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Is alkali–carbonate reaction just a variant of alkali–silica reaction ACR = ASR?

P.E. Grattan-Bellew [a,*], L.D. Mitchell [a], James Margeson [a], Deng Min [b]

[a] *Institute for Research in Construction, NRC, Ottawa, ON, Canada K1A0R6*
[b] *College of Materials Science & Engineering, Nanjing University of Technology, Jiangsu, 210009, China*

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ABSTRACT

The mechanism of the alkali–carbonate reaction (ACR) has been recognized as being different from that of the more common alkali–silica reaction (ASR). However, the identification of alkali–silica gel in ACR concrete from Cornwall, Ontario, Canada by Katayama, in 1992 raised the possibility that ASR was at least playing a role in the ACR reaction. The acid insoluble residues of the ACR aggregate from Kingston, along with two other aggregates were analyzed to determine what might be contributing to the reaction. The acid insoluble residue of the ACR Kingston rock contains 96% quartz of high solubility in NaOH. Good correlation was found between the amount of quartz and expansion of concrete prisms indicating that the expansion was due mainly to an alkali–silica reaction. This conclusion is supported by observations, in 2008, by Katayama of gel in thin sections of concrete made with the Kingston aggregate. It is concluded that ACR = ASR.

1. Introduction

1.1. Alkali–carbonate reaction

The term alkali–carbonate reaction (ACR) is somewhat ambiguous as it would appear to be applicable to reactions between the alkalis in Portland cement and any carbonate aggregate. However, since the early 1960s the term ACR has been reserved for reaction between alkalis and certain argillaceous dolomitic limestones. Dedolomitization was thought to be the underlying mechanism leading to expansion, without any reactive silica involvement, Hadley [1] and Swenson and Gillott [2]. In 1992, Katayama [3] reported gels in a sample of concrete from Cornwall Ontario, Canada that was made with alkali–carbonate reactive dolomitic limestone, similar to that from the well documented rock from the Pittsburgh quarry in Kingston Ontario. Katayama suggested that alkali–silica reaction (ASR) had a role in the alkali–carbonate reaction (ACR). At the time, our Canadian colleagues thought that the result obtained by Katayama was anomalous and that ACR was a separate type of reaction. However, in 2002 the first author observed gel filling a crack in dolomitic limestone from Kingston in a RILEM concrete microbar, Grattan-Bellew et al. [4]. In this case, the gel had to have formed in the dolomitic limestone particle as there was no other aggregate in the microbar. Katayama [5] extracted cryptocrystalline quartz from the Kingston ACR aggregate. In 2006 and 2008 Katayama [5,6] also reported gels in concrete microbars made with ACR aggregate from the Pittsburgh quarry. Evidence was mounting that ASR was involved in, if not the cause of, the ACR expansion and deterioration of concrete. Wu Ding-yan and Fang Kun-Hy concluded that "In some non-siliceous carbonate rocks even with low contents of SiO_2, the alkali–silica reaction can still happen" [7]. Tang Mingshu and Deng Min noted that in carbonate rocks containing microcrystalline or cryptocrystalline quartz it is difficult to confirm that the deterioration is caused by ASR or ACR [8].

In 2007 the first author took some cores from experimental sidewalks in Kingston, made with the ACR aggregate, Grattan-Bellew and Rogers [9]. One core broke during drilling and the broken surface appeared to be coated with gel. After coating with uranyl acetate the surface fluoresced brightly in UV light confirming the presence of ASR gel (Fig. 1A). In addition, examination of a polished surface of the core showed gel filling a crack in a particle of dolomitic limestone (Fig. 1B). There was now little doubt that ASR was at least a contributing factor in the so-called ACR reaction. If the evidence noted above for a role for ASR in the so-called ACR is correct, then there has to be some reactive silica in the dolomitic limestones that are subject to the so-called ACR. Accordingly, it was decided to examine the mineralogical composition of the acid insoluble residue of the most reactive horizon (#78-16) of the Pittsburgh quarry in Kingston, Ontario and compare it to that of the Spratt Canadian ASR reference aggregate and a Chinese ACR dolomitic limestone. The purpose of the investigation was to determine if the expansion of so-called ACR aggregates in concrete could be attributed to an alkali–silica reaction, and to investigate the correlation between the amount of crypto-crystalline, or micro-crystalline, quartz in the insoluble residues and the observed expansion of concrete prisms. Due to the great variability in the petrology and reactivity of the Pittsburgh quarry top lift horizons, the results of this investigation apply only to one of the top horizons, Pit-16 in Fig. 5 of Du-You et al. [10].

* Corresponding author.
E-mail address: p.grattanbellew@sympatico.ca (P.E. Grattan-Bellew).

