

The Formation of Rims on Dolomite Aggregate in Iowa Highway Concrete

PAUL G. SPRY, GUO-LIAN GAN, ROBERT D. CODY, AND ANITA M. CODY

Rims have formed on the margins of dolomite ($\text{Ca,Mg}(\text{CO}_3)_2$) aggregate in Iowa highways due to dedolomitization reactions between aggregate and concrete paste. These dedolomitization reactions are usually accompanied by a volume change, due to a conversion of dolomite to a calcitic dolomite, that results in the development of micro-cracks in the aggregate and the concrete paste. These cracks become channelways for solutions, often saline in nature due to the application of deicing salts, that result in further deterioration of highway concrete. Rim development on aggregate particles commonly results in highway concretes with short service lives. The most complete sequence of rims on aggregate in Iowa highway concretes occurs where individual reaction zones are up to 200 μm wide and consist of an inner dark-colored dolomite rim, an outer light-colored dolomite rim, and an outer light-colored Portland cement paste rim. These rims are superimposed on unaltered dolomite aggregate particles and cement paste. Nondurable concretes (service life of < 16 years) exhibit better developed and more abundant rims and a higher density of microcracks and contain dolomite with a more variable grain size and higher porosity than durable concretes (service life of > 40 years). The rims of light-colored dolomite aggregate show an increase in Ca content and a concomitant decrease in Mg adjacent to the aggregate-paste interface, along with the formation of calcite, brucite, and portlandite. The ability to distinguish dolomites that are susceptible to deterioration from those that are less likely to deteriorate should save expenditures since highway maintenance costs will be reduced. Key words: dedolomitization, rims, aggregate, highway, concrete.

Deterioration of highway concretes that contain limestone or dolomitic limestone has long been recognized and has been attributed, in part, to alkali-carbonate reactions between carbonate aggregate and alkaline cement paste (1-3). Rim formation around dolomitic limestone aggregate in Iowa highway concrete was first identified by Bisque and Lemish (4) and Lemish et al. (5).

The main objective of the present study is to evaluate the mechanisms responsible for the formation of reaction rims on dolomite aggregate in several Iowa highways that have been subjected to rock salt (NaCl) deicer applications. This objective has been accomplished by determining and comparing compositional changes across dolomite aggregate-cement paste interfaces of durable concretes (service lives of > 40 years before significant deterioration as suggested by the presence of D-cracking) with those of nondurable concretes (service lives of < 16 years) utilizing electron microprobe analyses (EMPA), scanning electron microscopy (SEM)

(with energy dispersive x-ray analysis (EDAX) capabilities), and x-ray diffraction (XRD) techniques.

The present investigation is requisite to the companion study by Cody et al. (6) in which the effects of various deicing salts NaCl, MgCl_2 , and CaCl_2 in experiments have been evaluated on the same Iowa highways. In recognizing the possible involvement of an alkali-carbonate reaction in the deterioration of Iowa highways, Dubberke and Marks (7) suggested that deicing salts, in particular NaCl, accelerated these effects.

GENERAL CHARACTERISTICS OF IOWA HIGHWAY CONCRETE

We have studied seven Iowa highway concrete cores that can be divided into two groups based on their service records. The first group consists of durable concretes which contain coarse aggregate from the Sundheim and Mar-Jo Hills quarries, and the second group is comprised of nondurable concretes containing aggregate from Smith, Paralta, and Garrison quarries and from the Ames gravel pit. Aggregate sources included rocks of Ordovician (Mar-Jo Hills quarry), Silurian (Sundheim quarry), Devonian (Smith, Paralta, and Garrison quarries), and Recent (Ames gravel pit) geological ages (Table 1).

Both petrographic and SEM studies revealed significant differences in the nature of the coarse dolomite aggregate used in durable and nondurable concrete. In nondurable concrete, > 90 percent of aggregate particles consist of fine-grained dolomite with abundant void spaces between poorly-formed dolomite crystals. Dolomite crystals in nondurable concrete aggregates typically fall within the diameter of 0.005 to 0.05 millimeters. In durable concrete, by contrast, dolomite crystals are coarser, extremely well crystallized, and more tightly intergrown. Typically these large crystals are anhedral because of the interlocking fabric. Individual dolomite crystals commonly exhibit maximum diameters between about 0.05 and 0.40 millimeters. The abundance of void spaces, as well as subhedral and euhedral dolomite crystals, and the scarcity of tightly interlocking crystals are evident in dolomite that forms in less durable concrete.

Microfractures and larger fractures are considerably more common in the paste of nondurable concretes than in the durable concretes. Cement paste shows major textural differences between durable and nondurable concretes. Small concentric-laminated, spherical bodies (composed of hydrated cement phases) are common in the durable concrete pastes, whereas they are almost lacking in the nondurable pastes.

