Alkali-Aggregate Reaction in Concrete: A World Review

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So-Called Alkali-Carbonate Reaction (ACR)

Publication details
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Published online on: 13 Jul 2017

How to cite :- Paddy E. Grattan-Bellew, Tetsuya Katayama. 13 Jul 2017, So-Called Alkali-Carbonate Reaction (ACR) from: Alkali-Aggregate Reaction in Concrete: A World Review CRC Press
Accessed on: 20 Dec 2018

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3.1 INTRODUCTION

The term ‘alkali-carbonate reaction’ (ACR) would appear to apply to a reaction between the alkaline pore solution in concrete and any aggregate made from carbonate rocks such as limestones or dolostones (dolomite rocks). However, the term alkali-carbonate reaction is really applied only to the reaction between certain argillaceous dolomitic limestones and the alkaline pore solution in concrete that gives rise to rapid expansion and cracking of concrete. In North America the ACR dolomitic limestones are of Ordovician age, but in the Sichuan Province of China, some are of Triassic age. RILEM considered the use of carbonate-aggregate reaction (CAR) instead of ACR, but the latter was too established.

The argillaceous dolomitic limestones, that are quite rare, form in shallow intertidal or lagoon environments adjacent to the edge of an ancient continent (Tang et al., 2000). The Pittsburg quarry in Kingston, Ontario, Canada, from where the ACR aggregate was first encountered, is in the Ordovician Gull River formation that lies unconformably upon the Pre-Cambrian Canadian Shield and is overlain by limestones formed deeper in the basin. The presence of gypsum in the rock of the Pittsburg quarry is consistent with the formation of the rock in a shallow marine environment. Evidence from thin sections indicates that the deposit was initially laid down as limestone and only later became dolomitized. Fossils are generally rare or absent from the reactive argillaceous dolomitic limestones. In the Pittsburg quarry, the expansivity of aggregates in concrete varies considerably from layer to layer, but the pit-run aggregate from the entire first lift of the quarry is deleteriously expansive.

The term ‘alkali-carbonate reaction’ (ACR) has been in use since the 1960s, but recent research indicates that the expansion and cracking of concrete caused by this reaction is actually due to the formation of alkali-silica gel by reaction of the alkaline pore solution and cryptocrystalline quartz in the argillaceous dolomitic limestone (Katayama, 1992, 2004, 2006, 2010a, 2011; Katayama & Sommer, 2008; Grattan-Bellew et al., 2009; Katayama & Grattan-Bellew, 2012; Grattan-Bellew & Chan, 2013; Katayama et al., 2016). In 2004 and 2006, Katayama coined the term “so-called ACR” to take into account that the expansion was due to an alkali-silica reaction and not, as originally thought, some other type of reaction involving dolomite, as envisaged by Swenson (1957).

Retention of the term “so-called ACR” to distinguish it from typical alkali-silica reactive limestones may be justified, because of its different behaviour in the mortar-bar test and also because the proportions of supplementary cementitious materials (SCMs)
that are effective in reducing expansion in alkali-silica reactive limestones are not
effective in concrete made with the “so-called ACR” dolomitic limestones. This may,
in part at least, be due to the formation of additional alkaline hydroxide in the
dedolomitization reaction, equations (i, ii).

Reaction rim within aggregate: $\text{CaMg(CO}_3\text{)}_2 + 2\text{MOH} \rightarrow \text{CaCO}_3 + \text{Mg(OH)}_2 + \text{M}_2\text{CO}_3$  

(i)

Carbonate halo within surrounding cement paste: $\text{M}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow 2\text{MOH} + \text{CaCO}_3$  

(ii)

Expansion of typical ASR aggregates in concrete can be prevented by the use of a low
alkali-cement, (ASTM 0.60% Na$_2$O equivalent), but in the case of ACR aggregates
such as those from the Pittsburg quarry, the alkali content of the cement has to be less
than 0.31% to reduce the expansion of concrete prisms below 0.04%, Swenson (1957).
Grattan-Bellew, unpublished results, has shown that the expansion of concrete prisms
made with ACR aggregate (Pittsburg) can be significantly reduced by use of high-
alumina cement (HAC), Figure 3.1. In these concrete prisms, dedolomitization occurs
on the coarse aggregate mixed with HAC (Figure 3.2a), but ASR gel forms when used
with high alkali Portland cement (Figure 3.2b).

3.2 HISTORICAL PERSPECTIVES

ACR was first described by Swenson (1957) in a paper entitled ‘A Reactive Aggregate
Undetected by ASTM Tests’. On the basis of a different response in the mortar-bar test
method ASTM C227, Swenson apparently assumed that the reaction was different from that of the classical alkali-silica reaction as described by Stanton (1940). The term ACR was not used by Swenson in his original paper. The ACR aggregate evaluated by Swenson came from the Pittsburg quarry in Kingston, Ontario, Canada which is of Ordovician age. The term ‘alkali-carbonate rock reaction’ was first used by Swenson and Gillott (1964).

There was considerable research on the problem of the reactivity of carbonate rocks in the U.S.A. in the 1960s. In 1962, Newlon and Sherwood described the occurrence of Alkali-Reactive Carbonate Rock in Virginia, USA. In 1964, Hadley reported on Alkali-Reactive Carbonate Rocks in Indiana and Lemish and Moore, (1964) reported on alkali-carbonate reactions in Iowa, USA. In 1969, Buck reported on the potential alkali reactivity of carbonate rock in Virginia and Kentucky. Subsequently, the ACR problem in the U.S.A., was, for the most part, forgotten apart from a few papers by Ozol (1974, 1994), until a large number of cases of concrete deterioration were investigated by the present authors in Kentucky during the period 2006 to 2008 (Katayama & Grattan-Bellew, 2012). The petrology and expansivity of the Kentucky argillaceous dolomitic limestone is almost identical to that of the Kingston aggregate (Figure 3.3).

