



Comparison of the morphology of alkali–silica gel formed in limestones in concrete affected by the so-called alkali–carbonate reaction (ACR) and alkali–silica reaction (ASR)

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ABSTRACT

The morphology of alkali–silica gel formed in dolomitic limestone affected by the so-called alkali–carbonate reaction (ACR) is compared to that formed in a siliceous limestone affected by alkali–silica reaction (ASR). The particle of dolomitic limestone was extracted from the experimental sidewalk in Kingston, Ontario, Canada that was badly cracked due to ACR. The siliceous limestone particle was extracted from a core taken from a highway structure in Quebec, affected by ASR. Both cores exhibited marked reaction rims around limestone particles. The aggregate particles were polished and given a light gold coating in preparation for examination in a scanning electron microscope. The gel in the ACR aggregate formed stringers between the calcite crystals in the matrix of the rock, whereas gel in ASR concrete formed a thick layer on top of the calcite crystals, that are of the same size as in the ACR aggregate.

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1. Introduction

An expansive reaction in concrete made with dolomitic limestones that appeared to be different from the classical alkali–silica reaction (ASR) was first reported by Swenson in 1957 [1] and 1960 [2]. The term alkali–carbonate rock reaction was first used by Swenson and Gillott in 1964 [3]. A mechanism for the alkali–carbonate reaction (ACR) was proposed by Gillott and Swenson in 1969 [4]. Their conclusion was that “moisture uptake by previously un-wetted clay minerals is responsible for the expansion in alkali of certain argillaceous dolomitic limestones”. This explanation of the mechanism was never very convincing particularly as the main clay mineral in the rock is non-expanding illite. In 1986 Tetsuya Katayama collected a sample of concrete affected by ACR in Cornwall, Ontario, Canada. He observed alkali–silica gel in this concrete suggesting that ASR might have a role in the so-called ACR reaction [5]. Additional research by Katayama appeared to confirm that ACR was a special case of ASR, [6–9]. This hypothesis was supported by research by Grattan-Bellew [10].

In the results of the research reported here the morphology of alkali–silica gel formed in a dolomitic limestone particle extracted from concrete affected by ACR, from the experimental sidewalk in Kingston, Ontario, Canada, was compared with gel from a siliceous limestone particle from a sample of concrete, affected by ASR, from Quebec, Grattan-Bellew & Rogers [11], and Fournier et al. [12].

2. Materials used

The concrete core from which the dolomitic limestone aggregate was extracted was taken from a section of a 22 year old experimental sidewalk made with low alkali cement in 1985 [10]. The aggregate used in the concrete was taken from a stockpile derived from the top lift of the Pittsburgh quarry, Kingston, Ontario, Canada. The section of the concrete sidewalk had expanded considerably and was severely cracked. The broken surface of the core fluoresced when treated with uranyl acetate indicating that it was coated with silica gel due to some ASR having occurred [10]. A sample of untreated rock was taken from the most expansive layer of the Pittsburgh quarry (Sample #78–16) so that its microstructure could be compared to that of the dolomitic limestone from the concrete. For comparison purposes, a piece of siliceous limestone aggregate extracted from a core of a 30 year old concrete structure, affected by ASR, built with Quebec siliceous limestone was also examined. Both the Quebec limestone and the dolomitic limestone particles extracted from the cores exhibited marked reaction rims.

3. Methodology

Particles of aggregate with a well-defined reaction rims were extracted from both concrete cores. These particles and a small piece of the untreated rock were polished and sawn to a size suitable for examination in the SEM. The grinding and polishing of the pieces of aggregate resulted in the generation of random surfaces from the interior of the particles. The samples were etched with very dilute HCl (2%)

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for about 2 s and then washed to remove any remaining acid. The samples were dried and given a light gold coating to prevent charging in the SEM. The samples were examined in an Hitachi S-4800 SEM equipped with an EDX detector for semi-quantitative elemental analysis. The operating conditions for the SEM photographs were 2 kV and 5 μ A, those for the EDX spectra and X-ray maps were 20 kV and 10 μ A.

4. Results

4.1. Etched sample of raw dolomitic limestone rock sample, (Pittsburgh 78–16)

The calcite crystals mostly appear to have an irregular shape and there are gaps between the crystals, Fig. 1a. It is uncertain if the gaps occur naturally or if they were widened due to the acid etching. Due to the volume excited by the electron beam being larger than the calcite crystals, the EDX spectrum, Fig. 1b is composed mainly of calcium but also shows a small amount of silica, aluminum and magnesium, that may originate in the clay minerals and chert present in the rock [10].

