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CONSTRUCTION MATERIALS CONSULTANTS, INC.

Investigation of Concrete Surface Scaling by Laboratory Examinations of Two Concrete Cores

Germantown Mill Lofts
Louisville, Kentucky

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TABLE OF CONTENTS

Suggested Reading:

Jana, D., "Concrete, Construction or Salt – Which Causes Scaling? Part I: Importance of air-void system in concrete", *Concrete International*, American Concrete Institute, November 2004, pp. 31-38.

Jana, D., "Concrete, Construction or Salt – Which Causes Scaling? Part II: Importance of finishing practices", *Concrete International*, American Concrete Institute, December 2004, pp. 51-56.

EXECUTIVE SUMMARY

Reported herein are the results of detailed laboratory examinations of two (2) hardened concrete cores identified as 'north' and 'south' received from scaled concrete sidewalks at Germantown Mill Lofts located in Louisville, Kentucky.

Field photographs of concrete surface distress at the locations of 'north' and 'south' cores showed severe scaling of concrete surface and exposures of coarse aggregate particles at scaled locations of 'north' core in the top photo, relatively lesser degree of surface scaling but exposure of coarse aggregate particles at the scaled location of 'south' core (bottom photo), and, noticeably sound concrete slabs adjacent to the scaled ones of this investigation separated by construction joints.

The cores were examined by detailed petrographic examinations *a la* ASTM C 856 to evaluate the concrete quality (e.g., aggregates, water-cementitious materials ratio, air contents, air-void systems), construction practices followed (e.g., placement, consolidation, finishing, and curing), and the potentially deleterious effects of salts. Additionally, profiles of water-soluble ions from the top, mid-depth, and bottom locations of cores were done by: (a) potentiometric titration, for water-soluble chloride contents *a la* ASTM C 1218, (b) anion chromatography, *a la* ASTM D 4327 for water-soluble fluoride, chloride, nitrate, nitrite, bromide, phosphate, and sulfate ions, and (c) cation chromatography for water-soluble alkalis (sodium, potassium), and calcium ions.

Based on petrographic examinations, the concrete in both cores is determined to be compositionally similar, **non-air-entrained**, and made using: (a) crushed limestone coarse aggregate having a nominal maximum size of $^1/_2$ in. (12.5 mm) which is well-graded and well-distributed; (b) natural siliceous-calcareous sand fine aggregates having major amounts of siliceous components (quartz, quartzite, feldspar, chert, siltstone), subordinate amounts of calcareous components (limestone, dolomite), and minor amounts of argillaceous and ferruginous components (shale, ferruginous siltstone), having nominal maximum sizes of $^3/_8$ in. (9.5 mm) which too is well-graded, well-distributed, and sound; (c) hardened Portland cement paste having cementitious materials contents similar in both cores and estimated to be 8 to $8^1/_2$ bags per cubic yard of which 15 to 20 percent is estimated to be fly ash, and, water-cementitious materials ratios (*w/cm*) similar in both cores and estimated to be 0.40 to 0.44 in the interior bodies but higher at the scaled surface regions (0.44 to 0.50); and, most importantly, (d) lack of air entrainment having estimated 2 to maximum 4 percent air as opposed to common industry (e.g., ACI, ASTM)-recommended minimum air content of $4^1/_2$ percent for an outdoor concrete intended to be exposed to cyclic freezing and thawing and deicing chemicals at critically saturated conditions.

Due to the lack of air entrainment, the observed and reported **surface scaling of concrete is determined to be due to cyclic freezing and thawing of a non-air-entrained concrete at critically saturated conditions**. Scaling could have been aggravated in the presence of deicing chemicals and exposure to winter weather conditions prior to the attainment of concrete maturity, which is defined as a period of air drying and a compressive strength of at least 4000 psi at the exposed surface regions prior to the first exposure to freezing, salts, and snow.

Chemical profiles of cores showed no significant enrichment of chloride in the exposed surface regions of cores compared to the interiors, indicating perhaps a chloride-based deicer was not used. However, scaled surface regions of both cores showed noticeable enrichment in water-soluble sulfates, sodium, and calcium ions, indicating perhaps a sulfate-based salt (or a salt having sulfate contaminants) was used that could have caused chemical and physical deterioration of surface region by chemical and/or physical salt attacks at the surface.

Based on detailed laboratory investigations, the reported surface scaling of concrete slab from field photographs to examined cores are judged to be due to a combination of one or several of the following factors:

a. **Lack of air entrainment in concrete**, which has affected the durability of concrete in a moist outdoor environment exposed to cyclic freezing and thawing at critically saturated conditions.

b. **Premature finishing prior to the evaporation of bleed water from the surface** that has created soft, porous, high *w/cm* paste at the scaled surface regions susceptible to scaling during freezing at critically saturated conditions.

c. **Potential exposures to non-chloride-containing deicing salts**, that might have caused the observed noticeable enrichment of water-soluble sulfate, sodium, and calcium ions at the scaled surface regions compared to the interiors of both cores, which could have caused chemical and/or physical salt attacks at the surfaces, probably aggravated by the lack of air entrainment of concrete to release any salt-related distress of concrete, especially if salts were applied at an early stage prior to the attainment of concrete maturity.

d. Due to the lack of air entrainment all throughout the depths of cores, **scaling will continue during future winter months of cyclic freezing and thawing at critically saturated conditions.**

INTRODUCTION

Reported herein are the results of detailed laboratory examinations of two (2) hardened concrete cores identified as 'north' and 'south' received from scaled concrete sidewalks at Germantown Mill Lofts located in Louisville, Kentucky.

BACKGROUND INFORMATION

The cores were, reportedly, obtained from outdoor concrete sidewalks that have experienced severe scaling. The owner of the apartment development wanted to know the cause of the distress that is occurring in areas and if it is related to the deicer. The deicer used is reportedly not supposed to damage concrete.

