

**ALKALI-AGGREGATE REACTION COMBINED WITH FREEZE/THAW  
IN NEWFOUNDLAND, CANADA -- PETROGRAPHY USING EPMA**

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**ABSTRACT**

Detailed petrographic examinations coupled with EPMA measurements were made of unhydrated cement minerals, hydrated C-S-H gels and ASR gels in seven deteriorated 50-70 year old concrete structures in Newfoundland, Canada, to relate their chemical compositions with their origin and petrographic characteristics. It was found that the compositions of the ASR gels and C-S-H gels are strikingly continuous, particularly in the weathered portions of these concretes. Under weathering conditions, both alite and belite hydrate to leach calcium down to a Ca/Si ratio 1.2, while ASR gels during migration absorb such liberated calcium and transform into pozzolanic C-S-H gels having a Ca/Si ratio of 1.0-1.2. This suggests that an apparent chemical equilibrium is attained between the C-S-H and ASR gels within concretes that are undergoing combined deterioration from ASR and freeze/thaw weathering.

**Keywords:** alkali-silica reaction, ASR gels, C-S-H gels, deterioration, EPMA

**INTRODUCTION**

In Newfoundland, Canada, some concrete structures more than 50 years old are undergoing severe deterioration from alkali-silica reaction (ASR) combined with freeze/thaw weathering (Bragg & Katayama 1993, Bragg 1995) (*Table 1, Fig. 1*). Various types of reaction products have been reported from these concretes (Katayama & Bragg 1995).

To clarify the relationship between the type and the process of chemical reactions in these old deteriorated concrete structures, as well as to interpret the origin of the reaction products, detailed petrographic examinations coupled with a total of 600 EPMA measurements were made of unhydrated cement minerals, their hydrates and alkali-silica gels found in concretes. As a result, a continuous series of calcium silicate gel products predicted by Urhan (1987), ranging from typical ASR gels through intermediate pozzolanic C-S-H gels to typical C-S-H gels, were confirmed from each concrete structure.

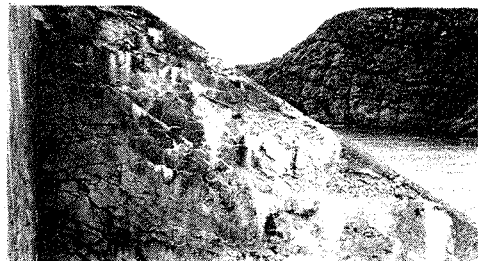
This paper discusses the process of a long-term alteration of cement hydrates and ASR gels in these old concretes, with emphasis on the usefulness of petrography and EPMA analysis of both cement minerals and gel products in diagnosing chemical reactions in the deteriorated concrete structures.

**Table 1 Deteriorated concrete structures near St. John's**

**Fig. 1 Concrete structure undergoing ASR and freeze/thaw**

Location	Structure	Year	F	ASR
Red Cliff	Radar base	1941	I	W
Water Street	Retaining wall and gate	1923	W	I
Fort Amherst	Gun bunkers	1941	I	I
Cape Spear	Gun bunkers	1941	I	I
Petty Harbor	Reservoir dam	1923		W
Tors Cove	Bridge (old)	1935	I	I
Cape Broyle	Bridge (old)	1935		I

F: freeze/thaw, I: intense, W: weak



## PETROGRAPHY OF REACTED AGGREGATES

Petrographic examination of the deteriorated concrete revealed that late Precambrian siltstone and sandstone coarse aggregates containing crypto- to microcrystalline quartz (Katayama & Bragg 1995), have reacted deleteriously in these concretes, due to late-expansive alkali-silica reaction which was formerly called the alkali-silicate reaction in Eastern Canada (e.g. Lewczuk et al. 1990). Rhyolites in the sand, originally glassy but now devitrified to a cryptocrystalline state, have also reacted. However, metarhyolite did not react because of its coarsely recrystallized texture (*Table 2*). Sea shells and wood fragments were occasionally found in these concretes.

