

A CRITICAL REVIEW OF CARBONATE ROCK REACTIONS -- IS THEIR REACTIVITY USEFUL OR HARMFUL ?

Tetsuya Katayama
Cement/Concrete Research Laboratory, Sumitomo Cement Co., Ltd.
585 Toyotomi, Funabashi, Japan 274

The contradictory nature of a wide range of carbonate rock reactions has been reviewed and re-interpreted. It has been pointed out that deleterious expansion of the carbonate rocks is independent from a dolomite content and clay mineralogy, but is only related to a high insoluble residue. It should not be called alkali- "carbonate" reaction. In contrast, dedolomitization, accompanied by rim formation, is not an "alkali"- carbonate reaction, but a hydroxyl reaction. It has no particular relation with the rock expansivity. It has been suggested that classic alkali-carbonate reaction should be reviewed in light of alkali-silica reaction, focusing on the reactivity of cryptocrystalline quartz hidden in the insoluble residue of the carbonate rocks. It has also been noted that carbonation phenomena of outer rims should be carefully correlated to the carbonate rock reactions.

1. INTRODUCTION

Since the discovery of alkali-carbonate reaction at Kingston, Ontario, Canada, by Swenson (1), various types of carbonate rock reactions have been recorded from Paleozoic formations in North America (Berard and Roux (2), Mather et al. (3)), and from Mesozoic and Neogene formations in the Middle East (French and Poole (4), Alsinawi and Murad (5)). These reactions could be classified into three types: 1) alkali-carbonate reaction of impure dolomitic limestone (1), 2) alkali-silica reaction of impure limestone (2), and 3) carbonate reaction of pure limestone (3). The former two are often accompanied by a deleterious expansion and/or rim formation, while the last one seems to develop only rim.

Because reactive carbonate rocks cover a wide range of lithologies, from non-dolomitic to dolomitic or from pure to argillaceous or siliceous, the nature and manifestations of their reactions have been sometimes gradational and complex, or even confusing. It was felt necessary to review and clarify the characteristics of the carbonate rock reactions described in the literature, before a systematic study can be made in other countries, for example, Japan. A suggestion for re-examining the classic alkali-carbonate reaction in light of alkali-silica reaction, will be given in this paper.

2. REACTION OF ARGILLACEOUS DOLOMITIC LIMESTONE

Potential alkali reactivity has been reported from impure carbonate rocks, where expansion is strongly alkali dependent and lacks a pessimum phenomenon (Swenson and Gillott (6)). The harmful expansion occurs irrespective of the dolomite content and clay mineralogy. It is only related to a high content of acid insoluble residue, and would not be alkali- "carbonate" reaction. Thus the mineralogy of reactive phases in the insoluble residue should be high-lighted. Some carbonate aggregate develops rim, accompanying with dedolomitization, but rim formation has no correlation with their deleterious expansion. It is not always alkali dependent, but is essentially a hydroxyl ion reaction. Thus dedolomitization has no bearing on the expansion of carbonate rocks.

2.1 Petrography of Expansive Rocks

Early research of alkali-carbonate reaction in North America (Hadley (7), Newlon and Sherwood (8), Swenson and Gillott (9), Lemish and Moore (10)) emphasized that deleteriously reactive carbonate rocks have in common the following petrography: 1) fine-grained dolomitic limestone, with silt sized dolomite rhomb floating in the micro- to cryptocrystalline matrix of calcite and clay, 2) dolomite constituting 40-60% of the carbonate fraction, and 3) acid-insoluble residue, ranging from 10-20%, mostly composed of quartz and illite. This holds well for early expansive rocks, represented by a dolomitic limestone of Kingston, Ontario. But subsequent research suggested exceptions to be present so that the feasibility of screening reactive rocks by these petrographic criteria has been questionable (Axon and Lind (11), Smith (12), Dolar-Mantuani (13)).

Lithology. The Ordovician Gull River (Lower Black River) Formation in Ontario, Canada, contains alkali-carbonate reactive rocks. It is thinly bedded with shaley intercalations, or sometimes, chert nodules, and is heterogenous even in hand specimens, carrying argillaceous laminations and *stylolite* seams where acid insoluble materials are concentrated (13, 14). Expansivity of the rock cylinder in alkaline solution is different bed by bed, and specimens cut normal to the bedding plane expands more than those cut parallel to this plain (6). Dolar-Mantuani (13) reported that a clayey *stylolite* part had caused early expansion to crack rock cylinders, suggesting that the insoluble materials may be responsible for the expansion. These lithological and expansionary behaviors are common to reactive carbonate rocks of Paleozoic formations in North America.

Carbonate composition. Compositions of the Gull River Formation are plotted in Figure 1, from modifying a diagram for the rapid chemical screening test proposed by Rogers ((15), from his Figure 8 where CaO/MgO ratio is used). Potentially expansive rocks appear to occupy the range between 15-70% dolomite in the carbonate fraction and between 5-30% insoluble residue, which is wider than previously believed. Limestones with more than 5% dolomite of this formation are also known to be expansive (Ryell et al. (16)). Sandy to silty dolostones containing 20-35% insoluble residue may be late expansive, whose expansion starts after several months of contraction in alkaline solution (Dolar-Mantuani (14, 17)), but this type has no cases of concrete distress (Walker (18)). Highly dolomitic rocks generally develop a well-crystallized interlocking texture of carbonates, which tends to prevent penetration of alkaline solution and thus reduces expansion (Hilton (19)).