FIELD PHOTOGRAPHS

Figure 1 shows field photos of concrete surface distress at the locations of 'north' and 'south' cores. Figure 1 shows:

a. Severe scaling of concrete surface and exposures of coarse aggregate particles at scaled locations of 'north' core in the top photo,
b. Relatively lesser degree of surface scaling but exposure of coarse aggregate particles at the scaled location of 'south' core (bottom photo), and,
c. Noticeably sound concrete slabs adjacent to the scaled ones of this investigation separated by construction joints.

PURPOSE OF PRESENT INVESTIGATION

Based on the background information provided, the purposes of the present investigation are to determine:

a. The composition, quality, and overall condition of concrete in the cores;
b. Evidence of any physical or chemical deterioration of concrete in the cores; and,
c. Based on detailed laboratory investigation, investigation of all possible reasons to explain the observed and reported surface distress of concrete slabs.

Figure 1: Field photographs of concrete surface scaling at the locations of two cores (circled) marked as 'north' (top photo) and 'south' (bottom photo). Notice: (a) severe scaling of concrete surface and exposures of coarse aggregate particles at scaled locations of 'north' core in the top photo, (b) relatively lesser degree of surface scaling but exposure of coarse aggregate particles at the scaled location of 'south' core (bottom photo), and, (c) noticeably sound concrete slabs adjacent to the scaled ones of this investigation separated by construction joints.

SAMPLES

PHOTOGRAPHS, IDENTIFICATION, INTEGRITY, AND DIMENSIONS

Figures 2 and 3 show the two cores as received.

The cores have nominal diameters of $3^5/_8$ in. (90 mm) and nominal lengths of $3^1/_2$ in. (88 mm) and $3^7/_8$ in. (100 mm) for 'north' and 'south,' respectively.

END SURFACES

Both cores show scaled surfaces at the exposed top ends and adhered crushed stone of subbase in the bottom ends.

Scaling is more pronounced in the 'north' core with exposures of coarse aggregate particles.

CRACKING & OTHER VISIBLE DISTRESS, IF ANY

There are no visible cracks, joints, or large voids observed in the cores, as received.

EMBEDDED ITEMS

No reinforcing steel, wire mesh, fibers, or other embedded items are present in the cores.

RESONANCE

The cores have a ringing resonance, when hammered.

TESTING STRATEGY

Each core was tested for detailed petrographic examinations and chemical profiles from the top scaled surface region, mid-depth location, and bottom end. Details of testing methodologies are provided in the next section.

