

# ASR GEL IN CONCRETE SUBJECT TO FREEZE-THAW CYCLES - COMPARISON BETWEEN LABORATORY AND FIELD CONCRETES FROM NEWFOUNDLAND, CANADA

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## Abstract

A comparative EPMA analysis was made of ASR gel between 6 deteriorated concrete structures in Newfoundland and laboratory concrete prisms, to assess to what extent the frost action aggravates ASR in concretes. Normal-strength concrete prisms stored in alkaline solution presented more crack-filling ASR gel than high strength prisms, and a narrow compositional range of ASR gel toward CSH gel in the  $[Ca/Si]-[Ca]/[Na+K]$  diagram. When freeze-thaw cycles were superimposed, cracks and ASR gel developed near the concrete surfaces along with expanded compositional range toward a "convergent point", where a chemical equilibrium was attained with CSH gel due to migration of interstitial water during the cycles; a result of enhanced leaching of alkalis from ASR gel and absorption of calcium from cement paste. Similar trends of ASR gel occurred in the field concretes, which suggest that the combined processes of ASR and freezing and thawing enhanced deterioration in these structures.

**KEYWORDS:** ASR gel, cryptocrystalline quartz, EPMA analysis, freeze-thaw, CSH gel

## 1 INTRODUCTION

Newfoundland is one of the best places to investigate the combined effects of frost action and alkali-silica reaction on concrete structures. Katayama and Bragg reported that ASR gel in concretes in the St. John's area as a whole exhibits a continuous series of compositions merging into typical CSH gel [1][2]. Langdon demonstrated that a highly reactive aggregate from Newfoundland considerably reduced the tensile strength and freeze-thaw durability of normal strength concrete based on the laboratory study [3]. Because it is useful to correlate the laboratory properties with the field performances of concretes, the present paper examined the materials used by these authors by means of detailed EPMA (EDS) analysis of ASR gel, to assess and reply to the questions raised by Dan Bragg: 1) what field age the laboratory specimens in alkaline solution represents, 2) to what extent the frost action aggravates ASR in concretes, and 3) what stage of alkali-silica reaction the ASR gel in field concretes represents[4]. This paper summarizes results of the study.

## 2 MATERIALS AND METHODS

### 2.1 Sample origin

Field concrete specimens, both blocks from previous repair and from weathered surface (collected by the author in 1992) and drilled cores from the interior of the structure (mostly dia. 100mm, supplied by Dan Bragg in 1994), came from 7 deteriorated structures, including two bridges, three abandoned installations, one gate and one reservoir dam on the Avalon Peninsula, Newfoundland (Table 1). Concrete prisms prepared by Sheldon Langdon were also examined, which consisted of normal and high strength concretes with reactive gravel aggregates from Newfoundland, some having been immersed in the solutions for 12 weeks ( $80^{\circ}\text{C}$ , 1M NaOH or distilled water) after initial curing of 4 weeks ( $23^{\circ}\text{C}$ ), while others subjected to NaOH solution for 6 weeks and then to 300 freeze-thaw cycles in 1997 [3].

### 2.2 Methods of investigation

*Polarizing microscopy, SEM observation, EPMA analysis*

Polished thin sections ( $20 \times 30\text{mm}$ , thickness  $15\mu\text{m}$ ) of field concretes, which were used for EPMA (WDS) analysis in the previous studies [1][2], and of concrete prisms were examined by polarizing microscopy to identify reaction products, then subjected to SEM observation to check the presence of

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cryptocrystalline quartz in the reacted aggregate and morphological changes of ASR gel due to freeze-thaw. Compositions of ASR gel and cement hydrates in these concretes were analyzed in detail by EPMA (EDS) which became available in 1998 (JEOL JSM 5310LV/JED 2140: at 15KV, mainly 0.8 nA,  $\times 2000$ , ZAF correction), but some data on the field concretes were previously obtained by WDS (JEOL JCMA 733: at 15KV,  $\times 400$ , 10nA, ZAF correction, partly 12nA with Bence-Albee correction). Because no apparent difference was noted between the EDS and WDS data, excepting that WDS presents one digit more precise values, both data were jointly plotted on the same [Ca/Si]-[Ca]/[Na+K] diagram (Fig. 4).

### 3 RESULTS

#### 3.1 General petrography

Under the polarizing microscope, reacted aggregates in concrete were mainly sandstone and siltstone, with occasional presence of rhyolitic welded tuff, all of which have been known to cause typical late-expansive ASR (Table 1) [1][2][5]. Table 2 outlines the storage conditions of concrete prism specimens prepared by Sheldon Langdon, and what examinations were performed. The result of thin section polarizing microscopy was briefly shown in Table 3. ASR gel formation was most evident in the normal strength concrete prism, subjected to freeze-thaw cycles after immersion in the alkali solution. In this case, cracks parallel to the surface of concrete prism (depth 4mm), suggestive of freeze-thaw-related deterioration, but often aligned with ASR gel, were found. However, ASR was present throughout the section of this specimen. Other specimens after the freeze-thaw cycles had shallower cracks (depth 1mm).

SEM observation on the same polished thin sections directly identified the presence of cryptocrystalline quartz and microcrystalline quartz that are reacting to form ASR gel in both field concrete (Fig.2F) and in concrete prisms (Fig.3D). ASR gel was generally amorphous where [Ca]/[Si] ratio was high, such as air void-filling gel (Fig.2C) and crack-filling gel in the reacted aggregate in the weathered concrete containing calcite veins (Figs.2A,H). However, in the concrete prisms, void-filling ASR gel may be alkali-rich, when it appeared in the surface area of the prisms immersed in NaOH solution (Figs.3B,H).