Potentially expansive carbonate rocks of North America have varying compositions from region to region, with the major compositions of higher reactivity as follows: Missouri, dolomitic limestones with 5-40% dolomite and 5-10% insoluble residue (11); Virginia, dolomitic limestones containing 25-75% dolomite and 10-30% insoluble residue (Sherwood and Newlon (20)); Indiana, dolostones with more than 80% dolomite and more than 10% clay (Hadley (21)); Quebec, limestones with less than 15% dolomite or dolostones with more than 85% dolomite, both containing 5-20% insoluble residue (Durand and Berard (22)). This would suggest that reactive carbonate rocks cover the whole range of dolomite ratio, and there are no correlations between the expansion and dolomite content in these rocks.

Insoluble residue. Clay minerals of North American reactive carbonate rocks are dominantly illite, with subordinate mixed-layer clay or chlorite (7). However, the type of clay mineral is not a determining factor in the reactivity of carbonate rocks, because it is similar to both reactive and non-reactive rocks (7), and is also common to alkali-silica reactive limestones in Quebec (Pournier et al. (23, 24)). There is apparently a "minimum clay content" necessary for causing expansion, usually more than 10%, where the clay means the fraction of insoluble residue finer than the silt size (Hadley (21, 25)). Thus, in the alkali-carbonate reaction, a higher content of insoluble residue, at least 5-10%, appears to be the sole common characteristic among expansive carbonate rocks. It is in this portion that deleteriously alkali reactive materials exist.

Insoluble residue of reactive carbonate rocks consists mainly of silica, ranging from about 70% SiO₂ in Ontario (15), to 90% SiO₂ in Iowa where chert is common (Bisque and Lemish (26)). Most of this silica has been attributed to detrital quartz of the silt

size (7,10), while cryptocrystalline quartz of authigenic origin has seldom been reported. However, the result of a quick chemical test of the insoluble residue of a Kingston dolomitic limestone, suggests the presence of crypto- to microcrystalline quartz in this rock, because it showed a potential alkali-silica reactivity (6). It is very likely that authigenic cryptocrystalline quartz is present in the argillaceous to siliceous impurity parts in the Paleozoic carbonate rocks, because this type of quartz is formed in association with mixed-layer clay or chlorite from argillaceous impurities during diagenesis, as known in the siliceous sedimentary rocks (Katayama and Futagawa (27)). Cryptocrystalline quartz is likely missed, either by the optical microscopy using thin sections, or by the XRD analysis because it gives diffraction patterns of quartz. A more detailed examination would be necessary by means of SEM observations of the insoluble residue to explain the potential alkali reactivity of the residue.

2.2 Rim Formation of Dolomitic Rocks

The process of dedolomitization sometimes develops reaction rims on the periphery of carbonate aggregates in concrete, but the tendency for this development is not always alkali dependent. Dolomitic limestone from Kingston (6) and Virginia (Newlon et al. (28)), developed conspicuous rim when low alkali cement was used. Some of rim forming rocks in Indiana had a low resistivity to freezing and thawing (21), suggesting that the process of rim formation is also related to the permeability of rocks. Rim is classified into positive, neutral, and negative rims, according to the resistance to acid-etching. In general, dolomitic rocks form positive rim, while highly calcitic rocks negative rim, but there is no apparent relationship between the rim development and expansivity of these rocks (18, 19). This is probably because rim formation is based on a hydroxyl ion reaction of carbonate minerals, while expansion is closely related to alkali reaction of particular phases of insoluble residue in the rock. It is therefore necessary to distinguish rim formation and expansivity of carbonate rocks.

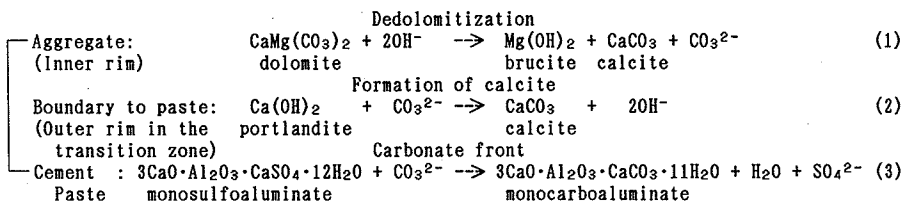
Positive rim. This rim is formed in some of the impure dolomitic rocks that contain a large amount of insoluble residue. Bisque and Lemish (26) first described this in a distressed concrete in Iowa, where dolomitic limestone of the Devonian Rapid Member was used. It is enriched in silica and has a resistance to etching by dilute hydrochloric acid, showing a positive relief against the interior aggregate on the sawed surface of concrete (26, 29). Some rocks developing this rim are deleteriously expansive (26), while others are not (21). A non-expansive dolomitic limestone in India, developed a white rim enriched in potassium and silicon, in addition to crystalline calcium aluminate hydrate (Samuel et al. (30)). Positive rim can be reproduced either by low-alkali (29,31), or high-alkali cement (20, 21) in the mortar and concrete. In the former case, the aggregate did not expand. It is therefore suggested that the process of dedolomitization, accompanied by rim formation, has nothing to do with the deleterious expansivity of carbonate rocks.

Positive rim is formed in the presence of reactive silica, or perhaps, clay minerals like illite, in the impure dolomitic rocks. Lemish et al. (32) showed, with XRD analysis, that finely divided impurity quartz in the rim zone decreases in parallel with dedolomitization toward the interface with the cement paste. Hadley (25) suggested that dissolved silica is fixed by brucite to form magnesium silicate hydrate, which presents a siliceous rim after etching. This explains the absence of siliceous rim in non-dolomitic limestones, because such rocks can not produce brucite. EPMA analysis by Poole and Sotiropoulos (33) revealed that the site of reaction between silicon and magnesium clearly exists, but away from the aggregate in the case of a pure dolostone.

