rhodesite (3.52Å)[21]. Because the 12Å phase forms a glass at 955°C after heating by DTA [17,18], about 220°C higher than the melting point of mountainite and rhodesite [19], this was not identified as such by the original authors. However, their cation ratios recalculated from the published data are closer to mountainite (Table 3)[21].

From the above discussion, a relatively wide compositional range of the ASR rosettes observed within cracks in the studied concrete (Figure 4b) is assumed to have originated from a solid solution, which most probably inherited continuous compositions of ASR gels through their crystallization.

5 CONCLUSIONS

The RC basement of the PC structure underwent severe ASR of late-expansive cryptocrystalline quartz in the sedimentary aggregate, superimposed by early-expansive ASR of cristobalite in the volcanic rocks. The accelerated concrete core expansion test confirmed their reactivity. The most active swelling ASR gel, which popped out the glassy rhyolite, had most alkali-rich and Ca-poor compositions with higher silica/alkali ratio, which explains the most viscous and expansive nature. Alkali-rich gels in other rock types, now present as non-expansive rosette crystals on the [Ca/Si]-[Ca]/[Na+K] diagram, apparently constitute a solid solution from mountainite (1/4, 2/3), but mainly from fedorite (1/4, 4/5), to shlykovite (1/4, 1) by the cation ratio.

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TABLE 1:	1: Minimum alkali content of cement clinker in concrete by EDS analysis on polished thin section (wt%)												
		Alite		Belite			Aluminate				Total		
	С	с	60%	а	а	20%	с	С	10%	а	С	10%	
SiO ₂	24.17	25.92		32.66	32.09		5.72	5.86		5.79	5.02		
TiO ₂	0.62	0.00		0.04	0.39		0.65	0.13		1.88	1.51		
Al ₂ O ₃	0.77	0.63		1.50	1.99		26.01	26.90		18.62	21.99		
Fe ₂ O ₃	0.60	0.63		0.95	1.24		9.16	6.50		23.01	18.04		
MnO	0.37	0.00		0.02	0.00		0.00	0.00		0.35	0.86		
MgO	0.25	0.42		0.00	0.00		1.35	1.29		3.06	3.87		
CaO	67.78	67.93		61.72	60.56		52.40	53.36		46.66	45.55		
Na ₂ O	0.36	0.17	0.27	0.68	0.39	0.54	2.04	1.59	1.82	0.13	0.52	0.33	0.48
$K_{2}O$	0.04	0.09	0.07	0.50	0.44	0.47	0.56	0.51	0.54	0.00	0.49	0.25	0.21
SO ₃	0.00	0.00		0.60	1.26		0.02	0.00		0.21	0.20		
Total	94.36	95.79		98.67	98.35		97.90	96.14		99.72	98.04		
Na2Oeq			0.31			0.84			2.17			0.49	
Na ₂ Oeq*			0.19			0.17			0.22			0.05	0.62
* in clinker, assumption: alite 60% belite 20% aluminate 10% ferrite 10%													
	$N_{a2}O: 0.27 \times 0.60 + 0.54 \times 0.20 + 1.82 \times 0.10 + 0.49 \times 0.10 = 0.48$												
	K	$_{2}O: 0.0$)7x0.60	+ 0.47 x 0.2	20 + 0.54x	0.10 + 0).25x0.10 :	= 0.21,	Na2Oeq :	= Na2O+	0.658xK ₂ 0	D = 0.62	