Rosette-like crystalline phases have been identified from crack-filling ASR gel in the reacted aggregate in both field concrete (Figs.2B,D,G) and in concrete prism (Figs.3A,E,F). In the surface area of the concrete prism, these rosettes leached alkalis after the freeze-thaw cycles, retaining a pseudomorphic texture (Fig.3D). In the weathered concrete, alkali-depleted rosette-like ASR gel was also found (Fig.2E). In some case, amorphous ASR filling reacted aggregate was locally crystallized into rosettes, without changing compositions (Fig.2D, Fig.3G).

The result of EPMA (EDS plus WDS) analysis of ASR gel and CSH gel in both concrete prisms and field concretes is described below, to examine and compare the evolutionary trends of these compositions on the [Ca/Si]-[Ca]/[Na+K] diagram developed by the first author (Figs.3, 4) (e.g.[2][7][8]). In this analysis, the ratio of [Ca]/[Na+K] ranged between  $10^{-1}$  and  $10^4$ , and the capacity of EDS was generally up to  $10^3$  around 700, while WDS up to  $10^4$  around 7000.

#### 3.2 EPMA analysis of ASR gel in concrete prisms

The compositions of ASR gel and cement hydrates (CSH gel) in the concrete prisms prepared by Sheldon Langdon were plotted on the [Ca/Si]-[Ca]/[Na+K] diagram (Fig.3). All corresponds to the *Type I evolution* to be described later.

##### *Normal strength concrete*

In the normal strength concrete prisms, calcium silicates alite and belite hydrated to CSH gel, from the least hydrated state with [Ca/Si] atomic ratio of 3.0 and 2.1, respectively, down to final hydration products at around [Ca/Si] =1.7-1.8, [Ca]/[Na+K]=100, by liberating calcium and alkalis (Figs.3A,B,C,D).

In the concrete prism immersed in NaOH solution (80°C, 12 weeks), ASR gel filling air voids were most enriched in sodium, presenting a horizontal compositional line between 0.1 and 1 on the abscissa [Ca]/[Na+K]. However, ASR gel filling cracks in the reacted aggregate migrated into cement paste, forming an oblique compositional line, by absorbing calcium from cement paste and leaching alkalis. This line was shorter for the surface area of the concrete prism (depth <5mm)(Fig.3A) but was longer for the interior of the same prism (depth >5mm)(Fig.3B), approaching compositions of CSH gel. Crack-filling ASR gel in the cement paste was rich in calcium.

The concrete prism subjected to 300 freeze-thaw cycles after immersion in NaOH solution (80°C, 6 weeks), presented a distinct difference in the compositions of ASR gel, i.e. the horizontal line of the air void-filling ASR gel disappeared. Instead, air void-filling ASR gel lost alkalis and gained calcium, occupying the most calcium-rich areas (upper right corner) on the oblique line of ASR gel compositions. In the surface area of the concrete prism (depth <5mm)(Fig.3C), this compositional line extended upward the CSH gel, forming a “convergent point” with CSH gel at around  $[Ca/Si]=1.5$ ,  $[Ca]/[Na+K]=100$ . However, in the interior of the same prism (depth >5mm)(Fig.3D), compositions of ASR gel were not continuous with those of CSH gel and there was a compositional gap between these two gels.

#### *High strength concrete*

In the high strength concrete prisms, both alite and belite hydrated to CSH gel down to final hydration products at around  $[Ca/Si] = 1.5-1.6$ ,  $[Ca]/[Na+K]=50-100$ . During hydration, the  $[Ca]/[Na+K]$  ratio of CSH gel slightly decreased, i.e. alkalis being slightly increased, producing steep lines on the  $[Ca]/[Si]-[Ca]/[Na+K]$  diagram (Figs.3 E,F,G,H). This is a distinct feature of the cement hydration of this concrete.

In the prism immersed in NaOH solution (80°C, 12 weeks), ASR gel was generally scarce in this high-strength concrete, and air void-filling ASR gel was almost absent. Hence, the compositional line of ASR gel was short for the surface area of the concrete prism (depth <5mm)(Fig.3E), and was shortest for the interior of the same prism (depth >5mm)(Fig.3F) where only crack-filling ASR gel in the reacted aggregate was identified and analyzed. This is another distinct feature of this high strength concrete. The most alkali-rich ASR gel, i.e.  $[Ca]/[Na+K]< 1$ , was crack-filling ASR gel in the aggregate.

In the prism subjected to 300 freeze-thaw cycles after immersion in NaOH solution (80°C, 6 weeks), air void-filling ASR gel appeared commonly, but the compositional range of ASR gel was narrow, presenting a wide compositional gap with CSH gel, irrespective of the concrete surface (Fig.3G) or the interior (Fig.3H).

### 3.3 EPMA analysis of ASR gel in field concretes

Three types of compositional lines of ASR gel, representing evolutionary trends in each concrete, have been identified on the  $[Ca]/[Si]-[Ca]/[Na+K]$  diagram. They were denoted as Type I, Type II and Type III evolution, respectively (Fig.4).