Neutral rim. Poole (34) reported a neutral rim in the relatively pure dolostones from Bahrain and Libya. On etching, this rim dissolves at the same time with the interior of aggregate. Calcite is formed in this rim by dedolomitization, but silica is not enriched. Rim formation is common in the dolomitic aggregates in the Middle East, but it has not been believed to be expansive reaction (Sims (35), (36)). A low content of clay (34), or, of insoluble residue, seems to be responsible for the non-deleterious nature of these aggregates, and for the low content of silica in this rim. This suggests that the process of dedolomitization itself is not a harmful process that causes expansion of concrete.

2.3 Reaction Products of Dolomitic Rocks

The process of dedolomitization forms brucite and calcite in the reacted dolomitic aggregate, and monocarboaluminate in the concrete. The main reactions, including a concept of "carbonate front" by Hadley (7, 25), could be written as follows:



Brucite. This is formed through dedolomitization (formula 1), but is independent of the expansivity of rock cylinders of dolomitic rocks in alkaline solution (10). Swenson and Gillott (6) first described this reaction experimentally by XRD analysis in the dolomitic limestone from Kingston. Though brucite was first considered as a cause of deleterious expansion of dolomitic limestone, this hypothesis was abandoned because the total of unit cell volume of brucite and calcite is less than dolomite (9). Brucite is formed by a rather "in-situ" reaction, coating the surface of dolomite crystals (Carles-Gibergues et al. (37)). It occurs as sheet-like crystals arranged parallel to the surface of dolomite (Tang et al. (38)), suggesting that their c-axes are perpendicular to the surface, similar to the orientation of portlandite crystals formed on a limestone aggregate (39). Brucite has been identified in the reacted aggregate from distressed concrete in Virginia by XRD (40), and in the reaction rim of dolostone aggregate in Bahrain by EPMA analysis (4).

Calcite. Calcite is also produced during dedolomitization (formula 1). It appears in the reaction rim within dolomitic limestone aggregates from Iowa (32) and Kingston (37) in laboratory concretes, and also within dolostone aggregate in the distressed concrete in Bahrain (4). Calcite occurs as fine-grained crystals, either of idiomorphic precipitates in the reaction rim (37), or of pseudomorphic replacements after dolomite rhombs in the rock cylinder that had long been in contact with alkaline solution (Walker (41)). Calcite increases in amount with a decrease in dolomite toward the interface with cement paste.

Hadley (7) postulated that carbonate ions released from a dedolimitizing aggregate would react with hydration products of cement (portlandite) to produce secondary calcite in the cement paste (formula 2), but he did not recognize this process in his experiment. Later, Poole and Sotiropoulos (33, 34) observed that calcite occasionally appears forming an outer rim in the cement paste immediately adjacent to the dolostone aggregate from Bahrain. They interpreted this calcite to be the product of the carbonation reaction (formula 2). Carles-Gibergues et al. (37) observed a similar carbonation process in the transition zone around reacted Kingston dolomitic aggregate in laboratory, and assumed a dissolution-diffusion-precipitation process of calcium to occur during dedolomitization. However, it may be generally difficult to determine the origin of carbonate ions whether they were derived from the carbonate aggregate or from the atmosphere, when the mortar and concrete have long been exposed to the room atmosphere at accelerated conditions.

Monocarboaluminate. This hydrate is formed in the cement paste that surrounds the coarse aggregate of dolomitic limestone (7), and of non-dolomitic limestone (3). It is formed from monosulfoaluminate through its carbonation by the carbonate ions released from dedolimitizing aggregates (formula 3), as well as from limestones that are reacting with hydroxyl ions in the cement paste, as discussed later. Hadley (7, 25) called this site "carbonate front". It has been observed that sulfur is released and concentrated in the cement paste far beyond the outer rims of dolostone aggregate in this reaction (33).

Alkali-silica gel. Although the presence of reactive silica is suspected in the insoluble residue of some dolomitic rocks, the occurrence of siliceous gels from reacted

aggregates has been rarely reported in the alkali-carbonate reaction, such as Kingston, Ontario (6), Bahrain (4), and Tennessee (Hugenberg (42)). General absence of the siliceous gels in the dolomitic aggregates could be interpreted as a result of the fixation process of dissolved silica by brucite in the siliceous rim of the aggregate.

3. REACTION OF SILICEOUS AND ARGILLACEOUS LIMESTONE

The Ordovician Trenton Group in the St. Lawrence Lowlands, Quebec, contains several horizons of alkali-silica reactive limestones. These limestones, beside inclusions of occasional chert nodules and veinlets (43), contain a siliceous and argillaceous matrix, composed of cryptocrystalline quartz intimately mixed with illite, mixed-layer clay and chlorite (Fournier et al. (23, 24)). This matrix constitutes an acid-insoluble, alveolar network of silica around fine-grained calcite, as revealed by SEM observations (23, 24).

In Ontario, a limestone of Lower Trenton age, containing 3% chert and chalcedony, is alkali-silica reactive (Rogers (44), (45)). Compositional ranges of some of Trenton limestones in Quebec, shown by Durand and Berard (22) (Figure 2), are overlapping with those of alkali-carbonate reactive dolomitic limestones of the Gull River (Lower Black River) Formation in Ontario (Figure 1, (16)). Thus, some of the reported cases of alkali-carbonate reaction may be grading into, or have an aspect of alkali-silica reaction.