Katayama (1992), based on literature reviews, predicted that ACR is a combined phenomenon of harmless dedolomitization and expansive ASR of cryptocrystalline quartz hidden in the dolomitic aggregate. Since then, this hypothesis has been examined in detail by various petrographic methods (polarizing microscopy, SEM observation and quantitative EDS analysis), using i) field ACR concretes from the type locality (Kingston) of ACR (Katayama, 2004, 2006, 2010a, 2011; Gratten-Bellew et al., 2009), ii) field reproduced ACR concretes containing the Kingston ACR aggregate (Katayama & Gratten-Bellew, 2012; Gratten-Bellew & Chan, 2013) and iii) laboratory produced ACR concrete specimens (Katayama, 2004). After all these efforts, however, a paradox was encountered, that the concrete deterioration meeting the original definition of ACR by Swenson & Gillott, that is, deleterious expansion other than typical ASR but associated with dedolomitization, had not been identified, even when typical ACR concretes from the type localities Kingston and Cornwall in Ontario.
were examined. Consequently, this led to re-defining the classical term ACR as “so-called ACR” in 2004 & 2006 by Katayama (2004, 2006) (Katayama et al., 2016).

ACR was reported by Milanesi et al., in Argentina in 1996. Qian et al. (2001) reported the occurrence of ACR aggregate from Jixian, Tianjin, China in 2001. However, before 2004, the mechanism of dedolomitization and expansion were not yet clearly distinguished based on detailed petrographic examination, hence early reports on ACR should be reviewed critically.

3.3 MECHANISM OF SO-CALLED ACR REACTION

3.3.1 General

The deleterious alkali-carbonate reaction occurs in argillaceous dolomitic limestones with porphyrotopic or mosaic textures (Swenson and Gillott, 1960; Buck, 1969; Melanesi et al., 1996). The rocks consist essentially of a matrix of fine grained micritic calcite crystals (2μm), intermixed with clay minerals, mostly illite with minor chlorite and cryptocrystalline quartz (chert), in which are embedded large dolomite rhombohedra (50 μm). According to Hadley (1964) the deleteriously expansive rocks generally contain over 7% clay minerals. Figure 3.4a shows a photomicrograph of a typical thin section of the Kingston dolomitic limestone taken through a petrographic microscope. A photograph taken of a polished section of the Kingston dolomitic limestone taken using SEM is shown in Figure 3.4b. Dolostone (dolomite rock) and dolomitic limestone with a mosaic texture produce marked dedolomitization but are not always expansive. Hence, it is important to distinguish two distinctive phenomena, i.e., reaction (dedolomitization) and expansion, Katayama (2004, 2006, 2010a, 2011).

Hadley (1961) showed that the dolomite content of the deleteriously expansive dolomitic limestones was about 50%. Lemish and Moore (1964) found that expansion

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![Figure 3.3](image-url)  
*Figure 3.3 Expansion of aggregates from Kingston and Kentucky in the CSA concrete prism test A23.2-14A.*

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was greatest at dolomite contents of 60% (Figure 3.5). However, Dolar-Mantuani (1964), using the rock prism test, found most expansive rocks in Ontario contain less than 40% dolomite. Katayama, (1992) reviewed the North American carbonate rocks and indicated that insoluble residue at least 5-10% is the sole common characteristic among expansive carbonate rocks, irrespective of whether it is a limestone or a dolostone. Katayama & Sommer (2008) found that the argillaceous dolomitic limestone in the most expansive layer of the Pittsburg quarry in Kingston (Pt-16) contained 16.8% of insoluble residue and 4.8% of mostly cryptocrystalline quartz by H₃PO₄ extraction (Figure 3.10a).

### 3.3.2 Dedolomitization

It was initially noticed that the ACR involved dedolomitization of the aggregates in an alkaline medium. Hadley (1961) reported that a large single crystal of dolomite

![Figure 3.4](image-url)  
**Figure 3.4** Kingston dolomitic limestone: a) [left]: Thin section photomicrograph showing a large dolomite rhomb in a matrix of fine grained calcite. b) [right]: SEM micrograph of dolomite rhombs in a matrix of fine grained calcite.

![Figure 3.5](image-url)  
**Figure 3.5** Dolomite content of aggregate vs expansion of concrete, adapted from Lemish and Moore (1964).
expanded by 0.15% after 100 days in 3M NaOH solution. Hadley concluded that “the expansion of the de-dolomitizing crystals themselves would be sufficient to account for the expansion of the reactive carbonate rocks”. However, Gillott and Swenson (1969) failed to reproduce the expansion of a dolomite single crystal and noted that the molar volumes of the products of dedolomitization were less than that of the reactants and hence they concluded that dedolomitization could not account for the expansion of dolomitic limestone aggregates in concrete. Deng and Tang (1993) calculated that the solid volume change on dedolomitization was -4.32 % (less than zero), however they noted that the products of dedolomitization are fine and enclose many voids. They calculated that the void space was 29.21 % and from this they calculated that the volume change for the dedolomitization reaction was 36.56 %. Walker (1978) concluded that “Dedolomitization can be an innocuous reaction but in specific kinds of carbonate rocks it can result in expansion of the aggregate particles and destructive expansion of the concrete”.

In his critical review of the published references on carbonate rock reactions before 1992, Katayama concluded that dedolomitization is an innocuous reaction, and that deleteriously expansive ACR had been confused with dedolomitization. In 2000, Grattan-Bellew and Rogers (2000) found that, after 13 years outdoor exposure, most of the dolomite in the Kingston ACR aggregate was unreacted and so it was most unlikely that dedolomitization could be the underlying mechanism of expansion.

### 3.3.2.1 Reaction rims

How, then, does dedolomitization proceed in concrete? Decomposition of dolomite crystals, equation (i), forms a reaction rim within the dolomitic aggregate. Figure 3.6a shows a conspicuous dark rim of dedolomitization developed within a reacted dolomitic limestone aggregate in the 6-month old field concrete in Saudi Arabia. At the interface between the dolomite crystals and cement paste, a thin rim of Mg-Al-bearing hydrate resembling hydrotalcite may be formed on the dolomite absorbing Al ions from the cement paste, instead of brucite (Katayama et al., 2008; Katayama, 2010a, 2012a).

