Alkali Reactive Carbonate Rocks: Is it Alkali Silica Reaction (ASR) or Alkali Carbonate Reaction (ACR)?

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ABSTRACT

The root cause of distress in two different concrete structures made from carbonate coarse aggregates that fit the textural and compositional criteria cited for ACR was found to be caused by ASR, not ACR. Stereo-optical examination and transmitted polarized light microscopy (PLM) analysis showed that the concretes contain some dark gray, fine-grained argillaceous dolomitic coarse aggregates in which secondary white deposit filling the cracks extending from these aggregates into the paste (as well as lining air voids) is ASR gel. Back scattered electron (BSE) imaging with EDS spectra and X-ray elemental mappings, clearly confirm that the white secondary deposits consist of ASR gel. BSE images with EDS spectra and X-ray maps of different samples for each element within areas occupied by the gel showed typical ASR gel. High magnification PLM examination showed the presence of cryptocrystalline to microcrystalline quartz in pockets in the matrix of the rock. The presence of Si-rich phases as finely divided interstitial cryptocrystalline silica minerals intermixed with the matrix and locally in pockets in the matrix of the rocks is confirmed by X-ray mapping, and these silica minerals are the source of silica for ASR. The uniform Mg concentration as reflected by the scan across the dolomite rhombs indicates no sign of dedolomitization, and there was no evidence of brucite formation. While the aggregates have the classic texture often cited for ACR, there is no evidence of the deterioration of the dolomite rhombs or migration of Mg into the rims/peripheries of the dolomite rhombs. Instead, in these cases there is compelling evidence that the concrete distress was caused by ASR and not ACR.

Keywords: ASR, ACR, Fine-grained dolomitic limestone, Cryptocrystalline quartz, PLM, SEM-EDS

1.0 INTRODUCTION

One common cited distress mechanism in concrete caused by reaction of certain carbonate rocks is conventionally referred to as “Alkali Carbonate Reaction” [ACR] (Deng & Tang, 1993; Hadley, 1964a; Ozol, 1994; Swenson, 1957; Tang et al., 1987). The term “distress” is widely used to describe material-related deterioration and damage in concrete (example, FHWA Publications: FHWA-RD-01-163, FHWA-RD-01-164, & FHWA-RD-01-165). These are dolomitic limestones consisting of small isolated dolomite rhombs disseminated in a fine-grained calcite, clay, and silt-sized quartz matrix. This type of texture has been referred to as a “classic texture” for ACR reactive aggregates, and used as a guide to identify alkali reactive carbonate rocks. The reactive component of the rock often occurs as thin layers locally in a large otherwise non-reactive carbonate formation. This makes it difficult to mine selectively the non-reactive portion of the carbonate. Although several researches have been conducted over the last 50 years, the mechanism of ACR and its resulting distress in concrete is controversial and still not well understood. A complete understanding of the mechanism of ACR is critical to selecting appropriate measures for preventing deleterious expansion in new concrete structures by designing concrete mixtures that minimize reaction risk, and to formulate or choose suitable technologies to mitigate or suppress the effects of deleterious expansion in existing structures. The current understanding is that while both ACR and ASR exhibit similar damage patterns in concrete, reaction products that cause the distress are different in composition (ASR gel for ASR vs. brucite formation for ACR). There are four proposed hypotheses for the mechanism of ACR and the resulting expansion of concrete: (1) Dedolomitization, without expansion, coupled with expansion due to swelling of clay minerals due to uptake of water (Swenson & Gildot, 1964; Gildot, 1964; Gildot & Swenson, 1969), (2) Expansion caused by de-dolomitization [Hadley, 1964a, Tang et al., 1987; Ozol, 1994], (3) Alkali Silica Reaction (Katayama, 2010; Grattan-Bellew et al., 2010), and (4) Expansion caused by a combination of ASR and clay/insoluble-rich microbeds (Fecteau et al., 2012).

