Explaining the difference in freeze-thaw resistance of two similar “high-quality” limestone aggregates

Evelyn Hussey
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/etd
Part of the Geology Commons, and the Transportation Commons

Recommended Citation
Hussey, Evelyn, "Explaining the difference in freeze-thaw resistance of two similar “high-quality” limestone aggregates" (2018).
Graduate Theses and Dissertations. 16380.
https://lib.dr.iastate.edu/etd/16380
Explaining the difference in freeze-thaw resistance of two similar “high-quality” limestone aggregates

by

Evelyn Hussey

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Geology

Program of Study Committee:
Franciszek Hasiuk, Major Professor
Paul Spry
Peter C Taylor
M Robert Dawson

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2018

Copyright © Evelyn Hussey, 2018. All rights reserved.
# TABLE OF CONTENTS

| LIST OF FIGURES | v  |
| LIST OF TABLES  | x  |
| NOMENCLATURE    | xi |
| ACKNOWLEDGMENTS | xii|
| ABSTRACT        | xiii|

## CHAPTER 1. INTRODUCTION
Concrete.................................................................................................................................1
History of Tests .........................................................................................................................2
Iowa DOT Coarse Aggregate Quality Rating .............................................................................3
Geologic basis for Iowa DOT quality tests. ..............................................................................5
Additional Rock Quality Observations ......................................................................................5
This Study .....................................................................................................................................7

## CHAPTER 2. GEOLOGIC SETTING
The Paleozoic .............................................................................................................................8
Iowa in the Devonian ....................................................................................................................10
The Spring Grove and Davenport Members ..............................................................................11
The Owen Member Source ..........................................................................................................13
Episodes of karstification and/or complex diagenesis .............................................................14
Burial depths ...............................................................................................................................15

## CHAPTER 3. METHODS
Equipment .................................................................................................................................17
Helium porosimetry ....................................................................................................................17
Mercury porosimetry ..................................................................................................................18
Petrography ..................................................................................................................................19
Sampling ......................................................................................................................................19
Aggregate...................................................................................................................................19
Core ...........................................................................................................................................20
Blockstones ................................................................................................................................20
Durability Beam ..........................................................................................................................21
Rock Properties and Description .............................................................................................21
Bulk Volume ...............................................................................................................................21
Mass ...........................................................................................................................................21
Helium Porosity ..........................................................................................................................22
Mercury Porosimetry ..................................................................................................................22
LIST OF FIGURES

Figure 1. Spring Grove blockstones (circled in red) show the deterioration that occurs when they are allowed to remain on the quarry floor. They developed the cracks, flakes, and tan coloration visible in the image over the course of a year. Photo: F. Hasiuk, August 2015. ............................................. 41

Figure 2. Section of the spalled concrete durability beam that was provided by the Iowa DOT. The spalling is indicated with a black arrow. ............................................. 42

Figure 3. Spring Grove Facies 3a from the studied source showing well developed bubble trains after being immersed in approximately 10 cm of deionized water for approximately one minute. The demarcations on the side of the container are ~3 mm apart ............................................. 43

Figure 4. Isopach map of Devonian sedimentary rocks in Iowa and surrounding states. Hatched areas denote Devonian outcrop belt, other patterned areas where Devonian has been eroded and younger strata were deposited (IP=Pennsylvania, J=Jurassic, K=Cretaceous). After Figure 3, Witzke et al., 1988. ............................................. 44

Figure 5. Quarry locations shown on the Bedrock Geologic Map of Iowa (Iowa Geological Survey, 1998). The Spring Grove source is located in Black Hawk County. The Owen Member source is located in Story County. ............... 45

Figure 6. Spring Grove source stratigraphic column. Created using information provided by the Iowa DOT. Beds 4 and 5 are “high quality” aggregate sources based on the Iowa DOT quality tests. ............................................. 46

Figure 7. Owen Member source stratigraphic column. Taken from core provided by Martin Marietta Company. Quarried section approximately from 124m to 131m. ............................................. 47

Figure 8. Overhead (A-W and B-O) and side view (B-W and B-O) of preliminary wettability test on the silt-sized calcite microcrystals that disaggregated from coarse aggregate pebbles of Spring Grove limestone during freeze-thaw cycles. A-W and B-W) Tests performed with water. Water was added to the microcrystals from the left. Material that did not mix with the water was pushed to the right of the image and is indicated with the blue arrows. A-O and B-O) tests performed with oil. Oil was added to the microcrystals from the left. The droplet is ~1 cm across. No material rose to the surface.
Some mixed with the oil, causing a cloudy appearance. Outlined in blue is the test performed with water.

Figure 9. Spring Grove porosity distribution from 36 blockstone plugs. The porosities of the mudstones and breccias are outlined in red. The porosities of the peloidal grainstones are outlined in blue. The breccias from the Spring Grove and Davenport (Facies 1) fall in the 2-4% range (red). Both Facies 2 and Facies 3a fall into the 5-8% range (blue and red), while Facies 3b is between 16 and 20%, and 3c is all those above 20% helium porosity.

Figure 10. Owen Member porosity distribution, from 11 blockstone plugs. All blockstones are from the same facies, a peloidal grainstone.

Figure 11. Davenport limestone breccia. The mudstone clasts are indicated by (MS), the stylolite in the bottom left is (Sty), and the spar cement is (Spar). B) Blue arrows point to the small, fine grained areas that remained unstained by Alizarin Red S, suggesting a dolomitic composition. The yellow arrow indicates a small fracture cemented with calcite. Large image (A) is 17.8mm across and inset image (B) scale bar is 200 µm.

Figure 12. Spring Grove Facies 2. The low clay limestone mudrock is labelled (MS), and the clay rich bands are labelled (Clay). There is no visible porosity in the clay-rich mudrock, and there are isolated micropores (green arrow, inset image) in the clay-rich areas. A cemented fracture is indicated with a yellow arrow. The image in the back is 17.8mm on each side and the inset image scale bar is 200 µm.

Figure 13. Spring Grove Facies 3a. The peloidal areas are indicated with “Pl” and the ropey algal structures are marked “Algal.” Two of the dolomite ghosts are marked with pink rhombuses. The blue arrow is indicating the presence of the fine minerals that did not take dye but that are not identifiable petrographically. The green arrow indicates an area of isolated micropores. A) 17.8mm on each side. B) scale bar of 200 µm.

Figure 14. Spring Grove Facies 3b. This is a moderately porous peloidal lime grainstone. There are peloids indicated with “Pl,” clay bands with “Clay,” and radial textures with “Rad.” The radial fabric indicated is inside an ostracod. The green arrow is pointing at porous areas. The green arrow in the inset is indicating an area of interconnected microporosity and the green arrow in the larger image is indicating a macropore. The pink rhombus highlights a dolomite ghost. A) is 17.8mm on each side. B) scale bar is 200 µm.
Figure 15. Spring Grove Facies 3c. A) 17.8mm on each side and the inset (B) image has a 200 µm scale bar. Helium porosity of 23%. This is a highly porous peloidal grainstone. An area of peloids is indicated in each image with “Pl” and the green arrows indicate porosity. There are many micropores, causing a “blue haze” in the slide.

Figure 16. SEM image of Facies 4 focusing on one of the microporous regions of the peloidal grainstone. This location has a larger calcite crystal (likely a blocky cement) embedded in it. The micrite crystals can be classified as “granular subhedral” according to the classification scheme of Kaczmarek et al. (2015).

Figure 17. Thin section photomicrograph of a concrete beam made with Spring Grove coarse aggregate, having been subjected to ASTM 666 freeze-thaw durability test. The bottom of the image is approximately 1cm across. The aggregate labelled “MR” corresponds to the Facies (2), and those labelled “Pl” correspond to the peloidal grainstones of Facies 3.

Figure 18. Microporosity deterioration. Scale bars 50 µm. A) Facies 3c blockstone. Microporous area indicated by green arrow. B) Coarse aggregate from the durability beam, presumed to be equivalent of Facies 3. A deteriorated area is indicated by the green arrow.

Figure 19. The two textures present in the mined section of the Owen Member. Both scale bars are 200 µm. A) Peloidal (Pl) lime grainstone, with birds-eyes (BE). B) Peloidal lime grainstone, with radial cement (Rad), often nucleated on oogonia.

Figure 20. Pore throat size distribution data measured via mercury intrusion data for Spring Grove samples. Facies 1/Davenport breccia has a peak in pore throat size at 0.03 µm (top, dark gray). Facies 2 has a variable pore throat size peak, with one sample peaking at 0.05 µm (dark brown) and another sample extended peak between 0.1 µm and 1 µm (light brown). Facies 3a has a pore throat peak at 0.09 µm (red). Facies 3b has a large range of pore throat sizes, with peak diameter increasing as porosity increases from 0.1 µm (pink) to a range of 0.1 µm to 1 µm in an asymmetric distribution (purple), to a 0.3 µm to 1 µm peak (blue). Facies 3c continues to increase the pore throat diameter, with a trimodal peak between 0.4 µm to 1.2 µm (light green) and a bimodal distribution from 0.7 µm to 1.2 µm (dark green, bottom).

Figure 21. Pore throat size distribution data measured via mercury intrusion data for the Owen Member sample. There is a peak between 70 µm, of macropores, and between 0.01 and 0.07 µm (micropores).
Figure 22. Image of micropores in the concentric layers of ooids. The scale bar is 100 \( \mu m \). The microporous areas are indicated with green arrows.

Figure 23. Fibrous texture present in Spring Grove Facies 3c. Outlined in green is an area where pores have developed along an area of fibrous calcite, possibly algal in origin. The crystals within the area do not go extinct together. A) plane polarized light, and B) is in cross polarized. The images show the same area. Both scale bars are 50 \( \mu m \).

Figure 24. Image of the microporosity present in Spring Grove Facies 3c. The images show the same area. The concentrically layered fabric is circled in yellow, while a microporous area lacking discernable fabric is circled in green. Both scale bars are 50 \( \mu m \). A) is in plane polarized light. Image B is in cross polarized light.

Figure 25. Photomicrograph of calcite microcrystals that disaggregated from coarse aggregate pebbles of Spring Grove during freeze-thaw tests, mounted as a strew slide. Scale bar is 20 \( \mu m \). The black arrows indicate some of the granular subhedral microcrystals that have not flocculated.

Figure 26. Image showing the twinning present in a thin section from Spring Grove Facies 1, the limestone breccia. Twinning can be a low temperature geothermometer, but in this case it is not useful because the crystals which show twinning are in fractures (Ferrill et al, 2004).

Figure 27. Materials used in this study included crushed rock (A) and core plugs from...

Figure 28. Rock type 1 from S1. The blockstone shows a limestone, peloidal grainstone texture with a pore throat peak (cc/g intruded) at 0.02\( \mu m \) and a peak above 10\( \mu m \). The aggregate sample shows essentially the same pattern, with a peak at 0.03\( \mu m \) and above 10\( \mu m \).

Figure 29. Rock type 1 from S2. Both are lime wackestone. Both have peaks at 0.3\( \mu m \). The aggregate also has a peak above 50\( \mu m \).

Figure 30. Rock type 2 from S2. Both are packstones, but the blockstone is of intermediate carbonate chemistry and the aggregate is pure limestone. Both have a pore throat peak at 0.05\( \mu m \).

Figure 31. Rock type 1 from S3. Both are fine grained, moderate porosity dolomites. Both have peaks at 3\( \mu m \) and a small peak at 0.03\( \mu m \). The noise in the aggregate graph may be due to the small size of the particle tested.

Figure 32. Rock type 2 from S3. Both are packstones. The blockstone has a bimodal peak at 0.03\( \mu m \) and 0.15\( \mu m \). The aggregate also has a bimodal peak, but
the peaks have shifted to the left toward smaller pores. The peaks are at 0.02µm and 0.07µm. The aggregate also has some noise in the data toward the larger pores. ................................................................................................................. 83

Figure 33. Map of logged wells that contain the Spring Grove, and their primary chemistry. Pink is dolomite, blue is limestone, red is gypsum or anhydrite. The yellow stars are quarry locations that source their material at least in part from the Spring Grove........................................................................................................ 92

Figure 34. Photomicrograph of pure limestones with original fabrics preserved. Both scale bars 200 µm. A) peloidal lime mudstone with dolomite ghosts and sparry cement, B) peloidal grainstone with dolomite ghosts. ...................... 93

Figure 35. Photomicrograph of A) pure dolomite and B) intermediate chemistry (calcite cement is stained pink). ................................................................. 94

Figure 36. Photomicrograph of dolomite grain size variation in pure dolomites, all scale bars 200 µm, A) has crystals of 25 µm, B) 100 µm and C) 200 µm....... 95

Figure 37. Photomicrograph of dolomite crystal size in intermediates (mixed dolomite and limestone). Dolomite crystals are 150 µm in (A) and up to 300 µm in (B)......................................................................................................................... 96

Figure 38. Photomicrograph of limestone with original fabric, with fracture cemented with calcite. Scale bar is 200 µm................................................................. 97

Figure 39. Photomicrograph of a fine crystalline dolomite with a stylolite. The clay in the stylolite is diffuse, and the crystals of dolomite along the stylolite do not show evidence of dissolution present (partially dissolved or truncated grains). Scale bar is 200 µm. ................................................................. 98

Figure 40. Photomicrograph of dolomite with quartz grains. The green arrow indicates a large quartz grain. Scale bar is 200 µm. ................................................................. 99

Figure 41. Photomicrograph of a limestone with a large organic inclusion, scale bar 200 µm........................................................................................................ 100
**LIST OF TABLES**

| Table 1. | Facies identified in the Davenport (1) and Spring Grove Members (1-3) of the Pinicon Ridge formation at the Spring Grove source. | 66 |
| Table 2: | Summary statistics for Aggregate Quality data. | 84 |
| Table 3: | Summary statistics for Source 1. | 85 |
| Table 4: | Summary statistics for Source 2. | 85 |
| Table 5: | Summary statistics for Source 3. | 85 |
| Table 6. | Summary of sampled cores | 101 |
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAV</td>
<td>Davenport</td>
</tr>
<tr>
<td>DOT</td>
<td>Department of Transportation (Iowa)</td>
</tr>
<tr>
<td>SG</td>
<td>Spring Grove</td>
</tr>
<tr>
<td>PCC</td>
<td>Portland cement concrete</td>
</tr>
</tbody>
</table>
ACKNOWLEDGMENTS

I would like to thank my committee chair, Dr. Franek J. Hasiuk, without whom I could not have completed my studies. His patience, support, and scientific and editing skills have been invaluable. I sincerely thank him for always going above and beyond for both me and my fellow students, to help us become better scientists and members of the scientific community. I would also like to thank my committee members, Dr. M. “Bob” Dawson, Dr. Paul G. Spry, and Dr. Peter Taylor, for their guidance and support throughout the course of this research.