*Table 2 Lithology of aggregates in the deteriorated NF concretes*

Rock type	Red Cliff pillar wall			Water Street	Fort Amherst		Cape Spear	Petty Harbor	Tors Cove	Cape Broyle old new		
	b	c	b c	b	b	c	b	c	b	b	c	c
Sandstone	S	S		C*	G	C*	G*	C*	G	G		G
Siltstone/sil. sh	G*	G*	G* G	C*	G*	G*	G*	S	G*	G*	G*	G*
Slate/phyllite	S	S			S		S		S	S		S
Quartzite		S	S	S	S							
Gneiss	S	S	S	S								
Basalt(alt/meta)	G	G	G G	S			S				S	S
Rhyolite	S	S	S*	S*	S*		S*	S	S		S*	G*
Metarhyolite	S	G	S S		S	S				S	S	S
Porphyrite		S	S	S	S		S			S		S
Granite	G	G	G G							S	S	G

\*: reacted, b: block sample, c: core, S: sand, G: gravel, C: crushed stone

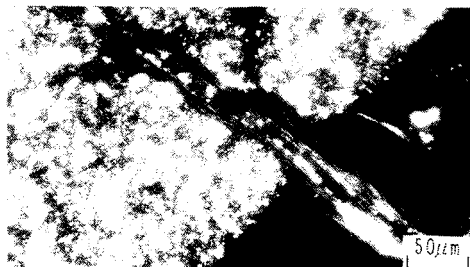
## ASR GELS IN CONCRETE

Five types of ASR gels were recognized in the deteriorated concretes, which represent different origins and stages of formation. They are 1) crack-filling in aggregate, 2) crack-filling in cement paste, 3) air void-filling/lining in cement paste, 4) gels interreplacing C-S-H gels, 5) gels replacing reaction rims of aggregate. The entire processes of chemical alterations of these gels in the concretes were characterized by polarizing microscopy of polished thin sections, coupled with about 600 quantitative measurements of compositions of these products using a WDS-type EPMA (Katayama & Bragg 1995).

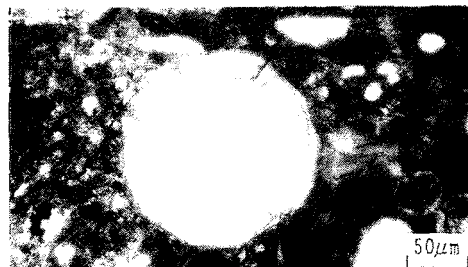
### *Crack-filling ASR gels in aggregate*

These gels filling cracks in the reacted aggregates are relatively fresh and contain a large amount of alkali and lower calcium (*Table 3*). In one example from the Petty Harbor dam, the Ca/Si ratio of a "gel vein" ranged from 0.2 to 0.4. The gel vein sometimes consists of several alternating layers of different crystallinity (*Fig. 2*), and their chemical compositions may differ layer by layer. Generally, inner layers of the gel vein represent a later formation, and have higher Ca/Si ratios than outer layers (gel-walls) of older generation.

*Fig. 2 Crack-filling ASR gels*



*Fig. 3 Air void-filling ASR gels*



### Crack-filling ASR gels in cement paste

Where a large crack extends from the reacted aggregate into cement paste, ASR gels often fill this crack as a continuous gel vein (*Fig. 2*). During migration from the reacted aggregate, these gels lose alkalis and gain calcium from the cement paste in a short distance (*Fig. 4*), sometimes losing transparency. In one case (Water Street), the Ca/Si ratio of such crack-filling gels increased from 0.7 at an aggregate/cement interface toward 1.2 in the cement paste, only within a distance of 0.5mm (*Table 4*). The crack-filling gels appear to gain crystallinity with an increasing Ca/Si ratio, particularly over 0.7.

### ASR gels replacing reaction rims of aggregate

This type of gel is often found in the periphery of reacted sand grains of rhyolite and rhyolitic tuff, but can be rarely seen in the reacted coarse aggregate of a sedimentary siliceous shale. In thin section, the reacted rhyolite has colorless and transparent reaction rims, which are replaced by ASR gels with a Ca/Si ratio between 0.7 and 1.1 (Water Street & Cape Spear). Calcium content is relatively high, because these gels have long been in contact with the cement paste and have probably altered their compositions.