Dedolomitization and the subsequent brucite crystallization appear to be the more favored theory
for the mechanism of ACR. Here the main chemical reaction in the rock is the decomposition of the dolomite CaMg(CO$_3$)$_2$ (dedolomitization) to brucite [Mg(OH)$_2$ and calcite (CaCO$_3$)]. While proponents of this mechanism all agree that, the mechanism of ACR is dedolomitization with formation of brucite and calcite, there are some disagreements about the spatial location where the actual dedolomitization and formation of brucite occur within the reactive carbonate rock aggregates. There are two different proposed mechanisms in the literature. The first and most widely recognized mechanism/model is that dedolomitization of dolomite rhombs occurs within the reactive carbonate rocks and formation of brucite and calcite around the rims of individual dolomite rhombs within dolomitic limestone exhibiting the classic ACR texture (Tang et al., 1987; Tang and Deng, 2004). In this case, the common understanding is that alkali ions and water molecules move into the areas surrounding the dolomite rhombs, followed by movement of these constituents into the dolomite rhombs to react with dolomite to form reaction products around the outsides/rims of the rhombs. It was reported that brucite produced by the reaction occurred in a “2-mm-thick ring of parallel-oriented, 2.5nm brucite crystals (with space between them) surrounding the euhedral dolomite rhombs of the classic reactive texture” (Tang and Deng, 2004). Due to the formation of brucite at the rims of the individual dolomite rhombs, it was claimed that Ca/Mg ratio decreases towards the rims of dolomite rhombs (Tang and Deng, 2004). The volume change due to the crystallization of brucite is believed to be the root cause of cracking in the concrete.

The second proposed mechanism/model states that dedolomitization occurs only at the rims of reactive coarse carbonate aggregates. According to this model, dedolomitization involves only dolomite crystals situated at the margins of reactive dolomitic aggregate particles, close to aggregate-paste interfaces. The authors believed that this led to extensive crack development at the dolomite aggregate-paste interfaces (Gan et al., 1996).

The purpose of this paper is to present two case studies on distress in two concrete structures made from carbonate coarse aggregates that fit the compositional and textural criteria of ACR. The sources of the coarse aggregates used in the concretes and the actual structures were from two geographically different regions.

2.0 METHODS

2.1 Reflected Light and Transmitted Light Microscopy

Concrete samples obtained from both structures were examined visually and using the stereomicroscope. Subsequently, two to three, 19.0 mm (3/4 in.) thick concrete sections were cut from each sample, and one of the resulting surfaces on each was lapped (polished) and examined using a stereomicroscope at magnifications up to 100X. Surfaces of freshly fractured concrete were also studied with the stereomicroscope. Multiples of small representative rectangular blocks were cut from areas of interests of each concrete specimen and placed on individual glass microscope slides with epoxy, and reduced to a thickness of approximately 20 micrometers (0.0008 in.). The thin sections were studied using a petrographic PLM at magnifications up to 500X to identify aggregate types and their mineralogical makeup, and identify secondary deposits that filled cracks and microcracks extending from aggregate particles into the paste.

2.2 Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS)

Thin sections used in the optical analysis and concrete billets were polished using successively finer 9, 6, 3, 1 µm diamond suspension; and the polished sections and polished thin sections were examined using SEM coupled with EDS. The samples were examined at magnifications of 100X to 2200X in the BSE mode. The qualitative SEM-EDS analyses were conducted as a complementory tool to optical microscopy for further investigation into the composition and extent of the gel in the cracks that extended from the argillaceous dolomitic limestone aggregates. Selected samples were also examined in the SEM using BSE signals, and specific compositional information was obtained through collection and processing of characteristics X-rays. EDS maps were collected from different samples to determine the location of phases discriminated by variations in elemental composition. In the EDS map, X-rays are displayed as colorized images assigning a different color to each element. The map for an element visually depicts the number of X-rays collected for an element at each pixel.

2.3 BSE Calcium and Magnesium Profile Analyses Across Dolomite Rhombs in Reactive Aggregates

BSE Ca and Mg counts per second were performed along profiles across dolomite rhombs in reactive carbonate coarse aggregates that possess the “classic texture” referred for ACR reactive carbonate rocks. The Ca and Mg counts along each traverse were plotted against the traverse length to determine if the Mg concentration was depleted in the interior of dolomite rhombs and increased towards or at the rims as proposed previously (Tang & Deng, 2004).

3.0 RESULTS

Visual and stereo-optical examination of lapped concrete cross sections prepared from a pavement and wharf (Beyene et al., 2013) concrete structures showed that some cracks and microcracks originated
from some dark gray, fine-grained dolomitic limestone coarse aggregates extending into the surrounding paste. Most cracks that extend out from the dolomitic limestone coarse aggregates are filled with a white secondary deposit (Figs. 1 & 2) shown by yellow arrows. Some air voids in the paste are linked with cracks, or are near cracks, are also lined with a white gel-looking secondary deposit (Fig. 1). Darker rims are also observed in some of these aggregates as shown by green arrows in Fig. 1.

PLM examination showed that the white gel-looking secondary deposits are ASR gel (Figs. 3 & 4). Figures 3A & 4 are plane-polarized transmitted light thin section photomicrographs showing ASR gel in cracks extending from a reactive, fine-grained, dolomitic limestone coarse aggregates into the paste (shown by arrows). As illustrated in Fig. 3B, under cross-polarized view, the ASR gel appears opaque, a typical characteristic that in most cases differentiates ASR gel from other crystalline secondary deposits.