In addition, I would also like to thank the department faculty and staff for making my time at Iowa State University a wonderful experience. I would particularly like to thank DeAnn, the best administrative specialist ever, for helping me to complete all of the forms required to graduate and to remember all of the important dates and deadlines.

Lastly, I would like to thank Brian. Moving to Iowa together was a gamble, but it was a good one.
ABSTRACT

Several hundred quarries throughout Iowa mine carbonate bedrock for aggregate, which is used in the construction of pavement and structures, as granular surface materials (i.e., “gravel roads”), or as rip rap to prevent erosion. This study focuses on coarse aggregate used in concrete pavement. The Iowa Department of Transportation employs a set of tests to predict the durability of pavement constructed with these aggregates. These tests factor in the bulk elemental chemistry of the carbonate (calcium-rich, magnesium-rich, or a mixture), the alumina percentage (a proxy for clay content), and the pore system (the volume of “micropores”). While these tests have been generally accurate in predicting the durability of a pavement since the 1980s, there have been some exceptions that require more specific exploration in a geologic and structural context.

The studied quarry removes the bulk of its material from the Spring Grove Member of the Middle Devonian Pinicon Ridge Formation, Wapsipinicon Group, with some from the Davenport and Kenwood Members of the same formation. Coarse aggregate from this source qualifies for the highest Iowa DOT quality classification, meaning it can be used on interstate highways and be expected to last at least 30 years. Despite this classification, anomalous behavior has been observed with this aggregate, including spalling during some freeze-thaw tests on durability beams (ASTM 666) and bubbling when placed in water. There is currently no evidence that it deteriorates unusually in roads—the Iowa DOT’s preferred method for predicting durability. To elucidate the reasons behind these anomalous behaviors, we compare it to another highly rated source (Late Devonian Owen Member of the Lime Creek Formation, Central Iowa) that performs equally well in aggregate testing yet does not spall in durability beams.
The Lime Creek Formation was selected for comparison to the Spring Grove because both were deposited in similar environments, tidal flats adjacent to shallow marine basins that show evidence of possible restriction during deposition. Both sources have relatively low clay content, and both are pure limestone lithologically. Helium porosity of Spring Grove material ranges from 0% to 26%, and modal pore throat size measured using mercury porosimetry ranges from 0.02 µm to 1 µm. The Iowa DOT’s pore system test measures the material as having a very low volume of micropores (average value: 11 mL). Owen Member coarse aggregate ranges in porosity from 2% to 5%, and a similarly small volume of micropores in the DOT’s pore system test (average value: 14 mL). It has a mercury-measured modal pore throat size of 0.03 µm.

One facies present in the Spring Grove is unique in comparison to the Lime Creek Formation. The high porosity peloidal algal grainstone from the Spring Grove has a uniquely interconnected and pervasive system of micropores that are hosted among calcite microcrystals, and may be responsible for the anomalous spalling behavior in durability beams, as well as other anomalous behaviors. This pore system likely stems from dissolution associated with episodes of karstification that have occurred in the vicinity of the Spring Grove source.
CHAPTER 1. INTRODUCTION

Concrete

Concrete is one of the most important materials used to build the modern world, making up significant portions of vital infrastructure like roads, bridges, and buildings (USGS, 1999). Portland cement concrete (PCC) is made up of four major components that dictate its properties: cement paste, coarse aggregate, fine aggregate, and air entrained in the cement paste during mixing (Langer, 2011). The properties of the paste and the fine aggregate have been well studied and well constrained, with the paste being a blended product of di- and tri-calc-silicates and the fine aggregate being mostly monomineralic fine sedimentary grains, in Iowa usually quartz or lithic sand (Smith, 1958; Taylor, 1990). The air entrained is atmospheric, and in equilibrium with atmosphere over time. Therefore, coarse aggregate, with its natural heterogeneity in terms of chemistry, texture, and porosity, can be the largest source of material-related heterogeneity in PCC. The variability introduced by coarse aggregate can affect PCC properties, such as resistance to compressive and tensile stress, chemical deterioration, freeze-thaw damage and so-called “D-cracking” (Özturan and Cengizhan, 1997; Poitenvin, 1999; Lee et al., 2005).

Limestones and dolostones are common bedrock in the Midwest and Northeast USA, and therefore they are often used as coarse aggregate in PCC (Langer, 2011). They are generally less vulnerable to the alkali-silica reaction, and reduce the drying shrinkage of concrete (Poitevin, 1999; Carlos et al., 2010). However, not all carbonate rocks make durable concrete pavements (Marks and Dubberke, 1980; Poitevin, 1999; Beshr et al., 2003). Poor performance can depend on a number of factors, and the Iowa Department of Transportation (DOT) tests coarse aggregates to predict the lifespan of a pavements and structures. High
quality aggregate can yield a pavement that lasts 30 years, while poor aggregates can result in pavement replacement in as little as seven years.

**History of Tests**

The Iowa DOT tests coarse aggregates to estimate the amount of time a pavement made with a given aggregate will last in service. These tests provide an estimate of durability, with service history as the ultimate arbiter. The tests rest on a series of field observations that link shorter service lives to various physical and chemical properties of coarse aggregate: low clay content (<0.6% aluminum oxide), end member carbonate composition (i.e., pure limestone or pure dolostone), and with a volume of micropores less than 30 mL as measured by water intrusion into 4.5 kg of coarse aggregate (Marks and Dubberke, 1980). The Iowa DOT has refined the interpretation of these criteria over time (Reyes and Dawson, 2010). A recent study has shown that favorable carbonate rock properties can be tied to depositional texture and diagenetic history of the rock (Ridzuan et al., 2017) and so are predictable to some extent based on the regional geology.

Historically, freeze-thaw resistance has been tested with the ASTM-666 method, which submerges a PCC block made with the test coarse aggregate in a water bath, and subjects it to 300 freeze-thaw cycles. In Iowa, this test is considered to simulate approximately 10 years of winter-related stress. Any cracking or deterioration observed at the end of the test is cause for concern. This freeze-thaw test was used in conjunction with proven service history as a basis for characterizing quarry rock quality, but was replaced with the Iowa Pore Index in the early 2000s.
Iowa DOT Coarse Aggregate Quality Rating

The Iowa DOT has identified three rock properties that correlate with coarse aggregate performance: expandable clay content, bulk minerology, and its pore system volume and structure.

First, the Iowa DOT seeks to find aggregates with a low content of expandable clay minerals because of the deterioration that occurs during repeated wetting/drying, and freezing/thawing cycles. The current procedure to obtain a coarse aggregate’s expandable clay content is to measure its alumina content using x-ray fluorescence (XRF) because of alumina’s presence in expandable clay. The amount of alumina in the sample is weighted in the calculation of the quality rating (IA 223B Quality Number, 2018). A “good” alumina content would be below 0.25 wt% and would be added as 1 point or less in the calculation of quality, which is based on the curve, where y is the quality points and x is the percentage of alumina:

$$y = 9.98x^2 + 1.26x + 0.04$$  
Equation 1

Generally, a result above 0.6 wt% will result in the coarse aggregate failing the test (IA 223B Quality Number, 2018). However, the possibility of alumina present in another mineral, like mica, could potentially make the alumina percentage high without expandable clay. This is corrected for using the IPI test. If the water imbibed by micropores is low, but the alumina is high, a correction may be applied because the alumina is probably not in expandable clay (IA 223B Quality Number, 2018).

Next, the lithological purity of the sample is determined. Most coarse aggregates used in Iowa are either limestone (low-Mg carbonate), dolostone (high-Mg carbonate), or a mixture of the two. The nature of the mixture is determined by the dolomite peak shift in XRD. There is a distinct peak for limestone with a d-spacing of 29.4, and one for dolomite at
30.9. When a peak is between these two, it indicates that there are impurities present in the crystal structure (IA 223B Quality Test, 2018). These impurities may be MgO (in dolomite), or include MnO (only in dolomite, correlates to deterioration through an unknown mechanism), sulfur (in pyrite), and strontium (only in limestone, correlates to deterioration in an unknown mechanism). These chemistries are assigned values and a weighting factor and are used in the overall equation. The XRD quality factor is calculated by 

\[ \text{XRD quality} = (\text{MgO} - 0.011) \times 70 \]

\[ \text{Magnesium quality} = (\text{MnO} - 0.011) \times 70 \]

\[ \text{Sulfur quality} = (\text{S} - 0.011) \times 52 \]

\[ \text{Limestone quality} = (\text{SrO} - 0.03) \times 238 \]

When all of these are taken together, they generate the XRD/XRF quality number (IA 223B Quality Test, 2018). Dolostone, especially in mixtures, is vulnerable to deterioration from deicing salts, which are used frequently in Iowa during the winters (IA 223B Quality Test, 2018).

Finally, the porous nature of the coarse aggregate is analyzed. Most coarse aggregates used in Iowa are to some extent porous, which can lead to water absorption and increased susceptibility to deterioration during winter months, especially if the pores are small (<1 \( \mu \text{m} \)). The IPI test used by the Iowa DOT uses water intrusion at a constant pressure (35 psi) to measure pore space in a 4.5 kg sample of coarse aggregate taken from a production stockpile. The amount of water absorbed by the coarse aggregate pore system is noted at two times over the course of the test, at one minute and at 15 minutes (IA 223B Quality Test, 2018). The value recorded at 1 minute is interpreted as the volume of water entering the largest pores (>50 \( \mu \text{m} \)) and that having entered the coarse aggregate at the later time (15 minutes), is interpreted as representing the volume of micropores (<1 \( \mu \text{m} \)) (IA 223B Quality Test, 2018). From the first 15 minute value, a Pore Index Quality Number is calculated with the portland cement concrete (PCC) durability class system. Higher water absorption (20mL
to 30mL) are associated with shorter pavement performance.

The outcomes of these individual tests are used to calculate an overall quality number. For pure limestones (MgO = 0%), only the IPI number and the alumina number are used, and they are each given a 50% weight. For coarse aggregates of intermediate lithology (MgO = 10%), all factors are used and weighted 50%/25%/25% with the XRD/XRF quality number having the larger share. For a pure dolostone (MgO > 18 wt%), each factor is given a one-third weight (IA 223B Quality Test, 2018).

Geologic basis for Iowa DOT quality tests.

A previous study (Ridzuan et al., 2017) laid the groundwork correlating these rock property tests performed by the Iowa DOT with geological attributes (e.g., depositional and diagenetic texture) as well as petrophysical properties (e.g., porosity, pore throat size distribution). It correlated the “secondary load” measured by the IPI index to micron-size pores, and that the total porosity of high quality limestone aggregates is overall less than 7% because most pore space in high-porosity limestones is in the form of micropores (which raise the secondary load index). High quality dolostones tend to have a total porosity over 12% because most these higher porosity dolostones tend to be coarsely crystalline, which results in a lower relative abundance of micropores.

Additional Rock Quality Observations

In Iowa, coarse aggregate that will make the most durable, highest quality pavement tends to be sourced from pre-Pennsylvanian Paleozoic bedrock, (Langer, 2011). Pre-Paleozoic formations are too deeply buried in most of the state for economic extraction, except in the extreme northwest where the Proterozoic Sioux Quartzite is exposed. Pennsylvanian strata tend to be microporous, clay-rich, and/or poorly cemented—all of which causes rapid deterioration in pavement especially under winter weather. Cretaceous
Seaway sediments present themselves mostly as poorly indurated argillaceous chalk. The lack of lithification makes them difficult to use as coarse aggregate because much of the material is lost during crushing. In the early 20th Century, glacially derived river gravels were commonly used in concrete pavement construction, their use has decreased in much of the state and has been replaced by crushed stone quarries for coarse aggregate. In northwestern Iowa, river gravels continue to be an important source for aggregate.

Additional factors can be used to identify potentially well-performing sources of coarse aggregate. One such criterion is a grainstone texture (presumed to have a large relative abundance of allochems and a small relative abundance of mud sized material). The coarse sand to gravel sized grains of a grainstone and low mud will have larger interlocking grains and lower surface area, as well as fewer micropores present between grains.

Another criterion is significant spar as either cement or recrystallization of grains. The presence of spar presumably indicates that the crystals of the material are well cemented and interlocking, suggesting that it will be more resistant to deterioration both physically and chemically.

The Iowa DOT has also provided anecdotal information on characteristics they have observed to be anomalous at the study locality. The observations include reports that:

- A petrolierous or fetid odor is released when the rock is crushed
- When concrete is mixed for road construction, the paste fails to adhere to some of the coarse aggregate pebbles (Figure 2)
- Blockstones weathering on the quarry floor can deteriorate to pebbles and dust over only one winter season (Figure 1)
- When the crushed aggregate is submerged in water, well formed “bubble trains”
develop from the upper surfaces of pebbles. The bubble trains resembling the bubbling rate and bubble size of champagne for the first 5 minutes or more (Figure 3). After bubbling becomes less frequent, the pebbles continue to absorb water for over 24 hours.

This Study

This study seeks to understand the anomalous behaviors of the Spring Grove aggregate from a quarry near Waterloo, Iowa, USA, by comparing its characteristics to a similar limestone source that lacks these behaviors. Unique characteristics of coarse aggregate from this location were identified based on petrographic and petrophysical data and connected to deterioration in aggregate grains from a concrete durability beam that has experienced 300 freeze-thaw cycles. These differences in performance can be traced to the microporosity formed during diagenesis, and to the character of those pores.

Being able to move beyond the current tests to better understand the depositional and diagenetic factors that contribute to coarse aggregate performance will enable quarry developers to better map and predict the quality of their deposits, as well as enabling government transportation officials to build roads more efficiently, both in terms of time and cost. This could also potentially reduce both false positives (when poor aggregate passes current tests), and false negatives (when good aggregate fails current tests).
CHAPTER 2. GEOLOGIC SETTING

The two formations analyzed in this study were the Spring Grove and Davenport Members of the Pinicon Ridge Formation at a source in Eastern Iowa, which are Middle Devonian, and the Owen Member of the Lime Creek Formation, an Upper Devonian unit, from a source in Central Iowa (Figure 5).

The Paleozoic

The Paleozoic had generally higher sea levels than today, with widespread carbonate deposition in epicontinental seas across Laurentia (Kendall and Schlager, 1981; Haq and Schutter, 2008). As the Tippecanoe sequence was deposited, sea level was at its highest during the Ordovician while slowly receding through the Silurian before reaching a sea level lowstand at the beginning of Kaskaskia sequence in the Early Devonian. Kaskaskia sea level increased to its maximum in the Mississippian before dropping again to reach its lowest at the end of the Permian (Sloss, 1963; Haq and Schutter, 2008). These long-term sea level changes are controlled by the formation and break up of continents and the rates of sea floor spreading, as the breakup of continents and creation of hot and buoyant seafloor causes the ocean to become shallower overall (Kendall and Schlager, 1981). High sea levels yielded large epicontinental marine environments, and the long period of high sea levels in the Paleozoic created ample accommodation for sediment to be deposited in what is now the midcontinent of the United States (Witzke and Ludvigson, 1996).