#### *Type I evolution*

Three concrete structures presented a single compositional line of ASR gel, with the  $[Ca]/[Na+K]$  atomic ratio steadily increasing with  $[Ca]/[Si]$  ratio. This is referred to *Type I evolution* here. In this case, a distinct “convergent point” was present between the ASR gel and the CSH gel, whose position with the  $[Ca]/[Si]$  and  $[Ca]/[Na+K]$  ratios ranged from 1.7, 100 (Petty Harbor dam)(Fig.4A), through 1.5, 1000 (Cape Broyle old bridge)(Fig.4B), to 1.2, 1000 (Cape Spear)(Fig.4C), respectively.

The inner part of less weathered concrete from Petty Harbor dam (core) contained ASR gel rich in alkali. By contrast, concretes from highly weathered structures undergoing severe frost action, presented shallower compositional lines, with lower  $[Ca]/[Si]$  and higher ranges of  $[Ca]/[Na+K]$  ratios. Highly weathered concrete (block) from Cape Spear contained ASR gel having a narrow and higher range of  $[Ca]/[Na+K]$  ratio between 100 and 1000. This indicates that essential part of alkalis in the ASR gel has been leached out from this concrete (Fig.4C).

#### *Type II evolution*

One structure (Water Street, gate) presented diffused and two parallel compositional lines of ASR gel (Fig.4D). This type of trend lines of ASR gel is defined as the *Type II evolution* here. This concrete has been severely map-cracked in the field, and both weathered part along cracks and fresh part distant from cracks, were contained in the same concrete block. In this case, one of the compositional lines was continuous with the hydration products of alite at  $[Ca]/[Si]$  ratio of 1.2-1.3.

Such parallel compositional lines of ASR gel have also been identified from deteriorated concretes undergoing so-called alkali-carbonate reaction in Cornwall and Gananoque, Ontario [6].

### Type III evolution

On the  $[\text{Ca}]/[\text{Si}]-[\text{Ca}]/[\text{Na}+\text{K}]$  diagram, two structures (Fort Amherst, Tors Cove old bridge) exhibited a deflected ASR gel composition line, composed of a slope line with a connecting horizontal line at around  $[\text{Ca}]/[\text{Si}] = 1.0-1.2$ . This type of the compositional line is denoted here as the *Type III evolution*. The  $[\text{Ca}]/[\text{Si}]$  ratio of the “deflection point” corresponds to that of the “convergent point” in the *Type I evolution*. It ranged from  $[\text{Ca}]/[\text{Si}] = 1.2$ ,  $[\text{Ca}]/[\text{Na}+\text{K}] = 100$  at Fort Amherst (Fig.4E) to  $[\text{Ca}]/[\text{Si}] = 1.0$ ,  $[\text{Ca}]/[\text{Na}+\text{K}] = 100$  at Tors Cove old bridge (Fig.4F).

In these concretes, weathering was intense and secondary calcite, which had been formed along cracks due to carbonation of cement paste and/or precipitated within interstices between cement paste and aggregate, was commonly found. Calcium silicates alite and belite in the cement particles had hydrated to CSH gel, and their final hydration products had a lower  $[\text{Ca}]/[\text{Si}]$  ratio around 1.3.

## 4 DISCUSSION

It was found from comparisons of ASR gel, based on SEM observation and EPMA (EDS) analysis, that reaction products (rosette-like ASR gel, amorphous ASR gel) between the laboratory and the field concretes were very similar, and that broadly similar trends of evolution of alkali-silica reaction have been reproduced in the laboratory concrete prisms.

As to the first question mentioned in the introduction, about what field age the laboratory concrete specimens in alkaline solution ( $80^\circ\text{C}$  1M NaOH) represents, the accelerating period of 12 weeks does not seem to be enough to reproduce the same degrees of ASR. Because normal strength prism did not develop conspicuous ASR (Figs.3A,B), compared with 50-70-year old field deteriorated concretes in Newfoundland (at the year of sampling)(e.g. Figs.4A,B,E,F). However, freeze-thaw cycles aggravated ASR by producing cracks and ASR gel in the surface part of the concrete prism.

Concerning the second question, to what extent the frost action (300 freeze-thaw cycles) aggravates ASR in concretes, normal strength concrete prism subjected to the freeze-thaw cycles after 6 weeks immersion in alkaline solution ( $80^\circ\text{C}$  1M NaOH) was found to be enough to reproduce ASR gel, having a typical type I evolutionary trend (Fig.3C), which closely resembled ASR gel in a nearly 70-year old Petty Harbor dam (at the year of sampling)(Fig.4A).

Expansive ASR gel rich in alkalis evolves into non-expansive calcium-rich ASR gel, leaching alkalis and absorbing calcium from the cement paste. This ASR gel approaches a “convergent point”, attaining at an apparent chemical equilibrium between ASR gel and CSH gel, although its position differs by the degree of weathering and leaching in concrete. When concretes are exposed to circulation of water, depleting alkalis from ASR gel, and to secondary carbonation on drying, precipitating calcites within interstices of the concretes, the  $[\text{Ca}]/[\text{Si}]$  ratio of ASR gel no longer increases and becomes constant, resulting in a horizontal compositional line on the right corner of the  $[\text{Ca}]/[\text{Si}]-[\text{Ca}]/[\text{Na}+\text{K}]$  diagram.