Figure 5 shows transmitted light thin section photomicrographs of representative reactive dolomitic limestone coarse aggregate particles from distressed concrete structures located in two different geographic regions. The two aggregate particles are similar both in texture and mineralogical composition. The aggregates are relatively fine-grained and consisting of isolated dolomite rhombs disseminated in a fine-grained calcite, clay, and silt-sized quartz matrix.
Fig. 5. Transmitted thin section photomicrographs showing two fine-grained reactive argillaceous dolomitic limestone coarse aggregate particles from two different concrete structures.

BSE imaging with EDS spectra, and x-ray elemental mapping, clearly confirms that the white secondary deposits filling cracks and lining some air voids, are ASR gel (Fig. 6). Fig. 6A is Back scattered electron (BSE) showing an ASR gel filled crack (yellow arrows) extending from reactive, fine-grained dolomitic limestone coarse aggregate into the paste and lining an air void as shown by green arrows. The morphology of the gel and EDS spectra are typical of ASR gel. The image also shows sparsely dispersed rhombic dolomite in the finer matrix of the reactive aggregate. Figure 6B is a close-up of Fig. 6A showing the area outlined by the closed curve (shown by red arrows) where EDS spectrum was collected (shown in C).

Figure 6 (D through G) show similar features and composition as shown in Figs. 6 A, B, & C although the sample was taken from a concrete structure situated in different geographic region. Figure 6D shows back scattered electron (BSE) image showing crack filled with ASR gel extending from reactive, fine-grained dolomitic limestone coarse aggregate particles into the paste, while 6E and 6F are EDS spectrum of ASR gel within the aggregate and within the paste, respectively. Figure 6G is X-ray map showing the distribution of Si in the reactive carbonate aggregate and ASR gel in the crack extending from the aggregate into the paste. The morphology of the gel and EDS spectra is typical of ASR gel. The map exhibits the relative abundance and dispersed nature of the Si phase in the matrix of the reactive coarse aggregate.

PLM examination (Fig. 7A & B) and X-ray elemental map (Fig. 8A) revealed that the dark gray, fine-grained argillaceous dolomitic limestone coarse aggregates are the source of reactive silica for ASR. Unlike traditional alkali reactive siliceous rocks, Si-rich phases in argillaceous dolomitic limestone can occur locally in small pockets and as extremely fine-grained, divided silica particles (cryptocrystalline quartz) intermixed with the matrix of the rock. Figs. 7A & B illustrate pockets of cryptocrystalline quartz locally in the matrix of the rock using high magnification (40X) PLM. The yellow arrows mark the cryptocrystalline quartz. However, most of the silica minerals displayed in the X-ray map (Fig. 8A) in the matrix of the rocks are not discernible using thin section optical petrography due to the very small sizes of these silica minerals. As shown in Figs. 8A, the Si occurs into two forms: (1) as relatively coarser particles, and (2) much smaller sizes, intermixed with the matrix. The coarser particles are detrital, non-reactive form of quartz, while the finer ones are potentially reactive silica minerals.

4.0 DISCUSSION

The validity of the traditional explanation of the reaction mechanism of ACR has become controversial as more and more research has been done in the last twenty years using integrated state-of-the-art methods (including optical microscopy, SEM-EDS, SEM elemental X-ray mapping, Microprobe, and XRD). Even at an earlier time, Gillott (1964) commented that brucite was observed in non-expansive carbonate aggregates and thus the presence of brucite does not confirm the presence of expansion in the concrete. Results of previous studies on concrete reportedly damaged by ACR showed that the root cause of the concrete distress was ASR, not ACR. Katayama (2010) and Grattan-Bellew et al. (2010) performed studies to investigate the mechanism of ACR; all concluded that the root cause of concrete distress in concrete made from reportedly ACR reactive carbonate aggregates is ASR, not ACR. In our current study, the uniform Mg concentration as reflected by the scan across the dolomite rhombs (Figs. 9 & 10) collected along a profile across each dolomite and in the reactive dolomitic limestone aggregate showed that there is no increase in Mg content at the margins/rims.
Fig. 6. Back scattered electron (BSE) image with EDS spectra of ASR gel filled cracks extending from reactive carbonate coarse aggregate particles into the paste.
Recent studies also confirmed that the cause of distress in concrete made from dolostone (Northwest Ohio) and dolomitic limestone (Ontario, Canada) is ASR, not ACR (Smeltz & Farver, 2017; Katayama et al., 2016; Sims, 2016). The reactive silica in both cases is cryptocrystalline quartz hidden in the carbonate rock. Results of our current case studies clearly show that the concrete distress was ASR. There are also case studies showing that a pavement made of dolomitic limestone coarse aggregate deteriorated without alteration of dolomite or formation of brucite (Wong, 1998). Brucite may not always be detected or be present in some concretes claimed to be damaged by ACR (Swenson & Gillott, 1964). Also, studies showed
that the volume of products is less than the reactants which has also raised many questions, and even some proposed alternative mechanisms (Swenson & Gillott, 1964; Gillott, 1964; Gillott & Swenson, 1969).