The sedimentary sequences deposited during the Devonian in the United States midcontinent formed in a shallow ocean near the equator, which had a warm climate and produced large amounts of limestone (Kendall and Schlager, 1981). Clastic material derived from the Appalachian Mountain Belt, and the Wisconsin and Ozark Domes is also found in
wedges in the early Kaskaskia rocks of Iowa (Witzke et al., 1988). This clastic input diminished into the Middle and Late Devonian as relief decreased and gave way to more carbonate deposition (Witzke et al., 1988).

Sea level oscillated on higher frequencies due to volcanism, fluctuations in orbital forcings, and patterns of climate variation (Haq and Schutter, 2008). These higher frequency oscillations were superimposed on an overall sea level drop in the Early Devonian that left most of what is now Iowa subaerially exposed. Erosion of Silurian units ensued, which precluded preservation of the Lower Devonian in the Iowa Basin except in small areas in central Iowa where chert beds are thought to be Early Devonian (Witzke et al, 1988). Middle Devonian sea level rise covered most of Iowa, leaving only a small area in the east above water, and allowing the deposition of evaporites and shallow water carbonates in the somewhat restricted basin (Witzke et al 1988; Bond and Kominz, 1991). Sea-level rise continued through the Late Devonian and into the Carboniferous, resulting in deposition of sandstones (clastics derived from the Ozark Dome and Wisconsin Dome), limestones (when clastic input decreased), and shales (in deeper areas in the center of the basin) throughout middle Laurentia (Collinson, 1967; Witzke et al., 1988).

The Carboniferous saw an increase in tectonic activity in the center of the continent. The Alleghenian (also referred to as Appalachian) Orogeny reactivated faults in the Midcontinent Rift, a Proterozoic aulacogen, and caused folding and faulting of the earlier beds. The best-known area of faulting in Iowa is in the Plum River Fault Zone (Bunker et al, 1985). The mountain building also increased the clastic sediment supply, depositing sandy carbonates and sandstones. This mountain building has also been linked to the ore deposition of the Upper Mississippi Valley Zinc-Lead District (Heyl et al, 1959).
**Iowa in the Devonian**

The Devonian (~420 to 360 Ma) is dominated by the Tippecanoe and Kaskaskia cratonic sequences (Sloss, 1963). The Tippecanoe Sequence ended with a regression in the early Devonian and the Kaskaskia began as sea levels rose again in the Middle Devonian (Sloss, 1963). This eustatic sea level increase flooded large areas of Laurentia, including the Iowa Basin (Sloss, 1963; Witzke et al., 1988).

The Iowa Basin accommodated the deposition of Devonian sediments from the adjacent uplifted areas (Figure 4) (Sloss, 1963; Witzke et al., 1988). The Devonian saw eustatic sea level at ~100 m higher than present in its beginning. The sequence continued with a subsequent rise to ~120 m higher than the present in the Late Devonian, before falling back to ~100 m higher than present during the transition to the Carboniferous (Haq and Schutter, 2008).

The landmass that is now Iowa was situated at 30°S (±15°) latitude throughout the Devonian (Witzke and Heckel, 1988; Blakey, 2008). This resulted in a warm, subtropical marine basin, optimal for the accumulation of thick carbonate deposits with cyclic clastic input driven by repeated sea level changes (Collinson, 1967; Kendall and Schlager, 1981; Richardson and Hansen, 1991). The basin formed on the west side of Sangamon Arch, and there are some fine-grained clastics derived from the Ozark Dome in the south, from the Wisconsin Dome to the northeast, and perhaps even from the Catskill Deltas in the East (Whiting and Steveson, 1965; Collinson, 1967; Witzke et al., 1988; Richardson and Hansen, 1991). These areas were lifted due to the stresses exerted by orogenic activity of the Appalachians along the East Coast United States (Whiting and Steveson, 1965; Collinson, 1967; Witzke et al., 1988; Richardson and Hansen, 1991).
In Iowa, the Devonian section consists of a series of 3rd-order sequences (Richardson and Hansen, 1991; Haq and Schutter, 2008). The basin varies from exposure above sea level to limey shale deposition during submersion. Unlike the nearby Appalachian Basin, there was no significant black shale deposition in Iowa during much of the Devonian as the basins were shallower and lacked long periods of hypoxia/anoxia (Witzke et al., 1988; Day, 1990). The early Devonian is rarely present in outcrop in Iowa or the subsurface due to either lack of deposition or erosion during subaerial exposure (Collinson, 1967).

**The Spring Grove and Davenport Members**

The Middle Devonian is characterized by a global sea level increase of 30 to 50 m, overlain by high frequency fluctuations (Haq and Schutter, 2008). The beginning of Kaskaskia deposition during this period produced a sequence of shallow marine limestones interspersed with evaporites containing halite and gypsum (Sloss, 1967; Witzke et al., 1988). This study focuses on the Pinicon Ridge Formation within the Wapsipinicon Group, which is composed of, in order of deposition, the Kenwood, Spring Grove and Davenport Members, though not all are present in all parts of the state (Witzke et al., 1988). The Pinicon Ridge Formation disconformably overlies Ordovician and Silurian carbonates in much of Iowa and surrounding states (Witzke et al., 1988; Day, 2013). The Spring Grove is a transgression and the Davenport is the following regression (Witzke et al, 1988).

In southeastern Iowa, the Davenport and Spring Grove members host thick evaporite accumulations that are mined for gypsum, while in other areas this interval is expressed as a disconformity (Richardson and Hansen, 1991; Day, 2013). Dissolution of these gypsum, anhydrite, and halite evaporites has been implicated in creating collapse breccia of Davenport material above the Spring Grove in northeast Iowa (Day, 2013). In most of Iowa, the Spring Grove Member is a dolostone, usually laminated, and the Davenport member is a limestone,
but in some areas they are both limestone (Day, 2013). The transition from Spring Grove to Davenport is less pronounced in areas where both members are limestone and may be arbitrary (Day et al., 2006; Day, 2013).

A stable isotopic study (Richardson and Hanson, 1991) suggested a complex exchange of oxygen isotopes in the evaporites of Iowa, without exchange of sulfur isotopes. It is speculated that the exchange was caused by the movement of warm or hot groundwater through the system at some time, but no definitive conclusion was drawn as to the timing of such diagenesis (Richardson and Hanson, 1991).

The age of Pinicon Ridge Formation is constrained to between the Late Eifelian and Middle Givetian based on conodont and chitinozoa biostratigraphy in the surrounding units (Urban and Newport, 1973; Witzke et al., 1988). No index fossils have been found in the Spring Grove or Davenport to further constrain this age (Urban and Newport, 1973; Witzke et al., 1988; Day, 2013). In Illinois, the Spring Grove Member has been further separated into upper and lower sections. Well-preserved fish fossils have been found in both, although they are more common in the upper section (Hickerson, 1994).

A study of Linwood Mine where Spring Grove limestone is removed for aggregate detailed the generations of alteration, particularly karst development, in the member to the south and east of the study locality (Gavin, 1995). While the Spring Grove in Linwood has areas of massive karst and fluvial channels filled with Pennsylvanian clay and mud, similar Pennsylvanian karst development has not yet been reported in other Spring Grove localities.

The Spring Grove source (Figure 5) is located near the city of Waterloo in Black Hawk County, Iowa, USA. Mining encompasses the Kenwood, the Spring Grove and the Davenport Members of the Pinicon Ridge Formation with some material being taken from
the Solon Member of the overlying Little Cedar Formation (Figure 6). Unlike most of the Spring Grove Member in Iowa, limestone is found at this location, which is purer than the organic-rich dolostone more common at other Spring Grove Member sections (Collinson, 1967; Witzke et al. 1988; Day, 2013). The regional extent of this limestone facies is unconstrained. The Davenport Member at this location is also limestone. The contact between the Spring Grove and Davenport Members is difficult to constrain here because of the similar lithology (Witzke et al., 1988).

**The Owen Member Source**

The Upper Devonian in Iowa is characterized by a fall in sea level, containing the local sea level low of the Kaskaskia sequence (Sloss 1963; Haq and Schutter, 2008). The craton-scale sea-level fall contains many higher frequency carbonate sequences 30 to 60 m thick (Collinson, 1967, Witzke, 1996; Day, 2013). The Lime Creek is bounded above and below by unconformities (Witzke et al 1988; Day, 2013). A lowstand between the Middle and Late Frasnian resulted in the disconformity found between the Lime Creek Formation and overlying Cedar Valley Group (Day, 2013). The late Frasnian Lime Creek Formation is present over a large area in the subsurface from Minnesota to Missouri and east into Illinois, where it grades into limey shales. It generally records carbonate shelf or shelf margin deposition in Iowa (Witzke et al., 1988; Day, 2013).

The Owen Member source is located in Story County, Iowa, USA (Figure 5). Material is removed from approximately 122 m (400 feet) below the surface (Figure 7) in the Owen Member of the Lime Creek Formation. The aggregate produced is pure limestone from a shallow, tidal flat depositional environment. The unit underlying the main mine horizon is a stromatoporoid-bearing lime rudstone to floatstone and the unit overlying it is a low porosity
dolostone. In other areas in Iowa, the Lime Creek Formation is a fossiliferous, limey shale to pure lime mudstone (Collinson, 1967).

After Lime Creek deposition, sea level fall continued into the Carboniferous, with areas on the edges of the basin exposed above sea level. As clastic input increased in the Pennsylvanian, clastic deltaic sequences of sandstones and coals were deposited in Central Iowa, while some carbonate deposition occurred further to the west and south (Greb et al., 2003; Anderson, 2010).

**Episodes of karstification and/or complex diagenesis**

It has been suggested that the Wapsipinicon of Iowa is one of the most complex sedimentary units in Iowa, if not the most complex (Bunker et al, 1995). This is due in part to episodes of alteration which occurred after deposition, although it is also complex in its depositional textures. The cycles of sea level rise and fall over the last 400 million years have caused parts of the Iowa basin to periodically be exposed and submerged, and for it to become restricted occasionally. In areas of the Iowa Basin, the total accommodation is many kilometers (Bunker et al, 1995).

This sea level variation is what facilitated the deposition of evaporites, as well as the development of karst and breccias by dissolution. There is paleokarst from the Pennsylvanian which is well known and has been observed in the Spring Grove at Linwood Mine, in Davenport, Iowa. The clays deposited in the karst contain spores that were used to biostratigraphically constrain the age to the Pennsylvanian (Garvin, 1995). The breccias, especially those of the Davenport Member formed from the dissolution of the evaporites, but the timing is not well constrained. It is known that the evaporites in southern Iowa show an excursion in the oxygen isotopes from the global curve, suggesting alteration, but again there is no time constraint (Richardson and Hanson, 1991).
The development of the Plum River Fault Zone caused flexures of the sedimentary beds in southeastern Iowa (Bunker et al, 1995). The development of the Zone is affiliated with the stresses coming from the east during the Appalachian Orogeny. The faults uplifted sections of central eastern Iowa by tens of meters by steep angle faulting (Bunker et al, 1995). This uplift, as well as the formation of anticlinal systems, is possibly linked to some of the karst dissolution in the area, as the uplift could have brought the carbonates into the phreatic. Once in the phreatic meteoric waters could move through the system and begin to dissolve crystal faces and to widen flow paths (Esteban and Wilson, 1993; Groves and Howard, 1994). The zone is approximately 150 km east of the Spring Grove source and 300 km from the Owen source.

The emplacement of the Upper Mississippi Valley Mineral District during the Carboniferous to Triassic were facilitated by movement of basinal brines through the porous beds belonging to the Ordovician and Silurian, with some alteration of Devonian beds along the eastern side of Iowa. This Devonian alteration is thought to include the deposits in Linwood Mine, which derives material from the Spring Grove (Middle Devonian). Linwood Mine is well known for its barite deposits and large vugs and cavities, as well as its karst. The area effected by the movement of the basinal brines when mapped by Heyl et al (1959) may have included the Spring Grove source. Thus, it is possible that the Spring Grove source was subjected to alteration by both cool meteoric fluids and hot basinal brines.

**Burial depths**

Determining the maximum burial depth for carbonates can be done in several ways. One method is isotopic: oxygen isotopes can indicate a burial temperature, and this can be extrapolated to a burial depth. Every two per mil increase in $\delta^{18}O$ correlates to approximately 10°C, which approximately equals 100 meters of burial. The heating upon burial can also
cause calcite crystals to develop twinning of varying thicknesses, which is a known low
temperature paleo-thermometer, but can only be used for twinning which develop in grains
(Ferrill et al, 2004). The temperature can again be extrapolated to a burial depth. Another
method is to examine the stylolites present in the formation. Stylolites form due to
compressional stress increasing the solubility of the material, and carbonates develop
stylolites due to burial between 300 m and 1000 m (Fabricius and Borre, 2007).

In Iowa, minimum burial depth is constrained by the current burial depth, but the
maximum is less constrained. The Wapsipinicon is currently buried at up to 200m, and the
Lime Creek is buried up to 100 m (Witzke et al, 1988). How much deeper these formations
have been buried or the temperatures they may have reached in the past is not constrained
tightly- Day (1990) does not mention the color of the conodonts (a paleo-thermometer)
collected from the Lime Creek, nor does Klapper and Barrick (1983) in the Middle Devonian
formations they describe.
CHAPTER 3. METHODS

Equipment

Helium porosimetry

Porosity was measured by helium pycnometry. Helium is pressurized in a chamber of known volume containing the sample and then released into a second chamber of known volume. By measuring the pressure change after the expansion, the volume of the sample can be calculated. The measurement of porosity using helium takes advantage of helium acting as an ideal gas obeying Boyle’s Law:

\[ P_1 V_1 = P_2 V_2 \]

Where \( P = \) pressure, \( V = \) volume

Equation 2

This law defines the proportionality of pressure and volume with which gasses behave. Helium in the primary chamber is held at 19.5 psi and the gas is allowed to expand into the secondary chamber (increasing volume). The secondary pressure is thus lowered by a proportional amount. With other variables (e.g., temperature) known, this change in pressure can be used to calculate the volume in the primary chamber that is occupied by the mineral skeleton of the plug (i.e., its grain volume). When the mineral skeleton volume and bulk volume are known, the difference between them can be to calculate the porosity (in \% of the bulk volume) in the plug.

\[ P = 1 - \frac{V_{\text{mineral skeleton}}}{V_{\text{bulk}}} \times 100 \]

Where \( P = \) pressure

Equation 3

\( V = \) volume
**Mercury porosimetry**

Samples with a range of the measured helium porosities were measured using a Quantachrome Poremaster 33 automated mercury intrusion porosimeter. This porosimeter reaches 33,000 psi (227 MPa) and measures pore throats from ~100 µm to ~5 nm in size.

