Factors Relating to Aggregate Durability in Portland Cement Concrete

Interim Report

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INTERIM REPORT

FOR

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FACTORS RELATING TO AGGREGATE DURABILITY IN PORTLAND CEMENT CONCRETE

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INTRODUCTION

Over the past several years we conducted a comprehensive study on the pore systems of limestones used as coarse aggregate in portland cement concrete (pcc) and their relationship to freeze-thaw aggregate failure. A simple test called the Iowa Pore Index Test was developed and used to identify those coarse aggregates that had freeze-thaw susceptible pore systems. Basically, it identified those aggregates that could take on a considerable amount of water but only at a slow rate. The assumption was that if an aggregate would take on a considerable amount of water at a slow rate, its pore system would impede the outward movement of water through a critically saturated particle during freezing, causing particle fracture. The test was quite successful when used to identify aggregates containing susceptible pore systems if the aggregates were clean carbonates containing less than 2% or 3% insolubles.

The correlation between service record, ASTM C666B and the pore index test was good, but not good enough.

It became apparent over the past year that there were factors other than the pore system that could cause an aggregate to fail when used in pcc. The role that silica and clay play in aggregate durability was studied.

SILICA (SiO_2)

Silica occurs naturally in many forms. It can range from amorphous (opal, glass) to completely crystalline (quartz). Some of the in-between forms are known as tripolitic chert, cryptocrystaline chert and crystobalite. All of these forms of silica can be found in Iowa carbonates although some are quite rare. Quartz has no adverse effects on concrete durability while all the others have apparent negative effects.

Silicon itself is easily identified by using X-Ray Fluorescence (XRF), atomic absorption or standard wet-chemical analysis. The problem of identifying silica's form is another matter. X-Ray Diffraction (XRD) can be used where "grains" are apparent but it is unreliable toward the amorphous end of the range. A scanning electron microscope (SEM) with an

elemental analyser would be able to identify and photograph all of the silica forms, but it would be expensive and time-consuming.

We plan on using the XRD, XRF and SEM units to identify silica on selected samples during 1983.

While our understanding is incomplete, the initial study of over 60 samples chemically analyzed by XRF would seem to indicate definite relationships between silica and aggregate durability.

Some of the younger Iowa carbonates from the Paleozoic Era contain microscopic silica. This microscopic silica may take the form of cryptocrystaline chert, tripolitic chert, or quartz. In the case of tripolitic and cryptocrystaline chert, the microscopic chert usually takes the same form as the bedded or nodular chert that may be present.

The pore index and high pressure mercury porosimeter tests have shown that cryptocrystaline chert may be very dense and nonporous. Carbonate units containing cryptocrystaline chert in amounts as high as 7% can pass all of the Iowa quality control tests and still be associated with deterioration when used in pcc on the primary road system. Initial testing indicates that NaCl may severely aggravate the breakdown of this stone when used in pcc. A special preparation prior to testing with the ASTM C666B test was developed to test for salt (NaCl) susceptibility. The special preparation is performed on the loose coarse aggregate prior to the manufacture of the test beams. It consists of 5 cycles of soaking in NaCl for 24 hours followed by oven drying at 230°F for 24 hours. Excess salt is then removed by a final flushing of the aggregate particles.

One aggregate tested was the carbonate fraction of a gravel that contained an excessive amount of microscopic cryptocrystaline chert. This aggregate has developed an extensive service record over the past 20 years. The service record has been contradictory, in that the pcc pavement on the interstate and primary road systems developed extensive D-cracking, while pcc pavement on the secondary road systems is still in good condition, free of D-cracking. Since interstate and primary highways are salted (NaCl) and secondary highways are not, the combination of salt (NaCl) and this particular aggregate seemed suspect.

XRF analysis of the carbonate fraction of this gravel shows a silicon to aluminum ratio of 11.32 and a silicon to potassium ratio of 20.95 which we feel indicates an excessive amount of free silica (i.e. potassium and aluminum correlate directly with clay content and there is more silicon than the clay can account for). The durability factor for the specially prepared sample (with NaCl) was 13, while the durability factor for the standard sample was 71. Additional samples from other sources containing excessive cryptocrystaline chert have been subjected to the special preparation process and are awaiting durability testing. Some of the poorer performance may be due to the presence of the non-illite clay. One other observation should be noted: One hundred pounds of pure, dense, cryptocrystaline chert was hand-picked from limestone at the Logan Quarry in western Iowa. Test beams using only this chert as the coarse aggregate achieved a durability factor of 83 on the ASTM C666B test, an indication of satisfactory durability. The crushed stone from the Logan Quarry contains less than 3% visual chert, passes both the ASTM C666B and pore index tests, has a low clay content, and has a bad service record when used in pcc pavements salted in wintertime deicing programs.

