

# FURTHER INVESTIGATION OF THE MECHANISMS OF SO- CALLED ALKALI-CARBONATE REACTION BASED ON MODERN PETROGRAPHIC TECHNIQUES

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## Abstract

Typical examples of so-called alkali-carbonate reaction (ACR) in the Canadian field concretes in Ontario, and RILEM concrete microbars containing Pittsburgh aggregate, were examined petrographically based on polarizing microscopy, SEM observation and quantitative EPMA (EDS) analysis of the reaction products. It was revealed that ASR gel was the main product responsible for the crack formation in concretes, and that this gel had a common nature to that in the typical ASR. The so-called ACR is a combination of deleteriously expansive alkali-silica reaction (ASR) of cryptocrystalline quartz, and harmless dedolomitization which produces brucite and carbonate halo. In laboratory specimens, fine dolomitic aggregate undergoes dedolomitization, and ASR gel is altered to non-expansive Mg-silicate gel, which explains why the mortar bar produces smaller expansion than the concrete microbar.

**Keywords:** Alkali-carbonate reaction (ACR), ASR gel, cryptocrystalline quartz, dedolomitization, EPMA

## 1 INTRODUCTION

The mechanisms of so-called alkali-carbonate reaction (ACR) have been controversial. In early 1990's, Katayama predicted that ACR is a combined reaction of deleteriously expansive ASR of cryptocrystalline quartz, and harmless dedolomitization of dolomitic aggregate [1], based on critical review of the published references on ACR, and subsequently extracted this quartz from ACR-reactive Pittsburgh aggregate by phosphoric acid treatment [2]. Recently, this theory was confirmed by means of polarizing microscopy, SEM observation and quantitative EPMA (EDS) analysis using the same polished thin sections of concretes [3][4][5]. The investigations revealed the key importance of the expansiveness of mortar and concrete of Mg-silicate gel formed by the interaction of ASR and dedolomitization products. However, in view of the fact that the field instances of ACR have become rare even in Canada, it was decided to gather and present as much analytical data about reaction products as possible to provide the background to understand the nature of the reaction. This paper will focus on the chemical compositions of the reaction products in the ACR, as analyzed by the quantitative EPMA (EDS) of the materials.

## 2 MATERIALS AND METHODS

### 2.1 Sample origin

Three Austrian gravel carbonate aggregates and Canadian Pittsburgh aggregate (collective, 1<sup>st</sup> lift, MTO stockpile), examined with RILEM AAR-5 concrete microbars (aggregate 4-8mm) and AAR-2 mortar bars (aggregate 0-4mm) at VÖZFI [6], were used here. Another batch of the Pittsburgh aggregate (most reactive layer Pit-16, 1<sup>st</sup> lift, CANMET stockpile) [7], tested with AAR-5 concrete microbars in prolonged storage (NaOH or KOH added to cement: Na<sub>2</sub>O<sub>eq</sub> = 1.5 wt%, 80°C, 1M NaOH, 28 days) at KGE, was also used. Of the field deteriorated concretes that had undergone typical alkali-carbonate reaction (ACR) in the past, a ballast wall concrete with the Pittsburgh aggregate (1<sup>st</sup> lift) came from a bridge in Gananoque (MTO collection, built 1957), and from a concrete curb in Cornwall (placed 1979), both in Ontario, Canada [3][4]. An old CSA concrete prism prepared by MTO (1992, two years) was also examined for comparison.

### 2.2 Methods of investigation

*Polarizing microscopy, SEM observation, EPMA analysis*

Polished thin sections (20×30mm, thickness 15μm) of the test specimens and field concretes were prepared for polarizing microscopy to examine the presence of reaction products in the carbonate aggregate. After completing this, SEM observation and quantitative EPMA (EDS) analyses were done on

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the reaction products (brucite, ASR gel, CSH gel and cement particles), using the same polished thin sections (JEOL JSM 5310LV/JED 2140: at 15KV, 0.12 nA, partly 0.8 nA,  $\times 2000$ , ZAF correction). Their compositions were plotted on the [Ca/Si]-[Ca]/[Na+K] diagram, and on the Si-Mg-Ca diagram.

### 3 RESULTS

#### 3.1 Polarizing microscopy

##### *Lithology*

The Austrian gravel aggregates were predominantly siliceous limestone containing chert fragments (9C), or dolostone rich (10C), or poor (12C) in disseminated cryptocrystalline quartz [3]. The Canadian Pittsburg aggregate (collective, 1<sup>st</sup> lift), used for the AAR-5 concrete microbar (15C) and AAR-2 mortar bar tests (15F), ranged widely in lithology from micritic limestone to dolostone, with 3.2 wt% of quartz based on the phosphoric acid treatment (Table 1). The most reactive horizon in the same quarry (Pit-16, 1<sup>st</sup> lift) used for the prolonged tests (Na28, K28) consisted essentially of argillaceous dolomitic limestone, and contained 16.8 wt% of insoluble residue by HCl and 4.8 wt% of quartz by H<sub>3</sub>PO<sub>4</sub>, the latter being mostly cryptocrystalline. This is a typical reactive lithology, with silt-sized dolomite rhombs scattered within argillaceous matrix, which was dominant in the CSA concrete prism that developed crack-lining gel in early 1990's at MTO, as well as in the ACR-affected curb in Cornwall. However, this rock type was less abundant in the ACR-affected bridge in Gananoque made with the Pittsburg aggregate (1<sup>st</sup> lift).