### Air void-filling ASR gels in cement paste

Along the crack in the cement paste, ASR gels migrate from the reacted aggregate to fill the air-void. This type of gel has a higher Ca/Si ratio than the crack-filling gel because it has long been in contact with cement paste (*Table 5, Figs. 3, 4*). Large air-voids are lined with transparent ASR gels with a cyclic zoning from amorphous to crystalline, but their compositions are not different from each other. Gels filling smaller air voids have higher Ca/Si ratios than those in the larger air-voids, and sometimes present a brownish tint in thin sections.

**Table 3 Crack-filling ASR gels in aggregates**

An. no:	Petty Harbor In sandstone			Fort Amherst In sandstone			Cape Broyle In siltstone			Cape Spear In sandstone		
	Pc422	Pc415	Pc420	Fc31	Fc27	Fc28	Cb136	Cb138	Cb137	Cb105	Cb104	Cb102
SiO <sub>2</sub>	62.19	60.36	56.46	59.20	55.14	51.11	50.55	52.72	50.71	52.34	49.96	44.77
Al <sub>2</sub> O <sub>3</sub>	0.07	0.08	0.09		1.24	0.08	0.03	0.12	0.01	0.19	0.10	0.03
Fe <sub>2</sub> O <sub>3</sub>	0.03		0.01		0.01				0.03	0.09	0.26	0.22
MgO		0.01	0.04			0.02		0.01	0.01	0.06	0.04	0.04
CaO	11.11	17.37	23.38	22.35	30.61	34.84	21.15	23.38	25.18	27.56	31.78	32.98
Na <sub>2</sub> O	3.47	2.70	1.19	1.42	0.50	0.06	1.23	0.20	0.18	0.16	0.18	0.01
K <sub>2</sub> O	4.82	4.09	3.02	3.68	2.12	0.32	6.64	2.28	1.43	0.39	0.22	0.13
SO <sub>3</sub>	0.02						0.03			0.09	0.06	
Total	81.73	84.61	84.20	86.65	89.60	86.43	79.64	78.70	77.55	80.07	82.55	78.18
Ca/Si	0.19	0.31	0.44	0.40	0.59	0.73	0.45	0.48	0.53	0.56	0.68	0.79

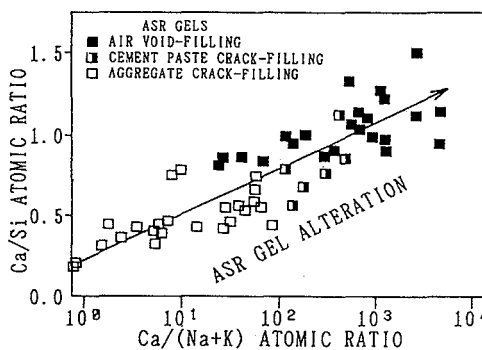
**Table 4 Crack-filling ASR gels in cement paste**

An. no:	Cape Spear From sandstone		Water Street From sandstone				Fort Amherst	Cape Broyle			
	Cb109	Cb108	Wb43	Wb51	Wb50	Wb52	Fb92	Cc124	Cc126	Cc127	Cc129
SiO <sub>2</sub>	52.47	37.94	48.58	38.90	39.25	30.64	35.90	38.59	38.43	36.82	31.99
Al <sub>2</sub> O <sub>3</sub>	0.05	2.27	0.03	0.11	0.22	1.92	1.65		0.08	1.01	0.23
Fe <sub>2</sub> O <sub>3</sub>	0.23		0.24	0.23	0.26	0.26	0.19			0.03	
MgO	0.10		0.05		0.03	0.04	0.01	0.04	0.01	0.04	
CaO	27.99	32.82	30.24	28.20	33.14	35.03	39.45	42.05	42.76	42.13	37.68
Na <sub>2</sub> O	0.07	0.03	0.10	0.05	0.03						0.25
K <sub>2</sub> O	0.17		0.34	0.02	0.03		0.01		0.03	0.02	0.50
SO <sub>3</sub>	0.03	0.19		0.06			0.04	0.07		0.03	0.05
Total	81.02	73.34	72.61	67.57	72.95	67.89	77.26	80.74	81.32	80.09	70.71
Ca/Si	0.57	0.93	0.67	0.78	0.90	1.23	1.18	1.25	1.28	1.31	1.35