Potential alkali-reactivity. In Quebec, a modified quick chemical test has been applied successfully to the acid insoluble residue of Trenton limestones (2, 23). Fournier and Berube (46, 47) found a good correlation to be present between the expansions in the concrete prism test and the dissolved silica (Sc), or corrected dissolved silica (Sc^*) calculated on the original rock basis. That is, more than 90% of Trenton limestones and more than 70% of Black River limestones in Quebec having $Sc > 100$, $Rc > 100$, or, $Sc^* > 10$, $Rc^* > 9.5$, were deleteriously expansive in their test. There was no good correlation, however, between the expansion rate and the values of these dissolved silicas (Sc , Sc^*). This is due probably to the wide variety of porosity and permeability of these carbonate rocks, that lead to produce different expansion behaviors in concrete.

Reaction of insoluble residue. Fournier and Berube (46, 47) revealed that siliceous limestones of the Ordovician Black River and the Trenton Groups in Quebec, containing more than 6% insoluble residue, are deleterious in both concrete bar and accelerated mortar bar tests. They confirmed by SEM observations that calcium-rich silica gels were formed in the cement paste of expanded mortars, and attributed the cause of expansion to alkali-silica reaction of cryptocrystalline quartz contained in the insoluble residue of these rocks (24). This finding presents important suggestions to the study of alkali-carbonate reaction. Because deleteriously expansive dolomitic aggregates, whose reaction has often been classified as alkali-carbonate reaction since the 1960's in North America, contain similar amounts of insoluble residues in the matrix of the rocks. The mineralogy and morphology of the insoluble part of these aggregates has not yet been fully examined by means of modern analytical techniques, such as SEM/EDXA, EPMA, etc. It will therefore be worth examining whether these rocks contain cryptocrystalline quartz or any other form of reactive silica, which is sufficient to produce alkali-silica reaction.

Alkali-silica gel. Calcium-rich alkali-silica gels have been reported from distressed field concretes in Quebec (22, Berube and Fournier (48)). Reacted limestone has dark reaction rim on the periphery of aggregate, and inner white gel deposits inside, or sometimes cracks filled with white gels. Exuded gels are deposited lining air voids of in affected concretes. Various types of the gel deposits have been found, ranging from calcium-rich to silica-rich and from massive to rosette-like, all of which are similar to the occurrence of a typical alkali-silica reaction (48). These gels may be also formed in the rock cylinders in alkali solution and mortar bars (23, 24). Durand and Berard (22) suggested that gels, filling veins within reacted aggregates, have a uniform composition among samples collected from several localities, i.e. SiO_2 51%, FeO 2%, CaO 12%, Na_2O 6%, K_2O 8% (wet base), so that analysis by EDXA/SEM observations could be helpful for diagnosing alkali-silica reaction caused by a reactive siliceous limestone.

4. REACTION OF PURE LIMESTONE

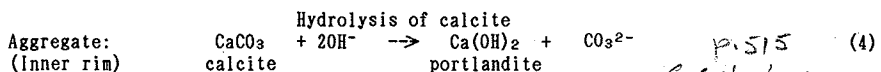
In the present knowledge of cement chemistry, calcite is not an inert substance but may react with portland cement paste to produce several types of calcium-bearing hydrates. Reaction products at the interface of limestone aggregate and cement paste, are sometimes effective for improving bond strength in this zone. Some limestone aggregates develop a reaction rim, but the rims have no detrimental effect on the properties of concrete. These calcite reactions are not alkali dependent, but a hydroxyl ion reaction, and it is not desirable to call these "alkali"-carbonate reaction.

4.1 Rim Formation of Pure Limestone

Development of dark rim in the limestone aggregate has been reported from concrete structures in Kansas and Nebraska, where low alkali cements were used (Mather and Mielenz (49), (3)). Such rim is slightly soluble to etching with dilute hydrochloric acid, leaving negative relief and thus called negative rim. These rocks were generally soft and porous, non-dolomitic limestones with low insoluble residue, having a fine texture of micritic calcite, sometimes showed an earthy appearance. Similar rims were formed on the cut surface of concrete core, stored more than one year at high humidity (3). The rims were interpreted as a leaching phenomenon, and there was no evidence of deleterious expansion.

Negative rim. Mather and Mielenz (49) noted that the bond between rimmed limestone and cement paste was excellent in a field concrete. Several researchers believe that negative rim represents a harmless (3), or a beneficial reaction that may develop bond strength (39). However, the presence of negative rim is not always a proof of innocuous sign of limestones, because data suggests that some dolomitic limestones in Virginia, which develop negative rim and contain 10-25% dolomite along with more than 5% insoluble residue, expanded in the rock prism test (comparison of Figures 9 and 13 of (20)).

Portlandite. Buck and Dolch (39) found experimentally that the negative rim was produced in a fine-grained limestone more conspicuously when low alkali cement was used, unlike alkali-silica reaction. In this rim, 0.5-1mm in thickness, hexagonal plates of portlandite were formed parallel to the surface of the limestone, with their c-axes arranged perpendicularly to the surface of aggregate. They found by XRD analysis that calcite decreased with increasing portlandite, and interpreted that the calcite crystals in this rim zone have partly been transformed into portlandite. They further suggested that this type of reaction may occur in all carbonate rocks to varying degrees when in contact with hydrated portland cement paste. Chen and Wang (50) observed by SEM that the surface of a crystalline limestone was dissolved to precipitate tabular portlandite on it. The reaction would be written as follows:



4.2 Development of Bond between Aggregate and Cement Paste

Carbonate rocks, especially limestone, often develop better bonding with cement paste than other rock types (Farran (51), Hsu and Slate (52), Zimbelmann (53)). The surface of the limestone aggregate in contact with cement paste, is often corroded during hydration of cement (50, 51, Grandet and Olivier (54), Monteiro and Mehta (55)). These observations suggest that certain chemical reactions occur at the interface between calcite and the cement paste, which may improve their bond.