Each core was sectioned longitudinally into multiple slabs with oil-cooled diamond saw. A sectioned slab was then lapped with successively finer diamond abrasives in metal and resin-bonded diamond lapping discs with water used as coolant. Additional sectioned slab was used to prepare blue dye-mixed epoxy-impregnated thin sections of concrete from the top 2 inches of each core. Finally, chemical profiles for water-soluble anions (chloride, nitrate, sulfate), and cations (sodium, potassium, calcium) are determined from the top, mid-depth, and bottom ends of each core.
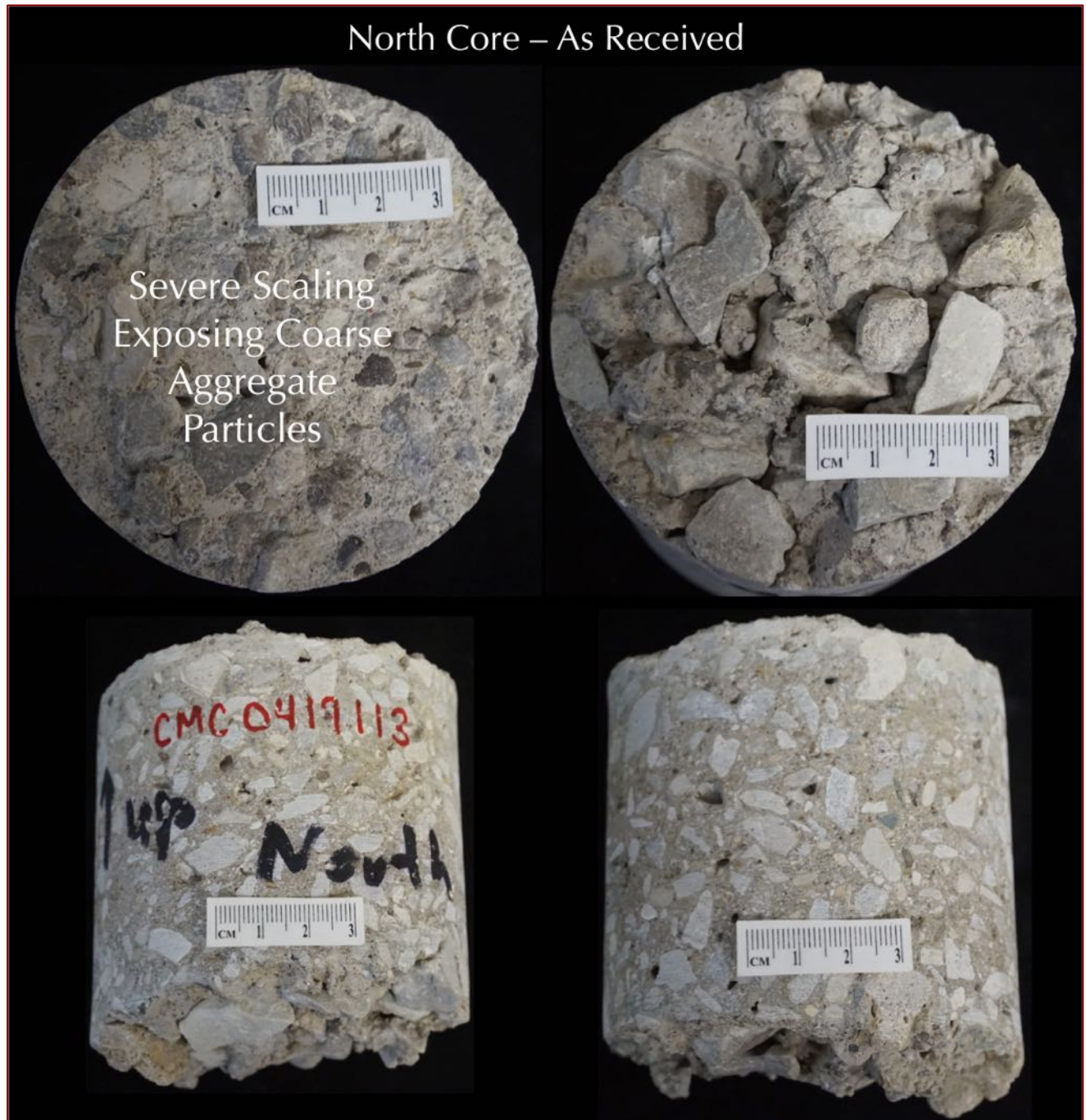
Figure 2: Photographs of North Core as received. Top left – Exposed surface with severe scaling and complete loss of the finished surface with exposed coarse and fine aggregate particles; Top right - bottom surface with adhered stones from subbase; and Bottom row - cylindrical side views of the core with identification.
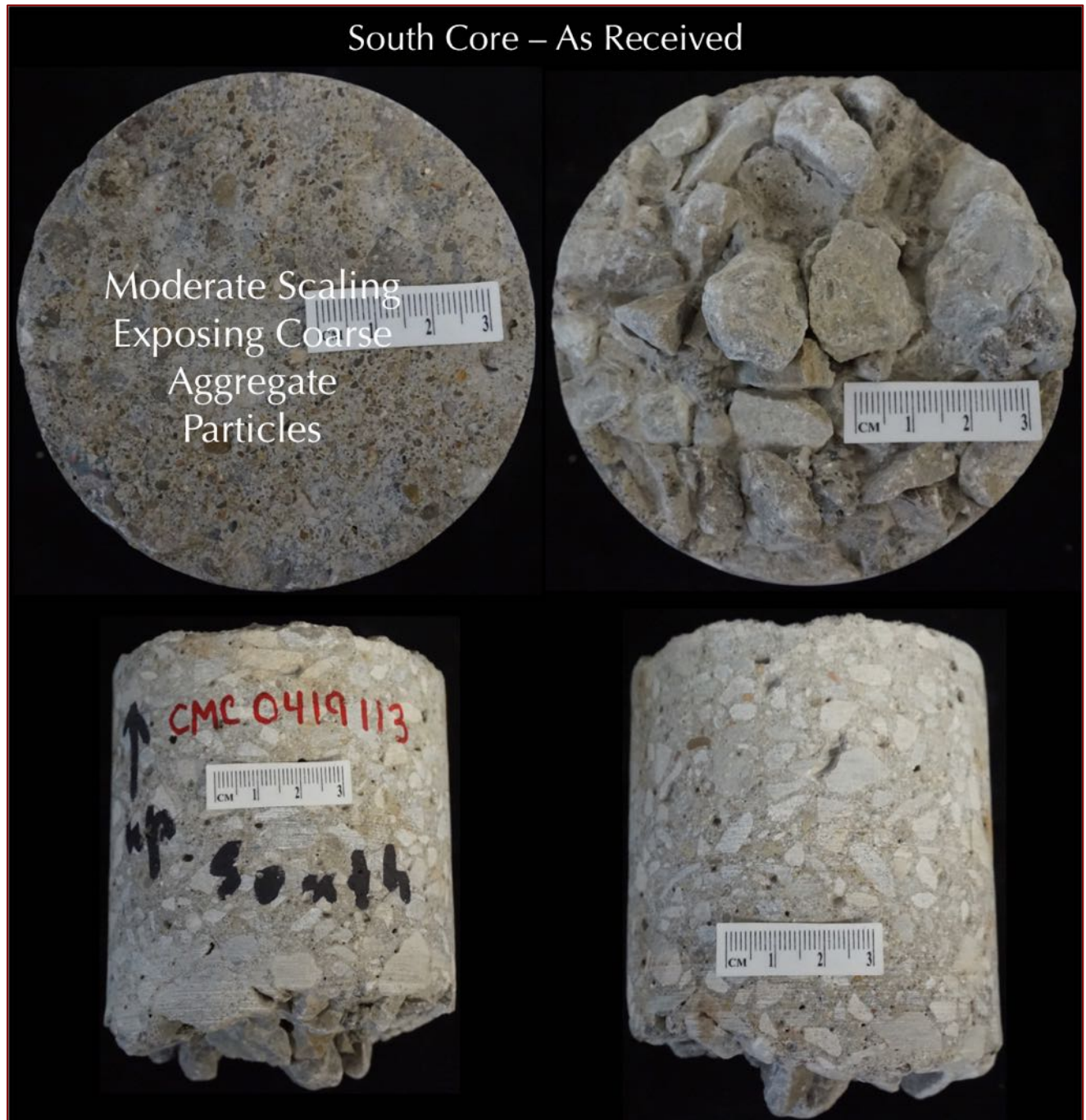
Figure 3: Photographs of South Core as received. Top left – Exposed surface with moderate scaling, loss of the finished surface with exposed coarse and fine aggregate particles; Top right - bottom surface with adhered stones from subbase; and Bottom row - cylindrical side views of the core with identification.

METHODOLOGIES

PETROGRAPHIC EXAMINATIONS

The cores were examined by petrographic examinations by following the methods of ASTM C 856 "Standard Practice for Petrographic Examination of Hardened Concrete." Details of petrographic examinations and sample preparation are described in Jana (1997a, b, 2001, 2004a, b, 2005a, b, 2006, 2007).