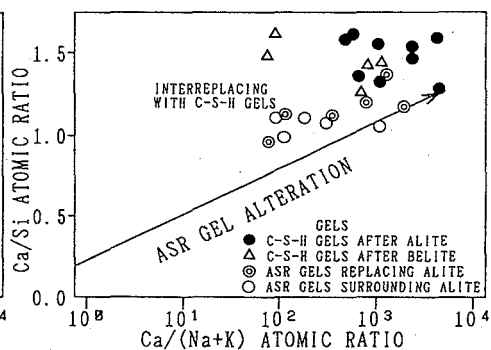
### ASR gels interreplacing C-S-H gels

Large gel veins occasionally replace C-S-H gels in the cement paste, leaving pseudomorphs of cement minerals surrounded by ASR gels. At this stage, both ASR gels and C-S-H gels have the same compositions with a Ca/Si ratio around 1.0-1.2 (Table 6), indicating that an interreplacement occurs between the two gels (Fig. 5). At this Ca/Si ratio, an apparent chemical equilibrium is attained between the C-S-H and ASR gels, the former leaching calcium while the latter absorbing the liberated calcium (Tables 9, 10, Fig. 11).

**Fig. 4 Alteration of ASR gels during migration in concrete**



**Fig. 5 Interreplacement between ASR and C-S-H gels**



**Table 5 Air void-filling ASR gels in cement paste**

An. no:	Tors Cove Large pore-lining			Water Street Pore-filling			Fort Amherst Pore-filling			Fort Amherst Pore-filling		
	Tb5	Tb9	Tb10	Wb73	Wb72	Wb74	Fb90	Fb91	Fb88	Fc53	Fc54	Fc55
SiO <sub>2</sub>	39.08	38.14	34.58	33.16	31.14	30.04	36.28	34.39	35.87	36.06	35.78	37.26
Al <sub>2</sub> O <sub>3</sub>	0.98	0.90	0.78	2.37	2.32	2.60	1.92	2.09	1.96	1.37	0.18	0.22
Fe <sub>2</sub> O <sub>3</sub>	0.13	0.09	0.23						0.40			0.04
MgO	0.01	0.05	0.02	0.03	0.04	0.03	0.05	0.03	0.05			
CaO	31.30	33.15	32.53	30.22	31.31	32.43	36.35	36.73	44.09	36.06	38.94	43.04
Na <sub>2</sub> O	0.22		0.09		0.06		0.01		0.03			
K <sub>2</sub> O	0.09	0.05	0.02	0.03	0.03	0.05	0.01	0.01	0.04	0.04	0.01	0.01
SO <sub>3</sub>	0.33	0.29	0.26	0.23	0.13	0.03	0.07		0.11	0.06	0.02	
Total	72.14	72.66	68.51	66.04	65.02	65.18	74.69	73.25	82.54	73.59	74.92	80.56
Ca/Si	0.86	0.93	1.01	0.98	1.08	1.16	1.07	1.14	1.32	1.15	1.25	1.33