![Figure 3.6 Dedolomitization rims around dolomitic limestone aggregate, a) [left] showing a brucite-rich dark zone with an invisibly narrow hydrotalcite layer at the very interface with the cement matrix, Saudi Arabia (Katayama, 2012a), b) [right] showing minute spots of brucite (dark) and calcite (bright) formed by dedolomitization of Austrian dolostone in a RILEM AAR-5 concrete microbar.](image-url)
By contrast, within the reaction rim of the dolomitic aggregate, or along the cracks extending from the periphery of the reacted aggregate into the interior of the aggregate, minute spots (<3 μm) of brucite and calcite are formed as a result of dedolomitization (Figure 3.6b) (Katayama, 2004, 2010a, 2011; Katayama & Sommer, 2008).

3.3.2.2 Carbonate haloes

In the dedolomitization, secondary calcite forms a carbonate halo, equation (ii), within the cement paste that surrounds the reacted dolomitic aggregate. It should be noted that no radiating crack suggestive of expansion is formed in the cement paste. In sufficiently thin polished thin sections (15μm), under the crossed polars, the carbonate halo has a high birefringence showing a bright yellow colour, characteristic of calcite (Figure 3.7a). This carbonate halo is a porous crust composed mainly of calcite that had precipitated from the interstitial solution and replaces CSH gel in the cement paste (Figure 3.7b). Elemental mapping of the carbonate halo by EDS revealed a zonal distribution of alkalis corresponding to the formula (ii) (Katayama, 2004, 2010a).

3.3.3 Evidence of expansion

Previous research on ACR was likely to be confused by believing that dedolomitization is evidence of expansive ACR. However, according to Katayama (2004, 2006, 2010a, 2011), wherever expansion cracks exist in concrete, ASR gel is always present. Katayama found that evidence of expansion in concrete is demonstrated by the formation of radiating cracks from the reacted particles of the aggregate, irrespective of whether it is typical ACR of argillaceous dolomitic limestone or typical ASR of andesite or another reactive siliceous rock. It has been shown, aided by SEM observations on polished thin sections, that there is no difference in the process of crack formation in concretes between ASR and ACR. Katayama and Katayama and Grattan-Bellew (2012), revealed that the sequence of the crack formation in ACR concretes is: 1) rim formation, 2) internal cracking with ASR gel within the aggregate, 3) cracking from

Figure 3.7 Carbonate halo in the cement paste surrounding the dedolomitized aggregate particle: a) [left] showing the distinctive colour indicative of calcite, RILEM AAR-5 concrete microbar with Austrian dolostone, b) [right] showing that the carbonate halo replaces CSH gel in the cement paste in a concrete building in Saudi Arabia.
aggregate into the cement paste exuding ASR gel, and 4) ASR gel lining air voids and cracks distant from the reacting aggregate.

With RILEM AAR-5 (in Nixon & Sims, 2016) concrete microbars, expansion continues even when brucite disappears, transforming into non-expansive magnesium-silicate gel, and exudation of ASR gel becomes prominent along radial expansion cracks (Katayama, 2006, 2010a; Katayama & Grattan-Bellew, 2011) (see Figure 3.8a).

3.3.4 Formation of alkali-silica gel in the concrete

In 1986, Katayama (1992) collected a piece of concrete from Cornwall, Ontario, Canada and examined ultra-thin sections (15 μm thick) made from it. He observed alkali-silica gel filling cracks in the concrete suggesting that ASR had at least a role in the deterioration of the concrete made with an ACR aggregate. During 2004 to 2006, Katayama, after examining a number of samples of concrete affected by the ‘so-called alkali-carbonate reaction’, including the typical ACR concrete from near Kingston constructed in the late 1950s, concluded that the “ACR could be a mixture of deleteriously expansive ASR of cryptocrystalline quartz, and non-expansive dedolomitization of dolomitic aggregates”, and that “ACR is believed to be ASR, influenced more (fine aggregate) or less (coarse aggregate) by dedolomitization” (Katayama, 2004).

Katayama identified ASR of crypto- to microcrystalline quartz in the dolomitic aggregates in several structures from Montreal to Quebec, Canada. He confirmed that ACR is a combined effect of deleteriously expansive ASR of cryptocrystalline quartz, and harmless dedolomitization, which produces brucite and carbonate haloes without accompanying expansion cracks (Katayama, 2004, 2006, 2010a; Katayama & Sommer, 2008). What is important is that dolomitic aggregates do not develop expansion cracks in the embedding cement paste, unless ASR is involved. Figure 3.8a shows the typical expansion crack filled or lined with ASR gel in the ACR aggregate in an AAR-5 concrete microbar (Katayama & Grattan-Bellew, 2012). In the Kingston experimental pedestrian pavement (sidewalk) at age 22 years, radial expansion crack is filled with veins of ASR gel within the reacted dolomitic limestone aggregate.
Note the dolomite rhombs are only slightly decomposed into a thin rim, consisting of brucite or magnesium silicate gel, whereas ASR gel is formed abundantly. Lu et al. (2006) also observed gel in samples of the ACR aggregate from the Pittsburg quarry autoclaved at 150°C in KOH solution.

### 3.3.4.1 Compositional trends of ASR gel in ACR concrete

According to Katayama (2010b, 2008) and Katayama et al. (2008), ASR gel in typical ACR concretes migrates along cracks from the reacted aggregate into the cement paste, absorbs calcium from cement paste, and approaches the composition of CSH gel. In principle, on the [Ca/Si]-[Ca]/[Na+K] diagram, alkali-silica reaction terminates at a convergent point of CSH gel at around Ca/Si=1.5, Ca/(Na+K)=100-200. It should be noted that there is no difference in the compositional trends of ASR gel between ACR concretes and ASR concretes. Figure 3.9a shows the data of typical ACR bridge near Kingston, while Figure 3.9b is typical ASR of andesite in Japan. In both cases, ASR gel crystallizes into the rosette-like aggregation at Ca/(Na+K) <1. Where leaching of alkalis occurs along cracks in concrete, a short parallel compositional line appears, irrespective of whether it is ACR as shown here (Katayama, 2010a), or ASR (Katayama, 2010b, 2008).