The steps of petrographic examinations include (Jana 2006):

  i. Visual examinations of samples, as received;
 ii. Low-power stereomicroscopical examinations of as-received, saw-cut and freshly fractured sections, and lapped cross section of cores for evaluation of textures, and composition;
iii. Low-power stereomicroscopical examinations of air contents and air-void system of concrete in the cores;
 iv. Examinations of oil immersion mounts in a petrographic microscope for mineralogical compositions of specific areas of interest;
  v. Examinations of blue dye-mixed (to highlight open spaces, cracks, etc.) epoxy-impregnated large area (50 mm × 75 mm) thin sections of concrete in a petrographic microscope for detailed compositional and microstructural analyses;
 vi. Photographing samples, as received and at various stages of preparation with a digital camera and a flatbed scanner;
vii. Photomicrographs of lapped section and thin section of samples taken from stereomicroscope and petrographic microscope, respectively to provide detailed compositional and mineralogical information of concrete.

Figure 4: Nikon Eclipse E600POL Petrographic Microscope with Jenoptik Gryphax Camera (left), Olympus SZH (middle), and Nikon SMZ-10A Stereomicroscope (right) used for petrographic examinations.

CHEMICAL PROFILES

Profiles of water-soluble ions from the top, mid-depth, and bottom locations of cores were done by: (a) potentiometric titration, for water-soluble chloride contents *a la* ASTM C 1218 by using Metrohm 751 DMS Titrino with attached 730 Auto Sample Processor (Figure 5), (b) anion chromatography, *a la* ASTM D 4327 for water-soluble fluoride, chloride, nitrate, nitrite, bromide, phosphate, and sulfate ions by using Metrohm 881 Compact IC Professional with attached 858 Professional Sample Processor (Figure 5) with a sodium carbonate-bicarbonate eluent, and (c) cation chromatography for water-soluble alkalis (sodium, potassium), and calcium ions by using Metrohm 861 Advanced Compact IC with attached 788 IC Sample Processor (Figure 5) with nitric acid/dipicolinic acid eluent.

For all these tests, a representative portion of concrete from top, mid-depth, and bottom end of each core was sectioned and pulverized to fine powders passing US No. 20 sieve. About 10 ± 0.01 gm. of powder sample was dispersed with 50-mL deionized water in a 250-mL beaker; stirring and breaking up any lumps with a glass rod, covered with a watch glass, and further stirred in a magnetic stirrer. The covered mixture in the beaker was then heated rapidly to boiling, but not more than a few seconds, then removed from hot plate, cooled down to room temperature, kept for further digestion for 24 hours while continuously stirring with magnetic stirrer preventing any evaporation with the covered watch glass. The digested sample solution was then filtered under vacuum, first through two 2.5-micron filter papers, followed by another filtration through two 0.2 micron filter papers to collect the filtrate. The filtrate thus obtained was diluted to a final volume of 200 ml in a volumetric flask.

About 50 mL from the final 200-mL filtrate was taken for ion chromatography. To the rest 150-mL filtrate to be used for potentiometric titration, a 3 mL of H_2O_2 (30%) and another 3 mL of HNO3 (1:1) were added, then heated rapidly to boiling but not more than a few seconds by removing from hot plate, cooled down to room temperature and used for titration for chloride content.

Metrohm equipments used for potentiometric titration and ion chromatography are all calibrated with known solutions, e.g., an 0.05N NaCl solution in 150-mL deionized water to run first for chloride titration, at least 7 to 10 standards of concentrations from 1-ppm to 100-ppm range to run for anion chromatography, and five standards from 2-ppm to 100-ppm range to run for cation chromatography.

Final results in terms of weight percent chloride by mass of concrete to the nearest 0.001% is determined for Cl, % = 3.545 [(V1-V2)N]/W, where V1 = milliliters of 0.05 N AgNO₃ solution used for sample titration (equivalent point), V2 = Milliliters of 0.05N AgNO₃ solution used for blank

Figure 5: Top: Potentiometric titration for water-soluble chloride contents (ASTM C 1218) with Metrohm 751 DMS Titrino, 730 Sample Processor, and Tiamo software. Middle – Ion chromatography of water-soluble cations with Metrohm 861 Advanced Compact IC with 788 Sample Processor, and MagIC Net software. Bottom – Ion Chromatography of water-soluble anions with Metrohm 881 Compact IC Professional with 858 Sample Processor and MagIC Net software.

titration (equivalent point); N = exact normality of 0.05 N AgNO₃ solution, and W = mass of sample in grams. This equation is equivalent to % chloride = (equivalent point from titration times 0.177) divided by sample weight in grams.

Final results of ion chromatography in terms of weight percent ions by mass of concrete are obtained from: [(ppm-concentrations from IC (which include appropriate dilution factors) × original filtrate volume (200 mL)] ÷ [(Sample weight, 10 ± 0.01 gm) × (10,000 to for conversion of ppm to wt. percent)].
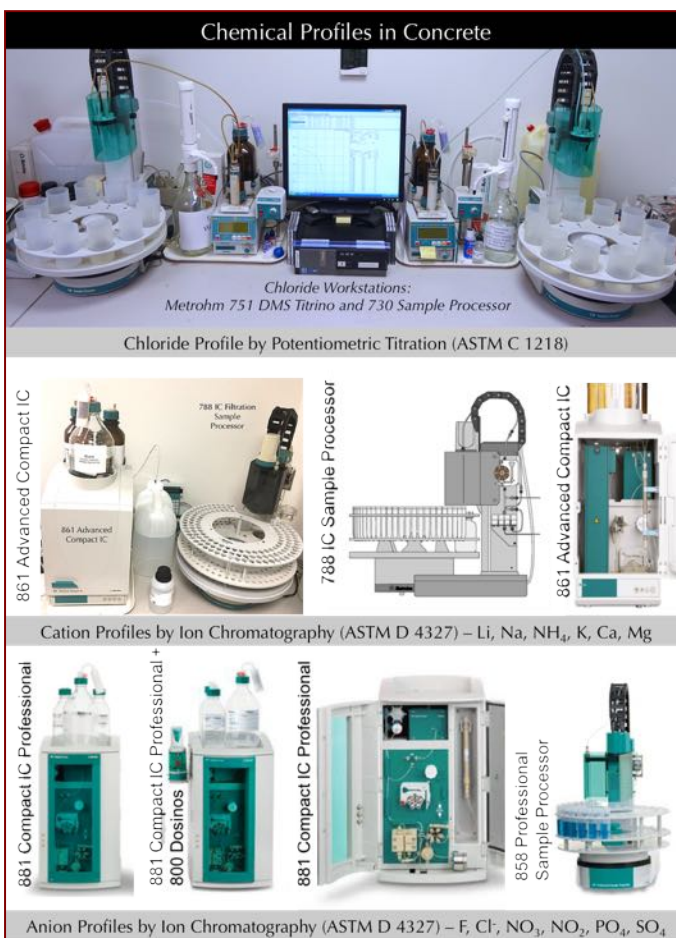
PETROGRAPHIC EXAMINATIONS