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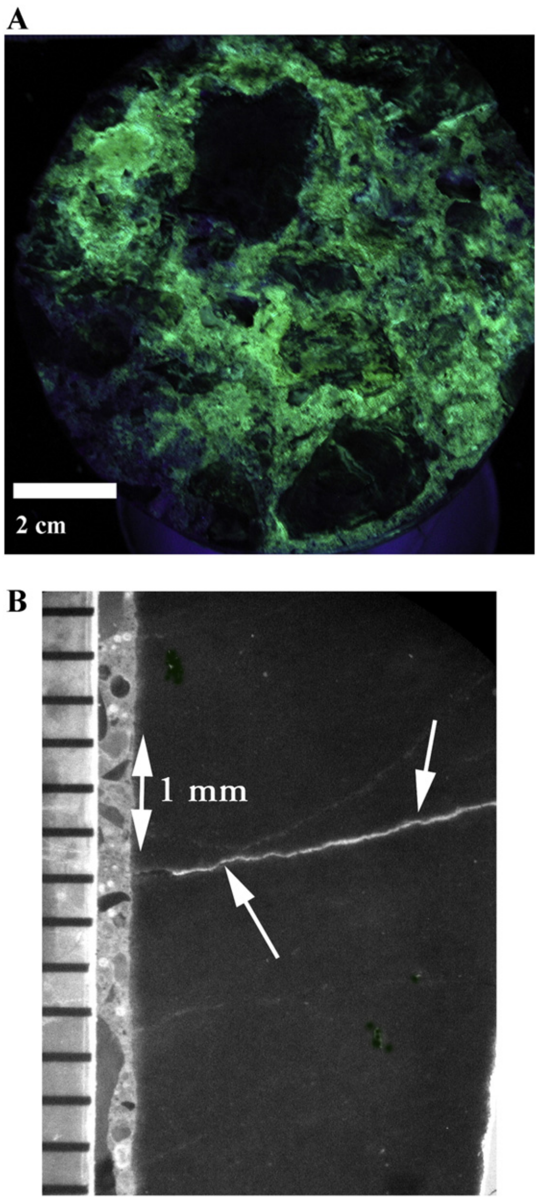

Fig. 1. A: Fractured surface of core from Kingston Sidewalk of coated with uranyl acetate and photographed in ultra-violet light showing fluorescence of the gel. Scale divisions in mm. B: Gel filling a crack in dolomitic limestone particle. Scale divisions in 0.5 mm.

2. Methodology

Four hundred grams of each rock were pulverized in a plate mill followed by 30 s in a shatter-box. The resulting material was sieved into two fractions: one passing a 300 µm sieve and retained on a 150 µm sieve; the second passing a 150 µm sieve. The separate fractions were stirred in dilute, 10% by volume, HCl until all the calcite was removed. The acid was then heated to 60 °C and the stirring continued; small amounts of concentrated HCl were added periodically until all the dolomite was dissolved, (effervescence stopped). The research was concentrated on the −150 + 300 µm fraction of the insoluble residues.

The mineralogical compositions of the samples were determined by X-ray diffraction (XRD). A Scintag XDS 2000 diffractometer configured with Bragg Brentano optics, Cu K alpha radiation and a graphite monochromator was used at an operating voltage of 45 kV and 35 mA. The samples for XRD were prepared by grinding in acetone in an agate pestle and mortar. The samples were mounted on low background holder. Quantitative analysis was undertaken using TOPAS a commercial Rietveld software from Bruker.

Microscopic examination was undertaken with a Hitachi S4800 field emission gun scanning electron microscope (FEG-SEM) equipped with an Oxford INCARx-Sight energy dispersive detector (EDS). The SEM micrographs were taken at an accelerating voltage of 1.2 kV. The EDS spectra were obtained with an accelerating voltage of 20 kV and 2 mA.

The SEM-EDS was used to augment the mineralogical information obtained by XRD rather than for complete chemical analysis.

The crystallinity index Ic of the quartz particles, which were not separated from the acid insoluble residues, was estimated from the relative intensities of the 5 peaks occurring in the diffractograms of quartz between 67 and 69° 2θ [11]. A reference clear euhedral quartz crystal from Brazil was crushed and used as a control for the Ic determinations. The percentages of quartz in the insoluble residues of the 3 aggregates were determined by Rietveld analysis. TOPAS, a commercial package from Bruker AXS, was used for the Rietveld analysis. It employs an instrument function approach (IFA) to Rietveld as opposed to a pseudo voigt.

The amount of silica dissolved, from the acid insoluble residues of the 3 aggregates, was determined by a modified version of The Standard Test Method for Potential Reactivity of Aggregates (Chemical Method), ASTM C 289. Only 15 g of each aggregate was used instead of the specified 25 g and 15 ml of NaOH was used in place of 25 ml. Due to the very viscous nature of the reaction product the filtrate was separated by centrifugation.

The amount of silica dissolved in the filtrate, from ASTM C 289, was measured by X-ray fluorescence (XRF) in a commercial laboratory as the in-house machine was out of commission.

The expansions of concrete prisms made with the three aggregates in the Canadian Concrete Prism Test CSA A23.2-14A were taken from earlier work [9].