### 3.3.5 Identification of cryptocrystalline quartz

In the ACR reactive argillaceous dolomitic limestone from Kingston, cryptocrystalline quartz is contained in an isolated form, and not as an aggregation like a chert. This explains why this form of reactive silica is difficult to identify in thin section, and had long been missed in the optical microscopy of the ACR aggregate from Kingston. This cryptocrystalline quartz was extracted from the Kingston rock by the phosphoric acid treatment, Katayama (2004, 2010a) (Figure.3.10a).

In field concretes undergoing ACR, cryptocrystalline quartz in the Kingston rock is difficult to identify, because this quartz reacts very fast (Katayama, 2004, 2010a, 2011;
Katayama & Sommer, 2008). However, in RILEM AAR-5 concrete microbars, some cryptocrystalline quartz occasionally remains, but mostly converts to ASR gel (Figure 3.10b) or Mg-silicate gel (Katayama, 2004, 2010a; Katayama & Sommer, 2008). In the siliceous argillaceous dolomitic aggregates undergoing ASR in Quebec, crypto- to microcrystalline quartz is abundant and is partly converting to ASR gel as revealed by SEM observation on the polished thin section, Katayama (2006).

### 3.3.6 Formation of magnesium silicate gel

The magnesium silicate gel (Mg-silicate gel) occurs as an intermediate product between ASR gel and magnesium hydroxide gel or brucite in the reacted dolomitic aggregate that contains reactive silica (Katayama, 2004, 2006, 2010a, 2011, 2012a). It is found within a dedolomitized rim or along cracks in the interior of the aggregate. Mg-silicate gel forms a thin inner rim of the reacted dolomite crystals (Figure 3.11a), or a

![Figure 3.10 Cryptocrystalline quartz from the Kingston dolomitic limestone aggregate: a) [left] extracted by phosphoric acid treatment, b) [right] in some AAR-5 concrete microbars, small amounts of cryptocrystalline quartz remain in isolated form, but most has converted to ASR gel.](image1)

![Figure 3.11 Magnesium silicate gel: a) [left] forming a thin inner rim around reacting dolomite particles (adapted from Katayama, 2006), b) [right] forming a pseudomorph after the original dolomite crystals and showing shrinkage cracks.](image2)
pseudomorph after the dolomite crystals keeping their original rhombohedral outlines (Figure 3.11b).

To identify the Mg-silicate gel, it is essential to perform a quantitative SEM-EDS analysis on the polished thin section at higher magnifications (e.g., >1500 x) to obtain a sharp image to distinguish the minute textures composed of dolomite, Mg-silicate gel, ASR gel, etc. In the aged concrete constructed in the 1950s near Kingston containing the ACR reactive Pittsburg aggregate, Mg-silicate gel became more or less crystalline, showing the transformation into sepiolite-like material or flakes of antigorite-like material as estimated by their composition, (Katayama, 2006, 2010a, 2011). Where dolomitic rock is argillaceous (Pittsburg aggregate), Al-Mg silicate gel forms (Katayama, 2006), and on aging this gel converts to a chlorite-like material.

There has been no evidence that Mg-silicate gel generates expansion, because no radiating cracks are found to accompany its formation, except for shrinkage cracks (see Figure 3.11b). The occurrence of the Mg-silicate gel in field concretes has been documented from variously reactive dolomitic aggregates in Ontario (deleterious), Austria (harmless) (Katayama, 2004, 2006, 2010a; Katayama & Sommer, 2008) and Saudi Arabia (harmless) (Katayama, 2012a), as well as in the ASR-reactive aggregates in Quebec and Japan (harmless) (Katayama et al., 2008) based on SEM-EDS analysis, but has not been identified by other researchers in a number of works before around 2000.

3.4 COUNTER ARGUMENTS AGAINST GEL FORMATION AS THE CAUSE OF EXPANSION DUE TO ACR

The arguments on this subject have been reviewed critically by Katayama (2010a, 2011) and Katayama et al., (2016). The main points of the problem are that 1) the conventional methods for preparation and examination of concrete thin sections are inappropriate, 2) general understanding on the expansion behaviours and remedial measures for a wide range of ASR remains stereotypical and has been reproduced by the papers without critical reviewing, and 3) interpretations on the expansion mechanisms related to dedolomitization lack support by petrographic evidence.

3.4.1 Why is gel not observed in thin sections of ACR concrete?

3.4.1.1 Thickness of thin section

The standard thickness of rock thin sections is generally accepted by geologists to be from around 30 μm in Europe and North America to 20 μm in Japan, and published optical properties for minerals usually relate to this range of thickness (although 30 μm is too thick for quartz, because it presents a pale yellow interference colour). However, whilst traditional 30 μm sections are usable for identification of the main mineralogy and types of coarse-grained rocks, they are often too thick for concrete petrography, particularly for the detailed study of AAR. For the petrographic examination of Portland cement clinker, thin sections with thickness of <15 μm have been accepted as standard (Insley & Fréchette, 1955). Similarly, the ideal thin section thickness for fine-grained alkali-reactive rock types (e.g., volcanic rocks, cherts, and carbonate rocks) is 15 μm, because most of the reactive constituents contained in them
(cristobalite, tridymite, volcanic interstitial glass, cryptocrystalline and microcrystalline quartz) are small (mainly <10μm) (Katayama, 2010a, 2012b; Katayama et al., 2016).