**Table 6 ASR gels interreplacing C-S-H gels in cement paste**

An. no:	Fort Amherst ASR* "alite"			Tors Cove ASR* "alite"			Cape Broyle ASR* "alite"			Water Street ASR* "alite"		
	Fc49	Fc41	Fc47	Tb110	Tb151	Tb152	Cc133	Cc134	Cc132	Wb253	Wb249	Wb247
SiO <sub>2</sub>	38.80	32.63	31.34	33.94	34.58	30.82	37.45	38.06	35.35	30.35	25.31	24.07
TiO <sub>2</sub>		0.04	0.24	0.02			0.05				0.29	0.20
Al <sub>2</sub> O <sub>3</sub>	0.16	2.22	2.85	1.08	0.65	0.64	0.08	0.28	0.58	2.44	2.44	1.87
Fe <sub>2</sub> O <sub>3</sub>		0.67	1.33					0.02	0.02	0.09	0.88	0.70
MgO		0.39	0.24	0.07	0.09	0.17	0.01	0.01			3.28	1.92
CaO	36.62	30.53	37.07	35.27	31.08	32.27	38.74	41.25	39.99	33.52	28.02	30.53
Na <sub>2</sub> O				0.06	0.15	0.08						0.02
K <sub>2</sub> O	0.08	0.18	0.14	0.09	0.12	0.10	0.13	0.11	0.05	0.01	0.01	
SO <sub>3</sub>		0.12	0.12	0.03			0.02			0.02	0.03	0.02
P <sub>2</sub> O <sub>5</sub>		0.05	0.08	0.06	0.01	0.05	0.13	0.26	0.24	0.01	0.15	0.05
Total	75.67	66.82	73.26	70.61	66.67	64.13	76.62	79.99	76.22	66.44	60.40	59.39
Ca/Si	1.01	1.00	1.27	1.11	0.96	1.12	1.11	1.16	1.21	1.18	1.19	1.36

\*: ASR gel surrounding replaced alite, "alite": C-S-H gel replaced by ASR gel

## CEMENT MINERALS IN CONCRETE

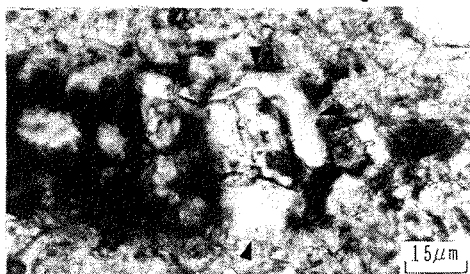
Polarizing microscopy of polished thin sections of deteriorated concrete from Newfoundland, revealed the common presence of unhydrated cement minerals along with hydration products. This method has a greater advantage to our SEM observations, because it is easy to identify mineral species and confirm the textural relationships between original clinker minerals and their hydrates. The EPMA has an optical microscope, convenient for work using thin sections.

### *Clinker minerals in hardened concretes*

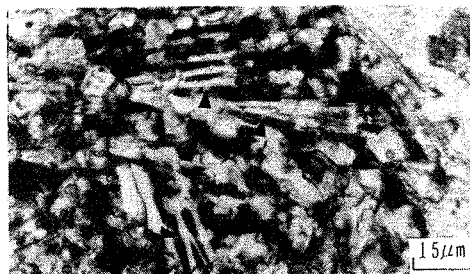
It is remarkable that the concrete field structures examined, even 50-70 years old, contain unhydrated alite, belite, aluminate and ferrite, except for water-soluble alkali-sulfates. Calcium silicates alite and belite are rimmed with hydration products in a cluster of cement minerals (*Fig. 6*). Aluminate occurs as optically anisotropic elongated crystals in all structures, and was identified as alkali-aluminate because of its optical properties (*Fig. 7*).

EPMA analysis indicated that the Ca/Si atomic ratio of unhydrated alite and belite generally exceeds 3.0 and 2.0, respectively, but this is due to solid solutions of these calcium silicates with other elements. Aluminate was confirmed to be the alkali-aluminate variety, containing 3.5% of  $\text{Na}_2\text{O}_{\text{eq}}$ . Alkali contents in the original cement (water-insoluble part) were estimated to be about 0.7%, based on the EPMA data (*Table 7*). But the cement alkali was probably higher, because water-soluble alkali-sulfates were also likely contained. Recent investigation showed that a Portland cement from this province contained about 1.0% of  $\text{Na}_2\text{O}_{\text{eq}}$  (Rogers 1989).