Bond between calcite and portlandite. Farran (51) assumed an epitaxial bridge to be produced between calcite and cement hydrates to explain the excellent bond of the limestone. SEM observations by later researchers indicate that a thin layer of portlandite is formed on the limestone aggregate, oriented parallel (c-axes perpendicular) to its surface. Such occurrence has generally been referred to epitaxial growth of calcite (55), and the better bonding of the limestone aggregate has been attributed to

this epitaxy (53). However, such epitaxy may be superficial, because no structural connection has been proved between the portlandite and the underlying calcite crystals of the limestone aggregate (50). The portlandite crystals precipitated from a water film around the aggregate in the early stage of hydration of cement. They can be formed on any type of material like polyethylene or quartz (Grandet and Olivier (56)). Monteiro and Mehta (55), based on XRD, attributed the strong bond between limestone and cement paste to the formation of basic calcium carbonate hydrate, $2\text{CaCO}_3 \cdot \text{Ca}(\text{OH})_2 \cdot 1.5 \text{H}_2\text{O}$, as a result of reaction between calcite and portlandite.

Monocarboaluminate. The formation of monocarboaluminate at the interface between limestone aggregate and cement paste has alternatively been believed to be responsible for the improved bonding of this aggregate (50, 54, Lyubimova and Pinus (57)). It is formed in the mortar and concrete that contain calcite, but may be also found in the weathered mortar and concrete that is devoid of carbonate aggregate. When calcite is present as a fine powder, monocarboaluminate is formed from ettringite, through an intermediate carbonate phase, taking up the carbonate ions released from calcite (54). In the case of coarse aggregate, it is formed from monosulfoaluminate in the cement paste around the aggregate, through the carbonation process similar to the carbonate front proposed by Hadley (7, 25). However, the release of carbonate ions is essentially based on a hydroxyl reaction of calcite, and is not dependent of alkali-content of cement.

Monocarboaluminate has been identified by XRD from the cement paste surrounding the coarse limestone aggregate in the field concrete (3). In Kansas and Nebraska, replacement of 30% of crushed limestone coarse aggregate to alkali-silica reactive sand-gravel aggregates, have been known to be effective for sweetening their reactivity. It is known as "limestone sweetening". Hadley (58) suggested that a reaction of the monocarboaluminate formation may be effective for suppressing the alkali-silica reaction, because this process may lower the alkalinity of pore fluids in concrete by releasing sulfate ions from sulfoaluminate hydrates. This aspect would suggest a need for further research, about whether or not the formation of monocarboaluminate around the carbonate aggregate accelerates the process of neutralization, which leads to the carbonation of concrete.

5. OUTER RIMS IN CONCRETE

There have been puzzling phenomena in the field concretes that develop outer rims around the carbonate aggregates. Outer rims are formed in the transition zone between the aggregate surface and cement paste. Because this zone has a porous and permeable structure at early ages of cement hydration, reflecting a high water/cement ratio around the coarse aggregate, it is generally believed to be the weakest zone in concrete, both mechanically and chemically. Thus the transition zone often becomes a site which is vulnerable to a carbonation process by a penetrating water that contains carbonate ions. This makes it difficult to identify whether the carbonated outer rims were formed solely by carbonate rock reactions, or by long term weathering of concrete.

Carbonate halo. During the setting of cement, portlandite precipitates from bleeding water and, later, it may be carbonated to form a white rim surrounding the aggregate. Bisque and Lemish (30) called such a rim "carbonate halo", and distinguished it from reaction rim. Segregations of this portlandite at the periphery of aggregate should not be mistaken as a reaction rim (McConnell et al. (59)). Dolomitic limestone aggregate having positive rim in deteriorated concrete in Iowa, had an outer rim of portlandite layer, which easily etched to produce a groove ditch (Lemish et al. (60)).

Carbonated rim. Mather et al. (3) found from old concrete structures in Kansas and Nebraska, that cement paste surrounding innocuous limestone aggregates has been intensively carbonated and portlandite was absent. They called this "carbonated rim". Similarly, Sims and Poole (33) noted "calclitic haloes", that surround innocuous dolostone aggregates in the field concrete in Bahrain, but have a poor bond with the cement paste. These rims and haloes, which consist of fine-grained calcite, present a brownish tint, suggesting that the concretes have been altered to some extent during weathering.

Intensive carbonation of cement paste has been also noted around the deleteriously reactive carbonate aggregates in the distressed concretes in North America (43, Lemish (61)). Such processes, characterized by the carbonated rim devoid of portlandite, have been considered as diagnostic of alkali-carbonate reaction (ASTM C856). However, in the field, it may be difficult to ascertain the origin of the carbonated rim, whether it is related to the reactions of carbonate aggregates (formula 2), such as dedolomitization (formula 1) or calcite hydrolysis (decalcitization, formula 4). Because there are several factors accompanying the reactions, e.g. freezing and thawing in North America (22, 60) and sulfate attack in the Middle East (4). It should be noted that these agencies weaken the bond between the cement and aggregate to produce a weak socket around the aggregate, where carbonation of cement paste may proceed selectively in the cracked concretes.