Mercury porosimetry takes advantage of the Washburn Equation (Washburn, 1921; Giesche, 2006), which relates pressure, surface tension, and cohesion of a liquid to the pore throat size into which it can be intruded:

\[ p = \frac{-4\gamma \cos \theta}{d} \]

where \( p \) = pressure 
\( \gamma \) = surface energy of the liquid, 
\( d \) = pore diameter, 
\( \theta \) = contact angle between liquid and solid

Equation 4

As the pressure is increased, the non-wetting liquid (mercury) is forced into smaller and smaller pore throats. Recording the volume intruded at a given pressure allows the calculation of the volume of pore throats at that size. The strong cohesive properties of liquid mercury and its lack of compressibility make this one of the most accurate methods to measure pore throat size (Roquerol et al., 1994). An inherent assumption in mercury porosimetry is that it assigns the volumes of pore bodies to the pore throat size needed to intrude that pore. Therefore, if there is a large pore, but the only way for mercury to enter the pore is through smaller pore throats surrounding it, then the measurement of the pore volume will be attributed to the smaller pore throats rather than the larger pore.
Petrography

One trim end from each core plug was sent for thin-sectioning (TPS Enterprises, Houston, Texas), and was stained with alizarin red-S (calcite stained red) and potassium ferricyanide (iron-rich calcite stained purple). They were imaged using an Olympus DP73 camera on an Olympus BX53 petrographic microscope and information about the texture, structures, and composition were described. The percentages of alumina were carried over from the Iowa DOT measurements using alumina from XRF.

Sampling

Four sets of samples were used for this study: ½- to ¾-inch aggregate provided by the Iowa DOT from both sources, blockstones collected by the Iowa DOT in the summer of 2015 from both sources, and a 2-inch (5-cm) diameter core taken form the Owen Member source by the mine operator in 2014. The Iowa DOT also provided a durability tested concrete beam made with Spring Grove aggregate from the same source.

Aggregate

Crushed aggregate was provided by the Iowa DOT from each quarry for previous studies (Ridzuan, 2017). Thin sections were made using the aggregate sorted by the different rock types from each quarry. These thin sections and corresponding mercury data (see above) were compared to similar data gathered for this study to determine what effect crushing had on the rock properties (APPENDIX A: EFFECT OF CRUSHING ON CARBONATE ROCK PROPERTIES).

One piece of each aggregate type was also selected for a freeze-thaw experiment that would not be influenced by the paste chemistry. The aggregate was typed based on texture and color. Six types were used. Those six samples were placed in deionized water and fully frozen and thawed several dozen times. The microcrystals which were exfoliated from the
aggregate during freeze-thaw settled into a film on the bottom of their container. The microcrystals were mixed into a slurry and two slides with two areas of crystals on each (Figure 8) were made with several drops of water and the slurry. A coverslip was not applied to slides, but rather the slides were allowed to dry at room temperature overnight.

**Core**

A 2-inch (5-cm) diameter core was taken during exploration drilling at the Owen Member source; it penetrates the Mississippian to Devonian strata present in the area. The core was provided for study by Martin Marietta Company. The provided section of core is approximately 140 meters long and has very few gaps, amounting to less than 5% of the total length, of which approximately 18 meters (60 feet) are relevant to the mining operation. This section includes the mined sections and the stabilized sections of the floor and ceiling of the mine. This study focuses on the Lime Creek Formation 116 to 134 m (380 to 440 ft). The core was plugged parallel to bedding through areas of interest. A Powermatic PM2800B drill press was used to cut 2.5 cm diameter plugs, which were trimmed to 2.5 cm long a low speed saw (ISOMET 11-1180). One of the trim ends was sent for thin sectioning (TPS Enterprises, Houston, TX, USA), and the middle portion was subjected to helium and mercury porosimetry (see above). The unused trim ends were used for isotopic analysis by the Iowa State University Stable Isotope Lab, and 1 was mounted for SEM. There are 13 plugs from the relevant section, and 13 thin sections.

**Blockstones**

The Iowa DOT collected blockstone samples from within the Owen Member source in the summer of 2015. These blocks were collected from walls and quarried stone and transported to Iowa State University for study. Where it was possible to discern bedding, plugs were drilled parallel to bedding. Plugs 2.5 cm in diameter and 1.2 to 6 cm long were
taken using a water-cooled Powermatic PM2800B drill press. The plugs were cut and trimmed to ~3.5 cm long on a MK-100 Tile Saw, Model 158189 high-speed wet-saw. After helium porosity measurement had been taken, the plugs were trimmed at each end with a low-speed saw (ISOMET 11-1180), leaving a clean 2.5 cm plug and two trim ends. One trim end was archived, and the other was thin sectioned (TPS Enterprises, Houston, TX, USA).

**Durability Beam**

The Iowa DOT also provided a concrete beam made with Spring Grove aggregate from the same source that was subjected to the standard freeze-thaw test (ASTM-666 performed at the Iowa DOT Materials Research Laboratory, Ames, Iowa, USA) and showed some spalling. This beam was sliced and plugs were taken for thin sectioning. Areas with spalled edges were also sampled for thin sectioning where they held together enough to be mounted. The slices taken have two series from exterior to interior of the most spalled area of the beam (there are two sets of three slices that move from the outermost layer of the beam to the more interior portion).

**Rock Properties and Description**

**Bulk Volume**

Once the cylindrical plugs were cut, their height and diameter were each measured three times using digital calipers (Mitutoyo Absolute Aos Digimatic) and averaged. Bulk volume was calculated geometrically from these measurements.

**Mass**

Core plugs were dried in an oven at a maximum temperature 75°C (minimum 30°C) for over five hours, and then cooled overnight in a desiccator. They were then weighed on an analytical balance (Mettler Toledo ME204E, precision ±0.0001g).
Helium Porosity

Helium porosity was measured on all blockstone core plugs when they were rough cut to 3.5 cm (1.5 in) long and again when the samples had been trimmed. The plugs were weighed and using the helium porosimeter (Micromeritics AccyPyc II 1340), the pore volume was calculated. The bulk and grain densities of the samples was calculated using sample weight and the bulk and grain volumes, respectively. Eleven samples from the Owen Member source were run (Figure 9), and 36 samples overall from all facies present at the Spring Grove source were run (Figure 10).

Mercury Porosimetry

Pore throat size distribution was measured on a subset of the plugs from both sources using mercury porosimetry. The subset was selected by the rock type as observed in thin section and based on the helium porosity. At least one sample of each rock type was run. If multiple samples of one rock type were run and showed no variation, only one run is used in this study.

Petrography

For each thin section, an overview photomosaic was taken at 2x. Further images were taken of areas of interest at magnifications up to 400x. The highest magnification was able to capture features as small as 10 µm, thinner than the slide thickness of 30 µm. Cross-polarized images were taken to identify calcite twinning, and twin morphology.

The strew slides made with the microcrystals sloughed off of the aggregate samples during freeze-thaw tests were imaged using the same microscope, with images taken at 400x.
SEM Imaging

One trim end from the most porous rock type from the Spring Grove, an area with micrite was cracked to reveal a fresh face and sputter coated with gold. These were mounted and imaged in a JEOL JSM-IT100LA compact scanning electron microscope (Geology Program, Iowa State University). The micropore system was categorized using the system developed by Kaczmarek et al. (2015).

Wettability

The wettability of the microcrystals from the aggregate freeze-thaw experiment was investigated by using a modified sessile drop technique (Nowak et al., 2013; Alghunaim et al., 2016). The test was performed by drying the microcrystals in two patches on a slide. On one side of the slide with two areas of dried microcrystals, a few drops of water were added and on the other side a few drops of oil were added. Drops were added from the left side, allowing the liquids to spread over the microcrystals from left to right. The slides were observed as the liquids spread across the slide. Once the liquid reached the edges of the areas of microcrystals, the slide was photographed from both above and obliquely (Figure 8).
CHAPTER 4. RESULTS

Previous Iowa DOT tests

Coarse aggregates from both sources score very highly on these tests, earning their highest quality rating indicating an anticipated service life in concrete pavement of at least 30 years. Overall, the Spring Grove has a mean alumina percentage of 0.04% and Ames had 0.22%. Both are nearly pure limestones. The Iowa Pore Index test for the Spring Grove has an average secondary load index of 11 mL; coarse aggregate from the Owen Member averages 14 mL.

Petrography

Davenport and Spring Grove Members

Thirty-six thin sections were made from quarry blockstones from the Spring Grove and Davenport, and 8 additional thin sections were made from the spalled edges of the concrete beam made with Spring Grove coarse aggregate. The thin sections revealed two main rock types: a dissolution collapse breccia that comes from both the Davenport and Spring Grove, and peloidal grainstones and mudstones from the Spring Grove.

The dissolution collapse breccia (i.e., an intraclast lime rudstone) from the Davenport and Spring Grove cannot be separated because of their similarity in chemistry and texture. The boundary between the Spring Grove and Davenport cannot be pinpointed easily where both members are limestone due to its gradational nature. The Davenport breccia (Figure 11) has no apparent fossils, yet shows rhombohedral ghosts of a precursor mineral, presumably dolomite, as well as areas of unstained microcrystals, presumably dolomite (indicated with blue arrows, Figure 11). The grains in the breccia are lime mudstones that have been completely cemented between the clasts with calcite spar (Figure 11). The breccia does not
show evidence of evaporite minerals (e.g., interlocked crystals of sulfates or halides), and this facies has little visible porosity (shown by blue-dyed epoxy in thin section). There are laminated facies and patches rich in clay minerals that appear dark brown with less distinct boundaries when compared to opaque pyrite. These clays may be concentrated in stylolites (Figure 11), while other clays occur diffused throughout the micritic portions of the breccia, making their presence difficult to identify or quantify in thin section.

The Spring Grove samples can be divided into four facies based on rock texture and properties. Petrographically, the facies were categorized based on grain size, grain type, visible porosity, pore structure and size, as well as chemistry and texture. Facies 1 is a solution collapsed limestone breccia similar to the Davenport facies described above (Figure 11). Facies 2 is a low porosity, well cemented lime mudstone (Figure 12) lacking any apparent grains such as fossils. Facies 2 has clay-rich laminae. Pores in Facies 2 are small, isolated, and present mainly in the clay-rich areas (green arrows in, Figure 12).

Facies 3 is composed of peloidal or algal lime grainstone. Some Facies 3 thin sections have ostracods, and rhombohedral ghosts are present in some as well. The peloids have diffuse edges, and range in diameter from 100 to 500 µm. Facies 3 has cryptalgal structures (ropey and flake-like textures) and radial cement in some samples.

Facies 3 can be subdivided by porosity. Facies 3a is the lowest porosity peloidal grainstone. This facies has dolomite ghosts (pink outline, Figure 13) algal structures (“Algal”), peloids (“Pl”), and finer grained areas that do not take dye (blue arrow) suggesting a dolomitic composition. It also has isolated micropores (green arrow). Facies 3b is a variably porous peloidal lime grainstone. Most pores are present in micron-size, appearing as a patchy “blue haze” in thin section. There is also spar, fossil ostrocodes, and radial cement
fabrics (Figure 14). Facies 3c has pervasive microporosity and abundant macropores (Figure 15).

Facies 3c was imaged using SEM to characterize the type of calcite microcrystals in that host the micro-scale pores in the high-porosity areas (Figure 16). The crystals displayed a granular subhedral texture (Kaczmarek et al., 2015), which are consistent with high-porosity, microporous limestones. Based on this texture, the permeability could be estimated as between 2 and 20 millidarcies (Kaczmarek et al., 2015).

**Spring Grove Durability Beam**

The thin sections of the concrete durability beam (Figure 17) have fracturing in the paste as well as both the high porosity peloidal (Facies 3c) and the low porosity mudstone (Facies 2) aggregate. The aggregate that resembles Facies 3c is the most severely fractured, with some fractures branching as they cross from the paste to the aggregate (upper right, labelled “Pl” Figure 17). The micropores in the Facies 3c aggregate in the durability beam appear larger than in blockstone thin sections, with less distinct boundaries (Figure 15).

**Owen Member**

The Owen Member core provided 13 plugs for thin section from the facies that are mined for aggregate and the immediate ceiling and floor (Figure 7). The only facies present in the Owen Member was a peloidal lime grainstone. There was birdseye texture throughout, peloids ranged from 100-200 μm, and the only fossils present are oogonia or similar structures (Figure 19). The birdseye texture occurs along laminations parallel to bedding. The birdseyes and interior parts of oogonia are filled with blocky, interlocking calcite spar. Thin sections have little visible porosity and are very well cemented. The oogonia may also have radiating fibrous calcite cement overgrowths.
Petrophysical Properties

Davenport and Spring Grove

The porosity of the quarried rock types varied with the facies. Facies 1, the breccia, is between 0 and 4%. Facies 2 is between 3% and 7%, Facies 3a is also 3% to 7%, 3b is 13% to 20% and Facies 3c is up to 26% porosity (Table 1). The distribution of bulk porosities for the blockstone samples produce a histogram with a bimodal distribution (Figure 9). This distribution was combined with petrographic data to delineate the four Spring Grove Facies.

Mercury porosimetry results show distinct patterns of pore throat distribution for each facies (Figure 20). Facies 1/Davenport breccia has a peak in pore throat size at 0.03 µm (top, dark gray). Facies 2 has a variable pore throat size peak, with one sample peaking at 0.05 µm (dark brown) and another sample extended peak between 0.1 µm and 1 µm (light brown).

Facies 3a has a pore throat peak at 0.09 µm (red). Facies 3b has a large range of pore throat sizes, with peak diameter increasing as porosity increases from 0.1 µm (pink) to a range of 0.1 µm to 1 µm in an asymmetric distribution (purple), to a 0.3 µm to 1 µm peak (blue).

Facies 3c continues to increase the pore throat diameter, with a trimodal peak between 0.4 µm to 1.2 µm (light green) and a bimodal distribution from 0.7 µm to 1.2 µm (dark green, bottom). Overall, for Facies 3 as the porosity increases, pore throat size distributions move from moves from smaller to larger size and from unimodal to multimodal distributions.

The porosity measured by mercury did not match the helium porosity (Table 1). The discrepancy may be due to the difference in measurable pore size. Helium will measure every pore down to the size of the helium molecule. Mercury will not enter pores smaller than 5 nm at the pressures applied, such as those found among clay minerals, nor does it measure pores over ~100 µm.
Spring Grove Durability Beam

The durability beam was subjected to 300 freeze-thaw cycles in the ASTM 666 test had significant deterioration starting around cycle 240, and the areas of deterioration were cut for thin sections. These thin sections have coarse aggregate resembling the facies identified from the Spring Grove blockstones (Figure 17). In particular, the high porosity peloidal limestones have microporous textures that occur along filaments or flakes of algal mats, but the microporous texture is less well defined in the durability beam thin sections (Figure 18).

Owen Member

Porosities overall for Owen Member samples were very low, less than 6% (Figure 10). The samples showed a consistent pattern in pore throat size distribution (Figure 21) with two peaks: one at ~0.01 μm and the beginning of a peak at ~100 μm (Figure 21). Multiple plugs were run, but there was little variation between them so only one sample is shown.