*Fig. 6 Partly hydrated alite rimmed with C-S-H gels*



*Fig. 7 Elongated crystals of alkali-aluminate*



*Table 7 Unhydrated cement minerals in concrete*

An. no:	Fort Amherst				Cape Broyle			Water Street		
	Alite Fc9	Belite Fb178	Alum. Fc13	Ferr. Fb214	Alite Cc102	Belite Cc113	Alum. Cc142	Alite Wb265	Belite Wb259	Alum. Wb279
SiO <sub>2</sub>	24.15	31.09	3.34	1.52	25.01	30.92	4.85	23.07	28.94	3.82
TiO <sub>2</sub>	0.19	0.13	0.28	1.67	0.16	0.20	0.03	0.31	0.36	0.11
Al <sub>2</sub> O <sub>3</sub>	0.97	1.64	29.23	21.72	0.88	1.50	29.27	1.38	2.14	29.90
Fe <sub>2</sub> O <sub>3</sub>	0.61	0.94	5.77	22.91	0.52	0.97	4.40	0.65	1.22	4.68
Mn <sub>2</sub> O <sub>3</sub>				0.51		0.01	0.03	0.05	0.08	0.04
MgO	0.88	0.17	0.59	2.37	1.48	0.52	0.92	1.64	0.33	0.52
CaO	70.82	63.81	53.73	46.77	69.77	60.99	53.74	67.04	58.43	50.70
Na <sub>2</sub> O	0.14	0.45	2.54	0.07	0.12	0.71	2.53	0.18	0.60	3.02
K <sub>2</sub> O	0.03	0.61	1.25	0.05	0.06	0.70	1.39	0.05	0.50	0.90
SO <sub>3</sub>	0.05	0.37		0.02		0.06	0.05	0.04	0.30	
P <sub>2</sub> O <sub>5</sub>	0.26	0.33	0.08		0.08	0.41	0.14	0.35	0.61	0.02
Total	98.03	99.84	96.81	97.61	98.04	97.02	97.35	94.70	93.52	93.71
Ca/Si	3.14	2.20			2.99	2.11		3.11	2.16	
Na <sub>2</sub> O <sub>eq</sub> *	0.10	0.17	0.34	0.01	0.10	0.23	0.34	0.13	0.19	0.36
	(Total Na <sub>2</sub> O <sub>eq</sub> =0.62%)				(Total Na <sub>2</sub> O <sub>eq</sub> =0.67%)			(Total Na <sub>2</sub> O <sub>eq</sub> =0.68%)		

\* Assumed content in cement: alite 60%, belite 20%, aluminate 10%, ferrite 10%

**C-S-H gels in hardened concretes**

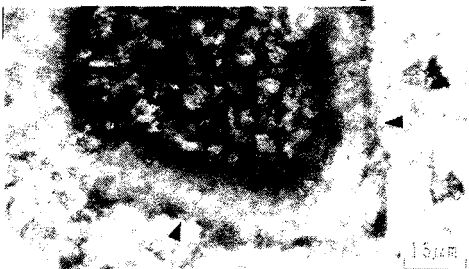
Both alite and belite hydrate to similar, optically amorphous, transparent C-S-H gels, leaving pseudomorphs of their original outlines (Figs.8,9). Table 8 shows the results of EPMA analysis of the C-S-H gels, with a distinctive compositional changes during hydration of alite and belite in the deteriorated concretes. These calcium silicates hydrate to a Ca/Si ratio down to 1.2, irrespective of whether they were originally alite or belite, and Ca, Na and K are leached from these silicates while Al and Mg are concentrated.

In cement chemistry, both alite and belite are known to hydrate to a Ca/Si ratio, down to 1.6-1.5 under normal calcium-saturated conditions (Brunauer & Kantro 1964). Thus, the C-S-H gels with a lower Ca/Si ratio ranging 1.5-1.2 in these concretes are suggestive of products under calcium-depleted conditions, such as leaching and weathering. Petrographic examinations revealed that these low Ca/Si gels were actually confined to weathered portions of concrete, severely exposed to freeze/thaw and rain-water percolation around cracks.