##### *Reactions versus expansion*

In the concrete microbars, dedolomitization was pronounced in less argillaceous dolomitic limestone, producing conspicuous *reaction rims* within the inner periphery of the dolomitic aggregate (Fig.1 C) and reaction zones along pre-existing cracks (Fig.1 A), together with *carbonate haloes* in the surrounding cement paste (Fig.1 C). Cracks extending from the reacted aggregate into cement paste, suggestive of expansion, appeared only when ASR was involved. These cracks were filled or lined with ASR gel, irrespective of whether it was a dolostone (Fig.1 A), a dolomitic limestone (Fig.1 E), or a siliceous limestone (Table 1). Prolonged storage developed wider gel-filled cracks (see SEM, Figs.2 A,B).

In the field concretes, ASR gel occurred in various lithologies of coarse aggregate, including limestone, shaley limestone, dolomitic limestone and argillaceous dolomitic limestone [4][5]. However, ASR gel in these cracks was often carbonated due to weathering and later forming carbonate haloes, and was obscured by high-birefringent calcites within carbonated cement paste and carbonate aggregate.

#### 3.2 SEM observation

Combined examination of SEM and mapping of elements by EPMA (EDS) on the same polished thin section was very effective in identifying the details of products in the carbonate aggregate.

##### *Dedolomitization*

Dolomite crystals in the reaction rims and in reaction zones had been more or less decomposed into a combination of dark spots of brucite ( $< 3\mu\text{m}$ ) and secondary calcite, leaving a mottled texture pseudomorphic after dolomite rhombs. Unless ASR was involved (Fig.1 B), dedolomitization did not accompany any expansion cracks in the surrounding cement paste, as shown by the Austrian dolostone coarse aggregate without excessive silica (Figs.1 C,D) [3][4]. Deleteriously expansive argillaceous dolomitic limestone from the Pittsburg quarry (collective, 1<sup>st</sup> lift) also produced no expansion cracks, when used as fine aggregate, but had been entirely dedolomitized within aggregate particles (Figs.1 G,H).

##### *Alkali-silica reaction*

Cryptocrystalline quartz had altered to ASR gel, forming gel-vein (Fig.1 F). In the concrete microbar made with the most reactive layer in the Pittsburg quarry (Pit-16, 1<sup>st</sup> lift) and stored in the prolonged period (28 days), as shown by the Si image, ASR gel had originated from cryptocrystalline quartz, migrating into ASR gel that lines large crack within the reacted aggregate (Figs.2 B,C,D). Mg-silicate gel (Fig.2 C, dark spots) formed replacing the rim on the dolomite rhombs (Figs.2 C,E).

Some of the ASR gel remained around the cryptocrystalline quartz (Fig.2G). Although the process of grinding thin sections tended to wear off such fragile reaction products in the weathered field concretes, SEM observation was effective in detecting the presence of ASR gel that had filled or lined cracks within the reacted argillaceous dolomitic limestone aggregate in concretes from Gananoque (Fig.2 F) and Cornwall (Figs.2 H, I). Within the reaction rims or near cracks, Mg-silicate gel occurred surrounding dolomite rhombs pseudomorphic after dolomite, replacing the original rims of brucite, while pure brucite was generally confined to areas distant from the cracks containing ASR gel (Fig.2F).

### 3.3 EPMA analysis

Compositions of reaction products, including brucite  $[\text{Mg}(\text{OH})_2]$ , Mg-silicate gel, ASR gel and reacted quartz, were plotted on the Si-Mg-Ca triangular diagram in atomic ratios (Fig.3). Brucite occupies the Mg-corner of the diagram, while unaltered cryptocrystalline quartz represents the Si-corner when it has not been altered. Carbonate minerals calcite and dolomite were omitted from this diagram. To clarify the chemical characteristics of the ASR gel in detail, reaction products with essential amounts of Si and Ca will be examined hereafter on the  $[\text{Ca}/\text{Si}]-[\text{Ca}]/[\text{Na}+\text{K}]$  diagram developed by the first author (Fig.4).

#### *Brucite and Mg-silicate gel*

Brucite has been found in the concrete microbar (15C: Fig. 2A), made with the Pittsburgh aggregate (collective, 1<sup>st</sup> lift) and stored for a normal period (14 days), as well as in the field deteriorated concretes from Gananoque and Cornwall (Figs. 2 E, F). Brucite was absent in the concrete microbars (Na28, K28: Figs. 2C, D) made using a highly reactive layer in the Pittsburgh quarry (Pit-16, 1<sup>st</sup> lift) and stored for a prolonged period (28 days), but was rare in the mortar bar (15F: Fig. 2B).

Mg-silicate gel occupies wide areas in the triangular diagram and was collectively shown as “dolomite rim”, together with brucite (Fig.3). Mg-silicate gel is very common in concretes that have undergone advanced reaction, such as the concrete microbars stored for a prolonged period (Figs.3 C,D) and the field concretes from Gananoque (Fig.3E) and Cornwall (Fig.3F). Mg-silicate gel was generally confined to the shell of the coarse aggregate (4-8mm) (Fig. 3A), while it was present in the entire section of the particle of fine aggregate (<4mm) that had undergone dedolomitization (Fig. 3B)[5].