The particle size distribution of the insoluble residues was measured using a Malvern Instruments Mastersizer 2000S particle analyzer coupled to a wet cell.

The effect of particle size of quartz on the amount of dissolved silica in ASTM C 289 was determined by crushing and sieving euhedral clear quartz crystal from Brazil. After sizing, the lattice strain due to pulverizing was reduced by annealing at 600 °C. Removal of the surface dust was attempted by washing briefly in dilute HF.

3. Results

The particle size distribution of the insoluble residues of the three aggregates is shown in Fig. 2. The particles in all three samples range in size from about 0.4 to 100 µm with a mean value of ~10 µm.

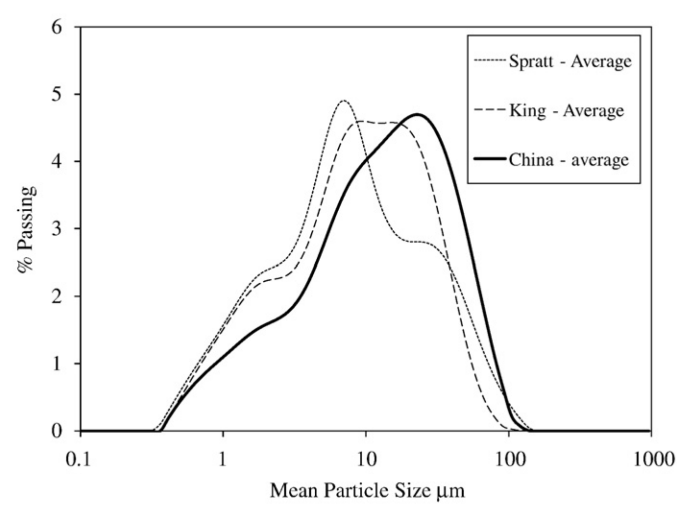

Fig. 2. Particle size distribution of acid insoluble residues of Kingston, Spratt and Chinese limestones.

Table 1
The amount of quartz, the index of crystallinity, the amount of dissolved silica, the insoluble residue, the mean particle size of the acid insoluble residues of the three aggregates and the expansion of concrete prisms containing the three aggregates.

	Kingston	Spratt	Chinese
Quartz vol.% determined by XRD	96	39	12
Crystallinity index Ic of quartz	4.5	9.3	7.4
Dissolved silica Sc mM/l	750	30	180
Insoluble residue as wt.% of rock	11	8	44
Mean particle size as determined by particle size analyzer in µm	10	10	10
Expansion % in concrete prism	0.616	0.275	0.064

Note: The mean particle size, 10 µm is larger than the size of the particles, 1 µm, observed in the SEM. This is probably due to coagulation of the particles in the analyzer.

The amount of quartz in the −300 + 150 µm fractions of acid insoluble residues of the three aggregates and the amount of silica dissolved in the ASTM C 289 test are shown in Table 1. The XRD diffractograms of the three limestones are shown in Fig. 3. The 2θ range 66.8 to 69.8 from the diffractograms was used to determine the indices of crystallinity Ics of the three aggregates and a reference quartz. The Ics are shown in Fig. 4. The amounts of dissolved silica, measured by ASTM C 289, in the insoluble residues of the three aggregates are compared with the crystallinity indices in Fig. 5. Good correlation was found between the amounts of quartz in the insoluble residues and the expansions of concrete prisms, stored at 38 °C and ~100% humidity, made with the whole rocks (Fig. 6). The minerals identified in the Rietveld analysis of the Kingston limestone are shown in Table 2.

4. Discussion

4.1. Kingston dolomitic limestone

The Kingston dolomitic limestone has both the highest content of dissolved silica in the acid insoluble residue and the highest amount of quartz 96 wt.% as determined by XRD. The remaining 4 wt.% is mostly composed of clay minerals. In addition, the quartz in the Kingston limestone is the most reactive.

It may appear surprising that the Spratt, a moderately reactive ASR limestone, has a lower amount of quartz than the Kingston limestone. The solubility of the quartz in the insoluble residue, as measured in ASTM C 289, is much lower than that in Kingston ACR aggregate. (It should be noted that some large quartz grains in the Spratt insoluble residue may have resulted in a large error in the amount of quartz determined by Rietveld analysis). However, once the reactivity of the Kingston dolomitic limestone is recognized as being due to an alkali–silica reaction the expansivities of the three aggregates are proportional to the amounts of quartz in the rocks (Fig. 6). A SEM photograph showing some typical quartz grains in the acid insoluble residue of the Kingston aggregate is shown in Fig. 7. The mean particle size in the SEM micrographs appears to be about 1 µm or less even though the laser particle size measurement showed the mean size to be ~10 µm. The differences are most likely due to particle coagulation. It is well known that silica will coagulate with varying pH. In addition multivalent metal ions such as calcium or magnesium drastically enhance the effects of coagulant stability due to their higher charge density. The solubility of quartz in NaOH increases quadratically, as the particle size of quartz decreased below about 100 µm (Fig. 8).