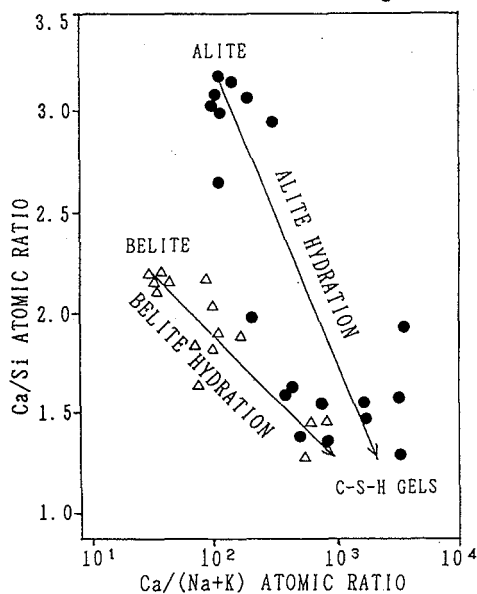
**Fig.8 Alite pseudomorph of C-S-H gel**



**Fig.9 Partly hydrated belite rimmed with C-S-H gels**



**Fig.10 Hydration of alite and belite into C-S-H gels**



**Table 8 C-S-H gels forming pseudomorphs of alite and belite**

An. no:	Port Amherst			Water Street			Cape Broyle			Tors Cove		
	Alite pseudomorph.	Alite pseudomorph.	Alite pseudomorph.	Belite pseudomorph.	Belite pseudomorph.	Belite pseudomorph.	Belite pseudomorph.	Belite pseudomorph.	Belite pseudomorph.	Belite pseudomorph.	Belite pseudomorph.	
	Fc36	Fc37	Fc51*	Wb233	Wb224	Wb261	Cc121	Cc115	Cc119	Tb146	Tb94	Tb89
SiO <sub>2</sub>	25.78	30.62	28.54	23.28	24.80	25.56	26.84	26.52	25.97	26.79	28.01	28.76
TiO <sub>2</sub>	0.22	0.30	0.29	0.50	0.40	0.22	0.39	0.15	0.50	0.19		0.31
Al <sub>2</sub> O <sub>3</sub>	1.44	1.83	2.10	2.70	3.04	3.88	3.67	3.09	4.23	2.53	3.10	5.84
Fe <sub>2</sub> O <sub>3</sub>	0.88	0.80	1.09	0.92	0.81	0.57	1.18	0.62	1.28	0.97	0.56	0.92
MgO	1.07	1.15	2.03	3.44	3.15	5.16	0.70	1.00	2.95	1.99	2.87	3.52
CaO	48.39	45.86	35.21	35.03	34.02	29.63	45.80	42.48	40.36	41.29	38.28	32.23
Na <sub>2</sub> O	0.07			0.03			0.09			0.16		
K <sub>2</sub> O	0.08			0.08			0.09			0.15	0.04	
SO <sub>3</sub>	0.14	0.13	0.16	0.69	0.20	0.21	0.22	0.08	0.43	0.06	0.32	0.32
P <sub>2</sub> O <sub>5</sub>	0.33	0.30	0.14	0.10	0.29	0.23	0.30	0.15	0.27	0.19	0.27	0.14
Total	78.38	81.01	70.54	67.76	66.70	65.38	80.26	74.08	75.99	74.31	73.46	72.02
Ca/Si	2.01	1.60	1.36	1.66	1.50	1.24	1.87	1.71	1.67	1.65	1.46	1.20

\*: Structure surface of core, Wb & Tb: weathered concrete blocks

## DISCUSSION

### Alteration of ASR gels

A general process of alteration of ASR gels in the deteriorated Newfoundland concretes is shown in **Table 9**. ASR gels lose alkalies and gain calcium during migration from reacted aggregate into cement paste: the Ca/Si ratio of the ASR gels increases from 0.2 in the reacted aggregate to 0.8 in the cement paste, and further reaches 1.0 or more after a long contact with cement paste. At a Ca/Si ratio around 1.0-1.2, ASR gels even replace the C-S-H gels which correspond to products of a pozzolanic reaction. Such a transformation of ASR gels into C-S-H gels has been found in a laboratory experiment (Dent Glasser & Kataoka 1982), but little has been documented from field concretes.