Wettability

Strew slides composed of disaggregated microcrystals from Spring Grove coarse aggregate that had been exposed to repeated freezing and thawing were used to perform a basic test of the crystals’ wettability. When the microcrystals were allowed to pull in either water approximately half of the microcrystals were rejected. The rejected microcrystals floated to the surface of the water drop, flocculated, and remained at the surface of the drop until it dried (Figure 8, A-W). When oil was added to another strew slide of Spring Grove microcrystals, no microcrystals were pushed to the surface (Figure 8, A-O). The microcrystals remained at the interface between the oil and slide. There was some mixing of microcrystals and oil producing a slightly cloudy appearance (Figure 8, A-O).
CHAPTER 5. DISCUSSION

The Pinicon Ridge Formation is known to contain a complex distribution of rock types, and the Spring Grove is not well characterized where it is limestone. The anomalous behaviors of certain facies of the Spring Grove at the studied quarry may be due to local characteristics or could be due to aggregate production processes or testing procedures.

**Is it the production of aggregate?**

The production of coarse aggregate is a stressful process for a rock. Quarries and mines drill into bedrock, detonate explosives, and crush the rubble until it reaches the desired size. This repeated stressing of the rock could reasonably be expected to cause changes in rock properties in a way that is similar to physical weathering. Microcracks and fractures could develop within the rock that do not result in through-going fractures, but yet could interconnect pores. These fractures and cracks could change the connectivity of its pore system.

A preliminary study (APPENDIX A: EFFECT OF CRUSHING ON CARBONATE ROCK PROPERTIES) compared blockstones collected from several quarries to the aggregate produced at the same quarry using petrographic and petrophysical analysis. No significant changes were identified in thin sections or in petrophysical properties (e.g., porosity, pore throat size distribution) to have resulted from the crushing process.

**Was it durability beam construction and testing?**

Since the crushing process does not appear to change the relevant rock properties, the process of making the concrete durability beam could have affected the Spring Grove aggregate in such a way that would explain the noticed spalling (Figure 2). The beam was produced in accordance with the specifications of the ASTM-666 test by a technician well-
versed in concrete preparation as well as test procedures (M.R. Dawson, personal communication) nor was there evidence of unusual performance of other durability beams constructed with the same batch of cement or run contemporaneously with the Spring Grove durability beam. It is possible that other rock properties (e.g., the oft-noticed petroliferous odor) may indicate that the Spring Grove Member at the studied source would react in an anomalous way to the test. However, it was beyond the scope of this study to evaluate the effect of these properties on durability beam construction.

**Is it the lithology and chemistry?**

Deterioration in concrete has been linked to intermediate-lithology carbonates (mixed limestone and dolostone), high expansive clay content, and abundance of micropores (i.e., microporosity). The chemistry of the Spring Grove peloidal grainstones are unremarkable, with low clay and MgO content consistent with a pure limestone lithology. There is no difference in minerology or trace chemistry that would suggest a greater prclivity to chemical deterioration. There is no reactive silica or chert in any samples that might cause an alkali-silicate reaction to occur nor did petrographic analysis of the durability beam show such deterioration.

**Is it the facies?**

If neither the production of aggregate nor the production of the durability beam itself is changing the Spring Grove aggregate, there might be something inherent to the facies of the Spring Grove at this location that makes it perform poorly. Here, the comparison between the similar facies at the two locations shows that a peloidal grainstone produced in a tidal flat or lagoon does not have inherent qualities that make it perform badly. No durability beams from Owen Member aggregate have spalled like those beams that have been made with
Spring Grove coarse aggregate from the studied source (M.R. Dawson, personal communication).

Peloids often start their journey into the rock record as amalgamations of mud- to silt-sized grains of calcite. The type and extent of cementation can turn a soft and porous sediment into a very durable material. Both the Spring Grove and the Owen Members have sparry cement holding their peloids together that has reduced interparticle porosity significantly. The Owen peloids and some of the Spring Grove peloids (e.g., Facies 3a) also have reduced intraparticle porosity due to cementation. This comparison between Owen and Spring Grove peloidal limestones suggests that there is nothing inherent about tidal flat or lagoon facies that leads to the anomalous behaviors that have been seen in the Spring Grove.

The maximum burial depth and stress that the Spring Grove and Owen sources have experienced appear to be similar based on the occurrence of stylolites in both sections, with the Owen being slightly deeper in the past (as well as currently). The Owen has many horizontal, laterally continuous stylolites and the Spring Grove has fewer, and they are less continuous.

**Is it the Spring Grove?**

The Spring Grove and Davenport are a transgression-regression sequence. The transgressive Spring Grove was deposited in a deepening, shallow marine basin in Eastern Iowa. During deposition the basin was frequently hypersaline, with the most common fossils being algal with a few ostrocodes. At one Spring Grove locality in Eastern Illinois, fish remains have been identified in the upper part of the unit (Hickerson, 1994). The presence of fish may suggest that the hypersalinity was less severe to the east or at the peak of transgression. The regression of the Davenport consists of interbedded carbonates and evaporites suggesting more restricted conditions. However, outside of the southeast of Iowa,
the evaporite deposits of the Spring Grove and Davenport have dissolved leaving collapse breccias (Witzke et al., 1988).

Evaporate minerals are not viable for concrete production in the climate of Iowa, nor are they common in the Iowa stratigraphic column. Across most of Iowa, the Spring Grove-Davenport sequence is not typically thought of as ideal for concrete due to the presence of evaporites, but where the evaporites have dissolved there is nothing to suggest that they would perform poorly in concrete.

The Spring Grove is also quarried for coarse aggregate in other areas of Iowa. Linwood Mine removes limestone Spring Grove for aggregate and no any anomalous behaviors have been reported. Other quarries remove dolostone or intermediate Spring Grove and have also not reported any of the anomalous behaviors of the Spring Grove at the studied source. Lithology of the Spring Grove Member has proved to be highly variable both regionally and even within a single core (APPENDIX B: SPRING GROVE REGIONAL STUDY). Thin sections made from cores in Eastern Iowa show that the Spring Grove can vary from limestone to dolostone within a single core, and over distances of only a few kilometers (APPENDIX B: SPRING GROVE REGIONAL STUDY). The variability in minerology is not apparent on the scale of the single quarry, though there is textural variation.

**Is it the petrophysical properties (e.g., pore volume, size, and structure)?**

Facies 3c in particular is highly porous (20%–26%) and the pore throat sizes when measured by mercury display a mode of ~0.7 μm (Table 1). This 0.7 μm pore throat size and helium porosity >7% have been postulated to be correlated with low durability by a previous study (Ridzuan, 2017).
In thin section, pores and porosities in Facies 3b and 3c do not appear to agree with the pore throat peak and porosity measurements made by mercury. A discrepancy between pore throat size and pore size is expected, because pores are generally much larger than the pore throats. The lack of homogeneity apparent across a single thin section may explain why even though there are large volumes of locally well-connected pores in Facies 3 of approximately 5 µm, the pore throats when measured by mercury are between 0.7 and 1 µm. The mercury entered the larger pores though small pores causing this character of mercury data, and the long paths the mercury would need to traverse to enter the innermost pores may have caused the porosity to be under-measured by mercury.

These types of micropores observed in the Spring Grove are not observed in thin sections prepared from other Iowa aggregate sources. The most similar pore structures occur in some ooids (Figure 22). This unusual pore structure explains the bubbling because the fine, long, convoluted pores conduct air out of the rock slowly and uniformly. The air exits the micropores as fine, rapid bubbling over a relatively long period of time (hours to days). The pore structure is also connected with the deterioration of the aggregate in the concrete beam. The most fractured coarse aggregate is similar to Facies 3c, and microcrystals that form the micropores in that aggregate have deteriorated and lost their structure (Figure 18). The pore structure and heterogeneity of Facies 3 at a fine scale may also explain the discrepancy between the helium pore volume and the mercury measured pore volume. There may be a core of pores that the mercury could not reach because they were not connected with a large enough pore throats to the exterior. The helium molecule is much smaller than the 5-nm minimum pore throat that mercury can access at 30 kpsi (200 MPA). The impact of any error in the measurement of porosity is probably negligible to understanding the general
trend, especially when the error is understood. The mercury is accurately measuring the pores throats it can reach, it is simply that mercury may fail to enter some pores. This knowledge allows for a general awareness of the types of errors that are possible - that pores that are not well connected and those that are in the center of the samples may not be measured.

A simple explanation for the anomalous behavior of a subset of the Spring Grove material is that all of the behaviors (e.g., bubbling when placed in degassed, deionized water, the lack of paste adhesion, and the rapid weathering when exposed in the quarry) arise from the same cause. The pore system in Facies 3b and 3c is different, based both on comparison to similar facies elsewhere suggesting local factors may be responsible for its formation. It is reasonable to think that the bubbles are being released from the pores (causing the bubbling behavior), and that the pores advance freeze-thaw deterioration by ice segregation. The bubbles that develop are not caused by formation of gasses upon exposure to water - water at equilibrium with the atmosphere is not acidic enough to cause carbon dioxide to form in such quantities. Probably there are favorable channels through the pore systems that conduct the air within out, and they allow for the bubble trains to develop. Ice segregation can be extensive in rock where the pores are large enough to take up water, but small enough to hold onto the water by capillary action.

The freeze-thaw deterioration should occur in the same way in the beam and in the quarry. In Facies 3, porosity is inversely correlated with degree of cementation. The lack of paste adhesion could thus be explained by the crystalizing paste peeling off layers of poorly cemented microcrystals.
What diagenetic history produced this rock type?

Diagenetic alteration of the peloidal algal grainstone pore systems of the Spring Grove could have caused characteristics in the material that hasten the deterioration of coarse aggregate in the durability beam. The alteration history of the Spring Grove when compared to that of the Owen provides evidence that alteration of a similar facies can radically change its characteristics, without a change from limestone to dolostone.

The micropores in Facies 3 that are visible in thin section take on three general forms. In one, the pores are along the edges of crystal faces in radial or fibrous fabrics. These radial, fibrous crystal growths look similar to the fabrics that form around some oogonia in the Owen Member, but the Spring Grove fabrics are porous, and in cross-polarized light do not exhibit extinction clearly, indicating they did not begin in an area with only one crystal orientation (Figure 23). The second form are concentric porous layers, where pores occur in concentric rings, with continuous rings of calcite surrounding it (Figure 24). The third type are those that do not have an apparent structure (Figure 24), having formed throughout an area without orientation or directionality. All the pores have sharply defined edges and appear to be due to non-fabric selective dissolution. In cross-polarized light, the extinction of the calcite crystals is uniform across the concentrically laminated pores and some of those without clear structure, which suggests that what is now porous was connected, and was all in one orientation (Figure 24).

Microcrystals that sloughed off of the aggregate when frozen and thawed repeatedly presumably came from the microcrystalline areas of the peloids and radial cement, and probably from the areas of microporosity. The microporosity would reduce the resistance of the microcrystals to freeze-thaw deterioration. The strew slide shows the crystals to be not
euhedral and are less than 5 µm in diameter (Figure 25), like those seen in the SEM image of Facies 3c (Figure 16).

The process that formed these pore systems resembles the initial dissolution of karst development, when meteoric waters begins widening flow paths (Groves and Howard, 1994). There is known pre-Pennsylvanian karst development in the Spring Grove in Linwood Mine near Davenport, Iowa (Garvin, 1995). This karst is filled with clastic mud and surface debris, and is extensive within the mine (Garvin, 1995). Mud-filled karst cavities were noticed in the core from the landfill near Waterloo (APPENDIX B:SPRING GROVE REGIONAL STUDY). The Mississippian-Pennsylvanian boundary is a major erosional surface in Iowa. It leads to both the evaporite dissolution as well as the one of the episodes of karstification of the Devonian. There are at least three known karstification events which impact the Devonian in Iowa (Garvin, 1995).

Constraining the ages of the alteration of the Spring Grove is difficult. Modern analogues show that the pore sizes noted in the Spring Grove at the studied source could have formed in as little as 5,000 years (Esteban and Wilson, 1993). There are no pores or vugs large enough or interconnected enough to have trapped sediment at the study locality to have accumulated datable fossils.

The dissolution that formed the pores could also be tied to an event that altered the δ¹⁸O of the Wapsipinicon Group gypsum and anhydrates in southern Iowa (Richardson and Hansen, 1991). The δ¹⁸O in the samples was slightly lower than a global synthesis of contemporaneous anhydrite δ¹⁸O and may have been caused by warm groundwater moving through the system (Richardson and Hansen, 1991).
The Owen Member source does not seem to have been subjected to meteoric waters or any phase of karstification. Although the Lime Creek in which the Owen resides is bounded by erosional surfaces, once deposition resumed there is no evidence that the Owen underwent such extensive alteration by meteoric waters. Diagenesis seems limited to stylolite formation parallel to bedding. The presence and pervasive nature of stylolite development suggests moderate burial, and while there are calcite twins present, they are not within fossils and so cannot be used to constrain burial temperatures.

The repeated exposures and influence of meteoric waters percolating through the Spring Grove have probably made its unique pore system, influenced by its fine peloidal depositional texture.

**Could wettability impact the properties?**

The wettability of the microcrystals around the microporous areas would alter the way the micropores take up water. If the microcrystal surfaces that face the pores are mostly water-wet, meaning that the contact angle between the mineral surface and a drop of water is greater than 90°, the pores will take up water rapidly and may not drain as quickly as if they were oil-wet (contact angle of less than 90°). If grains on the surface of a piece of coarse aggregate are oil-wet, they may fail to bond well with the paste when concrete is mixed, which has been reported by the Iowa DOT.

The wettability of microcrystals was preliminarily tested using the microcrystals sloughed off during a basic freeze-thaw test. Approximately half of the grains were rejected from the water suggesting that their surfaces are not strongly water-wet. When oil was added to the microcrystals, none were rejected and the oil readily moved over the entire area covered by the crystals (Figure 8). This suggests that the surfaces of the microcrystals are more oil-wet than water-wet, but a more detailed investigation should be undertaken to verify this
observation. If the microcrystals in the porous facies of the Spring Grove are oil-wet, this may explain the paste adhesion behavior.
CHAPTER 6. CONCLUSIONS

The Spring Grove as it is present at the study locality exhibits anomalous behaviors. During regular testing of aggregate, it has been observed to bubble vigorously. The bubbles were similar in size and pattern to champagne. Concrete durability beams made with the aggregate showed signs of spalling after the ASTM 666 freeze-thaw test. It was also noticed that blockstones left out on the quarry deteriorated to pebbles and dust after being exposed to weathering for one winter season.

By examining blockstones and aggregate, as well as a concrete durability beam, this study tested several potential causes of these anomalous behaviors. The Spring Grove Member is not inherently anomalous. When compared to a similar facies in the Owen Member, it is clear that these behaviors do not arise solely from its facies. Differential diagenetic alteration likely caused changes observed in the Spring Grove, which does differ from that present in the Owen Member.