Occasional small quartz grains with crystal faces were observed in the micrographs of the insoluble residue from Kingston. A very small amount of clay (tentatively identified as illite) was also observed. Under a petrographic microscope most of the quartz grains are too small to be resolved. However a few larger grains were found to consist of clusters of micro-crystalline quartz (chert) (Fig. 9). The coincidence between the quartz content in the insoluble residues and the expansions of concrete prisms made with the whole rock aggregates is linear and surprising good. In addition to having the most quartz in the insoluble residue, the quartz in the Kingston aggregate also has the lowest crystallinity (Fig. 4) and hence the greatest reactivity.

The low crystallinity of the quartz in the Kingston dolomitic limestone, Ic 4.5, also undoubtedly increases the solubility of the quartz compared to that of the Spratt and Chinese limestones with Ics of 9.3 and 7.4 respectively. (The index of crystallinity of a reference single crystal of clear euhedral Brazilian quartz, IC 10 was measured at the same time as the other samples.) The problem with the index of crystallinity of quartz as measured by XRD is that it is an empirical method with no obvious relation to any crystallographic parameters. For a silica particle to be reactive the emphasis should probably be placed on the strain rather than the crystallite size. This hypothesis is supported by Broekmans who found that there was no straight forward correlation between the index of crystallinity Ic of quartz and expansion in accelerated tests of a suite cherts and mylonites [12]. The correlation between the amount of dissolved silica in ASTM C 289 and the crystallinity indices Ics of the acid insoluble residues of the Kingston, Spratt and Chinese limestones is therefore rather surprising. It suggests that the crystallite size of the silica in all three reactive rocks examined in this study is similar and that the differences in reactivity are due to the strain, or vice versa. Further study is required for a conclusive answer.

4.2. Spratt siliceous limestone

The insoluble residue of the Spratt limestone, as determined by XRD, consists of quartz 40 wt.% and clay minerals 54 wt.% (mostly

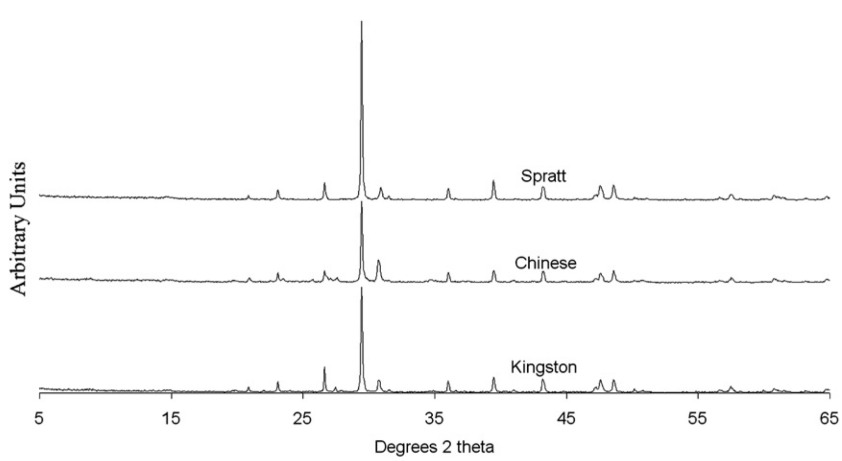

Fig. 3. X-ray diffractograms of the three limestones.

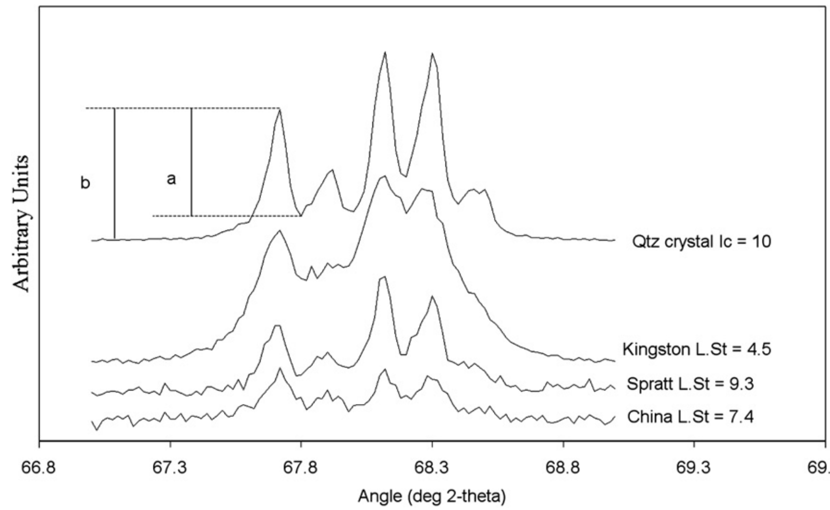

Fig. 4. X-ray diffractograms used in the determination of the crystallinity indices (Ics). $Ic = 10a/b*1.76$.