#### *Cement hydrates*

The compositions of ASR gel and cement hydrates (CSH gel) were plotted on the  $[\text{Ca}/\text{Si}]-[\text{Ca}]/[\text{Na}+\text{K}]$  diagram, excluding the Mg-silicate gel (>5 wt % MgO, Fig.4). In the concrete microbar (15C: Fig. 4C), calcium silicates alite and belite hydrated to CSH gel with a  $[\text{Ca}/\text{Si}]$  atomic ratio down to 2.0, corresponding to “final” hydration products. This  $[\text{Ca}/\text{Si}]$  ratio was even higher than that of the ordinary concretes not subjected to the immersion in NaOH solution. Abundant portlandite  $[\text{Ca}(\text{OH})_2]$  surrounded the CSH gel, suggesting that they had originated from the hydrated cement particles and the pore solution was oversaturated with OH ions. By contrast, the Canadian field concretes contained CSH gel with lowest  $[\text{Ca}/\text{Si}]$  ratios and chloride, i.e. Gananoque with  $[\text{Ca}/\text{Si}]$  down to 1.5, Cl 1.9-3.5 wt% (Fig. 4G), and Cornwall with  $[\text{Ca}/\text{Si}]$  down to 1.3 (Fig. 4H), Cl 0.4-2.2 wt% (Table 2). The concrete microbar (Na28: Fig. 4E) stored for a prolonged period (28 days), presented  $[\text{Ca}/\text{Si}]$  ratio of CSH gel of 1.8, being intermediate between the field concretes and the concrete microbars stored in two weeks.

#### *ASR gel*

Cryptocrystalline quartz, which altered to ASR gel leaving a pseudomorphic texture, is noted as “quartz rim” in the triangular diagram (Fig.3). It also reacted with brucite to form Mg-silicate gel. On the other hand, ASR gel, which appears as crack-filling or crack-lining materials in the carbonate aggregate, occupies the Si-Ca tie-line (Fig.3). On the  $[\text{Ca}/\text{Si}]-[\text{Ca}]/[\text{Na}+\text{K}]$  diagram (Fig. 4), ASR gel exhibits a narrow range of the compositional lines, directed toward the CSH gel with a distinct compositional break (Fig.4). This tendency was common to the siliceous (Austrian Figs.3 A,B) and argillaceous aggregates (Canadian). The Pittsburgh aggregate (collective) presents the same inclined lines in both mortar bar (15F: Fig. 4D) and concrete microbar (15C: Fig. 4C), with a wider range in the former. But the prolonged storage (28 days) (Pit-16, most reactive) resulted in less inclined lines (Na28: Fig. 4E, K28: Fig. 4F), with a “convergent point” between ASR gel and CSH gel at around  $[\text{Ca}/\text{Si}] = 1.8$ ,  $[\text{Ca}]/[\text{Na}+\text{K}] = 100$ .

Field concretes presented scattered distributions of ASR gel, but their compositions were generally continuous with the CSH gel, with a “convergent point” at around  $[\text{Ca}/\text{Si}] = 1.5$ ,  $[\text{Ca}]/[\text{Na}+\text{K}] = 100$  for Gananoque (Fig. 4G), and at around  $[\text{Ca}/\text{Si}] = 1.3$ ,  $[\text{Ca}]/[\text{Na}+\text{K}] = 100$  for Cornwall (Fig. 4H). The compositional lines of ASR gel sloped more gently than those of the laboratory concrete microbars.

## 4 DISCUSSION

Earlier researchers in Canada and USA in the 1960's, and more recently in China, believed that the following features distinguish ACR from ASR, that is, in ACR-affected concretes, 1) ASR gel is absent, 2) larger aggregate expands more than fine aggregate, 3) lithium and other additives are not effective, and 4) reaction takes place even with low alkali content. However, all these aspects also apply to typical ASR, as discussed below. Modern petrographic techniques applied here are useful in examining them.

#### 4.1 General exceptions to ASR

These are, 1) Concretes undergoing late-expansive ASR, some formerly called *alkali-silicate reaction* in the 1970's, lack conspicuous ASR gel which is invisible on the ground surface of concrete. 2) Some aggregates (British flint and Canadian Potsdam sandstone) produce less expansion in the mortar bar than in the concrete prism made with coarse aggregate, a result of segregation of reactive silica during crushing of the aggregate due to inhomogeneity of the texture. 3) Lithium compounds do not suppress deleterious expansion of some late-expansive aggregates [8]. Similar inefficiency is also known with slag and fly ash applied to ASR-reactive coarse aggregates, depending on their mix proportion and the pessimum proportion of reactive minerals (some Japanese andesites). 4) Cryptocrystalline quartz (Canadian Spratt limestone) [9] and highly reactive opal and occasionally cristobalite produce ASR even in cement or concrete with low alkali levels ( $\text{Na}_2\text{O}_{\text{eq}} < 0.6\%$ ,  $< 2.0\text{kg/m}^3$ ). In the previous discussions of ACR, however, these exceptions to ASR have been used as a proof of ACR without counterargument.

#### 4.2 Mechanisms of ACR

##### *Dedolomitization*

The process of dedolomitization, typically the formation of brucite, is thought to be a harmless reaction, because no expansion cracks formed in the cement paste with the Austrian dolostone aggregate (Fig.1C). With the most reactive Pittsburg aggregate rich in cryptocrystalline quartz (Pit-16, 1<sup>st</sup> lift), both dedolomitization and expansion of concrete microbars continued steadily with time (0.21% at 28 days [6]), but all brucite altered to Mg-silicate gel due to interaction with ASR gel (Figs.4 C,D), whereas ASR gel formed abundantly filling expansion cracks (Figs.2 A,B). Mg-silicate gel is deemed non-expansive or less expansive than the real ASR gel, because it accompanied no cracks [3][4][5]. Mg-silicate gel has also been identified from a marine concrete as a less-expansive material replacing ASR gel [10]. Though dedolomitization does not cause expansion, it maintains a high level of alkalinity. This may contribute to the speed of ASR and diminish the effectivity of fly ash and other additives to counteract ASR.