4.2. Etched dolomitic limestone particle extracted from a concrete core, made with low alkali cement, taken from the experimental sidewalk in Kingston

The appearance of the etched dolomitic limestone from the core is shown in Fig. 2a. As expected, the calcite crystals look similar to those in the raw rock sample shown in Fig. 1a except for stringers of material between the calcite crystals that appear white in the photograph Fig. 2b. The similarity of the size and shape of the calcite crystals in the reacted dolomitic limestone to those in the raw rock indicate that this is primary calcite and not that derived from dedolomitization. The calcite derived from dedolomitization might be expected to have a smaller crystal size. Some of the dolomite crystals have a rhombic shape, but others are irregular. The area outlined at the bottom left of Fig. 2a is shown enlarged in Fig. 2b which shows stringy white material filling the space between the calcite crystals. An enlarged view of the white gel (G) in Fig. 2b is shown in Fig. 2c. The EDX spectrum of the white gel (G) is shown in Fig. 2d. It is evident that silica is the main component in Fig. 2d. The volume of material excited by the electron beam is greater than the width of the siliceous particle and hence elements of some of the underlying calcite, dolomite and clay minerals are also detected. Although the EDX spectrum indicates that clay minerals are present, they were not directly observed in this investigation. Earlier research showed that illite was the main clay mineral in the rock [4]. As quartz does not occur in a stringy format the white material shown in Fig. 2b and c must be alkali silica gel which has squeezed between the calcite crystals. The EDX analysis of the silica gel is broadly similar to those reported by Katayama [8]. A calcite particle at a higher magnification is

shown in Fig. 2e. An elemental map of calcium from the same area is shown in Fig. 2f. The dark area surrounding the calcium grain is occupied by silica gel. Due to the presence of small amounts of gel on the calcite crystals a satisfactory EDX map of silica could not be obtained. The source of the silica that generated the silica gel could not be determined from this investigation, but Gillott in an unpublished internal report from the National Research Council of Canada in 1961, observed and determined the chert content of the rock from the Pittsburgh quarry. The chert content of the rock was also charted by Grattan-Bellew [10]. Non-reactive detrital quartz grains also occur in this rock, but none were observed in the small sample examined.

4.3. Siliceous limestone particle extracted from concrete affected by ASR

The morphology of the alkali–silica gel in this limestone is quite different from that in the dolomitic limestone. It appears as a massive layer covering part of the surface of the limestone which is composed mainly of small irregularly shaped grains of calcite with a size range of ~1 to 3 μ m, Fig. 3a. The calcite matrix of this rock is broadly similar to that of the Kingston ACR aggregate except for the absence of dolomite grains. Elemental maps of calcium and silica of the area shown in Fig. 3a are shown in Fig. 3b and c.

5. Discussion

5.1. Alkali–silica gel

It is evident that the cherty silica present in the dolomitic limestone has reacted with alkalis from the Portland cement to form an alkali–silica gel. The gel absorbed water and expanded squeezing between the calcite crystals. It is easy to visualize how the gel has forced the calcite crystals apart thus causing the aggregate particles and hence the concrete to expand. In contrast, the gel formed in the Quebec limestone sample appears to be more abundant and coats much of the surface of the interior of the aggregate particle, Fig. 3, where it also caused the aggregate particle to expand.

5.2. Lack of observation of gel in thin sections

The reason why the gel in the so-called ACR concrete was not identified in standard 25 to 30 μ m thin sections is that due to the small size of the calcite crystals (~2 μ m) that comprise the matrix of the rock, a petrographer is viewing the thin section through 12 to 15 layers of calcite which obscures the view. A similar observation was made by Katayama [8].

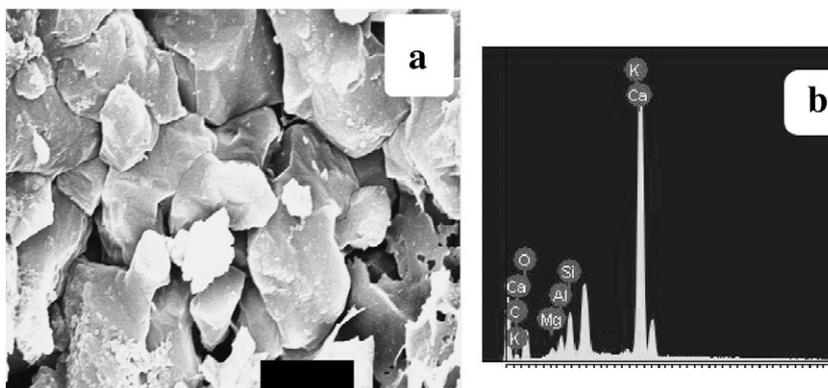


Fig. 1. a) SEM image of calcite matrix in raw dolomitic limestone. Scale bar 2 μ m. b). EDX spectrum of calcite.