illite) and 6 wt.% albite feldspar. The appearance and texture of the insoluble residue within the Spratt limestone is shown in Fig. 10 along with the corresponding EDS spectrum. The crystallinity index Ic of 9.3 of the quartz in the acid insoluble residue of the Spratt (ASR) limestone appears to indicate that it is quite well crystalline. This is borne out by the low amount of dissolved silica 35 mM/L determined in ASTM C 289. This is a surprising result as the Spratt limestone is alkali–silica reactive and causes expansion and cracking of concrete, Rogers and Hooton [13]. A possible explanation for this apparent discrepancy may be that the XRD Rietveld method only measures crystalline quartz and if there is any amorphous silica (opal) it would not be detected. However, if there were a significant amount of amorphous silica (opal) in the aggregate, the amount of dissolved silica would be expected to be higher than the 35 mM/L that was measured. However it is conceivable that the acid digestion may have preferentially dissolved any amorphous silica, skewing the 35 mM/L result. Further X-ray work to determine the amorphous content of the rock would provide more evidence on this point. Experience has shown that the Spratt limestone is moderately reactive and generates a significant amount of silica gel in concrete made from it indicating that there is sufficient reactive silica in the aggregate to sustain ASR.

4.3. Chinese limestone

The insoluble residue of the Chinese dolomitic limestone, as determined by XRD, contains 12 wt.% quartz, 48 wt.% albite feldspar, 28 wt.% illite and 12 wt.% other clay minerals. A typical view showing the platy clay particles is shown in Fig. 11 along with the corresponding EDX spectrum.

4.4. General

The Kingston limestone sample under investigation contains 11.4% by weight acid insoluble residue. The insoluble residue consists of 96% quartz most of it having a very small particle size. Assuming that 90% of this quartz is potentially alkali–silica reactive, it comprises 10% of the total rock. Recalling that less than 5% of some chert and opal in an aggregate is sufficient to cause deterioration in concrete, 10% of reactive quartz should be more than sufficient to cause the aggregate particles to expand in Portland cement concrete (In the current Dutch Guideline CUR-Recommendation 89. (2008) a limit of 2 vol.% is placed on opal porous flintstone and chalcedony.) [14].

Rock cylinders of the Kingston aggregate, containing 10% potentially reactive quartz, immersed in alkaline hydroxide solution expand significantly. This is presumably due to alkali–silica reaction. Evidence for this presumption is provided by copious amounts of precipitated

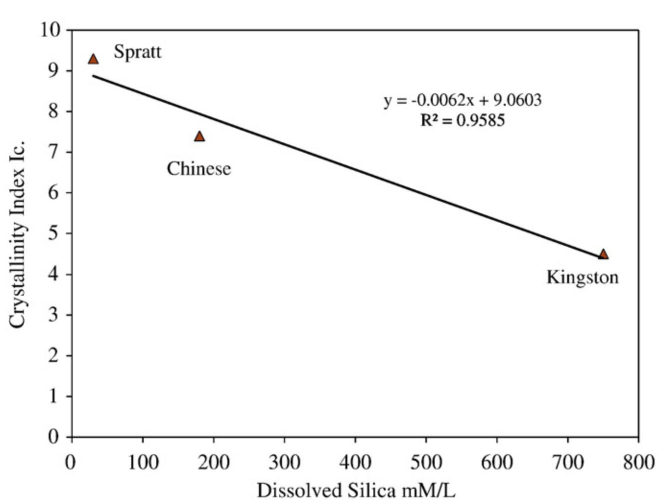

Fig. 5. Plot of dissolved silica (Sc) versus crystallinity indices of the acid insoluble residues of the three limestones.

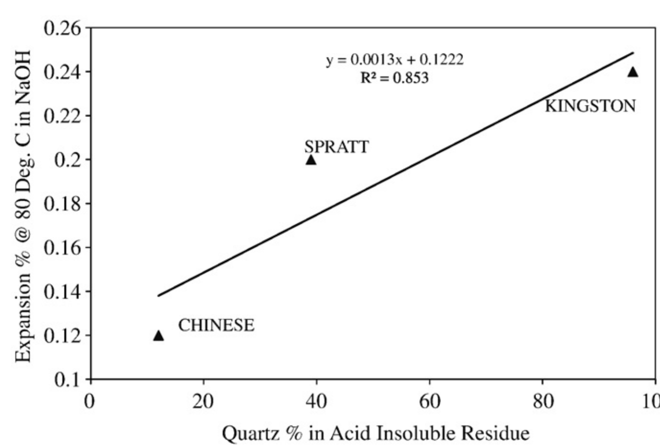

Fig. 6. Correlation between the quartz content of insoluble residues of the three limestones and the expansion of concrete prisms made with them.

Table 2
Modal mineral contents in the acid-insoluble residues from ACR carbonate rocks.