LAPPED CROSS SECTIONS

North Core – Lapped Cross Section

Crushed limestone coarse aggregate; Well graded and well-distributed

Figure 6: Lapped cross section of North Core showing: (a) severely scaled exposed surface at the top, (b) well-graded, well-distributed crushed limestone coarse aggregate, (c) dense and well-consolidated nature of concrete, (d) uniform color tone of paste in the body, but some lighter color paste at the scaled surface region at the top; and (e) adhered crushed limestone of subbase at the bottom of core.
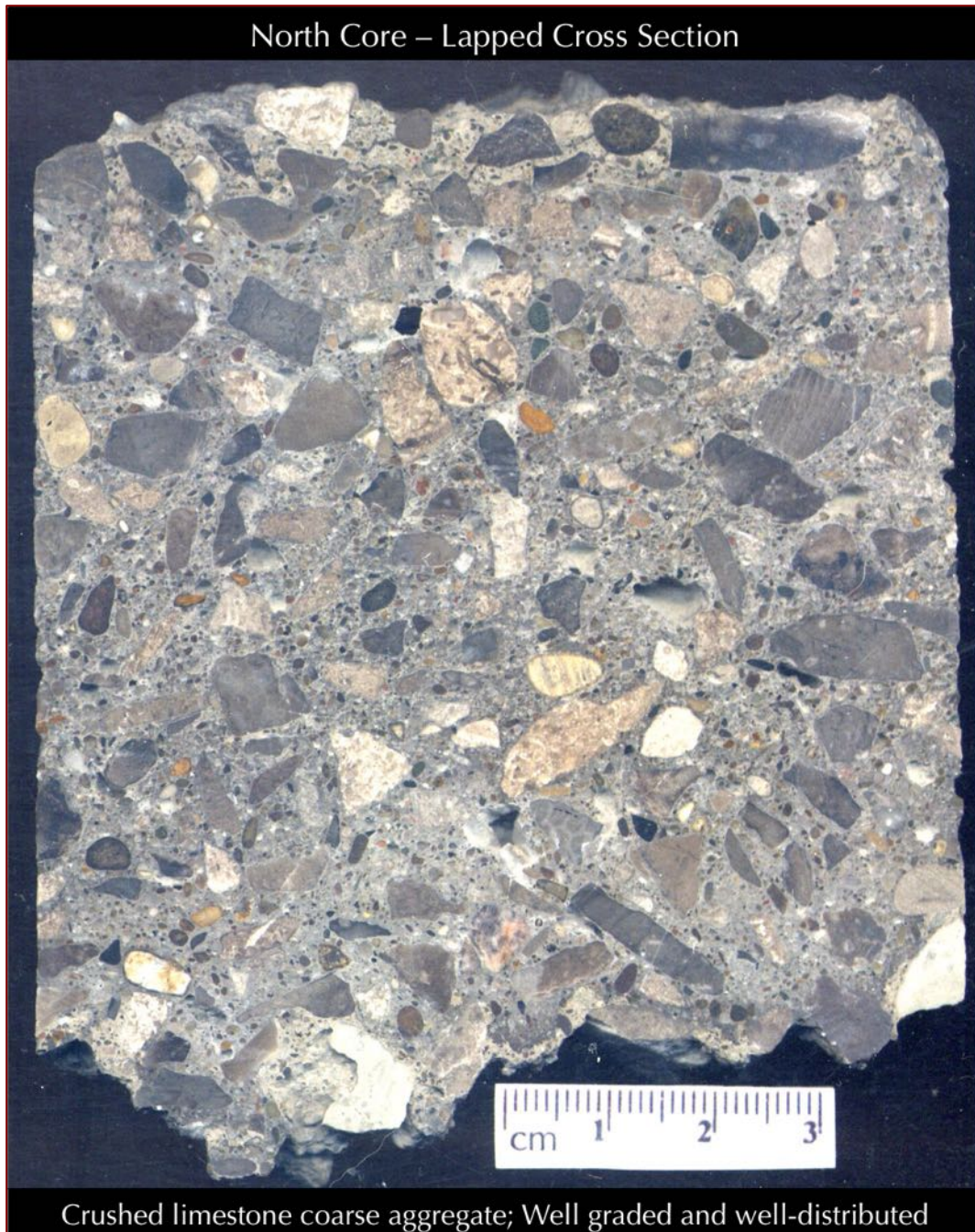
Figure 7: Lapped cross section of South Core showing: (a) severely scaled exposed surface at the top, (b) well-graded, well-distributed crushed limestone coarse aggregate, (c) dense and well-consolidated nature of concrete, (d) uniform color tone of paste in the body, but some lighter color paste at the scaled surface region at the top; and (e) adhered crushed limestone of subbase at the bottom of core.