TABLE	E 2: Petrogra	phic examination of concrete in	n thin section	to evaluate	the progr	ess of AS	R				
		Aconocato		Progress of alkali-silica reaction \rightarrow							
		Aggregate		Aggregate		Cem	ent paste	Grade of ASK			
Туре	Reaction	Rock type	Reaction	Reaction rim Gel halo Crack		illing gel	Void- filling gel	Micro- scopy	Field		
	Early- expansive	Dacite	х	х	XX	xx	XX	3			
		Meta-rhyolite (porphyry)	X					1			
Gravel		Rhyolitic tuff	XX					1	1		
	Late	Silicified tuff	X	X	х	х		2			
	expansive	Sandstone		X	х	х		2			
	expansive	Siltstone			X	X		2			
		Mudstone		X	Х	Х		2			
		Chert	Х	X	Х	Х	Х	2			
	Early- expansive	Andesite	Х		XX	XX		3			
		Dacite	Х	X	Х	Х		2			
		Glassy rhyolite*	Х	X	XX	XX		3			
		Rhyolitic pumiceous tuff		X	XX	XX		3	3		
		Andesitic tuff	Х	X	XX	XX		3			
		Meta-andesite (porphyrite)	X					1			
		Meta-rhyolite (porphyry)	X					1			
Sand		Rhyolitic welded tuff	X					1			
	_	Subcified tuff	X		XX	X		2			
	Late-	Sandstone	Х	Х	Х	Х		2			
	expansive	Siltstone	Х					1			
	-	Mudstone	X	X	X			1			
		Tuffaceous mudstone	Х	X	Х	Х		2			
		Siliceous mudstone	X		X	X	X	2			
		Chert	Х		х	X		2			
		General	evaluation					3			
* pop-ou	it after coring	Occurrence of ASR: xx conspic	uous, x comme	on, (x) rare,	Grade of A	ASR: 3 inter	1se, 2 moderat	e, 1 weak			

TABLE 3: Compositions of rosette crystals in concrete undergoing ASR and related natural minerals with tentative															
Identification based on cation ratios From [21]						т)			I)					
Mineral	Crueto	Natural m	Eodor	Shlukov	Phodos	Crupto	Mount	Mount	Mount	1) Fodor	Mount	Fodor	Ecdor	Eodor	Shlukov
wincia	phyllite	ainite	-ite	ite	ite	phyllite	-ainite	-ainite	-ainite	-ite	-ainite	-ite	-ite	-ite	ite
Host	Pegmat-	Pegmat-	Fenite	Pegmat-	Kimber-	Lime	Void	Void	Void		Chert	Dacite	Sand	Mud	Dacite
rock	-ite	-ite		-ite	lite	-stone	Meta-	around					-stone	-stone	
						av. 4	dolerite	Slate	av.101	av. 4					
						struc	av. 47	av. 4	points	coun-					
	[10]	[4 2]	[20]	[10]	[20]	-tures	points	points	[4:0]	tries					
SiOn	50.24	58.25	61.13	59.86	65.62	51.3	57.6	50.1	52.0	[0] 56.1	48.03	43.66	41.85	44.16	40.59
TiO ₂	50.24	50.25	01.15	57.00	05.02	51.5	57.0	50.1	52.0	50.1	0.10	0.35	0.39	0.06	0.25
Al ₂ O ₃	0.08		2.73				0.9	0.1	0.2		0.00	0.20	0.00	0.00	0.19
FeO *		0.74				2.3	0.3	0.0			0.13	1.05	0.16	0.00	0.40
MgO							0.6	0.0	0.1		0.00	0.00	0.00	0.00	0.00
CaO	11.59	13.98	15.01	13.70	15.31	12.4	10.4	15.7	12.1	16.1	15.99	9.25	9.25	10.21	8.16
Na ₂ O K:O	1.12	6.49	8.30	0.68	1.69	6.3	6.9	3.9	3.2	10.6	2.85	2.14	2.02	2.42	1.70
SO ₃	17.75	5.65	5.15	11.05	5.00	/.0	0.7	7.0	0.1	10.0	0.07	0.09	0.04	0.00	0.00
H ₂ O	19.24	14.71	9.04	14.73	13.53	19.9	14.2	22.6	20.4	17.2	0.00	0.02	0.01	0.00	0.000
F O=2E			1.27												
-O-2F Total	100.00	100.00	-0.54	100.00	100.00	100.0	99.7	100.0	100.0	100.0	73.83	64.22	61.04	64.33	58.00
Tetrahedra	8.01	7.97	8.07	7.98	7.98	7.94	8.09	7.84	7.93	7.91	7.75	7.92	7.91	7.96	7.95
S1 Al	7.99	/.9/	/.66	7.98	7.98	/.94	7.93	/.64	7.89	7.91	/./4	7.86	7.90	7.96	7.90
S	0.02		0.40				0.01	0.20	0.01		0.01	0.01	0.00	0.00	0.00
Octahedral	1.98	2.00	2.00	1.96	2.00	2.00	1.69	2.00	1.99	2.00	2.00	2.00	1.99	1.98	1.87
Ca	1.98	1.92	2.00	1.96	2.00	1.70	1.54	2.00	1.97	2.00	1.99	1.78	1.88	1.97	1.70
Fe		0.08				0.30	0.03		0.02		0.00	0.00	0.00	0.00	0.00
Ti											0.01	0.05	0.06	0.01	0.04
Mn Interlever**	3.05	200	2.54	2.06	1.02	3.80	3 39	3 21	3 27	2 34	0.00	0.02	20.02	$257^{0.00}$	2.000
Ca	5.95	0.13	0.02	2.00	1.02	0.36	5.56	0.57	5.27	0.44	0.77	0.01	2.47	2.37	2.2.3
Na	0.35	1.73	2.02	0.18	0.41	1.90	1.85	1.16	0.94		0.90	0.75	0.74	0.85	0.65
K	3.60	1.02	0.50	1.88	0.61	1.54	1.53	1.48	2.33	1.90	1.37	1.69	1.73	1.72	1.58
Cation	20.00	12.80	12.01	12.00	18.50	20.00	19.10	19.04	19.19	12.25	12.79	12.38	12.37	12.51	12.04
Ĕ	20.00	17.50	0.50	10.00	10.50	20.00	17.50	17.50	17.50	17.25	17.50	17.25	17.20	17.25	17.00
-O=2F	0.05	0.04	-0.25	0.05	0.05	0.04	0.40	0.04	0.05	0.21	0.04	0.00	0.04	0.05	0.00
Ca/M Ca/(Na+K)	0.25	0.26	0.26	0.25	2.00	0.26	0.19	0.54	0.25	0.51	0.36	0.23	0.24	0.25	0.22
* Total iror	as FeO	** in	cludes ca	ations of	void-fillin	g within	tetrahedr	al and oc	tahedral s	ites	1	0.75	0.70	0.17	0.11
[12] Pekov et al.(2010), [13] Zubkova et al. (2009), [20] Mineralogy Database, [6] Durand & Berard (1987), [17] Shayan & Lancucki (1987), [15]															