Mineral	LLD_{XRD} wt.%	ICDD card file number	Kingston dolostone	Spratt limestone	Chinese dolostone
Quartz		5–490	95	39	12
K-feldspar		31–966	n.d.	n.d.	n.d.
Albite		9–457	n.d.	n.d.	n.d.
Muscovite		6–263	n.d.	n.d.	n.d.
Kaolinite		29–1490	n.d.	n.d.	n.d.

n.d. — not determined.

gel observed at the surface of the prism. EPMA analysis of the gel showed that it consists of a calcium magnesium silicate and some brucite. The composition of the gel is similar to that reported by Katayama [5].

Concrete made with the Kingston aggregate shows massive cracking, expansion and deterioration, hence large amounts of gel would be expected, filling cracks in the concrete. However, comparison of polished surfaces of concrete made with Kingston and Spratt ASR aggregates shows that the Kingston concrete usually exhibits much less gel. Katayama explained that the apparent low gel content observed at low magnification was due to the inadequacy of the method in observing the gel [5].

The results shown in Fig. 8 indicate that the solubility of pulverized quartz in alkaline solution increases quadratically at particle sizes of less than ~100 µm. Accordingly, the solubility of quartz, with a mean particle size of 10 µm, in the insoluble residues of the three aggregates, might be expected to be about the same. However, as shown in Table 1, this is not the case as the solubility of the quartz from the Kingston aggregate is vastly greater than that of either the Spratt or Chinese insoluble residues. This discrepancy in solubility could again be attributed to the differing levels of crystallographic strain, as discussed earlier.

The solubility of acid insoluble residues of the three aggregates is proportional to the indices of crystallinity (see Fig. 5) indicating perhaps, that strain (perhaps in the form of defects) in the crystal lattices accounts for the discrepancies in the solubility in alkaline solution. It would also appear that the apparent quadratical increase in solubility with decreasing particle size below 100 µm of pulverized quartz shown in Fig. 8 may be due to lattice defects and surface dust despite attempts at annealing and rinsing in dilute HF rather than to the increased surface area.

There are several unsolved questions relating to ACR in concrete in addition to the small amount of gel that is observed: Why does the Kingston aggregate cause less expansion in mortar bars than in concrete prisms? Why does replacement of 50% of OPC by ground granulated blast furnace slag (GGBFS) not prevent expansion in concrete made with ACR aggregate and why do lithium salts not minimize or prevent expansion when they do in concrete containing ASR aggregate?

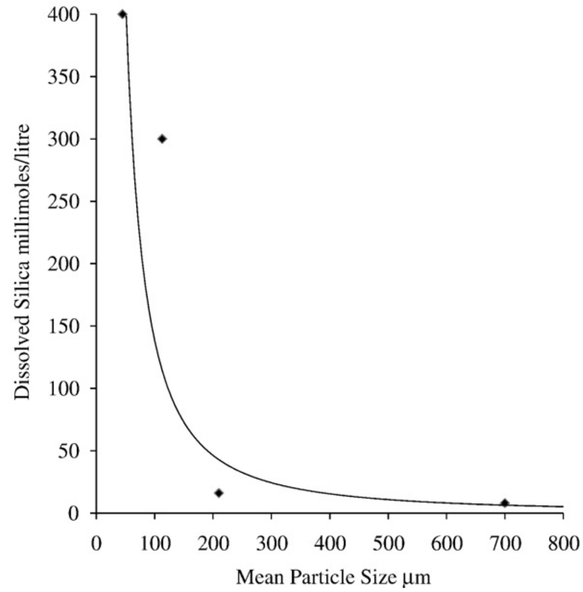

Fig. 8. Diagram showing the increased solubility of quartz with decreasing particle size.

Katayama and Sommer [6] postulated that due to the small particle size of the aggregate used in mortar bars gel formation and dedolomitization occur concurrently and produce a non-swelling magnesium silicate gel. In concrete, by contrast, due to the large size of the aggregate particles dedolomitization would only occur on the surface while gel production and expansion would occur in the interior of the particles.

Katayama and Sommer [6] found that replacement of 60% of Portland cement by a Japanese ground granulated blast furnace slag with a Blaine of 6050 cm^2/g reduced expansion by 30% in the RILEM AAR5 concrete microbar test made with the same Kingston aggregate used in this evaluation. The very high content of reactive quartz in the Kingston aggregate indicates that a higher amount of slag would be required to prevent excessive expansion than would be required, for example, for the Spratt siliceous limestone with lower quartz content.

Durand [15] observed that lithium salts were not effective in suppressing ASR in some aggregates so it is not too surprising that they are not effective with the Kingston aggregate containing a high content of very reactive quartz.