General cases of carbonation around aggregate. Carbonation of the cement paste around the aggregate, i.e. the aggregate socket, is brought about by many environmental factors, which are quite independent of the rock types: 1) carbonation of bleeding water (30), 2) solution/dissolution process of calcium from cement paste by repeated drying and wetting, or, drying out of concrete specimen after the coring (Idorn (62)), 3) weathering of concrete by repeated freezing and thawing (Jackson (63)), 4) replacement by calcite after leaching of water-soluble alkali-silica gels, formed during alkali-silica reaction of chalcedonic chert (Gilmore (64)), flint (62), and andesite (Iiyama et al. (65)), and 5) chemical corrosion by ground water containing carbonate ions (Idorn (66)). Such processes will proceed if the concrete has a higher water/cement ratio and a porous texture of hydrated gel. Thus, carbonate ions are available from everywhere during long term weathering of concrete, and evidence of carbonation around the aggregate can not always be the proof of carbonate aggregate reactions. We should therefore be careful to interpret the origin of the carbonated rims around carbonate aggregates.

6. SUMMARY AND SUGGESTIONS FOR FURTHER RESEARCH

A summary of the complicated nature of carbonate rock reactions is given, together with a suggestion based on the examination of a concrete sample taken from a locality of typical alkali-carbonate reaction.

6.1 Concrete from Cornwall, Canada

A small sample of distressed concrete from Cornwall, a typical locality of alkali-carbonate reaction (45), has been examined petrographically by the present author. This concrete contains coarse aggregates of various carbonate compositions, ranging from impure limestone to impure dolomitic limestone, the lithology of the latter being known as the typical alkali-carbonate reactive. In thin section, a crack similar to (13), was found running from an argillaceous lense of stylolite in a limestone aggregate into the cement paste. Transparent, partly carbonated gels were seen, lining air voids which contact this crack (Figure 3A) or another limestone aggregate (Figure 3B). EPMA analysis showed that these gels are calcium-rich silica gel, with less alkalis (wet basis): SiO₂ 37-40%, Al₂O₃ 1-3%, Fe₂O₃ 0.3-2.0%, MgO 1-3%, CaO 19-24%, Na₂O 0.2-0.8%, K₂O 0.2-0.4%.

The result indicates that the main visible reaction involved in this concrete is alkali-silica reaction of impure limestone, containing less than 10% of dolomite. Though the high calcium and low alkalis in these gels are fairly different from the typical products of alkali-silica reaction (22), this may be due to migration of these gels from the reacted aggregate into the cement paste. Feldman and Sereda (67) suggested that the reaction product of typical alkali-carbonate reaction in the Kingston dolomitic limestone, has a nature resembling alkali-silica gel. On the other hand, there is little possibility that clay minerals in the stylolite part caused expansion. Because silicates like the clay minerals are not expansive in alkaline solution, and the well-known "alkali-silicate reaction" has been proved to be alkali-silica reaction of crypto- to microstalline quartz in the argillaceous rocks (Tang et al. (68)). Thus, alkali-carbonate reaction also should be reviewed in light of alkali-silica reaction, focusing the nature of reactive silica and reaction products by means of modern analytical techniques such as EPMA and EDXA.

6.2 Summary of Carbonate Rock Reactions

- 1) Both calcite and dolomite may react with hydroxyl ions of cement paste to form several types of reaction rims. But such reactions are not responsible for abnormal expansion of concrete, nor alkali dependent in nature. It would not be desirable to call the reactions "alkali"-carbonate reaction. This is sometimes a useful reaction for limestone-aggregate concretes because it develops the bond strength of concrete.
- 2) Deleterious expansion is confined to impure carbonate rocks that contain more than 5-10% of acid insoluble residue. It is alkali dependent but quite independent from the category of carbonate rocks, whether it is a limestone or a dolostone or something else. The expansion is caused by ingredients other than carbonate minerals, thus the terminology of alkali-"carbonate" reaction is not suitable for denoting this process.
- 3) Scattered evidence of siliceous gels formed and the occasional association of cryptocrystalline quartz in the impure carbonate rocks, suggests that the deleterious expansion of these aggregates may be caused by this silica hidden in the rocks. It is therefore suggested that classic alkali-carbonate reaction should be reviewed in light of alkali-silica reaction of the cryptocrystalline quartz, focusing the mineralogical nature of the insoluble residue and reaction products by means of modern analytical techniques.
- 4) There are several confusing phenomena of carbonation processes of cement paste, that form outer rims around the aggregate in the field concretes. It is generally difficult to identify the origin of carbonate ions of these rims, whether they have been derived from carbonate rock reactions of aggregate or from the surrounding media such as water and atmosphere. Thus such rims are not always the proof of the carbonate rock reactions.

7. ABBREVIATIONS AND MODIFICATION

EDXA = energy-dispersive X-ray analyzer
 EPMA = electron-probe microanalyzer
 Rc = reduced alkalinity (m mol/l) (Rc* = corrected Rc on the original rock basis)
 Sc = dissolved silica (m mol/l). (Sc* = corrected Sc on the original rock basis)
 SEM = scanning electron microscope
 XRD = X-ray diffraction
 CaO/MgO ratio of carbonate rocks (15) can be changed into carbonate compositions (Figure 1), using the equation: $d = 56.03 \times 100 / (21.86 m + 25.62)$, where
 m = CaO/MgO, d = dolomite (%) in the carbonate fraction