##### *Alkali-silica reaction*

ASR of cryptocrystalline quartz is thought to be responsible for the expansion cracks in concretes, because this quartz was directly identified reacting in both laboratory and field deteriorated concretes from Gananoque and Cornwall. The compositions of ASR gel (Figs.4 G,H) were common to typical ASR in other areas of the world including Japan [11]. This means that ASR gel, during migration from the reacted aggregate, takes up calcium from the cement paste and leaches alkalis, approaching a "convergent point" where ASR gel and CSH gel attain an apparent chemical equilibrium. A wide scatter of ASR gel in compositions is due to leaching of alkalis during freeze-thaw weathering.

#### 4.3 Interpreting the conventional peculiarities of ACR

##### *Are reaction products really scarce?*

Classical petrographic techniques are inadequate for identifying reaction products in ACR-affected concretes. Because Mg-silicate gel that forms abundantly within dolomitic aggregate is too small to be detected by the stereomicroscopy on ground concrete (ASTM C457), and both cryptocrystalline quartz and cracks filled with ASR gel (often  $< 5\mu\text{m}$ ) are smaller in width than that of conventional cover-mounted thin sections ( $30\mu\text{m}$ : ASTM C856). In transmitted light, all these materials are overlapped by high-birefringent calcites in both carbonated cement paste and carbonate aggregate, thus hindering the details. There is no merit to using destructive HCl etching to check reaction rims on the carbonate aggregate (ASTM C856) and impregnation of fluorescent dye because they obscure the details of textures.

##### *Why does smaller expansion occur in the mortar?*

Alteration of ASR gel into non-expansive Mg-silicate gel in fine dolomitic aggregate is probably the reason why mortar bar produces smaller expansion than concretes. Both dedolomitization and ASR proceed faster in the mortar bar, forming Mg-silicate gel within the entire section of the fine aggregate. ( $< 4\text{mm}$ ). By contrast, in the concrete microbar, dedolomitization is limited to the surface of the coarse aggregate (4-8mm) forming reaction rims, but ASR gel inside the aggregate remains unaltered, thus causing expansion cracks in concrete. Where argillaceous material is dominant in the aggregate, Al-silicate gel with or without calcium also forms without producing cracks, which is deemed non-expansive [5].

##### *Why are additives ineffective?*

Lithium compounds do not suppress deleterious expansion of some aggregates that cause ACR (Pittsburg aggregate) or late-expansive ASR (Canadian Sherbrooke schist and Potsdam sandstone) [8] in the concrete prism. A common characteristic of these aggregates is a dense matrix around the reactive

silica, where Li ions in pore solution are either halted from penetrating, or absorbed by surrounding clay minerals, before ASR gel becomes inactive by the conversion into non-expansive Li-silicate gel, or both.

The ineffectiveness of slag and fly ash in suppressing the expansion of coarse aggregate may be due to two reasons: the slower rate of pozzolanic reactions in comparison to that of the ASR of the reactive silica, and the high alkalinity maintained by the dedolomitization process. According to Japanese experience with the most reactive layer of the Pittsburg quarry (Pit-16, 1<sup>st</sup> lift), a 50% substitution of a fine-grained Japanese blast furnace slag (Blaine finess 6050 cm<sup>2</sup>/g) to cement, reduced 30% of expansion of AAR-5 concrete microbar (0.11% vs. 0.16% at 14 days) with reduced exudation of ASR gel. But this may be a result of delayed ingress of alkali solution by a reduced permeability of cement-slag hydrates [12]. In Austria, the use of a super sulfated cement with 85% of slag with the Pittsburg aggregate prevented expansion both in the microbar test and the RILEM AAR-3 concrete bar test. Thus finely ground slag may suppress expansion of so-called ACR if sufficiently high amounts are used.

Deicing salt (NaCl) applied in winter supplies sodium and does accelerate AAR. In the field deteriorated concretes in Gananoque and Cornwall, the amount of locally concentrated chloride within CSH gel (Table 2), exclusive of the Friedel's salt, amounted to Cl 12kg/m<sup>3</sup> in concretes i.e. about 8kg/m<sup>3</sup> of Na, whereas this sodium was missing due to segregation in concretes, including the formation of ASR gel and leaching. The abundance in Cl and the lower [Ca]/[Si] ratios of CSH gel are indicative of long-term weathering of concretes, subjected to freezing and thawing, leaching and ingress of deicing salt.

Hence, to investigate ACR in detail, it would be useful to examine freshly cored concrete samples made with the Pittsburg aggregate, e.g. the experimental pavements in Kingston [9][12], based on the modern petrographic techniques adopted here (polarizing microscopy, SEM and EPMA analysis).

## 5 CONCLUSIONS

- Detailed petrographic examinations with EPMA analysis reconfirmed that so-called alkali-carbonate reaction is a combination of deleteriously expansive alkali-silica reaction of crypto-crystalline quartz, and harmless dedolomitization which produces brucite and carbonate haloes.
- ASR gel formed in the dolomitic aggregate is responsible for crack formation in concrete. This gel has a common nature to that in the typical ASR, which migrates within concrete taking up calcium from the cement paste and leaching alkalis, approaching the compositions of CSH gel.
- Fine dolomitic aggregate dedolomitizes and ASR gel that formed earlier alters to non-expansive Mg-silicate gel, which explains why mortar bar produces smaller expansion than concrete microbar.
- ASR was most evident with the most expansive argillaceous dolomitic limestone aggregate in the Pittsburg quarry, Ontario. The term alkali-carbonate reaction is misleading and should be placed in the museum of concrete history, like the former alkali-silicate reaction, both are forms of ASR.