The calcite crystals that comprise the matrix of the ACR aggregate are about 2 μm in size (see Figure 3.14b, Grattan-Bellew et al., 2009) and hence, in 30 μm thick thin sections, a petrographer is looking through about 15 layers of calcite that effectively obstructs the view, making it almost impossible to observe fine gel filled cracks. The 30 μm thin section of concrete gives an almost opaque appearance of cement paste (Figure 3.12a), whereas 15 μm section permits detailed observation by giving a transparent appearance of cement paste and argillaceous carbonate matrix of the dolomitic aggregate (Figure 3.12b).

Many papers on ACR, both published and submitted manuscripts to journals, are based on observations of either very thick thin sections, justifying the thickness of 30 μm in the references on petrography of natural rocks, or on the SEM observations on the fracture surface of concrete. In addition, enthusiasm for producing large-area thin sections (e.g., 12 cm by 18 cm, 30 μm thick) prevented preparation of sufficiently thin sections suitable for detailed petrographic examination. This is one of the main reasons why the presence of crypto- to microcrystalline quartz, which is responsible for the deleterious expansion due to ASR in the ACR (‘so-called ACR’ by the present definition), has long been missed in the petrography of concrete (Katayama, 2010a).

### 3.4.1.2 Carbonation of ASR gel

In the ACR concretes undergoing dedolomitization, both cement paste and ASR gel are most likely subject to secondary carbonation by the carbonate ions that are liberated from the reacted dolomite through dedolomitization (Katayama, 2010a). Because the carbonate minerals calcite and dolomite constituting the dolomitic aggregates have a high-birefringence, they overlap with fine cracks and ASR gel that lines or fills these cracks, as well as crypto- to microcrystalline quartz in the aggregate, thereby hindering...
the details of the microscopic texture in the transmitted light. In the concretes affected by more or less atmospheric weathering, such as field structures and concrete prisms stored for a long time, secondary calcite forms along the cracks often replacing veins of ettringite and ASR gel (Katayama, 2010a). As a result, ASR gel is likely to be missed by the thin section microscopy.

Although the above alteration processes obscure the presence of ASR gel in the transmitted polarizing microscopy, SEM observation on the polished thin section is able to reveal clearly the presence of the composite vein in which ASR gel is enveloped by its carbonation product calcite vein (Figure 3.13a, Katayama & Grattan-Bellew, 2012), as well as thin films of ASR gel intermixed with secondary calcite (Figure 3.13b). In the thick thin section (~30 μm) with a cover glass, none of fine cracks, ASR gel or cryptocrystalline quartz is detectable. To identify these fine textures and reaction products, combined petrographic examination is recommended, which consists of polarizing microscopy in both transmitted and reflected lights, SEM observation to characterize the reaction sites, and quantitative EDS analysis, using the same polished thin section (15 μm thick) (Katayama, 2004, 2006, 2010a, 2011).

3.4.1.3 Fluorescence method to identify thin films of ASR gel

Subsequent to Katayama, Grattan-Bellew et al. (2010) concluded on the basis of laboratory experiments that the formation of alkali-silica gel was the cause of the expansion and deterioration of concrete made with ACR aggregates. Data from Gillott (1961) and Swenson and Gillott, (1964) show that there is a direct correlation between the amount of chert in the insoluble residue of the Kingston aggregate and the expansion of concrete prisms. The fluorescence of alkali-silica gel on the fractured surface of a core, treated with uranyl acetate, from the 23 year old experimental sidewalk in Kingston made with the argillaceous dolomitic limestone and high alkali cement is shown in Figure 3.14a.

Further confirmation for the occurrence of ASR in concrete made with so-called ACR aggregates was presented by Katayama and Grattan-Bellew (2012) and by
Grattan-Bellew and Chan (2013), showing the presence of the thin films of alkali-silica gel between the small crystals of calcite in the matrix of the rock, Figure 3.14b.

3.4.2 Why does coarse aggregate expand more?

Why do ACR aggregates not cause expansion in mortar-bars if the mechanism of expansion is ASR? This subject has been discussed in detail by Katayama (2010a, 2011). According to Katayama and Sommer (2008) and Katayama (2010a), in mortar-bars the ~4 mm size of the aggregate results in more or less complete dedolomitization of the finer particles that produce brucite Mg(OH)$_2$, which reacts with the silica gel, produced by reaction of the crypto-crystalline quartz with the alkaline pore solution, to produce a magnesium silicate gel that is either less expansive or non-expansive and so expansion of mortar-bars is much reduced.

In general, typical ASR proceeds by the expansion generated in the interior of the aggregate. With the coarse aggregate, expansive alkali-rich ASR gel tends to remain within the interior of the aggregate particle, continues expansion, and generates wide cracks filled with ASR gel. By contrast, fine aggregate particles tend to lose the expansive nature rapidly through the replacement of alkali ions in the ASR gel by calcium ions from the surrounding cement paste, thus producing small cracks. In the alkali-immersion tests, the size of the aggregate is important. In the accelerated mortar-bar test (ASTM C1260: 2004), chert particles do not expand significantly due to dissolution of ASR sol into NaOH solution, whereas in the accelerated concrete microbar test [AAR-5 (in Nixon & Sims, 2016), Sommer et al., 2004] they produce expansion due to formation of ASR gel within the coarse aggregate. Nowadays, ASR gel is considered to be a universal product for generating expansion of all the traditionally known varieties of alkali-aggregate reaction, i.e., alkali-silica
reaction, alkali-silicate reaction, and alkali-carbonate reaction (Katayama, 2012b, 2012c).