PHOTOMICROGRAPHS OF LAPPED CROSS SECTIONS

Figure 8: Photomicrographs of lapped cross section of North Core showing: (a) overall non-air-entrained nature of concrete in all photos containing a few coarse near-spherical and irregularly-shaped entrapped air voids; (b) lighter gray tone paste at the top scaled surface region separated from darker gray paste in the body by white dashed lines, and (c) fine, near-surface surface-parallel microcrack at the scaled surface region (marked by arrows in right photo).
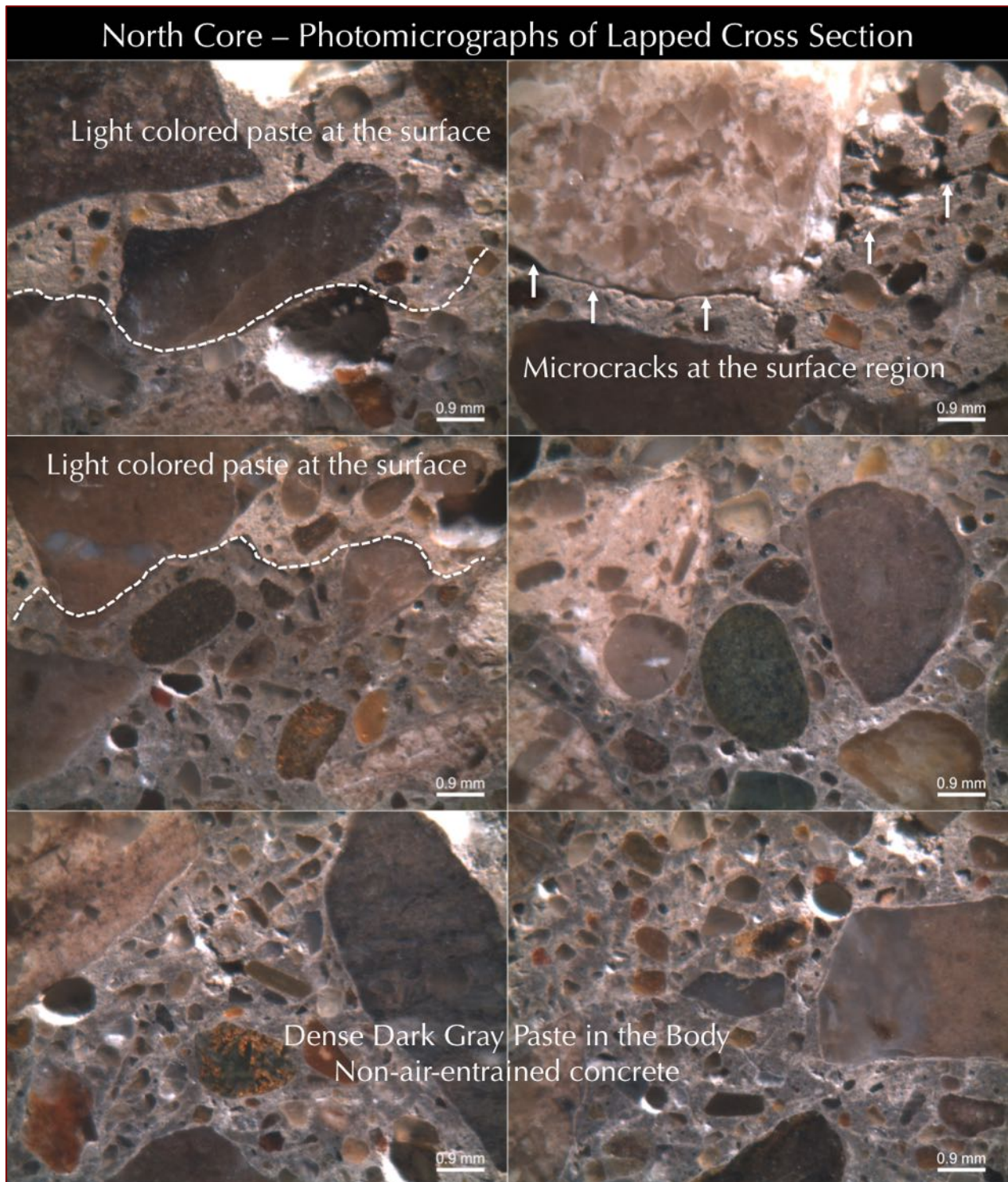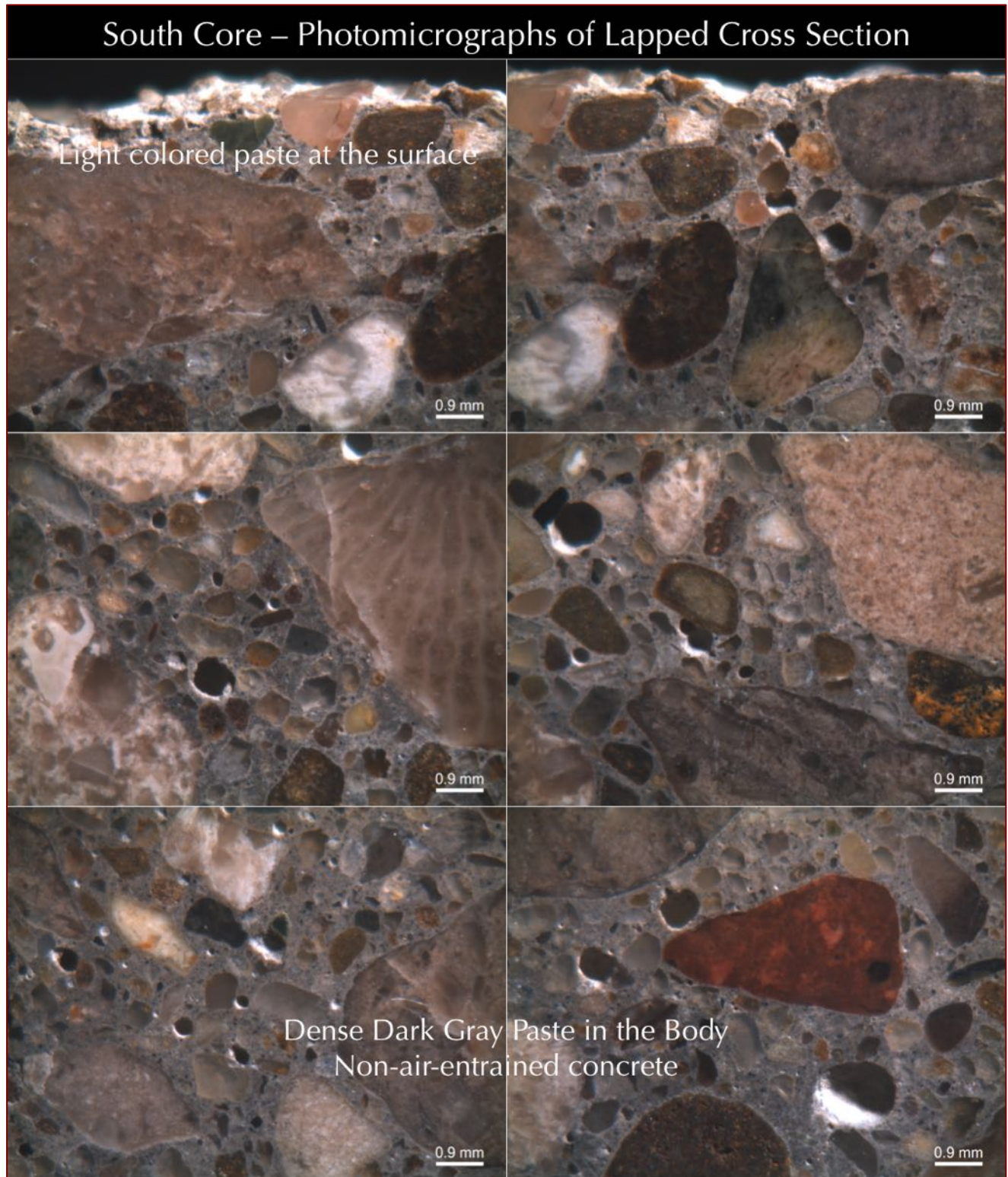
Figure 9: Photomicrographs of lapped cross section of South Core showing: (a) overall non-air-entrained nature of concrete in all photos containing a few coarse near-spherical and irregularly-shaped entrapped air voids; and (b) lighter gray tone paste at the top scaled surface region above the darker gray paste in the body.