Consequently, relevant to the third question about what stage of alkali-silica reaction the ASR gel in field concretes represents, field concretes with ASR gel with particularly higher  $[\text{Ca}]/[\text{Na}+\text{K}]$  ratios on the sloped compositional line (Cape Spear: Fig.4C) or on the horizontal compositional line (Fort Amherst: Fig.4E; Tors Cove old bridge: Fig.4F) are considered to represent a later stage of alkali-silica reaction. By contrast, concrete that abounds in ASR gel rich in alkalis, i.e. with low  $[\text{Ca}]/[\text{Na}+\text{K}]$  ratios, is assumed to have a potential of expansion if conditions are met.

It was also revealed that high strength concrete, unlike the normal strength concrete, did not remarkably develop ASR gel in the concrete prism, even when freeze-thaw cycles were superimposed. This explains why the high strength concrete was effective in suppressing ASR under the frost action [3]. The reason why the hydration of alite and belite presented a slight gain of alkalis relative to calcium in the compositional lines (Figs.3E,F,G,H), may be due to two reasons: that is, small permeability of the high strength concrete that prevented the leaching of alkalis, and supplied alkalis from hydrated alkali-aluminate and alkali-sulfates to the CSH gel, which came from increased cement mix and possibly being absorbed in the CSH gel.

## 5 CONCLUSIONS

- The evolutionary trends of ASR gel in field deteriorated concretes were classified into three types on the  $[\text{Ca}]/[\text{Si}]-[\text{Ca}]/[\text{Na}+\text{K}]$  diagram: i.e. The *Type I* with a single sloped compositional line; the *Type II* with parallel sloped lines; and the *Type III* with a deflected line composed of a sloped and a horizontal line.

- Expansive ASR gel evolved into non-expansive calcium-rich ASR gel, leaching alkalis and absorbing calcium from the cement paste. This ASR gel approaches a “convergent point” with CSH gel, attaining at an apparent chemical equilibrium, although its position differs by conditions.
- Field concretes with ASR gel with particularly higher [Ca]/[Na+K] ratios on the sloped compositional line or on the horizontal compositional line, represent a later stage of alkali-silica reaction.
- Laboratory produced normal strength concrete prism, subjected to 12 weeks immersion in 80°C 1M NaOH solution, did not develop intense ASR compared with 50-70-year old field deteriorated concretes in Newfoundland (at the year of sampling). But freeze-thaw cycles aggravated ASR by producing cracks and ASR gel in concrete.
- Normal strength concrete prism, subjected to 300 freeze-thaw cycles after 6 weeks immersion in 80°C 1M NaOH solution, reproduced ASR gel with the *Type I* evolutionary trend, closely resembling ASR gel in a nearly 70-year old dam (at the year of sampling).
- High strength concrete did not remarkably develop ASR gel in the prism, even freeze-thaw cycles were superimposed. This explains why high strength concrete was effective in suppressing ASR under the frost action.

## 6 ACKNOWLEDGEMENTS

This paper is dedicated to Mr. Dan Bragg, formerly at the Department of Mines and Energy, Government of Newfoundland and Labrador, Canada, who passed away in 2003. Mr. Sheldon Langdon, formerly at Memorial University of Newfoundland, prepared the concrete prism specimens.

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Table 1: Deteriorated concrete structures near St.John's on the Avalon Peninsula, Newfoundland, Canada[1][2][5]

Location	Structure		Deterioration		Aggregate			Sample
	Structure	Built	Freeze-thaw	ASR	Type	Reactive rock	Geologic origin	
Red Cliff	Abd.radar base	1941	intense		gravel	Sil. siltstone	Conception Gp	B,C
Water Street	Gate of residence	1923	weak	intense	crushed	Sandstone	Gibbett Fm, Signal Hill Gp	B*
Fort Amherst	Abd. gun bunker	1941	intense	intense	crushed /gravel	Sandstone /siltstone		B*,C*
Cape Spear	Abd. gun bunker	1941	intense	intense	crushed	Sandstone	Conception Gp	B*
Petty Harbor	Reservoir dam	1923		weak	crushed	Red sandstone	Black Head Fm, Signal Hill Gp	C*
Tors Cove	Bridge (old)	1935	intense	intense	gravel	Sil. siltstone	Conception Group	B*,C*
Cape Broyle	Bridge (old)	1935		intense	gravel	Siltstone/ sandstone		B*,C*

B: block; C: core  
 \* EPMA analysis

Table 2: Laboratory concrete specimens prepared by Sheldon Langdon used for the petrographic examinations in this study

No	Concrete specimen *			Storage (wks, 80° C)		Freeze-thaw cyc.	Petrography			Specimen obtained
	Aggregate	Form	Strength	1MNaOH	Water		Polarizing	SEM	EPMA	
10	A Reactive	Prism	Normal	12			x	x	x	1997
8			High	12			x	x	x	
11			Normal		12		x			
9			High		12		x			
12		Cylinder	Normal				x			1998
13			High				x			
3		Prism	Normal	6		300	x	x	x	
4			High	6		300	x	x	x	
5			Normal		6	300	x			
6			High		6	300	x			
1	B Less reactive	Prism	Normal	12			x		x	1998
2			Normal		12		x			
7		Cylinder	Normal				x			

\* All specimens were cured for 4 weeks before storage  
 Aggregate: Expansion of CSA A23.2-25A accelerated mortar bar test: A: 0.36%; B: 0.07% (informed by Bragg)  
 Compressive strength at 4 weeks: Normal strength: about 40 MPa; High strength: about 70 MPa (by Bragg)  
 Alkali content: Normal strength Na<sub>2</sub>Oeq 3.73kg/m<sup>3</sup>; High-strength 4.73kg/m<sup>3</sup> (calculated from data by Langdon)