FIGURE 1: a) Cracking of concrete foundation, b),c) Fracture of reinforcing steel bar at the bending position, d) SEM-EDS for quantitative analysis of ASR products and cement minerals in hardened concrete, e) Scanned core image indicating exudation of ASR sol/gel after sampling and wrapping in a cling film for storage (two days), f) Rock types of the coarse aggregate (gravel) exposed onto the core surface, and g) their constituents.



FIGURE 2: ASR gel filling cracks within aggregate particles: a) Andesite in sand and b) dacite in gravel. c) Glassy rhyolite in the sand popping out with radial expansion cracks. d) Silicified rhyolitic tuff, e) sandstone and f) mudstone in gravel, forming plugs of ASR gel within cracks at the aggregate-cement paste interfaces. g) Radiolarian siliceous mudstone precipitating ASR gel in the adjacent air void. h) Chert in gravel forming a plug of ASR gel exuding into cement paste.



FIGURE 3: a) Cristobalite particles in dacite converting to rosette crystals with fedorite to shlykovite composition. ASR products in sand stone: b) ASR gel and c) rosette crystals with fedorite composition. ASR products in mudstone: d) ASR gel, and e) rosette crystals with fedorite composition formed from cryptocrystalline quartz. f) Cryptocrystalline quartz in chert converting to ASR gel, now rosettes with mountainite composition. Unhydrated cement particles rich in g) alite, and in h) belite, commonly associated with fine-grained interstitial aluminate (dark) and ferrite.



FIGURE 4: a) Compositional trend of ASR products in reacted dacite, sandstone, mudstone and chert in concrete, and crystalline rosettes resembling the composition of fedorite, b) Cation site distributions of natural alkali-calcium silicate hydrate minerals and ASR rosettes ranging from mountainite to shlykovite, c) Compositions of ASR products in dacite, sandstone, mudstone and chert, d) Compositional changes of ASR gel veins in popped-out glassy rhyolite, e) Compositional changes of ASR gel veins within popped-out glassy rhyolite, f) Result of accelerated concrete core expansion test indicating a deleteriously expansive nature exceeding a threshold.