3.4.3 Why are supplementary cementitious materials not effective?

3.4.3.1 Blast furnace slag

Supplementary cementitious materials that are usually effective in minimizing expansion due to ASR are not effective when used in concrete made with ACR aggregates, which may be due to a number of causes. The crystallinity of the cryptocrystalline quartz in the ACR aggregate is lower than in typical ASR limestones, resulting in it being much more reactive and hence more difficult to suppress (Grattan-Bellew & Rogers, 2000). Katayama (2008) reported that replacement of 50% of Portland cement by fine grained Japanese blastfurnace slag reduced expansion by 30%, but that it failed to prevent the formation of cracks filled with ASR gel at later ages (Figure 3.15a,b). Because cryptocrystalline quartz in the Pittsburg aggregate occurs as isolated forms, rather than a massive aggregation like a chert, this quartz is considered to be more reactive than the particles of ground granulated slag and fly ash (Katayama, 2012b). Generally, blastfurnace slag is not always effective in preventing ASR: replacement of 40% of cement by slag could not suppress cracking due to late-expansive ASR in a mass concrete structure in Japan.

3.4.3.2 Fly ash

Fly ash is not effective in suppressing ACR in concrete. In Kentucky, high-calcium fly ash (40% CaO in glass, content 40%) was not effective in preventing cracking by the ACR aggregate and ASR of chert particles (Figure 3.16a, Katayama & Grattan-Bellew, 2012). In the reacted dolomitic aggregate, expansion cracks originated from the pool of ASR gel that had formed surrounding the calcite particles (Figure 3.16b). With typical ASR, even
low-calcium fly ash is not effective when the aggregate is highly reactive. In a Japanese case, low-calcium fly ash (<4% CaO in glass, replacement of 18%) was effective for the late-expansive ASR of the sandstone pebbles in concrete, but was not effective for the early expansive ASR due to the glassy bronzite andesite aggregate. The average SiO₂ content of the fly ash glass was 58%, while that of the rhyolitic interstitial glass in the andesite was 75%, which explains the low pozzolanic reactivity of this fly ash (Katayama, 2010b).

### 3.4.3.3 Lithium salt

The addition of lithium salts to concrete made with ACR aggregates is not effective in suppressing expansion (Tang & Deng, 2004). However, this is also the case with late-expansive ASR of orthoquartzite and greenschist in Canada (Durand, 2000). All these may be due to the presence of a dense matrix surrounding the reactive particles that either prevents the lithium ions from reaching them or the lithium is absorbed by clay minerals (Katayama, 2010a).

### 3.4.4 Dedolomitization-related mechanisms

#### 3.4.4.1 Hypothetical volume-increase dedolomitization

López-Buendia et al. (2006, 2008) claimed that dedolomitization itself is a volume-increase reaction, because calcite has a larger d-spacing (d104 = 3.03Å) than that of dolomite (d104 = 2.89Å). To compare the unit cell volumes of dolomite and calcite, mass balance should be considered, then one molar dolomite is equivalent to two molar calcites, expressed as equation (iii) (Katayama, 2011, 2010b). This is a hypothetical dedolomitization, in which complete ion-exchange takes place between Mg in the dolomite and Ca in the cement paste. Mg ions liberated from dolomite into solution do not precipitate as brucite, and more than 10% of volume increase may result (Katayama, 2010b). However, in concrete, such an entire replacement of dolomite by calcite in equation (iii) does not occur, as is evident from the microtexture of Figure 3.16.
3.6b which follows the equation (i). Actually, concrete specimens of López-Buendía et al. (2008) made with a Spanish dolomitic limestone aggregate presented contraction. For comparison, natural dedolomitization occurs in geological time by the near-surface weathering of dolomitic formations (Katayama, 2010b). In this process, calcite replaces the dolomite crystals, leaving a pseudomorphic texture of the original outlines of the dolomite rhombs (Figure 3.17a,b). This dedolomitization is a dissolution/precipitation process in the open system, and there is no volume change after the precipitation of calcite. Dolomites are dissolved into interstitial solution and secondary calcites are precipitated into the dissolution voids formed after the dolomite crystals. Mg ions liberated from the dolomite are carried away and do not precipitate as brucite, which is different from the dedolomitization in concrete. This reaction without volume change could be written as equation (iv) (Katayama, 2011, 2010b).

Hypothetical dedolomitization: \[ \text{CaMg(CO}_3\text{)}_2 + \text{Ca}^{2+} \rightarrow 2\text{CaCO}_3 + \text{Mg}^{2+} \] (iii)

Natural dedolomitization: \[ \text{CaMg(CO}_3\text{)}_2 + 0.75\text{Ca}^{2+} \rightarrow 1.75\text{CaCO}_3 + \text{Mg}^{2+} + 0.25\text{CO}_3^{2-} \] (iv)

### 3.4.4.2 Uptake of moisture and swelling of dry clay minerals in the dolostone

Gillott and Swenson (1969) concluded that dry clay minerals in dolomite crystals in the aggregate would become exposed to alkalis and moisture due to dedolomitization and the swelling of previously un-wetted, non-swelling clays (illite) could account for the expansion of the aggregates. However, if a swelling clay, typically smectite, is contained in the aggregate, this would produce distinctive shrinkage cracks of cement paste concentrically surrounding the aggregate through the repeated drying and wetting seasonally encountered in the outdoor conditions. Katayama (2011) reported that no such shrinkage cracks have been observed in the Kingston dolomitic aggregate in the typical ACR concretes from Ontario.

![Figure 3.17a & b) Natural dedolomitization, in which calcite pseudomorphs replace dolomite rhombohedra without producing brucite.](image-url)
3.4.4.3 Expansion due to dedolomitization and formation of brucite in confined space

Tong and Tang (1999) concluded that “brucite formed in a confined space and generated the force to cause the expansion of rock prisms and aggregate particles in concrete microbars”. This hypothesis appears rather unlikely as only a small amount of the dolomite limestone de-dolomitizes in the field deteriorated concretes.

The accelerated condition (150°C) of concrete microbars and compacted mortars produces portlandite and brucite in the particles of pure limestone and magnesite (Tong, 1994; Tang & Deng, 2000). They believed that the expansion was caused by a “topochemical reaction” that took place within a confined space to generate a pressure of crystallization of portlandite and brucite, claiming that the expansion of the ACR is due to the formation of brucite through the dedolomitization. However, if this mechanism is accepted, then pure limestone should also be regarded as deleteriously expansive, which contradicts the reality, since the expansion of this limestone aggregate in the autoclave is attributed to the thermal expansion of coarsely crystalline calcite (Mu et al., 1996). Hence, it is unlikely that brucite causes expansion, Katayama (2011).