As cryptocrystaline chert ages, it becomes grainy, develops a pore system and eventually turns into chalky tripolitic chert. When the cryptocrystaline chert is encased in porous carbonate rock the transition to tripolitic chert is faster. Coarse aggregates (carbonates) containing tripolitic chert (even in amounts of less than 3%) will nearly always fail the ASTM C666B durability test. Large pieces of tripolitic chert cause popouts in pcc pavements and may cause test beams to fracture. Carbonate particles containing microscopic tripolitic chert usually "disintegrate" within test beams when tested according to ASTM C666B as opposed to the sharp fractures in the clean, limestone aggregate particles with susceptible pore systems. Tripolitic cherts contain an extremely inferior pore system when tested using either the pore index test or the high pressure mercury porosimeter. Quartz is another form of silica. All of the natural sands in Iowa are made up of nearly 100% quartz grains. Quartz is also a major constituent of the igneous fraction of our gravel coarse aggregates.

Iowa also uses some limestones and dolomites containing minor amounts of sand (quartz) for coarse aggregate in pcc. Some quartzite (metamorphic sandstone) from South Dakota is also used. In every case, silica in the quartz form has proven to be a very durable aggregate.

CLAY

All of the carbonate pcc aggregates used in Iowa contain some clay. Iowa carbonates are all from the Paleozoic Era, which included the Pennsylvanian, Mississippian, Devonian, Silurian and Ordovician periods in order of increasing age. Grim, in his book of Clay Mineralogy, notes that montmorillonite clays occur in the eras younger than the Paleozoic. He further notes that Montmorillonites have been altered to illite in the Paleozoic era. Since most clays are rich in aluminum and illites are rich in potassium, any aluminum and potassium found in the carbonate could be assumed to be tied to clay mineral. Therefore, a K/Al ratio could be a rough indicator of illite content. According to Grim, the illite content of the clay fraction should increase at the expense of the other clays as we examine progressively older sediments. XRF chemical analysis of over 60 samples indicates that the above statements are generally true.

The Iowa and Illinois DOTs have known for a long time that crushed stone from the Silurian period is normally very durable when used in pcc. In Iowa, we have felt that this excellent durability was related to an open pore system which developed through the process of dolomitization. In addition, it now appears that the process of illite formation may be an important factor relating to durability. Also, the elimination of microscopic chert from the carbonate crystals seems to have taken place during the process. This microscopic chert may have been expelled from the crystal structures as dolomitization occurred. The silica could then be expelled through the newly developed pore system or, if retained, might be rendered harmless by the relatively large pore system. These older carbonate units still contain the larger nodules and beds of tripolitic chert, even though the microscopic chert has either totally disappeared, or disappeared from the carbonate crystal system.

The above explanation assumes that microscopic chert was originally in those carbonate units that contain the larger nodules and beds or layers of chert.

The presence of any clay influences the test results of the Iowa pore index test in a negative way and the presence of illite influences the test results of the ASTM C666B test in a positive way. It was known that the presence of clay affected the results of the pore index test in the early experimental stages, but we were unconcerned because we routinely screened and rejected aggregates with a clay content over approximately 5%. After conducting many tests on the Kankakee stone from Illinois as well as similar high (5%-15%) illitic carbonates here in Iowa, it appears that we may be guilty of "overkill" with our water-alcohol, freeze-thaw test specifications. However, the amount and type of clay encountered seems to be the critical issue. Our younger carbonate units apparently contain layers or mechanical mixtures of different clays. We have not analyzed these younger units for non-illitic clay types, but the Illinois Geological Survey identifies appreciable amounts of chlorite in their Pennsylvanian carbonate units. We expect to find kaolinite clay in these younger units also. The older stones with a high K/Al ratio (illitic carbonates) seem to do extremely well on the durability test (ASTM C666B) even with clay percentages over 10%. It would seem that high K/Al ratio clays enhance the durability (ASTM C666B) of the carbonate stones tested.