Table 3: ASR gel in the laboratory concrete specimens as examined by thin section polarizing microscopy

No	Concrete specimen				Surface(<5mm) with ASR gel				Interior with ASR gel				Paral crack	
	Aggr	Strg	Storage		Aggregate		Cement paste		Aggregate		Cement paste			
			NaOH	F-T	Rim	Gr	Crack	Void	Rim	Gr	Crack	Void		
10	A	N	O		xx	x	xx	xx	x	x	x	x	3mm	
8		H	O		x	x	(x)	(x)	x	(x)	(x)	(x)	2mm	
11		N												
9		H												
12		N												
13		H												
3		N	O	O	xx	x	xx	xx	x	x	x	x	4mm	
4		H	O	O	x	x	x	x	(x)	(x)	(x)	(x)	1mm	
5	B	N		O	x	x			x	x	x		x	
6		H		O	x	x	x		x	x				
1		N	O		x	x	x	x	x	x	x	x		
2		N												
7		N												

A: reactive; B: less reactive; Gr: sol/gel-like rimming on the cement paste  
 xxx: conspicuous; xx: common; x: rare; (x):trace

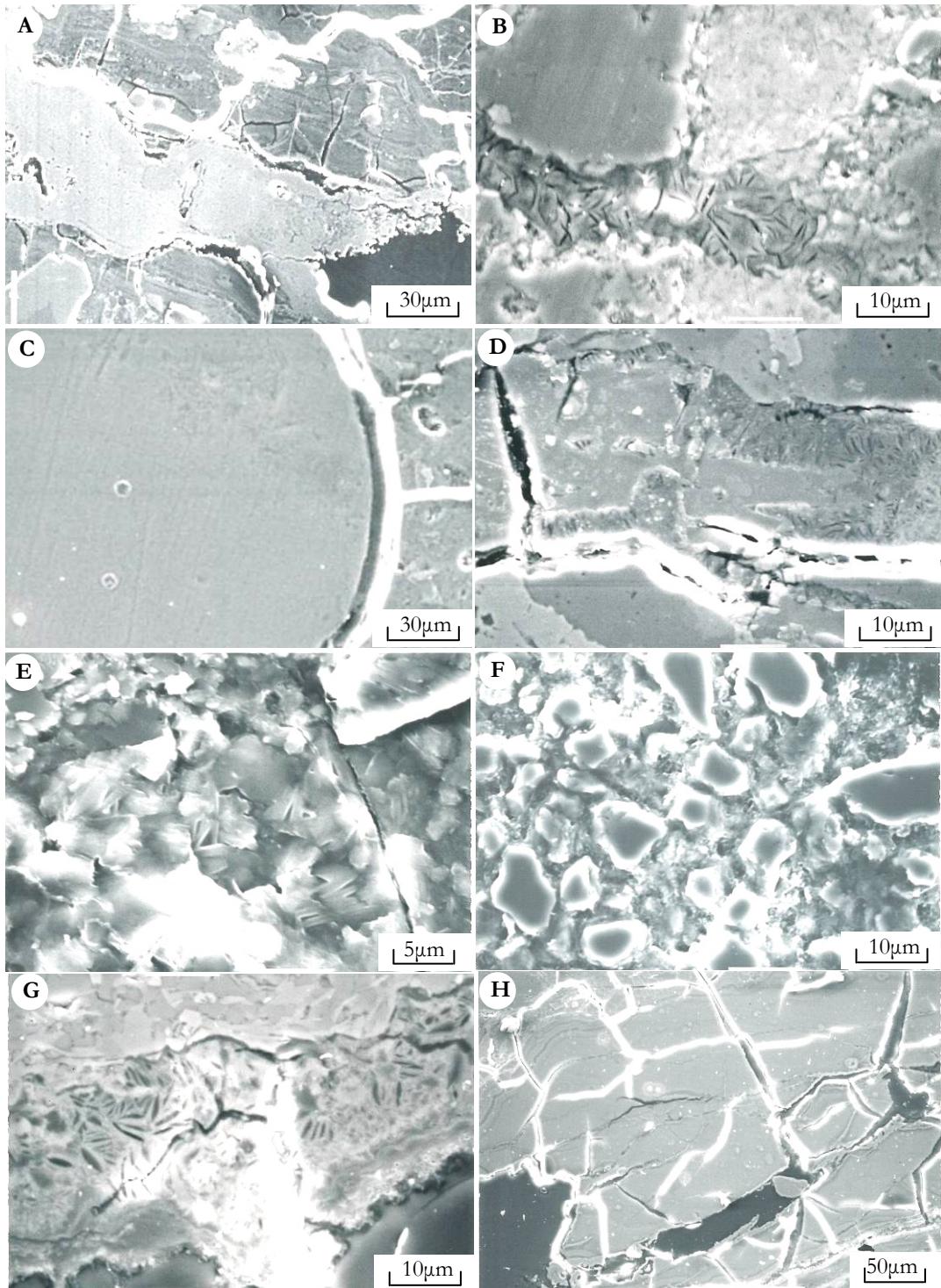


Figure 1: Field concretes: *Water Street, gate, block*: (A) Crack-filling ASR gel in sandstone (amorphous, alkali-depleted) inter-layered with calcite vein,  $[Ca]/[Si]$  0.68,  $[Ca]/([Na]+[K])$  77.15; *Fort Amherst, block*: (B) Crack-filling ASR gel (rosette) formed from cryptocrystalline quartz in sandstone,  $[Ca]/[Si]$  0.37,  $[Ca]/([Na]+[K])$  2.90, (C) Alkali-depleted void-filling ASR gel (amorphous),  $[Ca]/[Si]$  1.31,  $[Ca]/([Na]+[K])$  749; *Petty Harbor dam, core*: (D) Crack filling ASR gel in sandstone (amorphous and rosette),  $[Ca]/[Si]$  0.20-0.27,  $[Ca]/([Na]+[K])$  0.99-1.00; *Tors Cove old bridge, block*: crack-filling ASR gel in siltstone: (E) Alkali-depleted pseudomorph of rosette,  $[Ca]/[Si]$  1.06,  $[Ca]/([Na]+[K])$  135.0<sup>o</sup>; (F) Amorphous gel formed from microcrystalline quartz:  $[Ca]/[Si]$  042,  $[Ca]/([Na]+[K])$  13.84; *Cape Breyle old bridge, core*: Crack-filling ASR gel in siltstone: (G) Rosette,  $[Ca]/[Si]$  0.64,  $[Ca]/[Na+K]$  5.84, (H) Amorphous, alkali-depleted  $[Ca]/[Si]$  1.31,  $[Ca]/[Na+K]$  1124.