3.5 TEST METHODS

3.5.1 Rock Cylinder Test (ASTM C 586)

The first reported use of the rock prism test is by Hadley (1961). It was also used by Swenson and Gillott (2009), Dolar-Mantuani (1964), Walker (1978) and intensively by Rogers (1985). ASTM C586 (2006) specifies that the cylinders or prisms be stored in 1N NaOH at a temperature range of 20 to 27.5°C. The overall size of the specimens specified to be 9 mm diameter by 35±5 mm in length. However, Deng et al. (1993) stored the prisms at 80°C in 1N KOH. The relatively short length of the cylinders or prisms permits evaluation of individual layers in a quarry either by taking rock hand samples, or by evaluating cores, something that is difficult to achieve using other test methods. Hadley found good correlation between expansion of rock prisms after 14 days in 1M NaOH and the expansion of concrete prisms stored at 38 °C.

A modified miniature rock prism test was developed by Grattan-Bellew (1981) and this method was also used by Tang and Lu (1986), who tested prisms made from the Kingston Rock. They showed that expansion increased with temperatures from 20 to 80°C. It should be noted that laminated argillaceous carbonate rocks have a strong anisotropy in expansion by the direction of bedding. Rock cylinders cut perpendicular to the bedding plane produce expansion larger than those parallel to the bedding: e.g., 20% to 40% larger at age 28 days to 19 months with the Kingston ACR rock, whereas 7 times larger was found with a Japanese dolomitic limestone (Katayama et al., 1996).

This test does not necessarily reproduce ACR as recognized in concrete, because cement is not involved and interaction between the dolomitic rocks and calcium in the cement paste, e.g., formation of the carbonate halo, is thus not generated. Swelling of the clay minerals by water and alkali solution, may occur, but this is not relevant to ACR. In addition, NaOH solution used as the immersion medium tends to dissolve ASR sol before solidifying into ASR gel. On the basis of these differences from the tests
using concrete specimens, rock cylinder/prism test is not necessarily suitable for the study of the mechanism of ACR.

### 3.5.2 Concrete Prism Testing

The concrete prism test [ASTM C1105 (2006), CSA A23.2-14A (2014), French Standard NFP 18-454 (2004), RILEM AAR-3 (in Nixon & Sims, 2016)] is the most widely used method for the evaluation of the potential expansivity of argillaceous dolomitic limestones and probably comes closest to replicating the performance of concrete made with ACR aggregates in the field. However, the use of a specified mixture design of the concrete places some limitations on the use of this test method, for example, to predict the field performance of mixtures with lower cement contents and those using lower alkali cements. The CSA standard specifies the use of a non-reactive fine aggregate in the concrete prism test, however, Fournier et al. (2000), showed the importance of evaluating the potential expansivity of combinations of coarse and fine aggregates as the reactivity of the fine aggregate would likely have an effect of the expansion of the prisms. The Canadian Standard CSA A23.2-14A (2014) was developed from the work of Swenson (1957). The specified size of the prisms in the current standard is 75 x 75 x 275 mm or a maximum length of 405 mm (coarse aggregate: max.19 mm). The prisms are stored at 38 ºC as for testing for ASR. The specified cement content for the concrete prisms is 420 kg/m$^3$ and the alkali content of the cement is increased to 1.25% Na$_2$O equivalent by addition of NaOH.

In ASTM C1105 (2006), the specified cross section of the prisms is the same as in CSA, but the storage temperature is 23ºC. In the French standard NF P 18-454 (2004) the prisms are 70 x 70 x 282 mm. The prisms are stored in a “reactor” at 60 ºC to accelerate the reaction. In RILEM AAR-3 (in Nixon & Sims, 2016), the prisms are 75 x 75 x 250mm, and the storage temperature is 38ºC. An accelerated version, RILEM AAR-4, (in Nixon & Sims, 2016) was developed from the French method, which uses the prisms of 75 x 75 x 250mm stored at 60 ºC in a double container to avoid drying up and leaching of alkalis from the prisms.

Expansion curves of concrete prism tests often present a plateau at later ages, forming asymptote towards a certain expansion value, but this does not necessarily mean that reactive constituents in the aggregate were entirely consumed. Leaching of alkalis from the concrete prisms occurs during the long-term storage, perhaps in the order of 30-40% in some cases, irrespective of the temperature applied, 23ºC or 60 ºC. For this reason, late-expansive ASR aggregates present a sigmoidal expansion curve with apparent asymptote, whereas early-expansive ACR aggregates tend to give a simple convex curve with asymptote, rather than a sigmoid with an inflection point. At the same time, secondary carbonation proceeds along the cracks that were formed on the concrete prisms and calcite replaces ASR gel and ettringite in varying degrees (Katayama, 2010a).

#### 3.5.2.1 Correlation Between Expansions in the Concrete Prism Test & in the Field

There are only two papers on the comparison between expansions in the field and in concrete prisms made with ACR aggregates (Grattan-Bellew, 2000; Lu et al., 2008).
Both used data from the experimental sidewalk in Kingston, Ontario, Canada. Rogers and Hooton, (1992) noted that after one year the expansion of concrete prisms stored at 23 ºC was about the same as concrete slabs exposed outdoors under ambient conditions. However, after 5 years, leaching of alkalis from the concrete prisms stored at 23 ºC had reduced expansion significantly below that of the slab exposed outdoors, but in the case of one slab, the expansion of the prisms stored at 38 ºC was similar to that of the slab exposed outdoors, Figure 3.18. It is concluded from these results that the expansion of concrete prisms stored at 38 ºC and ~100% humidity provides a better prediction of the long term expansion of concrete in the field. The main disadvantage of the concrete prism test is that it takes up to one year to obtain results.