8. REFERENCES

1. Swenson, E.G., 1957, ASTM Bulletin 226, 48.
2. Berard, J., and Roux, R., 1986, Can. J. Civl. Eng. 13, 12.
3. Mather, K., Buck, A.D., and Luke, W.I., 1964, Highway Research Record 45, 72.
4. French, W.J., and Poole, A.B., 1974, Cement and Concrete Research 4, 925.
5. Alsinawi, S.A., and Murad, S., 1976, Proc 3rd Int. Symposium, London, on the Effect of Alkalis on the Properties of Concrete. 255.
6. Swenson, E.G., and Gillott, J.E., 1960, Highway Research Board, Bulletin 275, 18.
7. Hadley, D.W., 1961, Highway Research Board, Proceedings, 40, 462.
8. Newlon, H.H.Jr., and Sherwood, W.C., 1962, Highway Research Board, Bulletin 355, 27.
9. Swenson, E.G., and Gillott, J.E., 1964, Highway Research Record 45, 21.
10. Lemish, J., and Moore, W.J., 1964, Highway Research Record 45, 57.
11. Axon, E.O., and Lind, J., 1964, Highway Research Record 45, 114.
12. Smith, P., 1964, Highway Research Record 45, 126.
13. Dolar-Mantuani, L., 1964, Highway Research Record 45, 178.
14. Dolar-Mantuani, L., 1975, Ontario Division of Mines, Industrial Mineral Report, 42, 59p.
15. Rogers, C.A., 1986, Cement, Concrete and Aggregates, 8, 13.
16. Ryell, J., Chojnacki, B., Woda, G., and Koniuszy, Z.D., 1974, Transportation Research

- Record, 525, 43.
17. Dolan-Mantuani, L., 1971, Highway Research Record 353, 1.
 18. Walker, H. N., 1978, ASTM Special Technical Publication 169 B, 722.
 19. Hilton, M. H., 1968, Virginia Highway Research Council, Progress Report 7b, 61p.
 20. Sherwood, W. C., and Newlon, H. H. Jr., 1964, Highway Research Record 45, 222.
 21. Hadley, D. W., 1964, Highway Research Record 45, 196.
 22. Durand, M., and Berard, J., 1974, Can. Geotech. J. 11, 248.
 23. Fournier, B. F., Berube, M. A., and Vezina, D., 1986, Proc. 7th I.C.A.A.R., Ottawa, 23.
 24. Fournier, B. F., and Berube, M. A., 1991, Cement and Concrete Research, 21, 1069.
 25. Hadley, D. W., 1964, Highway Research Record 45, 1.
 26. Bisque, R. E., and Lemish, J., 1958, Highway Research Board, Bulletin, 196, 29.
 27. Katayama, T., and Futagawa, T., 1989, Proc. 8th I.C.A.A.R., Kyoto, 525.
 28. Newlon, H. H. Jr., Ozol, M. A., and Sherwood, W. C., 1972, Virginia Highway Research Council, Progress Report 5, VHRC 71, R33, 78p.
 29. Bisque, R. E., and Lemish, J., 1960, Highway Research Board, Bulletin, 239, 41.
 30. Samuel, G., Wason, R. C., and Mullick, A. K., 1989, Proc. 8th I.C.A.A.R., Kyoto, 235.
 31. Bisque, R. E., and Lemish, J., 1960, Highway Research Board, Bulletin, 275, 32.
 32. Lemish, J., Harwood, R. J., Hiltrop, C. L., and Werner, M. A., 1963, Highway Research Record, 3, 1.
 33. Poole, A. B., and Sotiropoulos, P., 1980, Q. J. Eng. Geol. London, 13, 281.
 34. Poole, A. B., 1981, Proc. 5th I.C.A.A.R., Capetown, S252/34, 9p.
 35. Sims, I., 1981, Concrete, 15, Oct. 27., Nov. 29.
 36. Sims, I., 1981, Proc. 5th I.C.A.A.R., Capetown, S252/13, 13p.
 37. Carles-Gibergues, A., Ollivier, J. P., Fournier, B., and Berube, M. A., 1989, Proc. 8th I. C. A. A. R., Kyoto, 161.
 38. Tang, M., Liu, Z., and Han, S., 1986, Proc. 7th I.C.A.A.R., Ottawa, 275.
 39. Buck, A. D., and Dolch, W. L., 1966, J. Amer. Concrete Institute, Proc., 63, 755.
 40. Sherwood, W. C., and Newlon, H. H. Jr., 1964, Highway Research Record 45, 41.
 41. Walker, H. N., 1974, Transportation Research Record, 525, 28.
 42. Hugenberg, T., Amer. Concrete Institute, SP.100, 1883.
 43. Durand, B., and Berard, J., 1987, Materials and Structures, 20, 39.
 44. Rogers, C. A., 1985, Ontario Ministry of Transportation and Communications, Engineering Materials Office, Report EM-31, 44p.
 45. Field Trip Guide Book, 1986, 7th I. C. A. A. R., Ottawa, Ontario Ministry of Transportation.
 46. Fournier, B., and Berube, M. A., 1989, Proc. 8th I.C.A.A.R., Kyoto, 363.
 47. Fournier, B., and Berube, M. A., 1990, Ontario Ministry of Transportation, Engineering Materials Office, Report EM-92, 118.
 48. Berube, M. A., and Fournier, B., 1986, Canadian Mineralogist, 24, 271.
 49. Mather, K., and Mielenz, R. C., 1960, Highway Research Board, Proceedings, 39, 205.
 50. Chen, Z., and Wang, J., 1987, Cement and Concrete Research, 17, 544.
 51. Farran, J., 1956, Revue des Materiaux de Construction et de Travaux Publics, 490-492, 155.
 52. Hsu, T. T. C., and Slate, F. O., 1963, J. Amer. Concrete Institute, Proc., 60, 465.
 53. Zimbelmann, R., 1985, Cement and Concrete Research, 15, 801.
 54. Grandet, J., and Olivier, J. P., 1980, Cement and Concrete Research, 10, 759.
 55. Monteiro, P. J. M., and Mehta, P. K., 1986, Cement and Concrete Research, 16, 127.
 56. Grandet, J., and Olivier, J. P., 1980, Proc. 7th Int. Congress on the Chemistry of Cement, Paris, 3, VII-85.
 57. Lyubimova, T. Y. and Pinus, E. R., 1962, Colloid J. USSR, 24, 491.
 58. Hadley, D. W., 1968, J. Portland Cement Association, Res. Devel. Lab., 10, 77.
 59. McConnell, D., Mielenz, R. C., Holland, W. Y., and Greene, K. T., 1947, J. Amer. Concrete Institute, Proceedings, 44, 93.
 60. Lemish, J., Rush, F. E., and Hiltrop, C. L., 1958, Highway Research Board, Bulletin 196, 1.
 61. Lemish, J., 1961, Trans. AIME, 220, 195.
 62. Idorn, G., 1964, "Studies of Disintegrated Concrete," The Danish National Institute of Building Research and the Academy of Technical Sciences, Progress Report N-6, 81p.
 63. Jackson, F. H., 1945, Public Roads, 24, 98.
 64. Gilmore, W., 1952, J. Amer. Concrete Institute, Proceedings, 49, 731.
 65. Iiyama, J. T., Kusano, M., and Tokunaga, Y., 1986, Proc. 7th I. C. A. A. R., Ottawa, 386.
 66. Idorn, G., 1957, Acta Polytechnica, 4, 48p.
 67. Feldman, R. F., and Sereda, P. J., 1961, J. Amer. Concrete Institute, Proceedings, 58, 203.
 68. Tang, M., Wan, J., and Han, S., 1991, Il Cemento, 88, 98.