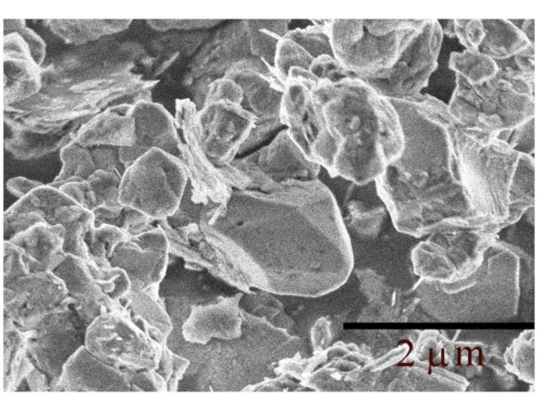

Fig. 7. SEM image of insoluble residue of Kingston aggregate showing a single crystal of quartz and irregularly shaped quartz grains and a few clay particles. Scale bar 1 µm.

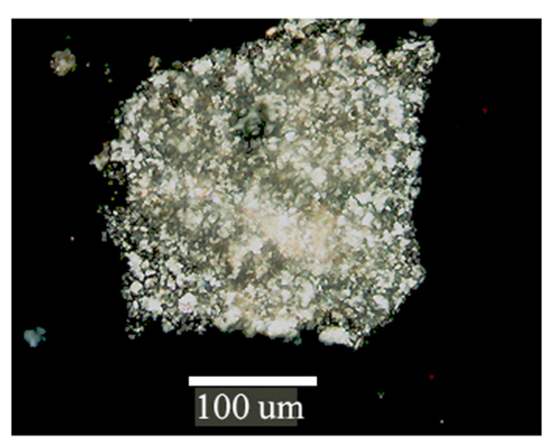

Fig. 9. Optical micrograph of particle of micro-crystalline quartz (chert) viewed between crossed polarizers showing the small size of the individual quartz crystallites.

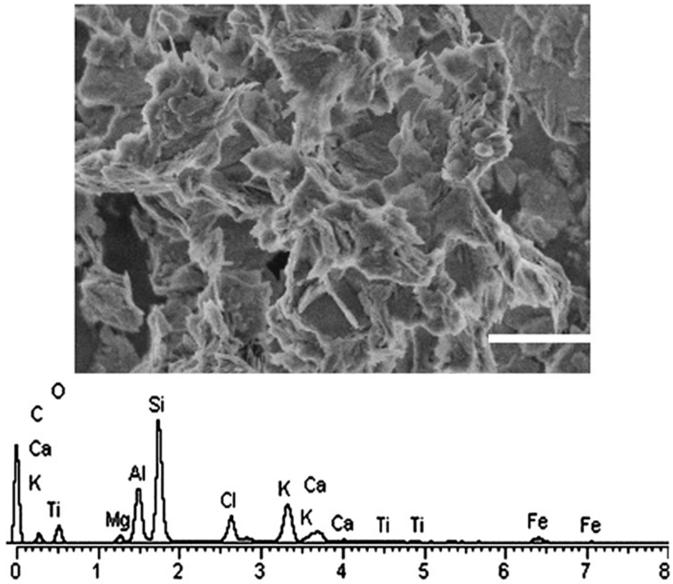

Fig. 10. SEM photograph of insoluble residue of Spratt limestone and the corresponding EDS spectrum. Scale bar 1 μm.

4.5. Earlier research supporting the hypothesis that expansion of ACR concrete is due to ASR

A review of the pioneering research conducted by Gillott in the 1960s [16,17], showed that the amount of chert in the rock from the Pittsburgh quarry correlated with the amount of expansion of concrete prisms (Fig. 12) (Gillott did not discuss the method that was used in determining the amount of chert.). In reference [17] the amount of expansion is plotted against the amount of quartz, but the percentages are the same as for chert. As in our work, Gillott also found that expansion correlated with the amount of SiO_2 in the rock. Evidently, at that time, the significance of the correlation between expansion and the amount of quartz and the chert content of the rock was overlooked.

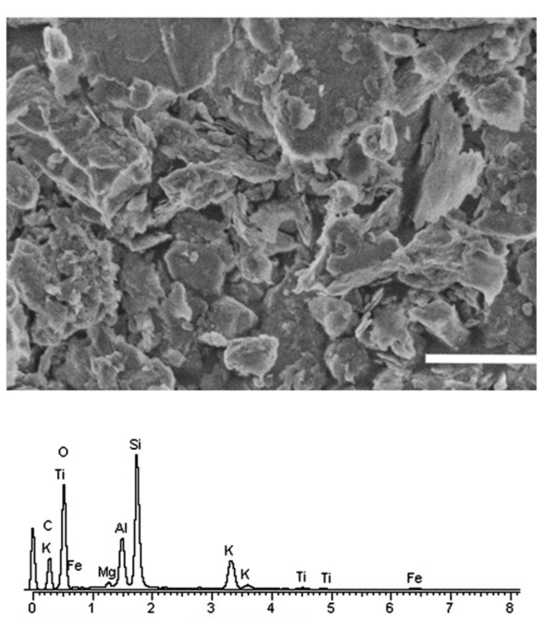

Fig. 11. SEM image of insoluble residue of Chinese limestone and the corresponding EDS spectrum. Scale bar 1 μm.