Unlike ASR, with ACR, there is no gel formation and damage lessens with decreasing coarse aggregate sizes (ACI 221, 1998). Grattan-Bellew et al. (2015) conducted comparison studies on ACR carbonate rocks from three sources after the observation of ASR gel in the Kingston Ontario sidewalk, which was placed to track long-term expansion of the concrete reportedly due to ACR. They compared the mineralogical composition of the acid insoluble residue of the most reactive horizon (#78-16) of the nearby Pittsburg quarry with that of the Spratt Canadian ASR reference aggregate and a Chinese ACR dolomitic limestone and performed concrete prism expansion tests as well. They found a direct correlation between the amount of quartz in the insoluble residues of the rocks from two different continents and the expansion of concrete prisms containing the whole rock aggregates. It seems to be a paradox that the Spratt limestone, which has been an ASR reference aggregate, has much lower silica than the Kingston Pittsburg ACR reference aggregate. However, the expansion results are consistent with the silica amounts – with lower concrete prism expansion (0.275%) of concrete made from the Spratt limestone and the relatively high concrete prism expansion of concrete made from Kingston ACR limestone (0.616%). Results of our preliminary PLM examination on the relative crystallinity of individual crystals of quartz (cryptocrystalline in the Pittsburg aggregate vs. microcrystalline in the Spratt) is consistent with solubility and crystallinity index findings of the two aggregates by Grattan-Bellew et al. (2015).

In carbonate formations, silica typically replaces or infills carbonate minerals during diagenesis (DeMaster, 1981 & 2005). Numerous studies confirmed that there are two sources of silica in
marine environments: biogenic silica and silica derived from deep-marine sediments from active swelling zones (DeMaster, 1981 & 2005). Studies showed that in carbonate rocks, the biogenic source is the major source of silica. Silicate is an essential chemical compound for certain biota, such as diatoms, radiolarian, siliceous sponges, and silicoflagellates, either to build their skeletal structures or as a waste product (DeMaster, 1981). These organisms are believed to extract dissolved silicate from the open ocean surface, and precipitate a biogenic silica referred as “opal-A”, which is a highly disordered and almost completely amorphous, to form siliceous tests [hard parts] (DeMaster, 1981 & 2005; Calvert, 1983; Williams et al., 1985) which accumulate on the sea floor after the organisms die to form siliceous oozes. Progressive diagenesis of opal-A deposits during burial has been well documented in the geological literature (Williams et al., 1985). During diagenesis, as this biogenic silica is buried in the seabed beneath meters to kilometers of sediment and subjected to higher pressure and temperature conditions over a time period of millions of years, the silica undergoes structural, mineralogical, and perhaps some chemical transformations (DeMaster, 1981 & 2005; Calvert, 1983; Williams et al., 1985). The sequence of this transformation during diagenesis is reported to be: opal-A (siliceous biogenic ooze) → opal-A’ (nonbiogenic amorphous silica) → opal-CT → better-ordered opal-CT→cryptocrystalline quartz or chalcedony (<5 micron) → microcrystalline quartz (5-20 microns). Results of our preliminary analyses showed that the reactive quartz in Spratt limestone can be considered as microcrystalline, while the reactive silica minerals in the Pittsburg is cryptocrystalline.

5.0 CONCLUSIONS

The root cause of concrete distress in the two different structures was ASR, not ACR. While the aggregates used in these concretes have the classic texture often cited for ACR, there is no evidence of the deterioration of the dolomite rhombs or migration of Mg into the rims/peripheries of the dolomite rhombs. Instead, in these cases there is compelling evidence that the concrete distress was caused by ASR of microcrystalline and cryptocrystalline reactive silica minerals or phases present in the matrix of the carbonate rock aggregate.

The mechanism of ACR in concrete is still controversial and requires further detail forensic research on concretes affected by ACR and on potentially reactive virgin aggregates from different geographical regions. One logical starting point is to perform petrographic and concrete expansion research with the reference ACR aggregate Pittsburg source from Ontario Canada. And added to the study should be several other identified or suspected ACR aggregates from other regions, such as the Midwest Region of the USA where there is extensive use of carbonate rocks as aggregates in many types of concrete infrastructure.

References


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