BLUE DYE-MIXED EPOXY-IMPREGNATED THIN SECTIONS
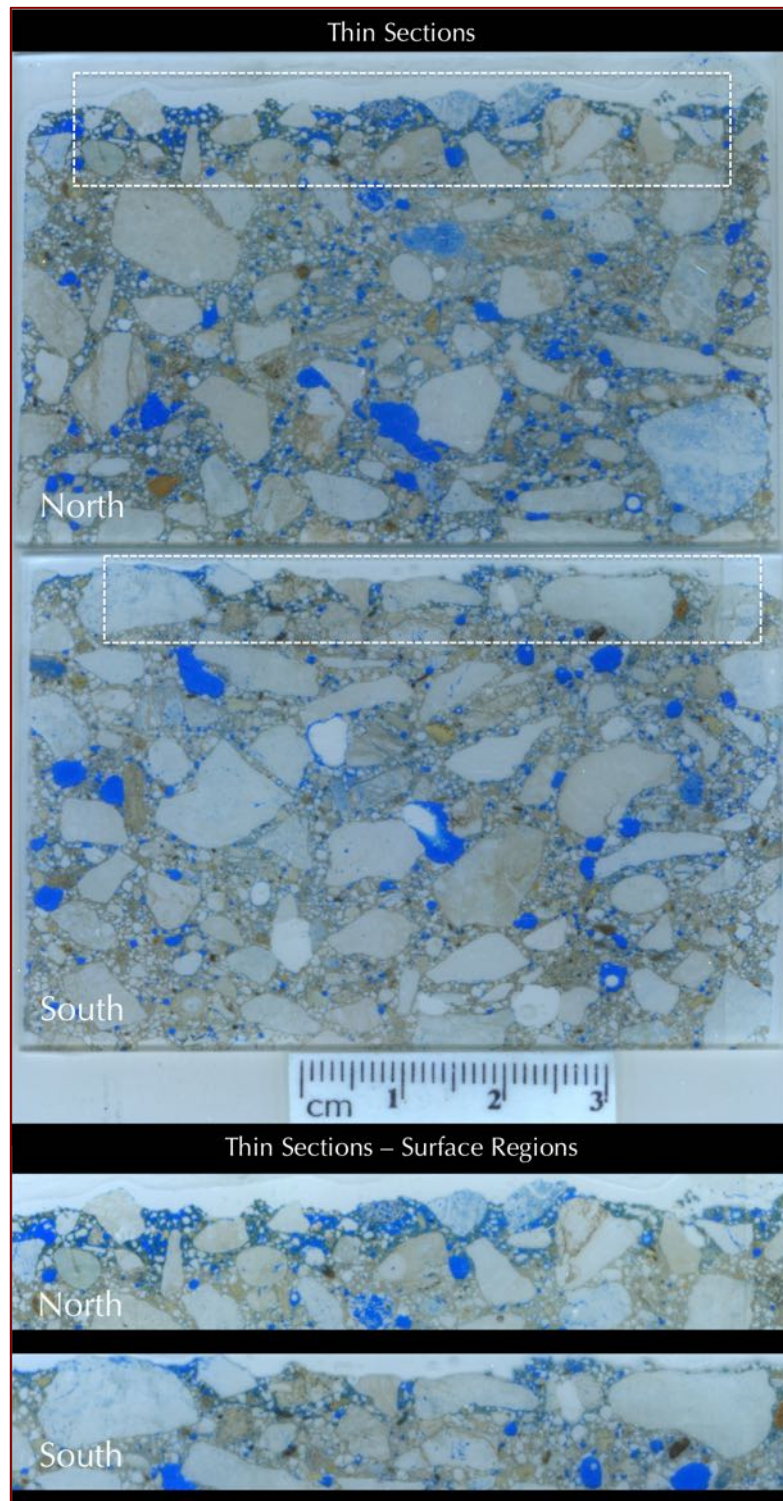
Figure 10: Blue dye-mixed epoxy-impregnated thin sections of 'north' and 'south' cores at the top and middle, respectively and enlarged views of surface regions of these cores at the bottom showing porous paste at the scaled surface regions highlighted by blue epoxy that has been absorbed more in the porous paste compared to denser interior. Blue epoxy has highlighted entrapped air voids and porous areas in concrete.