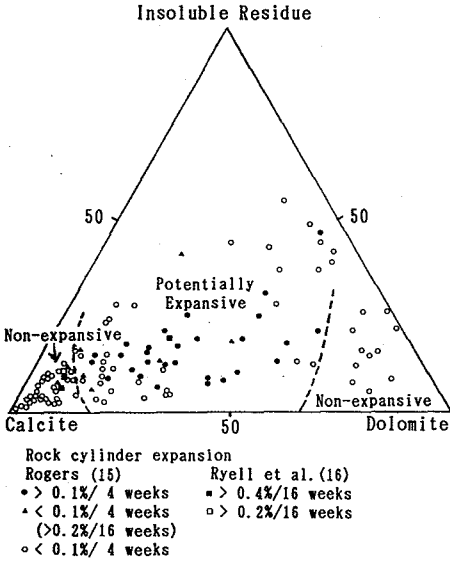


Figure 1 Carbonate rock reactivity of Ordovician Gull River Formation, Ontario, Canada (modified from Rogers (15))

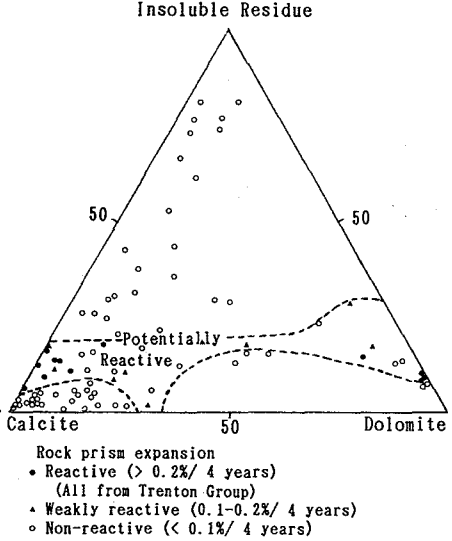


Figure 2 Carbonate rock reactivity of Ordovician groups in Quebec, including Trenton Group (Durand and Berard (22))

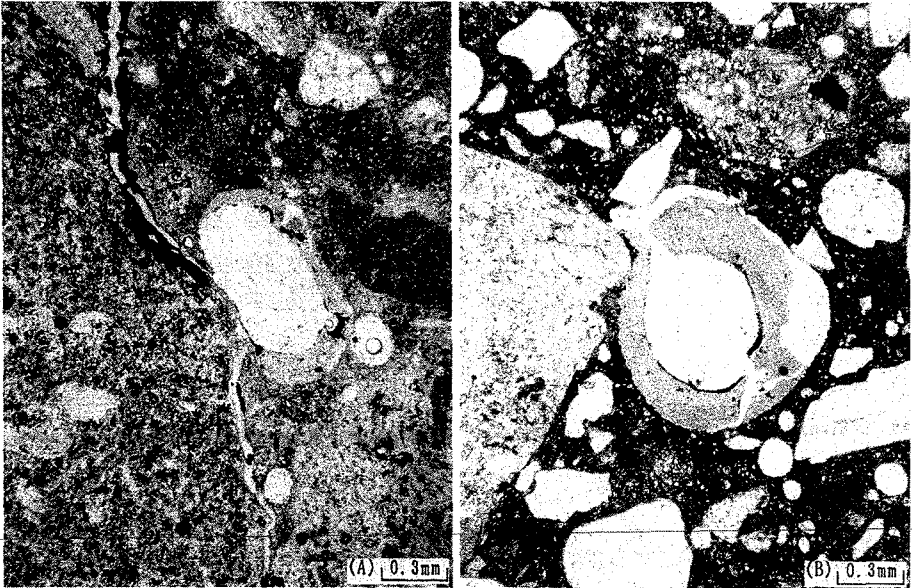


Figure 3 Calcium-rich silica gels lining air voids in concrete from Cornwall, Canada, an indication of alkali-silica reaction of impure limestone. (A) Gel migrated from a cracked stylolite seam (black) of a limestone aggregate. (B) Gel contacting a limestone aggregate.