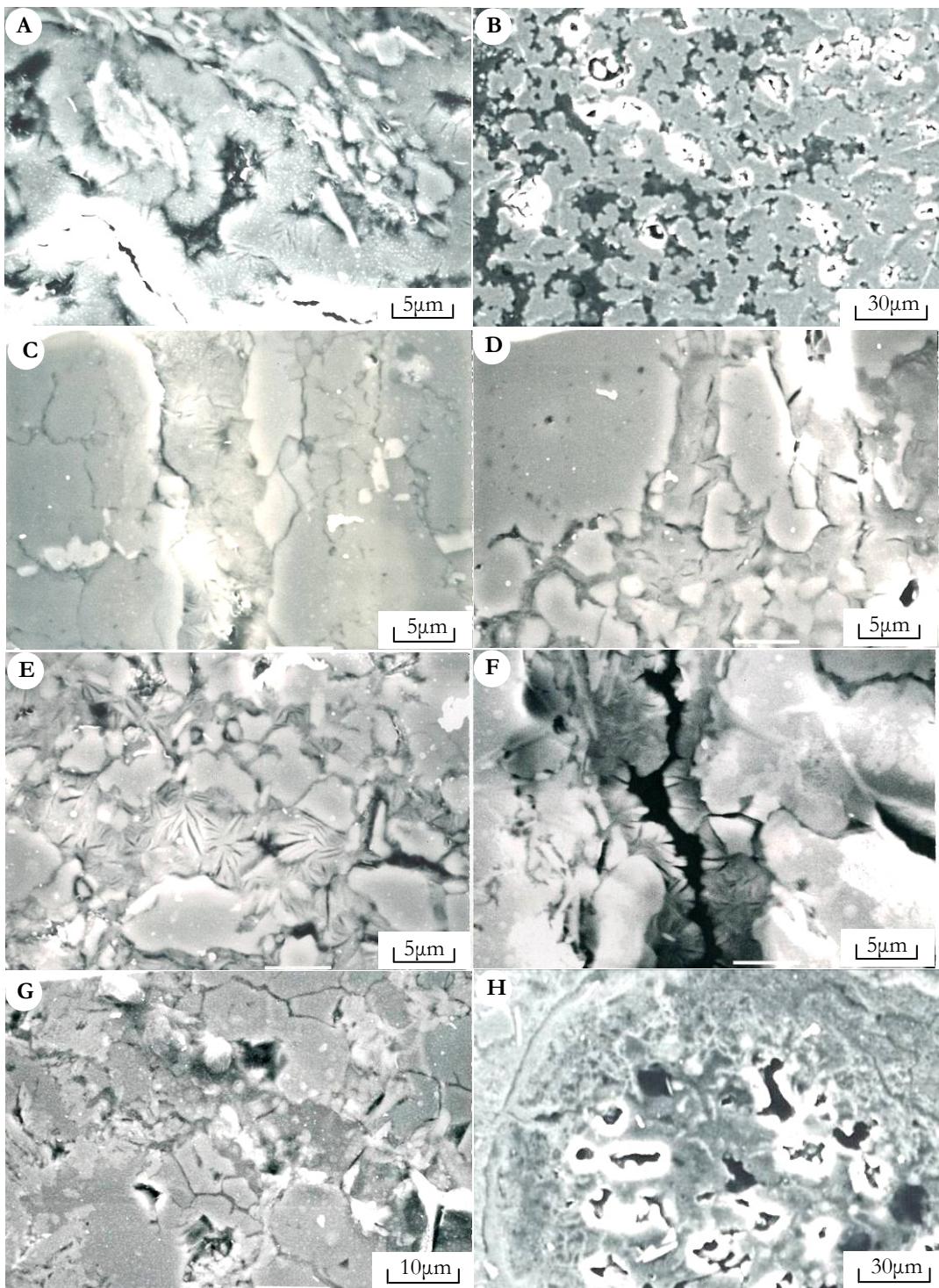


Figure 2: Normal strength concrete prisms:  $\text{NaOH}$  12 weeks (No.10), surface: (A) Crack-filling ASR gel (rosette) in siltstone,  $[\text{Ca}]/[\text{Si}]$  0.24,  $[\text{Ca}]/([\text{Na}]+\text{[K]})$  1.16, (B) Void-filling ASR gel,  $[\text{Ca}]/[\text{Si}]$  0.21,  $[\text{Ca}]/([\text{Na}]+\text{[K]})$  1.52;  $\text{NaOH}$  12 weeks (No.1), surface: (C) Crack-filling ASR gel (rosette) in rhyolitic tuff,  $[\text{Ca}]/[\text{Si}]$  0.24,  $[\text{Ca}]/([\text{Na}]+\text{[K]})$  0.89;  $\text{NaOH}$  6 weeks plus freeze-thaw (No.3): Crack-filling ASR gel (rosette) formed from cryptocrystalline quartz in sandstone: (D) Surface of prism: alkali-depleted,  $[\text{Ca}]/[\text{Si}]$  0.53,  $[\text{Ca}]/([\text{Na}]+\text{[K]})$  18.90, (E) Interior of prism: alkali-retained,  $[\text{Ca}]/[\text{Si}]$  0.25,  $[\text{Ca}]/([\text{Na}]+\text{[K]})$  1.32; High strength concrete prisms:  $\text{NaOH}$  12 weeks (No.8), surface: (F) ASR gel (rosette) in mudstone,  $[\text{Ca}]/[\text{Si}]$  0.22,  $[\text{Ca}]/[\text{Na}+\text{K}]$  0.55;  $\text{NaOH}$  6 weeks plus freeze-thaw (No.4), surface: (G) Crack-filling ASR gel in siltstone,  $[\text{Ca}]/[\text{Si}]$  0.36,  $[\text{Ca}]/([\text{Na}]+\text{[K]})$  1.18, (H) Void-filling ASR gel,  $[\text{Ca}]/[\text{Si}]$  0.53,  $[\text{Ca}]/([\text{Na}]+\text{[K]})$  4.82.