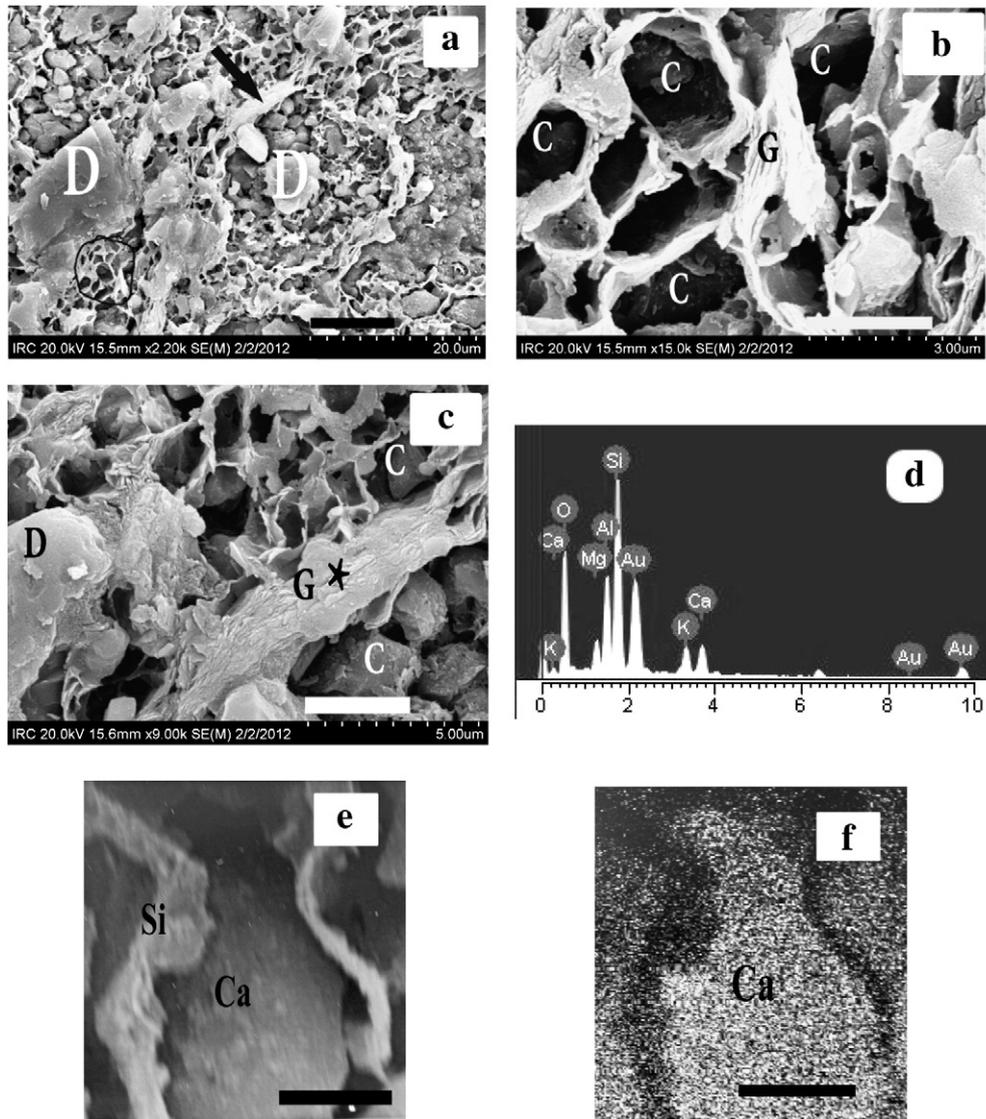


Fig. 2. a) Dolomitic limestone showing isolated dolomite crystals (D) in a matrix of calcite. Scale bar 10 μ m. b) Enlarged view of area outlined in black at lower left in subpanel a showing calcite crystals surrounded by gel. Scale bar 2 μ m. c) Enlarged view of gel (G). Scale bar 2 μ m. The star indicates the location of the EDX spectrum. d) EDX spectrum of the gel. e). SEM photograph of a calcite particle (Ca) surrounded by silica gel (Si). f). X-ray map of calcium from the area shown in subpanel e. Scale bars are 2 μ m.

6. Conclusions

- Chert in the ACR dolomitic limestone has reacted with the alkalis from the Portland cement to form alkali–silica gel.
- The gel absorbed water and swelled forcing its way between the calcite crystals that make up to matrix of the rock.
- The expanding gel between the calcite crystals caused the matrix of the dolomitic limestone and hence the concrete to expand.
- In contrast with the ACR dolomitic limestone, the gel formed in the siliceous limestone appears more massive coating sections in the interior of the limestone particles where it also causes expansion of the particle and hence the concrete.