## 6 ACKNOWLEDGEMENTS

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## 7 REFERENCES

- [1] Katayama T (1992): A critical review of carbonate rock reactions - is their reactivity useful or harmful? Proceedings, 9<sup>th</sup> International Conference on Alkali-Aggregate Reaction in Concrete. London, UK: 508-517.
- [2] Katayama T, Ochiai M, Kondo H (1996): Alkali-reactivity of some Japanese carbonate rocks based on standard tests. Proceedings, 10<sup>th</sup> International Conference on Alkali-Aggregate Reaction in Concrete. Melbourne, Australia: 294-301.
- [3] Katayama T (2004): How to identify carbonate rock reactions in concrete. Materials Characterization (53/2-4), Special Issue 29: 85-104. Printed version of proceedings, 9<sup>th</sup> EMABM 2003.
- [4] Katayama T (2006): Modern petrography of carbonate aggregates in concrete. - Diagnosis of so-called alkali-carbonate reaction and alkali-silica reaction. Marc-André Bérubé Symposium on Alkali-Aggregate Reactivity in Concrete, Montreal, Canada: 423-444. (available as a separate copy)
- [5] Sommer H, Katayama, T (2006): Screening carbonate aggregates for alkali-reactivity. Proceedings, 16<sup>th</sup> International Conference on Building Materials (IBAUSIL), Weimar, Germany: 2-0461-0468.
- [6] Sommer H, Grattan-Bellew P, Katayama T, Tang M (2004): Development and inter-laboratory trial of the RILEM AAR-5 rapid preliminary screening test for carbonate aggregates. Proceedings,

- 12<sup>th</sup> International Conference on Alkali-Aggregate Reaction in Concrete. Beijing, China: 407-412.
- [7] Lu D, Fournier B, Grattan-Bellew P (2004): Evaluation of the Chinese accelerated test for alkali-carbonate reaction. Proceedings, 12<sup>th</sup> International Conference on Alkali-Aggregate Reaction in Concrete. Beijing, China: 386-392.
- [8] Durand B (2000): More results about the use of lithium salts and mineral admixtures to inhibit ASR in concrete. Proceedings, 10<sup>th</sup> International Conference on Alkali-Aggregate Reaction in Concrete. Quebec, Canada: 623-632.
- [9] Hooton D, Rogers C, Ramlochan T (2006): The Kingston outdoor exposure site for ASR - after 14 years what have we learned? Marc-André Bérubé Symposium on Alkali-Aggregate Reactivity in Concrete, Montreal, Canada: 171-193.
- [10] Shayan A (2006): Expansion of AAR-affected concrete under aggressive marine conditions: a look at possible effects of complex interactions. Marc-André Bérubé Symposium on Alkali-Aggregate Reactivity in Concrete, Montreal, Canada: 369-389.
- [11] Katayama T, Sarai Y, Higashi Y, Honma A (2004): Late-expansive alkali-silica reaction in the Ohnyu and Furikusa headwork structures, central Japan. Proceedings, 12<sup>th</sup> International Conference on Alkali-Aggregate Reaction in Concrete. Beijing, China: 1086-1094.
- [12] Williams DA, Rogers CA (1991): Field trip guide to alkali-carbonate reactions in Kingston, Ontario. Ontario Ministry of Transportation, Report: MI-145..

phosphoric acid treatment of coarse aggregate (wt%) [3].

- \* Contains ASR gel
- # Contains reaction rims and carbonate haloes formed by dedolomitization
- + Quartz: extracted by phosphoric acid treatment, Insoluble residue: by HCl
- 1 38°C, 2 years, crack-lining gel
- 2 1000 Island Parkway Bridge (ballast wall, built in 1957, later replaced, MTO collection)
- 3 Water Street (placed in 1979)

and CSH gel in concrete as determined by EPMA (EDS) analysis [3][4]

1: Atomic ratio [Ca]/[Si], 2: Atomic ratio [Ca]/([Na]+[K])