The pore system present in a subset of the rock making up the Spring Grove are the result of the depositional and diagenetic history of the deposit. The pores in the highly porous (>20%) peloidal grainstones are pervasive and small (micropores). Micropores form an interconnected matrix, yet they are isolated from other microporous regions by the macropore network. The small size of the crystals around the micropores make them vulnerable to both physical and chemical deterioration.

The wettability of the microcrystals present in the microporous areas is implicated in the some of the reported anomalous behavior. The very high surface area of the microcrystals gives their surface properties an outsized influence on the overall physical properties of the rock. The failure of paste to adhere to some coarse aggregate the studied quarry, as has been
reported, suggests that the surface chemistry and structure may play a role in its behavior. It appears that the microcrystals are oil-wet, which could make bonding difficult for a water-based cement paste.

None of the tests performed can perfectly predict durability, and the Iowa DOT prefers past service history to any other metric where predicting future performance. However, it may be wise to have thin sections made of each rock type in a quarry or mine before using it because if this subset of material with pervasive micropores is detrimental, it may be that a small quantity could have an outsized effect on performance.

Further study of the effect of wettability on paste adhesion to micrites, particularly porous micrites, may further elucidate this phenomenon.
Figure 1. Spring Grove blockstones (circled in red) show the deterioration that occurs when they are allowed to remain on the quarry floor. They developed the cracks, flakes, and tan coloration visible in the image over the course of a year. Photo: F. Hasiuk, August 2015.
Figure 2. Section of the spalled concrete durability beam that was provided by the Iowa DOT. The spalling is indicated with a black arrow.
Figure 3.  Spring Grove Facies 3a from the studied source showing well developed bubble trains after being immersed in approximately 10 cm of deionized water for approximately one minute. The demarcations on the side of the container are ~3 mm apart.
Figure 4. Isopach map of Devonian sedimentary rocks in Iowa and surrounding states. Hatched areas denote Devonian outcrop belt, other patterned areas where Devonian has been eroded and younger strata were deposited (IP=Pennsylvania, J=Jurassic, K=Cretaceous). After Figure 3, Witzke et al., 1988.
Figure 5. Quarry locations shown on the Bedrock Geologic Map of Iowa (Iowa Geological Survey, 1998). The Spring Grove source is located in Black Hawk County. The Owen Member source is located in Story County.
Figure 6. Spring Grove source stratigraphic column. Created using information provided by the Iowa DOT. Beds 4 and 5 are “high quality” aggregate sources based on the Iowa DOT quality tests.
Figure 7. Owen Member source stratigraphic column. Taken from core provided by Martin Marietta Company. Quarried section approximately from 124m to 131m.
Figure 8. Overhead (A-W and B-O) and side view (B-W and B-O) of preliminary wettability test on the silt-sized calcite microcrystals that disaggregated from coarse aggregate pebbles of Spring Grove limestone during freeze-thaw cycles. A-W and B-W) Tests performed with water. Water was added to the microcrystals from the left. Material that did not mix with the water was pushed to the right of the image and is indicated with the blue arrows. A-O and B-O) tests performed with oil. Oil was added to the microcrystals from the left. The droplet is ~1 cm across. No material rose to the surface. Some mixed with the oil, causing a cloudy appearance. Outlined in blue is the test performed with water.
Figure 9. Spring Grove porosity distribution from 36 blockstone plugs. The porosities of the mudstones and breccias are outlined in red. The porosities of the peloidal grainstones are outlined in blue. The breccias from the Spring Grove and Davenport (Facies 1) fall in the 2-4% range (red). Both Facies 2 and Facies 3a fall into the 5-8% range (blue and red), while Facies 3b is between 16 and 20%, and 3c is all those above 20% helium porosity.

Figure 10. Owen Member porosity distribution, from 11 blockstone plugs. All blockstones are from the same facies, a peloidal grainstone.
Figure 11. Davenport limestone breccia. The mudstone clasts are indicated by (MS), the stylolite in the bottom left is (Sty), and the spar cement is (Spar). B) Blue arrows point to the small, fine grained areas that remained unstained by Alizarin Red S, suggesting a dolomitic composition. The yellow arrow indicates a small fracture cemented with calcite. Large image (A) is 17.8mm across and inset image (B) scale bar is 200 µm.
Figure 12. Spring Grove Facies 2. The low clay limestone mudrock is labelled (MS), and the clay rich bands are labelled (Clay). There is no visible porosity in the clay-rich mudrock, and there are isolated micropores (green arrow, inset image) in the clay-rich areas. A cemented fracture is indicated with a yellow arrow. The image in the back is 17.8mm on each side and the inset image scale bar is 200 µm.
Figure 13. Spring Grove Facies 3a. The peloidal areas are indicated with “Pl” and the ropey algal structures are marked “Algal.” Two of the dolomite ghosts are marked with pink rhombuses. The blue arrow is indicating the presence of the fine minerals that did not take dye but that are not identifiable petrographically. The green arrow indicates an area of isolated micropores. A) 17.8mm on each side. B) scale bar of 200 µm.
Figure 14. Spring Grove Facies 3b. This is a moderately porous peloidal lime grainstone. There are peloids indicated with “Pl,” clay bands with “Clay,” and radial textures with “Rad.” The radial fabric indicated is inside an ostracod. The green arrow is pointing at porous areas. The green arrow in the inset is indicating an area of interconnected microporosity and the green arrow in the larger image is indicating a macropore. The pink rhombus highlights a dolomite ghost. A) is 17.8mm on each side. B) scale bar is 200 µm.
Figure 15. Spring Grove Facies 3c. A) 17.8mm on each side and the inset (B) image has a 200 µm scale bar. Helium porosity of 23%. This is a highly porous peloidal grainstone. An area of peloids is indicated in each image with “Pl” and the green arrows indicate porosity. There are many micropores, causing a “blue haze” in the slide.
Figure 16. SEM image of Facies 4 focusing on one of the microporous regions of the peloidal grainstone. This location has a larger calcite crystal (likely a blocky cement) embedded in it. The micrite crystals are can be classified as “granular subhedral” according to the classification scheme of Kaczmarek et al. (2015).
Figure 17. Thin section photomicrograph of a concrete beam made with Spring Grove coarse aggregate, having been subjected to ASTM 666 freeze-thaw durability test. The bottom of the image is approximately 1 cm across. The aggregate labelled “MR” corresponds to the Facies (2), and those labelled “PI” correspond to the peloidal grainstones of Facies 3.
Figure 18. Microporosity deterioration. Scale bars 50 µm. A) Facies 3c blockstone. Microporous area indicated by green arrow. B) Coarse aggregate from the durability beam, presumed to be equivalent of Facies 3. A deteriorated area is indicated by the green arrow.
Figure 19. The two textures present in the mined section of the Owen Member. Both scale bars are 200 µm. A) Peloidal (Pl) lime grainstone, with birds-eyes (BE). B) Peloidal lime grainstone, with radial cement (Rad), often nucleated on oogonia.
Figure 20. Pore throat size distribution data measured via mercury intrusion data for Spring Grove samples. Facies 1/Davenport breccia has a peak in pore throat size at 0.03 µm (top, dark gray). Facies 2 has a variable pore throat size peak, with one sample peaking at 0.05 µm (dark brown) and another sample extended peak between 0.1 µm and 1 µm (light brown). Facies 3a has a pore throat peak at 0.09 µm (red). Facies 3b has a large range of pore throat sizes, with peak diameter increasing as porosity increases from 0.1 µm (pink) to a range of 0.1 µm to 1 µm in an asymmetric distribution (purple), to a 0.3 µm to 1 µm peak (blue). Facies 3c continues to increase the pore throat diameter, with a trimodal peak between 0.4 µm to 1.2 µm (light green) and a bimodal distribution from 0.7 µm to 1.2 µm (dark green, bottom).
Figure 21. Pore throat size distribution data measured via mercury intrusion data for the Owen Member sample. There is a peak between 70 µm, of macropores, and between 0.01 and 0.07 µm (micropores).
Figure 22. Image of micropores in the concentric layers of ooids. The scale bar is 100 µm. The microporous areas are indicated with green arrows.
Figure 23. Fibrous texture present in Spring Grove Facies 3c. Outlined in green is an area where pores have developed along an area of fibrous calcite, possibly algal in origin. The crystals within the area do not go extinct together. A) plane polarized light, and B) is in cross polarized. The images show the same area. Both scale bars are 50 µm.
Figure 24. Image of the microporosity present in Spring Grove Facies 3c. The images show the same area. The concentrically layered fabric is circled in yellow, while a microporous area lacking discernable fabric is circled in green. Both scale bars are 50 µm. A) is in plane polarized light. Image B is in cross polarized light.
Figure 25. Photomicrograph of calcite microcrystals that disaggregated from coarse aggregate pebbles of Spring Grove during freeze-thaw tests, mounted as a strew slide. Scale bar is 20 µm. The black arrows indicate some of the granular subhedral microcrystals that have not flocculated.
Figure 26. Image showing the twinning present in a thin section from Spring Grove Facies 1, the limestone breccia. Twinning can be a low temperature geo-thermometer, but in this case it is not useful because the crystals which show twinning are in fractures (Ferrill et al, 2004).
Table 1. Facies identified in the Davenport (1) and Spring Grove Members (1-3) of the Pinicon Ridge formation at the Spring Grove source.

<table>
<thead>
<tr>
<th>Facies</th>
<th>Description</th>
<th>He Porosity</th>
<th>Hg Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mudstone breccia with sparry calcite cement</td>
<td>0-4%</td>
<td>0-4%</td>
</tr>
<tr>
<td>2</td>
<td>Clay-rich fine grain crystalline limestone</td>
<td>4-7%</td>
<td>2-6%</td>
</tr>
<tr>
<td>3a</td>
<td>Fine peloidal grainstone with cryptalgal structures and dolomite ghosts</td>
<td>4-7%</td>
<td>3.3%</td>
</tr>
<tr>
<td>3b</td>
<td>Variably porous peloidal grainstone with sparry cement</td>
<td>13-20%</td>
<td>5-9%</td>
</tr>
<tr>
<td>3c</td>
<td>Highly porous peloidal grainstone with sparry cement</td>
<td>20-26%</td>
<td>10-11%</td>
</tr>
</tbody>
</table>
REFERENCES


Hickerson, W., 1994, Ptyctodontid Placoderms? From the Upper Spring Grove Member of the Pinicon Formation. Geological Society of Iowa Guidebook 79: 45-53.

Iowa Department of Transportation, 2018, IA 223B Quality Number: Method of Test: Determination of Salt Susceptibility Quality Number for Coarse Carbonate Aggregate in Portland Cement Concrete


Bond, G. C., & Kominz, M. A., 1990. Disentangling Middle Paleozoic Sea-Level and


APPENDIX A. EFFECT OF CRUSHING ON CARBONATE ROCK PROPERTIES

Introduction

Crushing rock to make aggregate relies on applying stress to the material until it fractures to a desirable size. The stress is compressional, and it is reasonable to assume that this stress might also cause physical changes to the rock’s pore system. Changes to pore systems could be of concern because it is currently assumed that both blockstones and core can be analyzed interchangeably with crushed rock aggregate when characterizing the quality of a source. To determine if any changes occur due to crushing, blockstone samples from three sources were compared to crushed aggregate sourced from the same quarries.

Localities

For the blockstone samples, the Iowa DOT worked over the summer and fall of 2015 to select blockstones from producing beds at each source. These samples were packed in bags and transported to Iowa State University before being laid out to fully dry. From the same sources, aggregate samples were provided from stockpiles. Ridzuan washed and sorted bulk aggregate. The aggregate sorting was based mainly on color, and most quarries had more than one rock type (Ridzuan, 2016).

Source 1

Source 1 (S1) is known for high-quality limestone. It currently generates aggregate from the Owen Member of the Upper Devonian Lime Creek Formation (Story County, Iowa, USA). In this area, it is pure limestone. The mine removes a limestone with low porosity and containing bird’s eye structures. It was selected because of its high-quality rating (secondary pore volume 13mL) and uniform limestone chemistry, without pyrite or clay (0.2%).
Source 2

This source (S2) was selected for analysis because it has a good pore system (secondary pore volume: 22mL) yet a high clay content (1.7%) and intermediate chemistry with both limestone and dolostone present. It comes from the Middle Devonian Spillville Formation (Wapsipinicon Group). The overall formation is intermediate. There are sections within the samples that are limestone, some slightly dolomitized, and some fully dolomitized.

This study selected two comparable sample sets from this quarry. The match was not perfect, due to a lack of overlap between the aggregate and the blockstone. The slight incongruity between the blockstone and aggregate samples sets was deemed negligible.

Source 3

The third source (S3) is almost entirely limestone source with a high clay content (2.9%) and high secondary pore index (88mL) (i.e., high microporosity). This quarry generates aggregate from a skeletal lime packstone and wackestone facies, which are both represented in both aggregate and blockstone. This quarry comes from the Bethany Falls Member of the Swope Formation (Bronson, Group, Middle Pennsylvanian), which runs through Kansas, Missouri and Iowa.

Methods

This study proceeded with two parallel workflows, one for aggregate and one for blockstones. They were similar, but the aggregate required visual sorting and that each test be performed on a subset of each sorted rock type whereas the blockstones were subdivided and tested from a large plug (see below) (Figure 27). Both the aggregate and the blockstone used in this study were provided by Iowa DOT. Visual sorting revealed that aggregate had
multiple rock types. Multiple samples were collected from blockstones in an attempt to identify multiple facies.

**Blockstone Plugging**

Between five and ten plugs were collected from several blockstones per source. Plugs were taken using a Powermatic drill press (model PM2800B).

Plugs were 2.5cm in diameter and 1 to 4 cm long. Some blockstones were impossible to sample due to their texture or breakdown. The plugs were cut using and trimmed to approximately 3 cm on a high-speed saw. Once a control helium porosity measurement had been taken, the plugs were trimmed at each end with a low velocity saw (ISOMET, 11-1180 LOW SPEED SAW), leaving a clean one-inch-long plug and two end pieces.

**Bulk Volume**

Once the plugs were cut, the plugs’ height and diameter were each measured three times using absolute Aos Digimatic calipers and averaged, and the bulk volume was calculated. The bulk volume of the pebbles used in the study was measured by means of the displacement of a fine powder (Ridzuan, 2016).

**Mass**

The plugs were dried in an oven at 135°C for 5 hours or more, and then cooled overnight in a desiccator. They were then weighed using a Mettler Toledo analytical balance (Model ME204E) with a precision of ±0.0001g.

**Pore Throat Size Distribution by Mercury**

As defined in the Washburn Equation, fluids (mercury, in this case) will enter capillaries at pressure proportional to the size of the capillary, based on the surface tension, viscosity and the adhesive properties of the fluid. Mercury will enter known pore throat sizes
at known pressures because of its cohesive and adhesive properties, if the initial state of the sample is defined. The data produced is the volume of mercury injected at a given pressure.