As with air entrainment, it is possible to have too much of a good thing, and this must also be true of the illite in carbonate coarse aggregate. Also, we must keep in mind that this improvement of durability may be caused by the absence of microscopic chert, or a totally different factor which merely relates to silica and/or potassium content. We have located a stone (Mohs Quarry) from the Ordovician system that is a fine grained limestone with a high K/Al ratio and a high Si/K ratio. Mohs Quarry durability factors have been run and the test results were very good. A sample with the special NaCl preparation will be tested. We should be able to determine the effect of NaCl on a fine grained limestone containing both microscopic silica and illite as the insoluble materials.

The Kankakee dolomite from Illinois, which contains a high percentage of pure illite but very little microscopic silica, tested very good with the special NaCl preparation prior to ASTM C666B testing. The Kankakee has a very good service record on primary roads.

CATION EXCHANGE

Soil scientists have known for a long time that it is possible to exchange ions in clay minerals and much has been written on this subject. The common water softener works on this principle. Theoretically, it should be possible to introduce potassium ions into the non-illite clays. Whether or not it would stabilize them, and if they would remain stable is still in question. Also a carbonate containing a non-illite clay with introduced potassium ions may or may not perform as if it contained a natural illite. Cation exchange was tried by soaking an argillaceous Pennsylvanian limestone in potassium chloride. The first test was positive but the next two were negative.

The XRF machine requires "known chemical standards" with which to compare samples to obtain accurate elemental percentages. Many of the mineral standards available from the government or private chemical labs report magnesium and calcium as calcium carbonate. Many of the clays contain calcium and magnesium as a part of their structure. The XRF machine reports total concentrations of elements regardless of the various compounds. Other elements such as iron and silicon may be found in more than one compound within a single "standard". When setting up a "standard" table for the XRF machine, extreme care should be used in working out the percentages for each element. A better method would be to blend pure, simple compounds to obtain the various elemental percentages needed for a comprehensive "standards" table.

Since clay and silica comprise a minor amount of the total carbonate sample in many cases, the accuracy of the results must be questioned. Since we are interested only in the insolubles for this study, removal of the carbonate portion of the sample by acid would seem to be an obvious solution. Unfortunately, acid may alter the clay structure and leave any test results open to question. Pulverization and flocculation has been

suggested, but ions in some flocculants could be a problem. As yet, an acceptable method to enhance the unaltered clay percentage so that we can obtain more accurate data on the insoluble portion of carbonate samples has not been identified.

FORMS OF SILICA (SiO_2)

Opal		Hydrated, Amorphous Silica
Chert	Cryptocrystaline	Dense, Fine Grained, Non-Porous Silica of Sedimentary Origin.
	↓ Weathering	
	Tripolitic	Chalky, White, Porous Silica
Quartz		Mostly of Igneous Origin, Relatively Large Crystals, Non-Porous Silica

Quarry or Pit	Service Record	ASTM C666B Durability Test		Si/K Ratio	K/Al Ratio
		Standard Preparation	NaCl Preparation		
Kankakee	Excellent	98	98	5.78	0.92
Stanzel 15C	Poor	98	39	11.86	0.39
Ames Pit (CO_3)	Poor	71	13	20.95	0.54

Si/K Ratio Correlates Directly With Excessive Silica and/or Non-Illitic Clay

K/Al Ratio Correlates Directly With Illitic Clay Content

GEOLOGIC ERAS AND PERIODS

Cenozoic		
Mesozoic		
Paleozoic	Permian	200 Million Years Old
	Pennsylvanian	
	Mississippian	
	Devonian	
	Silurian	
	Ordovician	
	Cambrian	500 Million Years Old
Proterozoic		
Archeozoic		

Total Sample					Insoluble Fraction		
Quarry	Geologic Age	Durability Factor ASTM C666B	Service Record	Pore Index Test	Percent Insoluble	K/Al Ratio	Si/K Ratio
Menlo	Pennsylvanian	Bad	Bad	Bad	Mod.	Low	High
Logan	Pennsylvanian	Good	Bad	Mod.	High	Low	High
Alden	Mississippian	Good	Good	Good	Low	Low	Low
Montour	Mississippian	Bad	Good	Good	Low	Low	Low
Plower	Devonian	Bad	Bad	Bad	Low	High	Low
Lamont	Silurian	Good	Good	Good	Low	High	Low
Kankakee	Silurian	Good	Good	Bad	High	High	Low

Si/K Ratio Correlates Directly With Excessive Silica and/or Non-Illitic Clay

K/Al Ratio Correlates Directly With Illitic Clay Content