TABLE 1 Concrete Core Locations, Service Records, and Aggregate Sources

Sample Number	Location of Core	Aggregate Source	Service Record
1	US 63, just north of Buckingham	Smith quarry (Basal Coralville Member, Cedar Valley Formation, Devonian)	12 years
2	US 151, near intersection with IA 13. NE of Cedar Rapids	Paralta quarry (Otis Member, Wapsipinicon Formation, Devonian)	8 years
3	US 218, near intersection with IA 8, east of Vinton	Garrison quarry (Basal Coralville Member, Cedar Valley Formation, Devonian)	15 years
4	US 20, west of Dubuque	Sundheim quarry (Hopkinton Formation, Silurian)	> 40 years
5	E 29, 1/2 mile east of US 65	Ames gravel pit (Skunk River gravels, Recent)	8 years
6	E 29 at junction with US 65	Ames gravel pit (Skunk River gravels, Recent)	8 years
7	US 52, south of Dubuque	Mar-Jo Hills quarry (Stewartville Member, Galena Formation, Ordovician)	> 40 years

REACTION RIM DEVELOPMENT IN CONCRETE

Although rims may be present on aggregate particles in durable concrete, they are best developed in nondurable concretes where both the coarse aggregate particles and the cement paste adjacent to the aggregate particles often exhibit discolored rims along the interface. Up to five zones can be distinguished, and are from the unaltered dolomite rock phase (Zone A) toward the unaltered portland cement paste (Zone E)(Figure 1):

1. A **dark dolomite rim** (zone B)—a relatively thick, typically 100–300 μm wide, dark-colored, dirty-appearing rim which occurs at or near the outer margin of the coarse aggregate particles. This rim is much darker and is more porous than the interior, presumably unaltered, dolomite. Fewer dolomite crystals are visible within the rim compared to the dolomite interior, so that some of the crystals may have dissolved or been absorbed by growth of other crystals during rim development. In aggregate where this rim is directly in contact with the paste, microfractures parallel to the boundary are common, and the outermost part of the dark dolomite rim is much less porous than the dolomite interior.

2. A **light-colored dolomite rim** (zone C)—a narrow, typically 20–50 μm wide, unstained, clean-appearing, light-colored rim which is located peripheral to zone B and which is in contact with the cement paste. Where absent, zone B occurs in contact with the paste. The light-colored dolomite rim is typically much lighter in color than the unaltered dolomite. Usually dolomite within zone C is less porous and exhibits fewer and smaller intercrystalline voids than unaltered dolomite interior or zone B. Abundant microfractures occur at the margin between the light and dark dolomite rims, and often the cracks parallel the dolomite/paste interface.

3. A **light-colored paste rim** (zone D)—a relatively thick, light-colored rim which occurs in the portland cement paste adjacent to

the outer margin of the dolomite aggregate. It is typically much lighter in color than the darker and dirtier-appearing, presumably unaltered, paste which occurs farther away from the dolomite aggregate. Although small microfractures may occasionally occur within the light-colored paste rim, most fractures occur in zone E.

An electron microprobe traverse across a nondurable concrete containing Smith quarry aggregate, for example, illustrates a chemical profile across the five zones typically found in nondurable concretes (Figure 2). In this traverse, CaO remains essentially constant, with minor irregularly spaced peaks and valleys, throughout zones A and B. The variation in MgO content shows an antithetic relationship with CaO. Variations in CaO or MgO content typically occur only in the outer light-colored dolomite rim where there is a distinct increase in CaO and a corresponding decrease in MgO compared to zones A and B. These chemical differences result from magnesium loss by dedolomitization within the dolomite aggregate immediately adjacent to the paste. Within the paste, Mg and Ca may increase locally, and is due, in part, to the formation of brucite ($\text{Mg}(\text{OH})_2$), calcite (CaCO_3) and portlandite (CaOH_2).

DISCUSSION

There can be little doubt from electron microprobe profiles and EDAX maps that the rims observed in concretes containing Smith, Paralta, and Garrison quarry dolomites result from chemical reactions between concrete paste and dolomite aggregates related to dedolomitization of the outer margins of the aggregate. Through these reactions, magnesium is released and then migrates into the cement phase. The most important of these reactions, the so-called alkali-carbonate reaction, is one in which dolomite is attacked by alkali derived from the high pH portland cement and produces brucite, calcite, and carbonate ions (2,3):