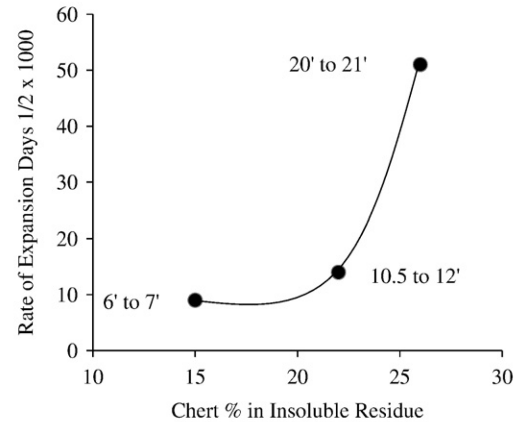

Fig. 12. Correlation between chert content of Kingston dolomitic limestone and expansion of concrete prisms. After Gillott [15,16].

A second piece of evidence supporting the concept that the expansion of the Kingston aggregate in concrete was due to ASR is that of Feldman and Sereda [18]. They measured the sorption and expansion isotherms of Kingston limestone from the Pittsburgh quarry in untreated, and in samples treated with sodium hydroxide, to simulate alkali–aggregate reaction. In the 24 to 30 foot horizon that corresponds approximately to our sample #78-16 that was used in this investigation, they found a marked increase in the amount of adsorption (Fig. 13). Their conclusion is that "the increase of sorbed water due to alkali treatment of the rock may be due to adsorbed water and the formation of a gel."

5. Current research

Katayama [19], recently reported significant amounts of gel in thin sections made from the cores that the first author took from the Kingston sidewalk, indicating that this appeared to be an alkali–silica reaction. The gel in these concretes is evidently finer than in typical ASR affected concretes and hence is not readily visible when viewed at low magnification. The first author also recently observed gel filling cracks on the surface of a concrete prism made with the #78-16 aggregate from the Pittsburgh quarry in Kingston confirming that ASR was occurring in this aggregate in concrete.

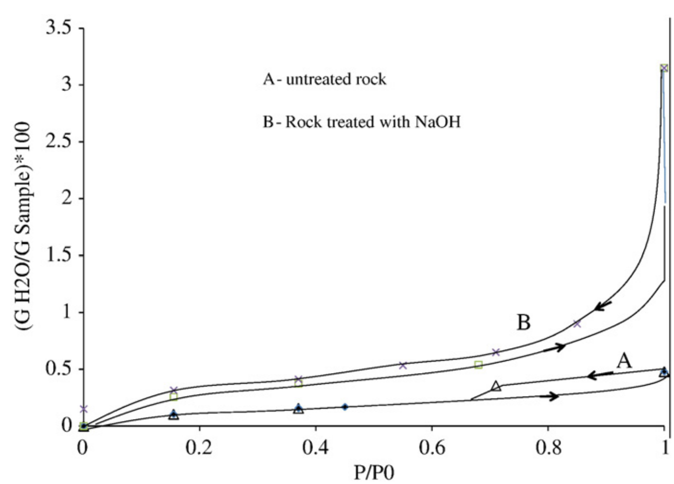

Fig. 13. Sorption/desorption of samples of Kingston dolomitic limestone showing the marked change after treatment with NaOH. After Feldman and Sereda [17].

6. Conclusions

- The particle size of the insoluble residue of the Kingston aggregate viewed in the SEM is 1 μm, but the mean particle size determined by a particle size analyzer, of all three aggregates is 10 μm. The larger size determined by the particle size analyzer is likely due to coagulation of the particles.
- The insoluble residue of the Kingston rock is composed of 96% quartz, compared to 39% in the Spratt and 12% in the Chinese limestone.
- The Kingston rock has a higher insoluble residue 11.4% compared to the Spratt with 8%, but lower than the Chinese ACR limestone with 44%.
- The amount of dissolved silica, Sc, in the insoluble residue of the Kingston aggregate was greater than that in the Spratt and Chinese aggregates.
- The Index of crystallinity Ic of the quartz in the Kingston is 4.5 compared to 9.3 for the Spratt and 7.4 in the Chinese limestone. The indices of crystallinity of quartz in the three aggregates correlated with the amounts of dissolved silica.
- There is a direct correlation between the amount of quartz in the insoluble residues of the rocks and expansion of concrete prisms containing the whole rock aggregates.
- The quantity and potential reactivity of quartz in the Kingston aggregate is an indicator that the reaction should produce a lot of gel. Gel was observed at low magnification in RILEM concrete microbars stored in NaOH solution but frequently not in many field concretes, although there are exceptions.
- In contrast to the gel produced in typical ASR affected concretes that consists of sodium/potassium calcium silicate hydrate, the gel found in the so called ACR affected concrete consists of calcium magnesium aluminum silicate hydrate.
- Based on the results obtained in this investigation it is concluded that the Kingston dolomitic limestone, at least from the horizon that was tested, exhibits a type of alkali silica reactivity.
- The final conclusion is: ACR = ASR.

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