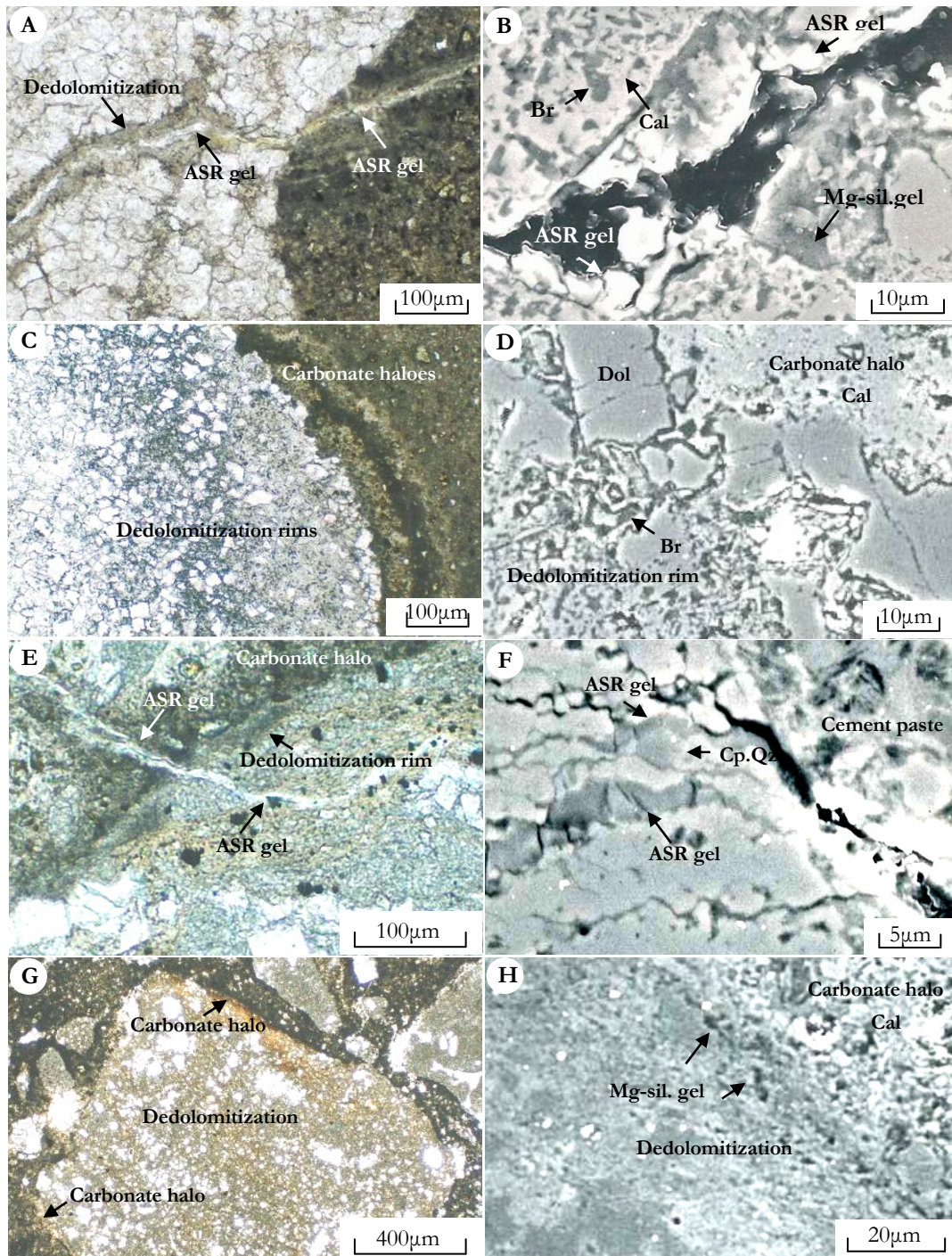


Figure 1: RILEM AAR-5 concrete microbars (aggregate 4-8mm) (A)-(F)[3][5]: Crack-lining ASR gel and reaction zone (dedolomitization) along the crack, composed of brucite spots (dark) and secondary calcite distant from the crack, and Mg-silicate gel (dark) near the ASR gel (10C) (A)(B). Pronounced reaction rims (dedolomitization) and carbonate haloes free from expansion cracks in the cement paste (12C) (C)(D). Both with the Austrian dolostone aggregates; Argillaceous dolomitic limestone in the Pittsburg aggregate (collective, 1<sup>st</sup> lift, MTO stockpile), Ontario, Canada (15C) (E)(F): ASR gel exuding along the crack from crypto-crystalline quartz, and faint reaction rim with diffuse carbonate halo; RILEM AAR-2 mortar bar (aggregate <4mm) with the collective Pittsburg aggregate (15F) (G),(H). Entire dedolomitization of fine aggregate of argillaceous dolomitic limestone, forming Mg-silicate gel on dolomite rhombs and carbonate halo in the cement paste without expansion cracks.