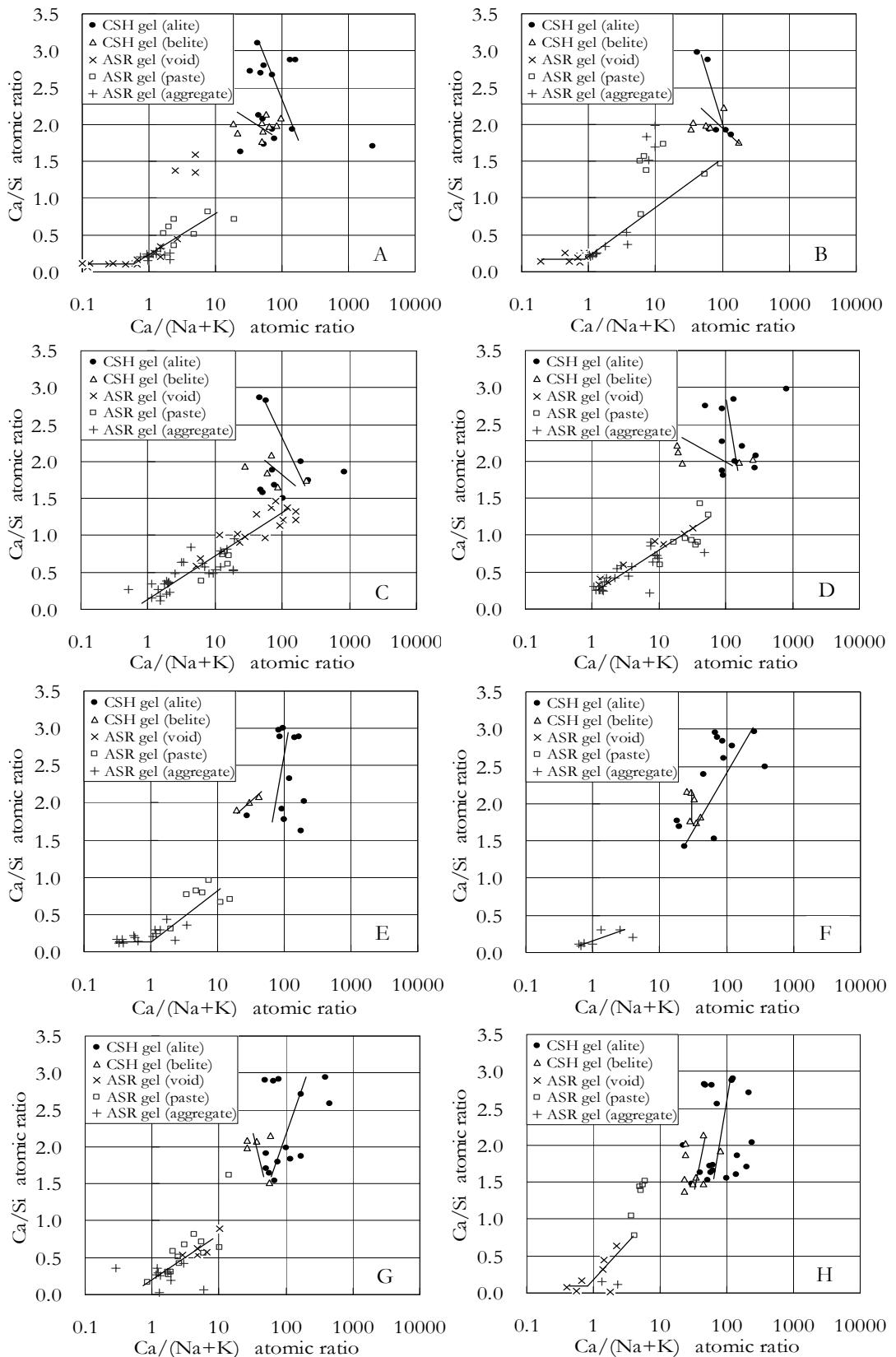


Figure 3: EPMA (EDS) compositions of ASR gel and CSH gel in concrete prisms, prepared by Sheldon Langdon: Normal strength: (A) NaOH surface (no.10), (B) NaOH interior (no.10), (C) FT NaOH surface (no.3), (D) FT NaOH interior (no.3); High strength: (E) NaOH surface (no.8), (F) NaOH interior (no.8), (G) FT NaOH surface (no.4), (H) FT NaOH interior (no.4).

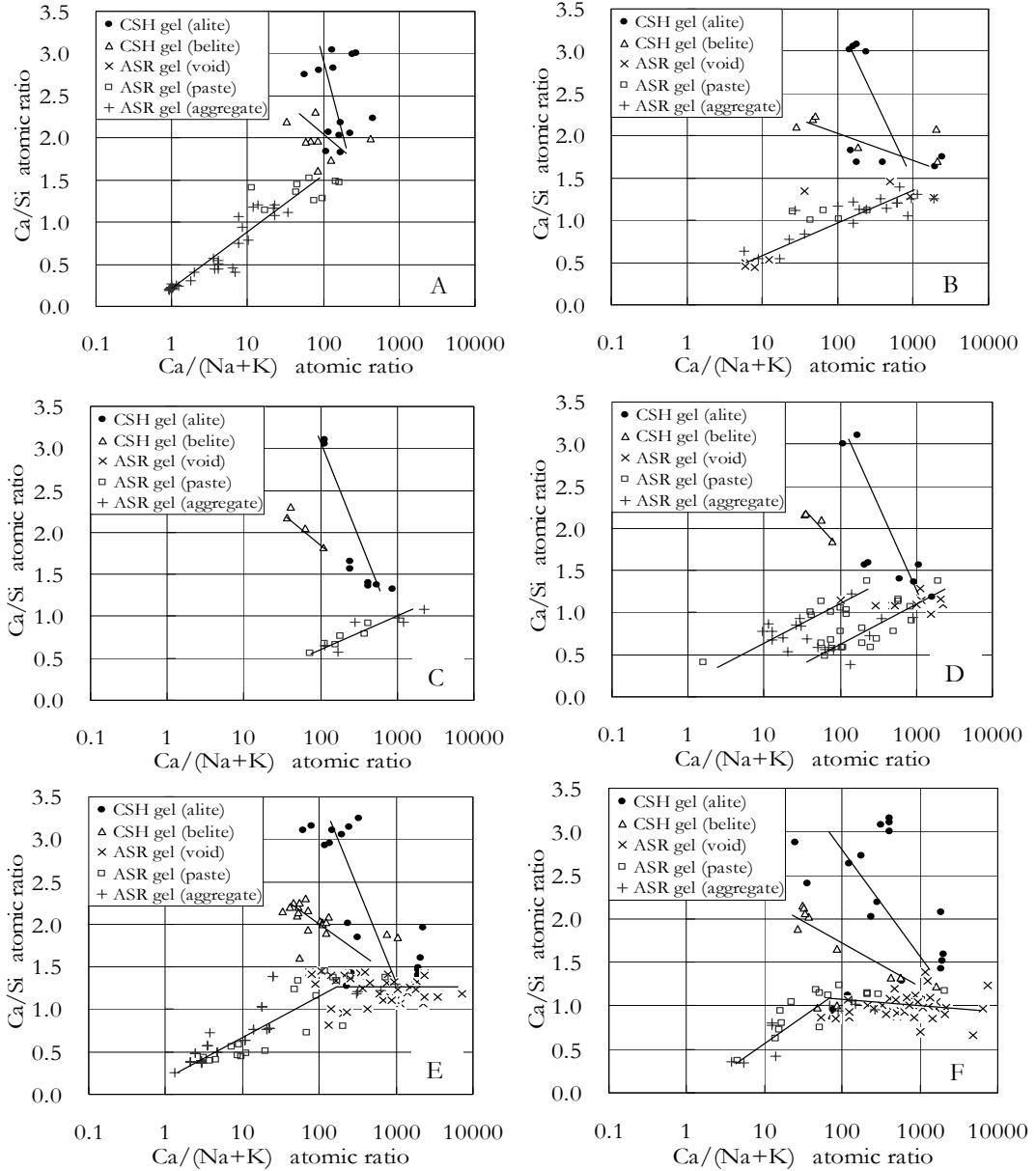


Figure 4: EPMA (EDS plus WDS) compositions of CSH gel and types of ASR gel in the field deteriorated concrete structures on the Avalon Peninsula, Newfoundland, Canada: *Type I evolution*: (A) Petty Harbor dam (core); *Type II evolution*: (B) Cape Broyle old bridge (core), (C) Cape Spear (block), (D) Water Street, gate (block); *Type III evolution*: (E) Fort Amherst (core, block); (F) Tors Cove old bridge (block).