### 3.5.3 Concrete Microbar Test

In this test procedure [RILEM AAR-5 (in Nixon & Sims, 2016), Tang & Deng, 2004], concrete microbars, 40 by 40 by 160 mm are made with a single size fraction of aggregate, 4.0 to 8.0 mm. The water to cement ratio is 0.33 and the aggregate to cement ratio is 1:1. The length change of the bars is monitored for 28 days in 1 M NaOH @ 80ºC. In Tang and Deng (2004), expansions of bars made with ACR aggregates in excess of 0.1% at 28 days are considered to be indicative of potentially deleterious expansion in concrete. Good correlation was found between the expansions of concrete microbars and concrete prisms (Lu et al., 2008). The similar procedure in RILEM AAR-5 is used to compare behaviour with the conventional accelerated mortar-bar test for ASR [AAR-2 (in Nixon & Sims, 2016)], on the basis that reactive carbonates will give greater expansion with the coarser aggregate particle size (4 to 8 mm) used in AAR-5.

During the storage, concrete microbar specimens are not affected by atmospheric carbonation. In this test, all the important features and reaction products characteristic
of the so-called ACR, *i.e.*, dedolomitization rims, carbonate haloes, brucite, Mg-silicate gel and ASR gel, can be reproduced. Besides, owing to the larger size of the aggregate than that in the mortar-bar tests (ASTM C1260, RILEM AAR-2), chert aggregates produce deleterious expansion without undergoing excessive dissolution of ASR sol/gel into the NaOH solution (Yamada *et al.*, 2015).

### 3.5.4 Chinese Autoclave Test

Concrete microbars 20 by 20 by 60 mm are used in this test (Tang *et al.*, 1994). The aggregate size is 5-10 mm, the aggregate:cement ratio is 1 and the water/cement ratio of 0.3. The alkali content of the cement is adjusted to 1.5% Na₂O equivalent by adding KOH to the mixing water. After demolding the bars are steamed at 100°C for 4 hours and then autoclaved at 150°C. Expansions in excess of 0.1% after 6 hours of autoclaving are considered to be indicative of potentially deleterious expansion of ACR aggregates, (Guangren, 2001). However, this condition (150°C) is too vigorous for well-crystallized carbonate aggregates with distinctive cleavage planes within them because it produces irreversible thermal expansion (Katayama, 2011). Coarsely crystalline, non-reactive limestone from Nanjing produced abnormal expansion, independent of the alkali level of the cement and curing conditions (Mu *et al.*, 1996), that is, coarser aggregate (5-10mm) gave larger expansion (0.09%), comparable to the threshold for deleterious expansion in this test (0.10%). Frequent heat treatment for measuring the length changes at various storage ages was responsible for the larger expansion.

According to Tong (1994), compacted mortar specimens (9 mm in diameter by 30 mm in length) containing the limestone or coarsely crystalline magnesite aggregate also produced significant expansion with the same autoclaving condition (150°C). Calcite and magnesite were decomposed into portlandite and brucite, although the total solid molar volumes should decrease after the reactions (Tang & Deng, 2004). Because the aggregates tested were coarsely crystalline rocks and the heat cycles applied were frequent, irreversible thermal expansion must have occurred with their specimens. Hence, care should be taken in interpreting the expansion data of the autoclave method.

### 3.5.5 Chemical Screening Test

This test procedure (CSA A23.2-26A: 2014) consists of determining the aluminum oxide, the calcium oxide and the magnesium oxide contents of pulverized carbonate rock samples and plotting a graph of Al₂O₃ versus the CaO:MgO ratio. The potential expansivity of the aggregate is determined from the position of the plotted point on the graph (Figure 3.19). This test procedure was developed by analysis of a large suite of carbonate rocks from Ontario for the Canadian Standards Association by Rogers (personal communication, 2000). This method was also used successfully by the authors to determine the potential expansivity of argillaceous dolomitic limestone from Kentucky, U.S.A.

According to Jensen (2009), about 6% of Norwegian carbonate aggregates tested was “considered potentially expansive” and therefore potentially ACR-reactive on this diagram, but ACR has not been diagnosed in Norway. Considering that ASR of
the cryptocrystalline quartz is the real cause of the deleterious expansion of the so-called ACR aggregates, and that metamorphic carbonate rocks common in Norway contain coarsely crystalline quartz with lower ASR reactivity, this diagram should better be applied to the non-metamorphosed carbonate rocks in North America. Another version of the screening diagram (CaO:MgO and insoluble residue) was proposed by Rogers (1986), which is equivalent to the ratio of calcite-dolomite-insoluble residue on the triangular diagram (Katayama, 1992), meaning that the dolomitic limestones in Ontario with a certain range of impurity are deleteriously expansive.

3.6 CONCLUSION

In 1992, Katayama reported on the occurrence of alkali-silica gel in concrete made with ACR argillaceous dolomitic limestone indicating that the formation of gel was at least a contributing factor in the expansion of the concrete. Up until 1992 ACR was generally considered to have a different mechanism of expansion from that of concrete made with classical ASR aggregates, and a number of mechanisms were put forward to explain the mechanism of expansion, particularly in Canada, the U.S.A. and China. Subsequently, Katayama (2004, 2006, 2010a) obtained more data to support the formation of gel as the underlying mechanism of expansion of concrete containing ACR aggregates, and Katayama’s work has been supported by observations of Grattan-Bellew (2009, 2013), Katayama and Grattan-Bellew (2012) and Katayama et al., 2016. It is concluded that the so-called alkali-carbonate reaction (ACR) is a special case of alkali-silica reaction similar to that occurring in siliceous limestones.

The long-standing confusion about ACR is due to the inappropriate methods applied in the sample preparation, observation and analysis, as well as to the misunderstanding that the distinctive chemical reaction (dedolomitization) is directly or indirectly responsible for the deleterious expansion.
REFERENCES