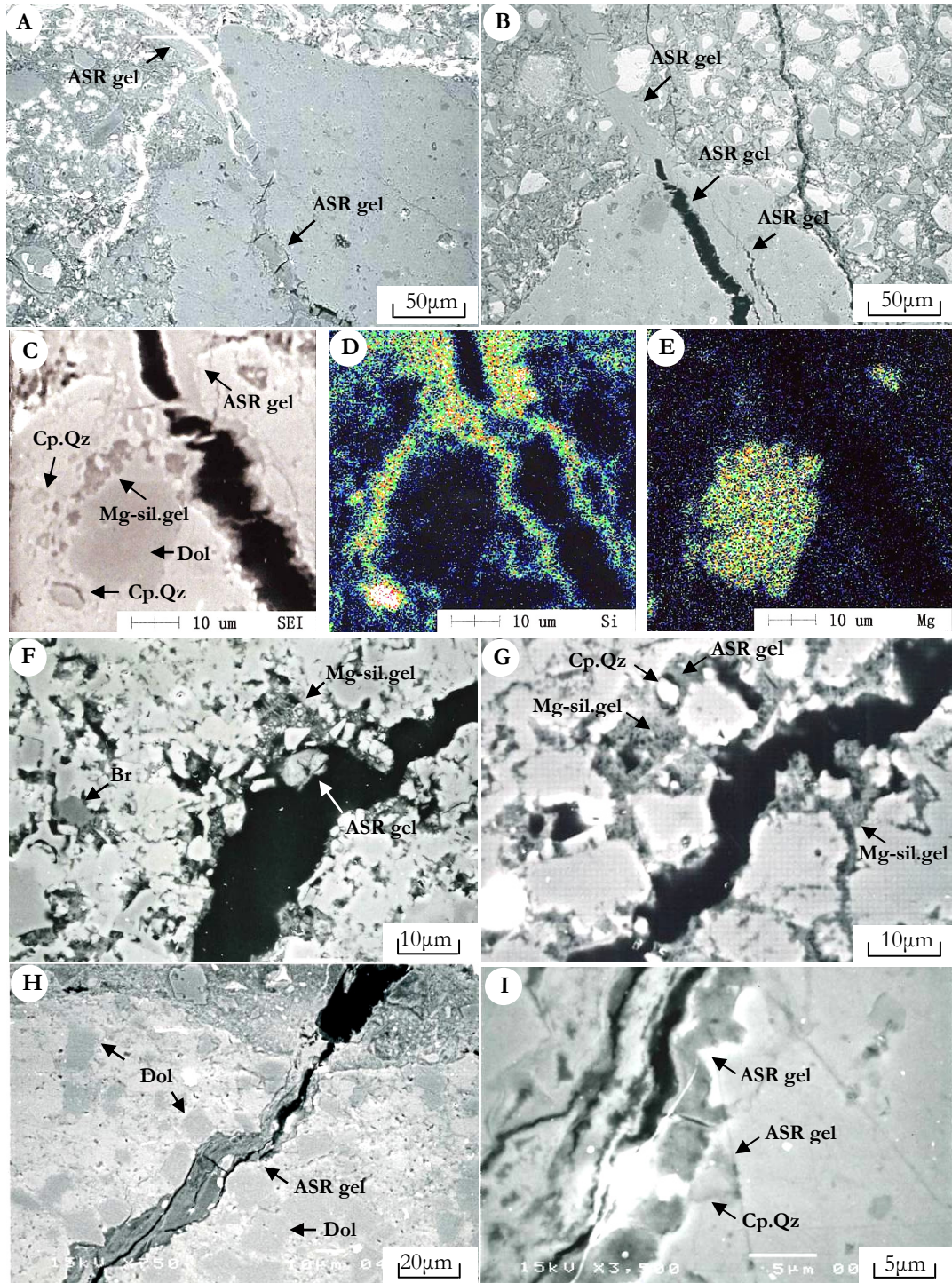


Figure 2: RILEM AAR-5 concrete microbars (aggregate 4-8mm) made with the Pittsburgh aggregate (most reactive horizon Pit-16, 1<sup>st</sup> lift, CANMET stockpile)(A)-(E)[5]: ASR gel filling wide crack formed through prolonged reaction (28 days) of argillaceous dolomitic limestone, with added NaOH (Na28) (A) or KOH (K28)(B)(C) to cement. Mapping of elements showing migration of ASR gel from crypto-crystalline quartz (D: Si image) into crack, and Mg-silicate gel (E: Mg image) on dolomite rhombs; Field deteriorated concretes in Ontario (F)-(I) [3][4]: Ballast wall of a bridge in Gananoque (built 1957) with ASR gel, spotted in the crack of argillaceous dolomitic limestone (F) and around cryptocrystalline quartz in dolomitic limestone (G). Dedolomitization along crack, forming brucite on dolomite rhombs distant from the crack, while Mg-silicate gel near the crack. Concrete curb in Cornwall (placed 1979) with cryptocrystalline quartz altering to crack-filling ASR gel in argillaceous dolomitic limestone (H),(I).