### Hydration of calcium silicates

In the normal hydration process (**Table 10**), both alite and belite hydrate to C-S-H gels, down to a Ca/Si ratio around 1.5, which are equivalent to the final hydration products of these calcium silicates under normal calcium-saturated conditions (Brunauer & Kanro 1964). However, where a weathering process dominates near the concrete surface, calcium is continuously leached from the C-S-H gels down to a Ca/Si ratio 1.2, and such liberated calcium is absorbed by ASR gels in concretes. Excess leaching of calcium may form stalactites and secondary coatings, composed of calcium carbonate on the structure surface.

### Apparent equilibrium between C-S-H and ASR gels

**Fig. 11** shows the entire processes of alteration of ASR gels and hydration of alite and belite in the deteriorated Newfoundland concretes. Final products of these alteration fall in the narrow range of the Ca/Si ratio around 1.0-1.2, intermediate between typical ASR and cement hydration. They correspond to products of a pozzolanic reaction predicted by Urhan (1987) to occur in concretes undergoing ASR. Probably, these pozzolanic products are stable under calcium-depleted conditions, such as weathering due to rain-fall and freeze/thaw. The Ca/Si ratio 1.0-1.2 represents an apparent chemical equilibrium between the leaching process of calcium from the C-S-H gels and the absorbing process of this liberated calcium by the ASR gels in concretes.

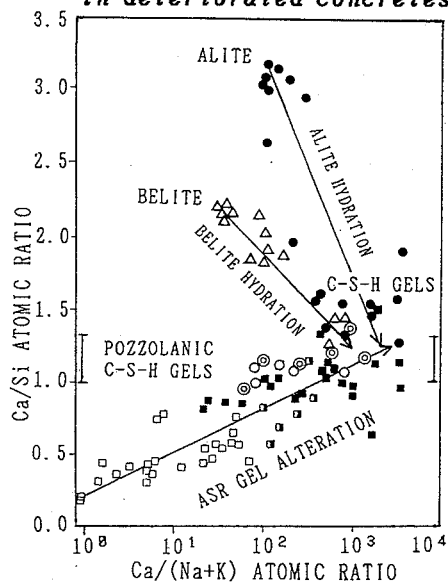
**Table 9 Alteration of ASR gels during migration**

Migration ASR gels	Weathering Pozzolanic C-S-H gels
Aggregate Crack- filling	Cement paste Crack- Air void- filling filling replac.
Ca/Si 0.2	0.8 → 1.0 → 1.1
Ca: leached from C-S-H gels & absorbed by ASR gels	
Na, K: leached out from concrete	

**Table 10 Alteration of cement hydrates during weathering**

Hydration Cement	Weathering C-S-H gels	Weathering C-S-H gels
	Ordinary	Pozzolanic
Alite Ca/Si 3.1	→ 1.5	→ 1.2
Belite Ca/Si 2.1	→ 1.6	→ 1.2
Leached Ca → absorbed by ASR gels → form stalactite & coating		

**Fig. 11 Chemical changes of gels in deteriorated concretes**



## CONCLUDING REMARKS

EPMA analysis of old deteriorated concrete structures in Newfoundland, undergoing ASR and freeze/thaw weathering, presented the following chemical and petrographical basis for diagnosing deterioration processes in concretes.

- Gel products in the deteriorated concretes have a continuous range of compositions from typical cement hydrates to typical ASR gels, particularly in the weathered portions exposed to freeze/thaw and rain-water percolation.
- Intermediate gel products, having a Ca/Si ratio of 1.0-1.2 and corresponding to products of a pozzolanic reaction, were formed at an apparent equilibrium between the C-S-H and ASR gels, due to long-term weathering of concretes.
- In this alteration process, calcium was leached from the C-S-H gels and entered ASR gels, transforming the latter gels chemically into pozzolanic C-S-H gels. Possibly, these pozzolanic C-S-H gels are stable and harmless to concrete under weathering conditions.
- Long-term weathering by freeze/thaw, coupled with rain-fall, likely enhances water-circulation, leaching and migration of soluble elements in concretes.
- Petrographic examinations coupled with EPMA analysis made it possible to estimate the cement properties in old hardened concretes, such as the water-insoluble alkali content of the cement used even more than 50 years ago.

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