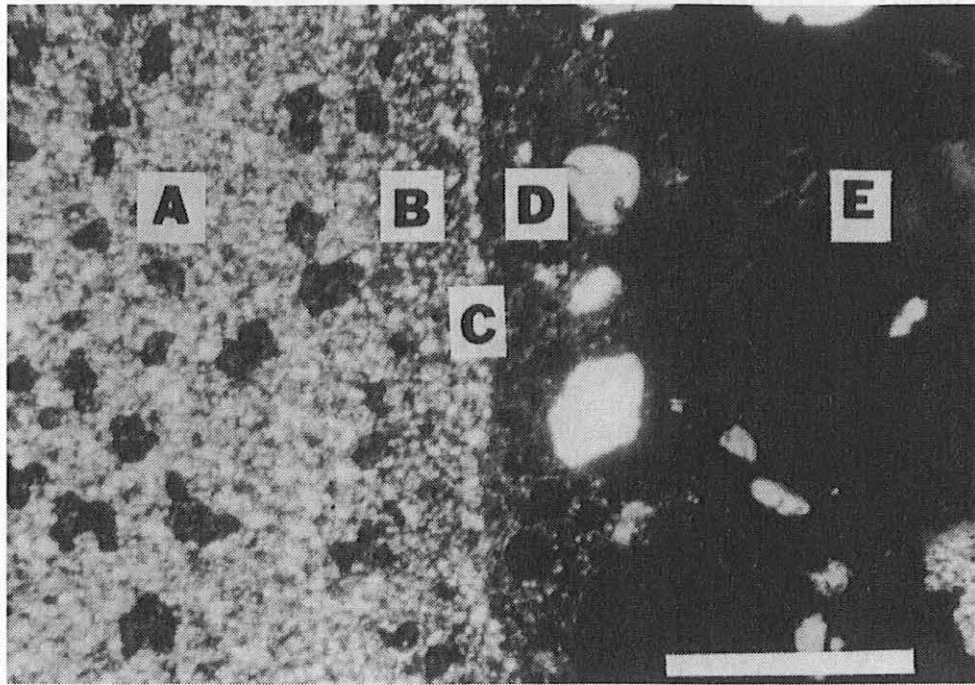


FIGURE 1 Light micrograph (between crossed-polarizers) of an aggregate-paste interface in nondurable highway US 63 (dolomite from Smith quarry) showing reactions rims B, C, and D (see text). Dolomite aggregate interior (A) and unaffected cement paste (E) are also shown. Scale bar = 250 μm . The larger crystals in zone D are quartz crystals.

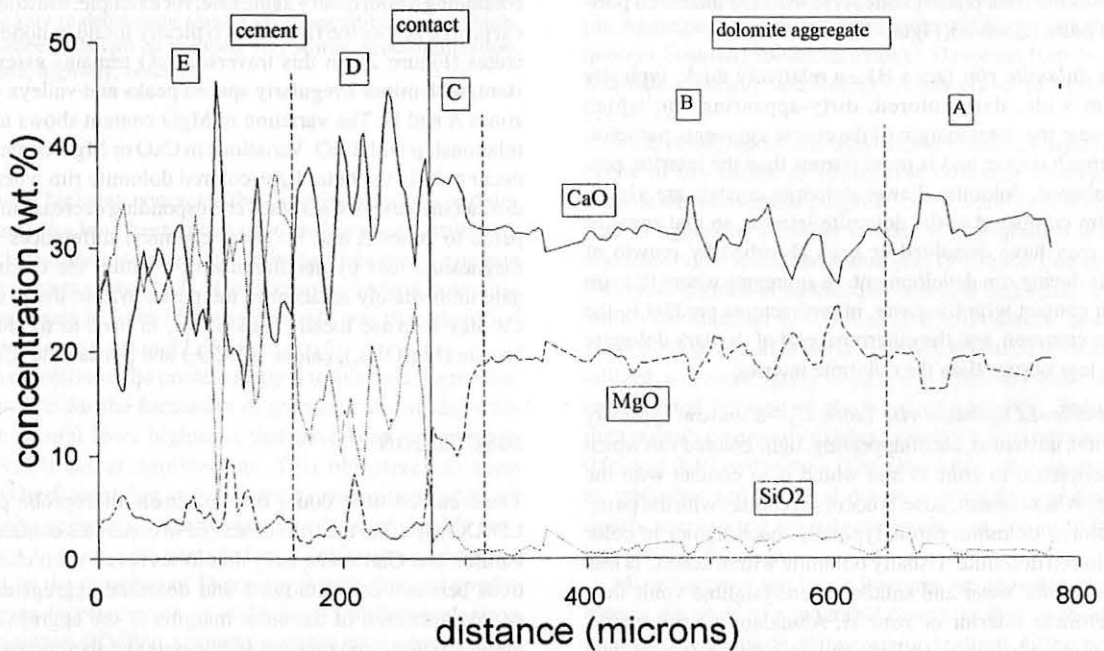


FIGURE 2 Electron microprobe traverse in nondurable concrete across an aggregate (Smith quarry)-paste interface which exhibits zones B, C, and D, as well as unaffected dolomite aggregate (zone A) and cement paste (zone E). The oxides shown in the traverses are CaO, MgO, and SiO₂.