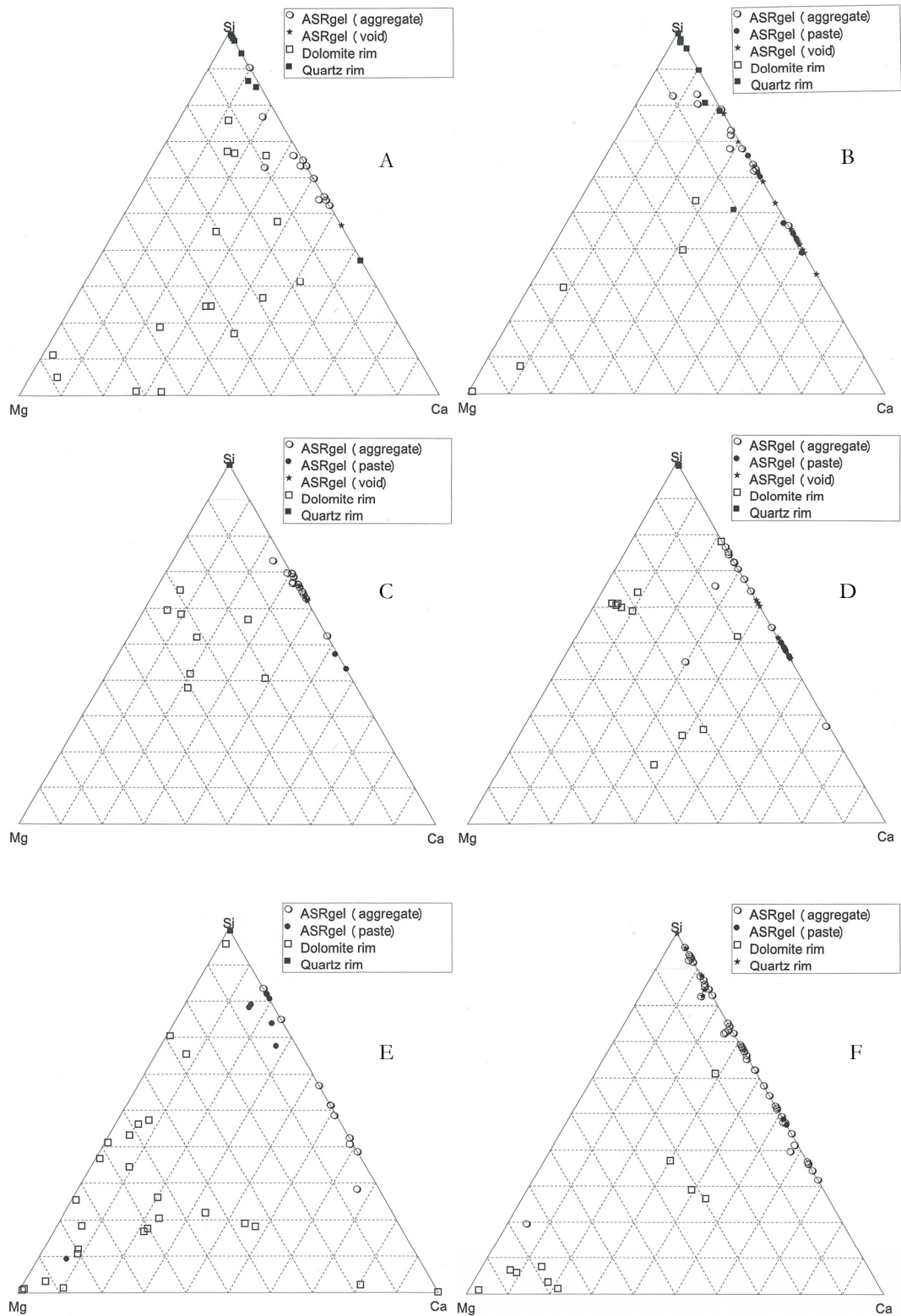


Figure 3: EPMA (EDS) analysis of reaction products in concretes. RILEM AAR-5 concrete microbar (A)(15C) and RILEM AAR-2 mortar bar (B)(15F), both with the Pittsburgh aggregate (collective, 1<sup>st</sup> lift, MTO stockpile); RILEM AAR-5 concrete microbar made with the most reactive layer in the Pittsburgh quarry (Pit-16, 1<sup>st</sup> lift, CANMET stockpile), with added NaOH (Na28)(C) or KOH (K28)(D) to cement and stored in a prolonged period (28 days); Field deteriorated concretes from the ballast wall of a bridge in Gananoque (E) and from the concrete curb in Cornwall (F), both in Ontario.

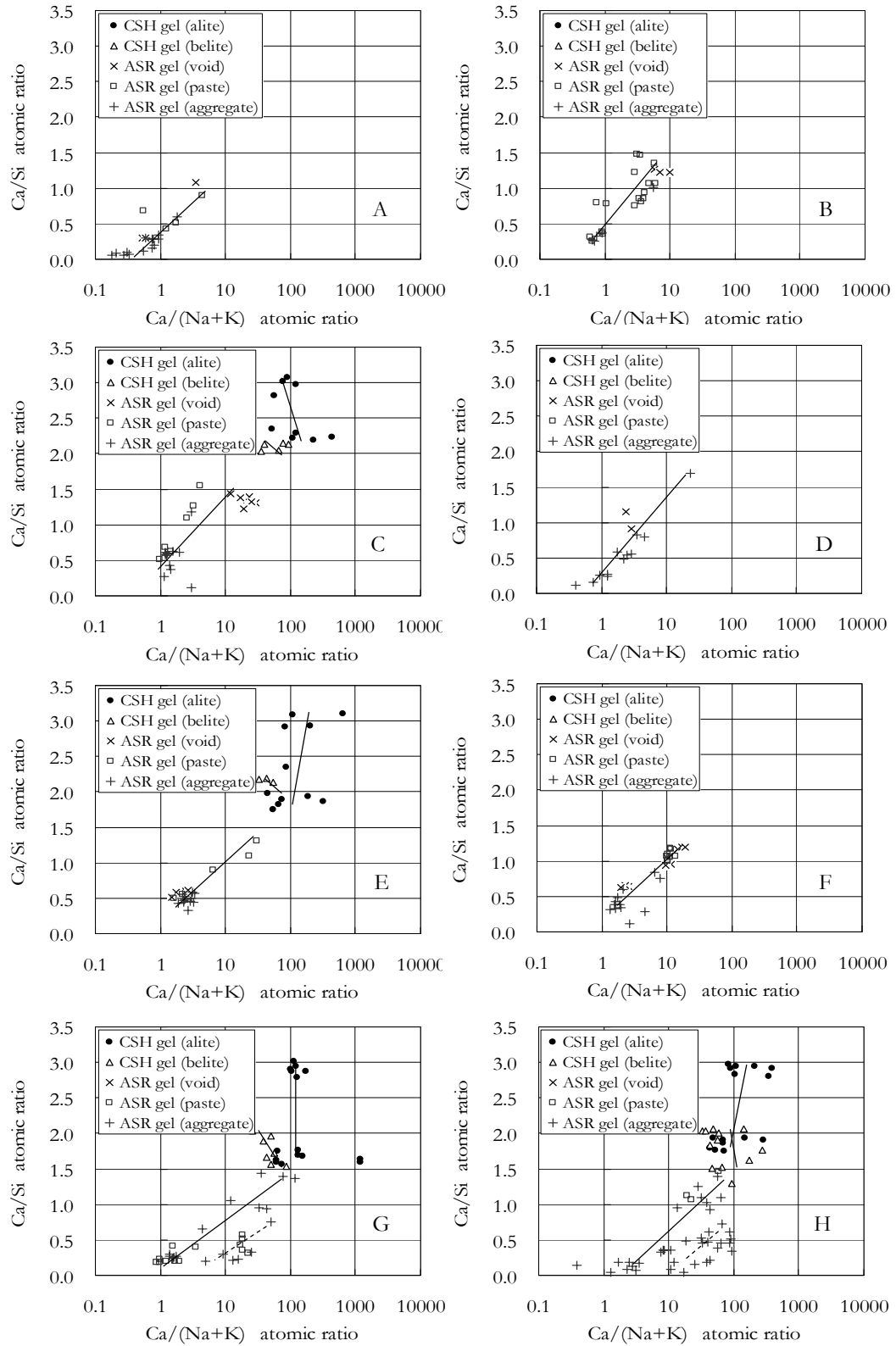


Figure 4: EPMA compositions of ASR gel. RILEM AAR-5 concrete microbars with Austrian dolomitic (9C)(A) and dolostone aggregates (10C)(B); RILEM AAR-2 mortar bar (15F)(C) and AAR-5 concrete microbar (15C)(D) with the Pittsburgh aggregate (collective, MTO stockpile); AAR-5 concrete microbars with the most reactive Pittsburgh aggregate (Pit-16, CANMET stockpile) stored in a prolonged period (Na28)(E), (K28)(F); Field deteriorated concretes from Gananoque (G) and Cornwall (H), Ontario.