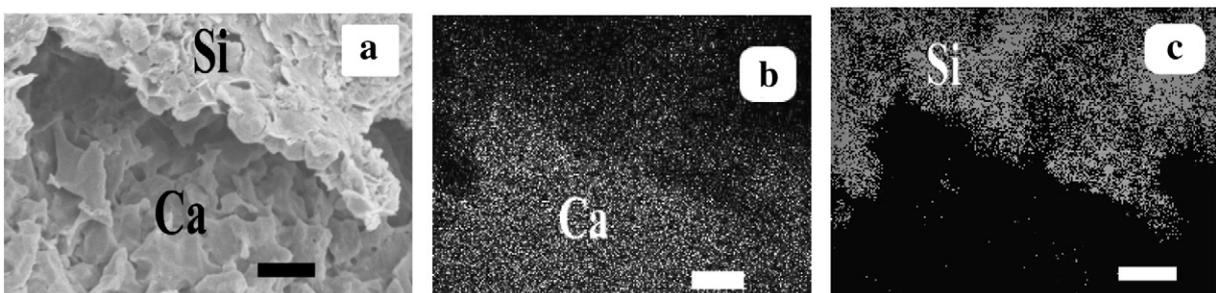


Fig. 3. a) Secondary electron image showing a layer of gel (S) overlying the calcite matrix (C). b) EDX map of calcium, (Ca). c) EDX map of silicon (Si). Scale bars 2 μ m.

References

- [1] E.G. Swenson, A Canadian reactive aggregate undetected by ASTM tests, *ASTM Bulletin* No. 226, 1957, pp. 48–51.
- [2] E.G. Swenson, R.F. Legget, Kingston study of cement–aggregate reaction, *Can. Consult. Eng.* 2 (8) (1960) 38–46.
- [3] E.G. Swenson, J.E. Gillott, Alkali–carbonate rock reaction, *Washington Symp. Hwy. Res. Bd.*, no 45, 1964, pp. 21–40.
- [4] J.E. Gillott, E.G. Swenson, Mechanism of the alkali–carbonate rock reaction, *J. Eng. Geol.* 2 (1969) 7–23.
- [5] T. Katayama, A critical review of carbonate rock reactions – is their reactivity useful or harmful? *Proc. 9th International Conference of Alkali–Aggregate Reactions in Concrete* London, July 1992, pp. 508–518.
- [6] T. Katayama, Modern Petrography of Carbonate Aggregates in Concrete – Diagnosis of So-Called Alkali–Carbonate Reaction and Alkali–Silica Reaction, in: B. Fournier (editor) in *Professor Marc-André Bérubé Symposium, on alkali–aggregate reactivity in concrete. 8th CANMET/ACI International Conference on Recent Advances in Concrete Technology*, Montreal, Canada. (May–June 2006), 1–22. (Oral presentation, unpublished).
- [7] T. Katayama, H. Sommer, Further investigation of the mechanisms of so-called alkali–carbonate reaction based on modern petrographic techniques, in: M.A.T.M. Broekmans, B.J. Wigum (Eds.), *Proc. 13th International Conference of Alkali–Aggregate Reactions in Concrete*, Trondheim, Norway, June 2008, (Published as a book ISBN 978-81-128-4).
- [8] T. Katayama, The so-called alkali–carbonate reaction (ACR) – its mineralogical and geochemical details, with special reference to ASR, *Cem. Concr. Res.* 40 (2010) 643–675.
- [9] Tetsuya Katayama, Patrick E. Grattan-Bellew, Petrography of the Kingston experimental sidewalk at age 22 years – ASR as the cause of deleteriously expansive, so-called alkali–carbonate reaction, *Proc. 14th International Conference on Alkali–Aggregate Reactions in Concrete*. Austin TX May 20–25, 2012, 2012.
- [10] P.E. Grattan-Bellew, et al., Is alkali–carbonate reaction just a variant of alkali–silica reaction ACR = ASR? *Cem. Concr. Res.* 40 (2010) 556–562.
- [11] P.E. Grattan-Bellew, C.A. Rogers, Expansion due to alkali–carbonate reaction: laboratory prognosis versus field experience, in: M.A. Bérubé, B. Fournier, B. Durand (Eds.), *Proc. 11th International Conference on Alkali–aggregate Reaction*, 2000, pp. 41–50, (Quebec City, June 2000).
- [12] B. Fournier, M.-A. Bérubé, D. Vezina, Investigation of the alkali-reactivity potential of limestone aggregates from the Quebec City Area (Canada). *Concrete alkali–aggregate reactions*, in: P.E. Grattan-Bellew (Ed.), *Noyes Publications Park Ridge, New Jersey, U.S.A.*, 1986, pp. 23–29.