A subset of the trimmed plugs was selected to be run in the Quantachrome Poremaster 33 automated mercury intrusion porosimeter. This instrument was capable of intrusion from 3 to 33000 psi (2.1x10^4 pascals to 2.3x10^8 pascals), which is equivalent to pore throats of ~100 µm to ~5 nm.

For most of the blockstones collected from quarries, three plugs were run for each quarry. Plugs chosen for analysis were selected using the helium porosity data—one from the high porosity end of the quarry’s plugs, one from the middle, and one from the low end. The aggregate was run based on the sorted samples, at least one pebble from each rock type from each quarry was run.

**Petrography**

One of the trim ends from the blockstones, and a portion of a piece of aggregate from each rock type was sent for thin-sectioning (TPS Enterprises, Houston, Texas). They were dyed with alizarin red-S and potassium ferricyanide. They were imaged for this study using an Olympus DP73 camera and Olympus BX53 petrographic microscope and information about the texture, structures, and composition were recorded.

There were four quarries in common between the previous aggregate research and the blockstones analyzed in this study. Each source had either one or two rock types.

**Results**

To identify comparable samples, the visually identified rock types from the previous aggregate study were narrowed down. Mixed aggregate samples that had been separated into up to six different rock types based on visual inspection were grouped using thin section
descriptions into one or two rock types. These broader rock types were compared to those from blockstone thin sections. Petrographically matched samples of aggregate and blockstone were then compared using helium and mercury porosimetry data.

**Source 1: Peloidal lime grainstone**

This is high-quality source for aggregate (Iowa DOT class 3i) has very low clay content ($\text{Al}_2\text{O}_3 = 0.05$-$0.25$ wt%) and is a very pure, low magnesium calcite ($\text{MgO} = 0.2$-$0.4$ wt%) (Table 2). There was only one rock type present in this sample: peloidal lime grainstone with equant calcite cement occluding the pores (Table 3). Peloids were 50 to 200 $\mu$m in size. No laminations, sedimentary structures, or fossils were identified petrographically.

Pore throat size distribution histograms from mercury porosimetry were similar in both the low pressure (>50 $\mu$m) and high pressure (<1 $\mu$m) regions (Figure 28). Between blockstone and crushed rock, modal pore throat size (0.02 $\mu$m) does not change in quantity (volume mercury intruded per gram at peak) or quality (broadness of peak or skewness). Porosity in crushed rock (4%) is little changed from blockstone value (2%) (Table 2).

**Source 2: Intermediate limestone**

This moderate-quality source (Table 2) also has two discernable rock types (Table 4). There is a skeletal lime wackestone with low clay content ($\text{Al}_2\text{O}_2 = 0.23$ wt%) and intermediate lithology ($\text{MgO} = 1.3$ wt%). In addition, a skeletal packstone was analyzed with higher clay content ($\text{Al}_2\text{O}_2 = 0.47$ wt%) and intermediate lithology ($\text{MgO} = 1.3$ wt%).

The blockstone wackestone had modal pore throat sizes of 0.3 $\mu$m and 50 $\mu$m; the aggregate had a modal pore throat size of 0.3 $\mu$m (Figure 29). Porosity was little change: 10% in blockstone and 12% in crushed rock (Table 4). The packstone had had a modal pore
throat size of 0.05 μm in blockstone and 0.05 μm in crushed rock (Figure 30). This rock type showed the largest difference in porosity between blockstone and aggregate: the blockstone had 24% porosity and the aggregate 17%.

**Source 3: Skeletal packstone and dolostone**

This source also had two comparable rock types and is classified overall as an intermediate source. There was a skeletal packstone that in the blockstone has a small amount of dolomitization and is pure limestone in aggregate. There was also a clay-rich crystalline dolostone with a very small amount of residual calcite. Overall, this is a moderate-quality source.

The clay content is variable, with the skeletal packstone having a low to moderate amount (Al₂O₃ = 0.11-0.43 wt%) and the dolostone being high (1.08-1.64 wt%). As one would expect, the dolostone had high magnesium content (MgO = 14.7-17.0 wt%) while the packstone was much lower (MgO = 2.4 wt%) (Table 1).

In terms of pore throat size distribution, the clay-rich dolostone pore throats had a bimodal distribution, with a larger pore throat peak at 3 μm (macropores) and a smaller peak at 0.03 μm (micropores) (Figure 31). The skeletal packstones both had a double peak, with the pure lime aggregate having peaks at 0.02 and 0.09 μm and the slightly dolomitized blockstone having peaks at 0.05 and 0.15 μm (Figure 32). Porosity was virtually unchanged for either rock type. The skeletal packstone 23% porosity in blockstone and 24% porosity in crushed rock, while the clay-rich dolostone had 10% porosity in blockstone and 11% in crushed rock (Table 5).
Discussion

Source 1: Peloidal limestone

These samples were selected for comparison due to their visual similarity in thin section. They are extremely low in clay, pure limestone, and very low porosity.

Since chemistry will not be altered by crushing, the main concern is if the pore throats, specifically the abundance of micropores, change when the rock is crushed. For these samples, the micropores are essentially unchanged. In addition, the larger pores (>10 µm) remain essentially the same. The volume of the pores per gram of sample is the same for the micropores and slightly lower for larger pores after crushing.

There is only a change in the larger pores, which decrease slightly in volume. This is possibly due to the propagation of fractures through larger pores during crushing.

Source 2: Intermediate and dolostone

The skeletal lime packstone has two peaks in pore throat diameter that do not change their place from the aggregate to the blockstone. However, the skeletal lime packstone’s two modes in pore throat diameters change significantly in volume per gram of rock. There is a very large peak in the macropore range in the aggregate sample, which is only a very small uptick in the blockstone.

The macropores present in the aggregate sample, but not in the blockstone, are not of concern because their large size is outside of the range thought to produce negative behavior in pavements. The size and abundance of micropore throats remain essentially unchanged.
Source 3: Skeletal packstone and dolostone

This quarry contains two very different rock types. However, each type varies little between blockstone and crushed rock when assessed in thin section. The dolostone pore throats remain the same in both size and volume per gram through crushing. In the dolostone, no new pores propagate and none appear to be preferentially destroyed. The skeletal lime packstone remains dominated by small pores.

There are two very different rock types present in this quarry. If one rock type (limestone or dolostone) is preferentially broken down during crushing, there could be a change in the ratios between the two components before and after crushing. However, the components within an aggregate grain will remain.

For this quarry, the dolostone’s pore throats remain essentially unchanged while the skeletal lime packstone shows a significant shift toward smaller pore throat size in the crushed rock. Interestingly, the bimodality of the pore throat peak remains, suggesting that perhaps some other aspect of the mercury intrusion process (e.g., contact angle) may have changed during crushing which could have resulted in moving the pore throat distribution.

Dolostones are often very homogenous due to the process of dolomitization, and the pores are generally consistent. The changes in the packstone might result from slight variation in the relative abundance of depositional components between where each sample was collected.

Conclusions

Based on the small suite of samples analyzed in this study, it does not appear that crushing significantly changes the pore throat size distribution of a carbonate rock with respect to the micropore system. Some variations were seen at larger pore throat sizes.
 (>50µm) which may result from crushing-induced damage at aggregate particle edges. Most differences between the blockstones and crushed rock seem to arise from minor textural differences that likely arise from spatial variation in the base material.

To control for this spatial variation, a future study could make crush a sample of blockstone after core plugging it. That way both the crushed and uncrushed sample would be from nearly identical facies. Such a study would need to assume that the crushing process in a laboratory-grade jaw crusher would impart the same stresses as that of a production-scale crusher found in a quarry or mine.

An aspect of coarse aggregate production that was not analyzed in this study in any way was the effect of the initial blasting on an aggregate’s pore system. Both blockstones and crushed rock have experienced the stress induced by blasting and that may impart some changes to the pore structure of the aggregate, especially near the shot hole itself. A future study could also assess the impact of this by collecting core plugs on a transect away from a blast hole.

References


Figure 27. Materials used in this study included crushed rock (A) and core plugs from blockstones (B) collected directly from producing beds.
Figure 28. Rock type 1 from S1. The blockstone shows a limestone, peloidal grainstone texture with a pore throat peak (cc/g intruded) at 0.02µm and a peak above 10µm. The aggregate sample shows essentially the same pattern, with a peak at 0.03µm and above 10µm.

Figure 29. Rock type 1 from S2. Both are lime wackestone. Both have peaks at 0.3µm. The aggregate also has a peak above 50µm.
Figure 30. Rock type 2 from S2. Both are packstones, but the blockstone is of intermediate carbonate chemistry and the aggregate is pure limestone. Both have a pore throat peak at 0.05µm.

Figure 31. Rock type 1 from S3. Both are fine grained, moderate porosity dolomites. Both have peaks at 3µm and a small peak at 0.03µm. The noise in the aggregate graph may be due to the small size of the particle tested.
Figure 32. Rock type 2 from S3. Both are packstones. The blockstone has a bimodal peak at 0.03µm and 0.15µm. The aggregate also has a bimodal peak, but the peaks have shifted to the left toward smaller pores. The peaks are at 0.02µm and 0.07µm. The aggregate also has some noise in the data toward the larger pores.
<table>
<thead>
<tr>
<th>Source</th>
<th>Average</th>
<th>SD</th>
<th>Max</th>
<th>Min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (n=31)</td>
<td>12</td>
<td>5</td>
<td>22</td>
<td>6</td>
</tr>
<tr>
<td>2 (n=2)</td>
<td>243</td>
<td>33</td>
<td>266</td>
<td>220</td>
</tr>
<tr>
<td>3 (n=6)</td>
<td>81</td>
<td>28</td>
<td>112</td>
<td>58</td>
</tr>
</tbody>
</table>

Table 2: Summary statistics for Aggregate Quality data.
### Table 3: Summary statistics for Source 1.

<table>
<thead>
<tr>
<th></th>
<th>Blockstone</th>
<th>Aggregate Type 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Blockstone</td>
<td>Peloidal Limestone</td>
</tr>
<tr>
<td>Porosity (Helium)</td>
<td>2%</td>
<td>4%</td>
</tr>
<tr>
<td>Micropore throat peak (μm)</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Al₂O₃ (percent)</td>
<td>-</td>
<td>0.02-0.22</td>
</tr>
<tr>
<td>MgO (percent)</td>
<td>-</td>
<td>0.2-0.4</td>
</tr>
</tbody>
</table>

### Table 4: Summary statistics for Source 2.

<table>
<thead>
<tr>
<th></th>
<th>Blockstone 1</th>
<th>Aggregate 1</th>
<th>Blockstone 2</th>
<th>Aggregate 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Skeletal lime wackestone</td>
<td>Skeletal intermediate packstone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity (He)</td>
<td>10%</td>
<td>12%</td>
<td>24%</td>
<td>17%</td>
</tr>
<tr>
<td>Micropore throat size (μm)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Al₂O₃ (percent)</td>
<td>0.47</td>
<td>-</td>
<td>0.29</td>
<td>-</td>
</tr>
<tr>
<td>MgO (percent)</td>
<td>1.3</td>
<td>-</td>
<td>1.3</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 5: Summary statistics for Source 3.

<table>
<thead>
<tr>
<th></th>
<th>Blockstone 1</th>
<th>Aggregate 1</th>
<th>Blockstone 2</th>
<th>Aggregate 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Skeletal Packstone</td>
<td>Dolomite (euhehdral)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity (He)</td>
<td>23%</td>
<td>24%</td>
<td>10%</td>
<td>11%</td>
</tr>
<tr>
<td>Micropore throat size (μm)</td>
<td>0.02/0.09</td>
<td>0.05/0.15</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Al₂O₃ (percent)</td>
<td>0.11-0.46</td>
<td>1.08-1.62</td>
<td>1.08-1.62</td>
<td>1.08-1.62</td>
</tr>
<tr>
<td>MgO (percent)</td>
<td>2.4-18.2</td>
<td>15.0-17.3</td>
<td>15.0-17.3</td>
<td>15.0-17.3</td>
</tr>
</tbody>
</table>
APPENDIX B. SPRING GROVE REGIONAL STUDY

The Devonian Spring Grove Member source for this thesis is in Black Hawk County, Iowa, USA. It is a highly microporous peloidal and algal grainstone facies, representing a restricted basin tidal flat environment (here, Facies 3c). Its pore system seems to have formed through the dissolution of the edges of calcite microcrystals. The regional extent of this microporous peloidal grainstone facies within the Spring Grove Member is important due to the economic value of the Spring Grove, which is used to produce high quality aggregate supplies for construction of pavement and structures in and around the City of Waterloo, Iowa’s sixth-largest metropolitan area.

The Spring Grove is known to be present in outcrop as both limestone and dolostone, and is present in the subsurface as limestone, dolostone, or evaporites, or a combination of these. Well logs cataloged by the Iowa Geologic Survey have the primary minerology of the Spring Grove as any of those three categories though dolostone seems to predominate, with limestone present around in the Davenport area, in Waterloo, and in southeastern Iowa (Figure 33). This suggests that the lithology and other properties of the Spring Grove Member may be predictable on a regional scale.

The logged wells do not have break down lithology data by relative abundance; it only provides what the major constituents are. This lack of detail necessitated further exploration of the Spring Grove by taking samples from cores stored by the Iowa Geological Survey Core Repository (Coralville, IA), particularly those that were taken from near Waterloo, near the Spring Grove source for this thesis. This study seeks to trace local and regional texture and diagenetic change. If the rock types present in the Spring Grove throughout
Iowa can predicted (as well as their properties), it can guide production at current operations as well as exploration for new resources.

**Methods**

**Core selection**

The Iowa Geological Survey’s online databases GeoSam and GeoCore were used to find cores in the Iowa Core Repository (ICR) that contained the Spring Grove Member (SG). Thirteen cores from around Eastern Iowa were selected because they contained the Spring Grove. The Spring Grove had been noted by the ICR, with depths in the core listed. High resolution photographs of each box of core are also available from the ICR.

In Iowa, hundreds of wells penetrate the Spring Grove and have chemistry logged (Figure 33), and 30 cores are available in the ICR. Of the cores with Spring Grove kept by the ICR, 13 were sampled for this study (Table 1).

**Data collection**

At the ICR, the SG as present in each core was viewed. Dilute HCl was sprayed on the cores to determine lithology. When there was rubble present in the core, a piece was dropped into still water to see if it had the same bubbling habit as the Spring Grove source 1 aggregate from the quarry studied for this thesis. The ICR allows up to half of the material present to be taken for study, and in each core at least one part of the Spring Grove was taken for further study. In most cases, a piece of core was cut in half parallel to the drilled direction. If the core was rubble, a piece of rubble was taken.