Reaction [1] results in a five percent decrease in volume; however, other dedolomitization reactions may be accompanied by volume changes as much as 14 percent. Alternative hypotheses have been proposed to explain the observed expansion associated with the alkali-carbonate reactivity. For example, Swenson and Gillott (8) suggested an indirect mechanism which assigns a trigger role to dedolomitization and invokes other factors as responsible for expansion.

However, Tang and his colleagues (9-12) proposed that the network of clay disseminated throughout impure dolomite furnishes channels through which H_2O , K^+ , Na^+ , and OH^- migrate into the interior of the reactive rock. They concurred that dedolomitization causes a reduction in volume, but they also pointed out that the reaction products of dedolomitization, calcite and brucite, were fine-grained and enclosed many voids. By including the void volume, their calculation revealed an increase in the overall volume of the solid skeleton plus voids during dedolomitization. Regardless of the mechanism responsible for the formation of cracks at the aggregate-cement paste interface, they provide pathways for cations released from alkali-dolomite reactions and further deterioration caused by deicing salts that are applied to highway concretes.

Although several studies have supported the conclusion that expansion of dedolomitized coarse carbonate aggregate is important in causing concrete deterioration, the question remains as to whether magnesium ions released by dedolomitization may also play a role in reducing concrete service life. Newly released magnesium undoubtedly leads to brucite precipitation in the concrete paste, and brucite growth may itself create crystal growth pressures which lead to expansion and deterioration (13). In addition, there may be adverse chemical reactions between magnesium and the paste, analogous to the effects of sulfate ions on concrete. Oberste-Padtberg (14) mixed magnesium chloride with cement paste and found the concrete rapidly deteriorated, perhaps partly due to magnesium reactions with the paste. An understanding of the effects of magnesium on concrete is especially pertinent at this time because magnesium chloride and/or calcium magnesium acetate have been proposed as road deicers and substitutes for rock salt.

IMPLICATIONS AND RECOMMENDATIONS

Cracks that allow alkali ions and various anions (particularly chloride ions) to penetrate and cause expansive, destructive growth to occur in concretes may be initiated within the concrete paste or at paste/aggregate interfaces. The processes that produce these cracks are complex but are, in part, related to dedolomitization reactions. The results of the present study and ongoing experimental investigations involving magnesium deicers (6) and high magnesium concretes suggest that excessive magnesium, in any form (including its release during dedolomitization reactions), should be avoided (or at least minimized) as it will contribute to rapid deterioration of highways. While we are currently working on establishing the nature of the complex reactions in the cement paste that result in deterioration, the following practical recommendations can be followed to help reduce the likelihood of utilizing dolomites that are less durable and that result in extensive crack development at dolomite aggregate/cement paste interfaces:

1. Before dolomite horizons are developed for use as highway aggregate, representative samples should be collected and made into polished thin sections that can be used for standard petrographic

and scanning electron microscopy. Such sections can generally be made for less than \$20/section at commercial laboratories. Dolomites that are porous or contain microfractures should be avoided. Those dolomites that are likely to be more durable exhibit low permeability, are generally coarser than 0.05 millimeters, contain a paucity of clays, are well crystallized, and show interlocking grain boundaries. The identification of these desirable physical properties is cheap and relatively easy.

2. After the physical and chemical characteristics of a prospective dolomite have been established, decisions can be made regarding the choice of dolomite beds to be mined in a given quarry. In some cases, these decisions may unavoidably have to wait until rims first appear on dolomite aggregate in highway concretes. Nonetheless, individual quarries may yield dolomite aggregate that will result in both durable and nondurable concrete. While the economics of an active quarry operation may dictate some aggregate be used in highway concrete that is likely more susceptible to deterioration, it may be practical in some operations to identify and subsequently avoid such horizons for use in highways that are to be built at a later date. The ability to recognize and distinguish these suspect dolomites should save expenditures in the long run for federal, state, and local highway departments, since highway maintenance costs will be reduced.

ACKNOWLEDGMENTS

This project was funded primarily by the Iowa Department of Transportation, Project No. HR-355. This support is gratefully acknowledged. We particularly want to thank Messrs. Vernon Marks, Jim Myers, and Wendell Dubberke, as well as Dr. Wallace Rippie for their advice, suggestions, and support of this project. Without their help the project would not have been possible. We thank Drs. Jerry Amenson and Scott Schlorholtz, of the Iowa State University Materials Research Laboratory, for their assistance with SEM analyses. Appreciation is also extended to Dr. Alfred Kracher for help with the electron microprobe studies, and to Mr. Scott Thieben for assistance with x-ray diffraction analyses and for reading an early version of this paper. Partial financial support was also provided to Guo-Liang Gan through the Iowa State Mining and Mineral Resources Research Institute program.

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