Twenty-eight samples were taken from the 13 cores for thin sectioning. Cores that appeared homogeneous were only sampled once, while those that were either close to Waterloo or displayed more complex textures had multiple samples taken.
Samples were brought back to Iowa State University, where they were plugged, trimmed, and measured for porosity when it was possible. The trim ends were sent for thin sectioning, which were then dyed using Alizarin Red S to identify calcite, and with potassium ferricyanide to identify Mg-rich calcite (dolostone and other minerals would remain unstained). Photomicrographs were taken of each slide, both an overview image of the entire slide and images of areas of interest at different magnification, especially of the pore systems and the texture.

**Results**

**Petrophysical and thin section**

The minerology of each sample falls into four broad categories: pure limestone, pure dolostone, mixed limestone and dolostone, and mixed dolostone and gypsum/anhydrite. Each of these can be further separated by both porosity and whether original fabric remains. Primary fabric would be any recognizable bedding, fossils, peloids, or other textures that developed at deposition.

In dolomites, porosities were between 15% and 50%. In limestones, porosities were between 3% and 25%, and the intermediates range from 5% to 30% (Table 1). The dolomite and anhydrite/gypsum had moderate porosity (5-15%).

All thin sections that appear to preserve original fabrics are limestone (Figure 34). No dolomites or intermediates have any discernable primary texture or grains (Figure 35). Dolomite crystal size varies significantly from 25 µm, to 100 µm, to 200 µm (Figure 36, A-C). In intermediate slides, the dolomite rhombs can vary from between 150 µm (Figure 37A) and 300 µm (Figure 37, B). Some limestone slides have dolomite ghost rhombs up to 350 µm (Figure 34, A).
Some of the limestone thin sections had fractures that had been cemented with limestone (Figure 38). Where primary fabrics are preserved in limestones are either mudstone or peloidal grainstone (Figure 34). One dolomitic slide shows a stylolite (Figure 39), but its texture is slightly diffuse within the crystals. Several dolomites have rounded quartz grains of between 50 µm and 300 µm (Figure 40). None of the limestone or intermediate lithologies had quartz grains present, but one limestone does have an organic inclusion (Figure 41).

**Stratigraphy**

Because of the heterogeneity of the cores, there is little that can be traced from core to core. The columns were only sometimes able to be correlated using depositional characteristics, textures, or minerology. Chert is present in the bottom of some SG cores. Some grade from gray to buff colored going up, while a few grade from gray at the bottom to buff at the top. Some have a sharp, erosional separation at the top and bottom of the Spring Grove, some of these show bioturbation.

**Discussion**

**Reasons for lack of homogeneity**

The northern-most core was taken in Mitchell County, Iowa. The southernmost was from Wapello County. The northernmost core and the southernmost core were taken approximately 300 km apart. The easternmost and westernmost cores used were approximately 100 km apart. This is an area of 30,000 square kilometers. Over this area, no sample from Spring Grove looks like exactly like another. Only 5 of the 10 cores that have more than one thin section taken from them have the same chemistry throughout. This indicates that the Spring Grove is highly variable regionally.
Variability at a regional scale is expected in a member or formation. Environments change over space (and time), and a patch reef might only be a few tens of meters across and might migrate kilometers over time. However, the variation in the Spring Grove does not appear to be in depositional environment. It does not seem that many samples of the Spring Grove have retained their original fabrics. This suggests that either the variation was caused by changes to an already variable member (erasing depositional texture, but controlled by previous variability), or something other than depositional environment have caused it (variable diagenetic history).

Analysis thus far indicates that either of these could have had the dominant effect. If porosity varied because of different grain sizes during deposition, for example, porous areas might be altered while less porous areas are not. This would seem to be supported by the fact all of the limestones with preserves fabrics seem to be peloidal or algal grainstones or mudstones—both of these were potentially deposited as fine-grained sediment, which would be more difficult for fluids to percolate through and alter. In areas where larger grains were deposited and mud was winnowed out, waters may have percolated through more easily, enhancing alteration and loss of depositional fabrics.

The second explanation is that the diagenetic history is very complex. Even the mudstones that retain original fabrics have dolomite ghosts (i.e., dolomite grew in them and was later replaced with calcite). The mudstones and peloidal/algal grainstones are also fully cemented with sparry calcite cement. The fossils that are present have recrystallized. If most of the material in the Spring Grove started as limestone, large swaths were dolomitized. This dolomite shows evidence of multiple stages of growth—many of the dolomite crystals are zoned. In some samples, the porosity within the dolostone has been completely occluded
with sparry calcite. In others, the dolomite has begun to or has been completely dissolved, leaving dolomoldic porosity or leading to complete dedolomitization. In still others, the calcite cement has been reduced by dissolution leaving patched of dolomite well cemented with calcite, while absent nearby.

It seems that both of these processes may have contributed to the final rock characteristics. Fine grained material with lower porosity and permeability are less likely to be altered by fluids moving through them. There were almost certainly multiple generations of fluids moving through the rock depositing different minerals, altering back and forth from limestone to dolostone. The many textures, some in different states of dissolution and recrystallization, also suggest a generation of diagenetic alteration. The dolomite with sparry calcite cement and the subsequent dissolution of either the calcite or the dolomite suggests at least one. In Linwood Mine, which removes some Spring Grove material, there are well known barite mineralization, as well as karst deposits and quartz lined vugs. This indicates that the Spring Grove in that area had had unique waters percolating through.

Overall, this suggests several changes in the pore waters that were moving through the system, with possible preferential preservation of depositional fabrics in lower permeability rock. At some point, probably before the first episode of dolomitization, there was at least some stylolitization due to stress form the overlying rock. Some of the limestones with original fabrics also contain cemented fractures—some due to dissolution collapse but others perhaps due to mudcracks or other external events.

**Conclusion**

The Spring Grove has been altered by a complex series of pore water changes, exposures, and stresses. Some depositional textures remain, but they do not appear to have significant control on alteration, other than where permeability may have been reduced by
small grain sizes. This lack of depositional control on the modern rock, especially on their pore structures, makes it difficult to predict with certainty where high quality aggregate may be sourced, even on a local scale.

Figures

Figure 33. Map of logged wells that contain the Spring Grove, and their primary chemistry. Pink is dolomite, blue is limestone, red is gypsum or anhydrite. The yellow stars are quarry locations that source their material at least in part from the Spring Grove.
Figure 34. Photomicrograph of pure limestones with original fabrics preserved. Both scale bars 200 µm. A) peloidal lime mudstone with dolomite ghosts and sparry cement, B) peloidal grainstone with dolomite ghosts.
Figure 35. Photomicrograph of A) pure dolomite and B) intermediate chemistry (calcite cement is stained pink).
Figure 36. Photomicrograph of dolomite grain size variation in pure dolomites, all scale bars 200 µm, A) has crystals of 25 µm, B) 100 µm and C) 200 µm.
Figure 37. Photomicrograph of dolomite crystal size in intermediates (mixed dolomite and limestone). Dolomite crystals are 150 µm in (A) and up to 300 µm in (B).
Figure 38. Photomicrograph of limestone with original fabric, with fracture cemented with calcite. Scale bar is 200 µm.
Figure 39. Photomicrograph of a fine crystalline dolomite with a stylolite. The clay in the stylolite is diffuse, and the crystals of dolomite along the stylolite do not show evidence of dissolution present (partially dissolved or truncated grains). Scale bar is 200 µm.
Figure 40. Photomicrograph of dolomite with quartz grains. The green arrow indicates a large quartz grain. Scale bar is 200 µm.
Figure 41. Photomicrograph of a limestone with a large organic inclusion, scale bar 200 µm.
Appendix Table 1: Summery of sampled cores

Table 6. Summary of sampled cores

<table>
<thead>
<tr>
<th>Well</th>
<th>Latitude &amp; Longitude</th>
<th>Depth to top of Spring Grove</th>
<th>Thickness of Spring Grove</th>
<th>Overall core description</th>
<th>Slide depths</th>
<th>Slide description</th>
</tr>
</thead>
<tbody>
<tr>
<td>27275</td>
<td>43.377240, -92.811850</td>
<td>80.1m</td>
<td>1.2m</td>
<td>Grey rubble (15cm) to massive (40cm) to rubble (40cm) again, then transitions to brown and porous for top 30cm</td>
<td>80.3m</td>
<td>31% porosity High porosity fine dolostone with fine quartz grains</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80.5m</td>
<td>Moderate porosity fine dolostone with medium and fine quartz grains</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>81m</td>
<td>Moderate porosity fine dolomite in dolomite mud matrix</td>
</tr>
<tr>
<td>32352</td>
<td>42.936498, -92.571936</td>
<td>75.9m</td>
<td>3.4m</td>
<td>Very porous, vuggy buff to brown colored</td>
<td>77.9m</td>
<td>50% porosity Highly porous vuggy dolomite with variable grain size (50 µm to 200 µm), clay rich</td>
</tr>
<tr>
<td>27274</td>
<td>43.181920, -92.732670</td>
<td>78.8m</td>
<td>2.7m</td>
<td>Bottom may have chert, gray (40cm) grades into highly porous/vuggy brown dolomite</td>
<td>79.5m</td>
<td>39% porosity Highly porous dolomite with some vugs, clay rich</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80m</td>
<td>Sparry calcite, with an oblong organic inclusion of 7mm thick and a few cm long.</td>
</tr>
<tr>
<td>27871</td>
<td>42.415104, -92.327594</td>
<td>~70.6m</td>
<td>~5.8m</td>
<td>Buff to brown at bottom (~300cm), some material lost from core,</td>
<td>70.7m</td>
<td>10% porosity Dolomite with calcite cement, some dissolution of calcite. Cores of dolomite very clay rich, some cores are converting back to calcite.</td>
</tr>
<tr>
<td>Depth</td>
<td>Latitude</td>
<td>Porosity</td>
<td>Description</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>-------------------</td>
<td>-----------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>71.5m</td>
<td></td>
<td>27%</td>
<td>27% porosity Highly porous dolomite with areas of calcite cement. Possibly calcite cement was partially dissolved.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>73.6m</td>
<td></td>
<td>20%</td>
<td>20% porosity Intermediate, large (&gt;100 µm) dolomite rhombs in fibrous limestone. May have some cryptoalgal structures. Some clay rich areas in limestone.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75.3m</td>
<td></td>
<td></td>
<td>Intermediate, with medium (&lt;150 µm) dolomite in bladed to micritic limestone. Limestone has some ropey texture.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27560</td>
<td>42.354817, -92.297972</td>
<td>~53.8m</td>
<td>~4.6m Interbedded gray and brown beds (5cm-60cm) going up,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>54.1m</td>
<td>Fine peloidal limestone, with some large (~1mm) pores (5-10%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>54.9m</td>
<td>Fine peloidal limestone, medium (0.5mm) pores (5-10%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>55.6m</td>
<td>19% porosity Dolomoldic (100 µm) porosity in sparry calcite. No dolomite apparent, fully dissolved.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>56m</td>
<td>19% porosity Dolomoldic porosity, but higher clay and some remaining dolomite (&lt;10%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.7m</td>
<td>Peloidal to micritic limestone with fractures, moderate porosity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23440</td>
<td>42.125942, -92.144135</td>
<td>Unknown</td>
<td>Unknown (~5m?) Brown breccia material in gray matrix, bottom 0.5m, grades into vuggy brown</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>88.4m</td>
<td>Peloidal limestone with porous areas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Location</td>
<td>Coordinates</td>
<td>Depth</td>
<td>Thickness</td>
<td>Description</td>
<td>Porosity</td>
<td>Notes</td>
</tr>
<tr>
<td>------------</td>
<td>-------------------------</td>
<td>-------</td>
<td>-----------</td>
<td>----------------------------------------------------------------------------------------------------------------------</td>
<td>----------</td>
<td>-------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>23925</td>
<td>41.814384, -91.714701</td>
<td>77m</td>
<td>5.2m</td>
<td>Dolomite/brown breccia of high porosity material at bottom. Beds of gray and brown with dark laminations all the way up, with gray increasing</td>
<td>4%</td>
<td>Lime mudstone with some peloids, with dolomite ghosts and at least one ostracod. Sparry cement.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23317</td>
<td>41.645516, -91.542065</td>
<td>36m</td>
<td>7.6m</td>
<td>Buff/brown highly porous dolomite at bottom (1m), patchy transition upward to gray (1.5m), top is laminated gray.</td>
<td>28%</td>
<td>Fine dolomite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fine, clay rich dolomite. Contains a stylolite with diffuse edges</td>
</tr>
<tr>
<td>Depth</td>
<td>Location</td>
<td>Interval</td>
<td>Interval</td>
<td>Description</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------------</td>
<td>----------</td>
<td>----------</td>
<td>-----------------------------------------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23254</td>
<td>42.165259 - 91.802293</td>
<td>24.4m</td>
<td>4.25m</td>
<td>Porous brown dolomite at bottom, gray and brown/buff interbedded all the way up. Clay/dark laminations present throughout.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26.2m Fine intermediate with some fine porosity</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>28.6m Vuggy fine dolomite with some areas of lower porosity, clay rich</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23183</td>
<td>41.901831, -91.802555</td>
<td>53.6m</td>
<td>7.3m</td>
<td>Low porosity, brown to buff at bottom, increasingly gray going up. Fine, dark laminations present throughout</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>52.9m Fine porous dolomite with clay/organic inclusions</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>58.8m 19% porosity. Fine peloidal grainstone with thin clay laminations, some calcite spar in areas. Some ghosts present.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23116</td>
<td>41.847825, -91.810600</td>
<td>71.3m</td>
<td>6.4m</td>
<td>Dark gray at bottom with possible chert bed and some breccia (~1.5m). Grades upward to highly porous brown dolomite and then back to gray for top 1m. has fine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>72.8m Porous dolomite, crystals approximately 100 µm. Cores of crystals are clay rich. Porosity evenly distributed</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>74m 15% porosity Porous dolomite, crystals approximately 100 µm. crystals are clay rich throughout, and porosity is lower in some areas than others</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Depth (m)</td>
<td>Coordinates</td>
<td>Thickness (m)</td>
<td>Description</td>
<td>Porosity (%)</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>--------------</td>
<td>---------------</td>
<td>------------------------------------------------------------------------------------------------------</td>
<td>--------------</td>
<td>---------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>36196</td>
<td>41.479704, -90.811277</td>
<td>78m 3.7m</td>
<td>Very dark brown at bottom, porous to vuggy, lightening and turning gray going up-core. Dark gray at top. Clay rich.</td>
<td></td>
<td>8% porosity Clay rich dolomite with calcite cement, dolomite crystals range in size from 150 µm to 300 µm</td>
<td></td>
</tr>
<tr>
<td>9030</td>
<td>41.083744, -92.361270</td>
<td>329m 4m</td>
<td>Interbedded gray and brown with cm-scale gypsum nodules. Darkens at top.</td>
<td></td>
<td>Dolomite crystals (150 µm) in dolomite and gypsum matrix, clay rich. Dolomite crystals uniformly clay rich</td>
<td></td>
</tr>
</tbody>
</table>