PHOTOMICROGRAPHS OF THIN SECTIONS

North Core – Photomicrographs of Thin Section – Porous Paste at the Surface Region

Field Width of Each Photo is 8 mm

Figure 11: Photomicrographs of blue dye-mixed epoxy-impregnated thin section of concrete in 'north' core taken with a reflected-light Stereozoom microscope showing porous areas of paste at the scaled surface region (which was also shown in Figure 10), which is responsible for the lighter gray tone paste at the surface shown in Figure 8.

Figure 12: Photomicrographs of blue dye-mixed epoxy-impregnated thin section of concrete in 'north' core taken with a reflected-light Stereozoom microscope showing crushed limestone coarse aggregate and natural siliceous-calcareous sand fine aggregate containing quartz, quartzite, feldspar, sandstone, shale, limestone, and dolomite particles in fine aggregate.

Figure 13: Photomicrographs of blue dye-mixed epoxy-impregnated thin section of concrete in 'south' core taken with a reflected-light Stereozoom microscope showing porous areas of paste at the scaled surface region (which was also shown in Figure 10), which is responsible for the lighter gray tone paste at the surface shown in Figure 9.
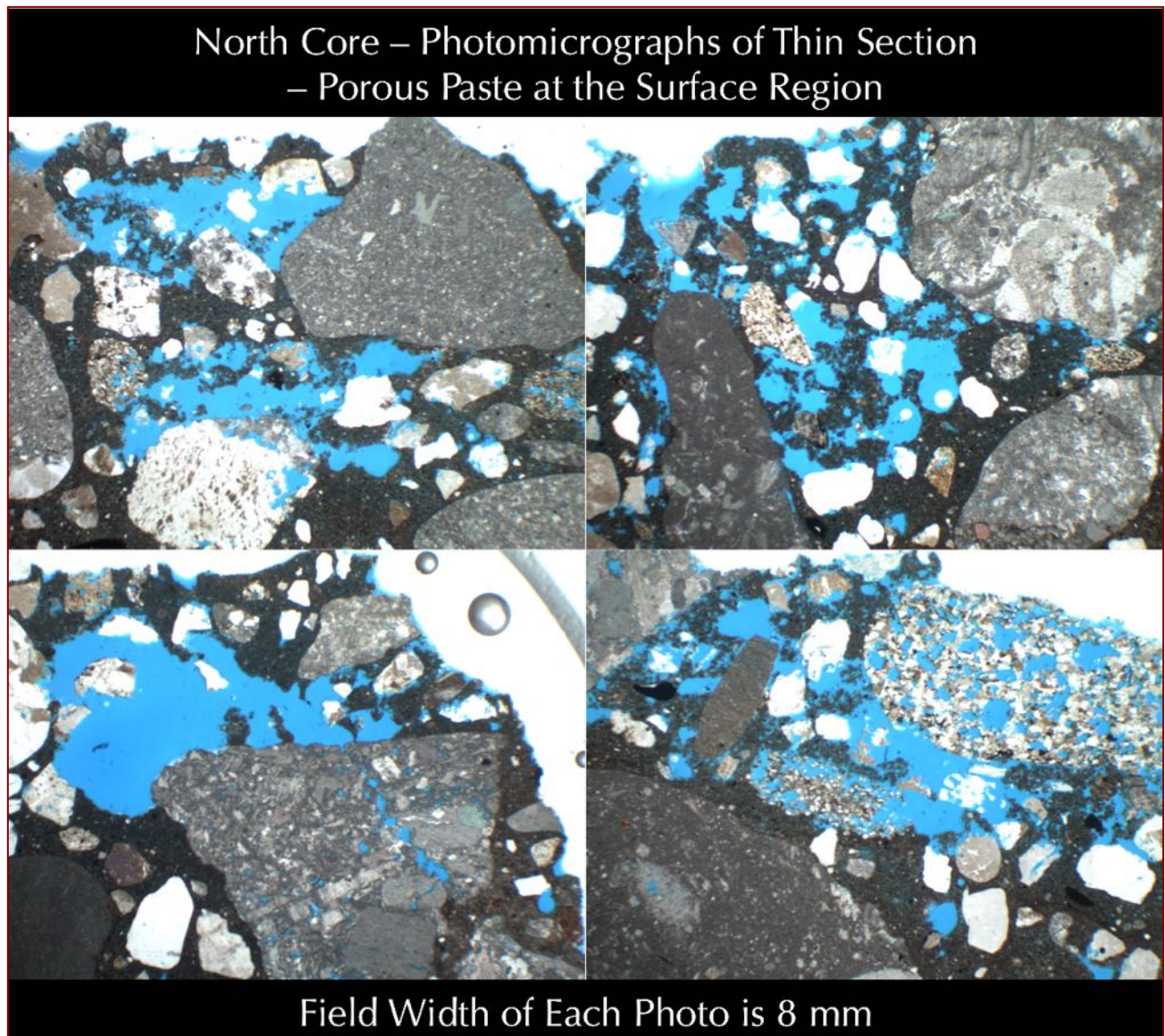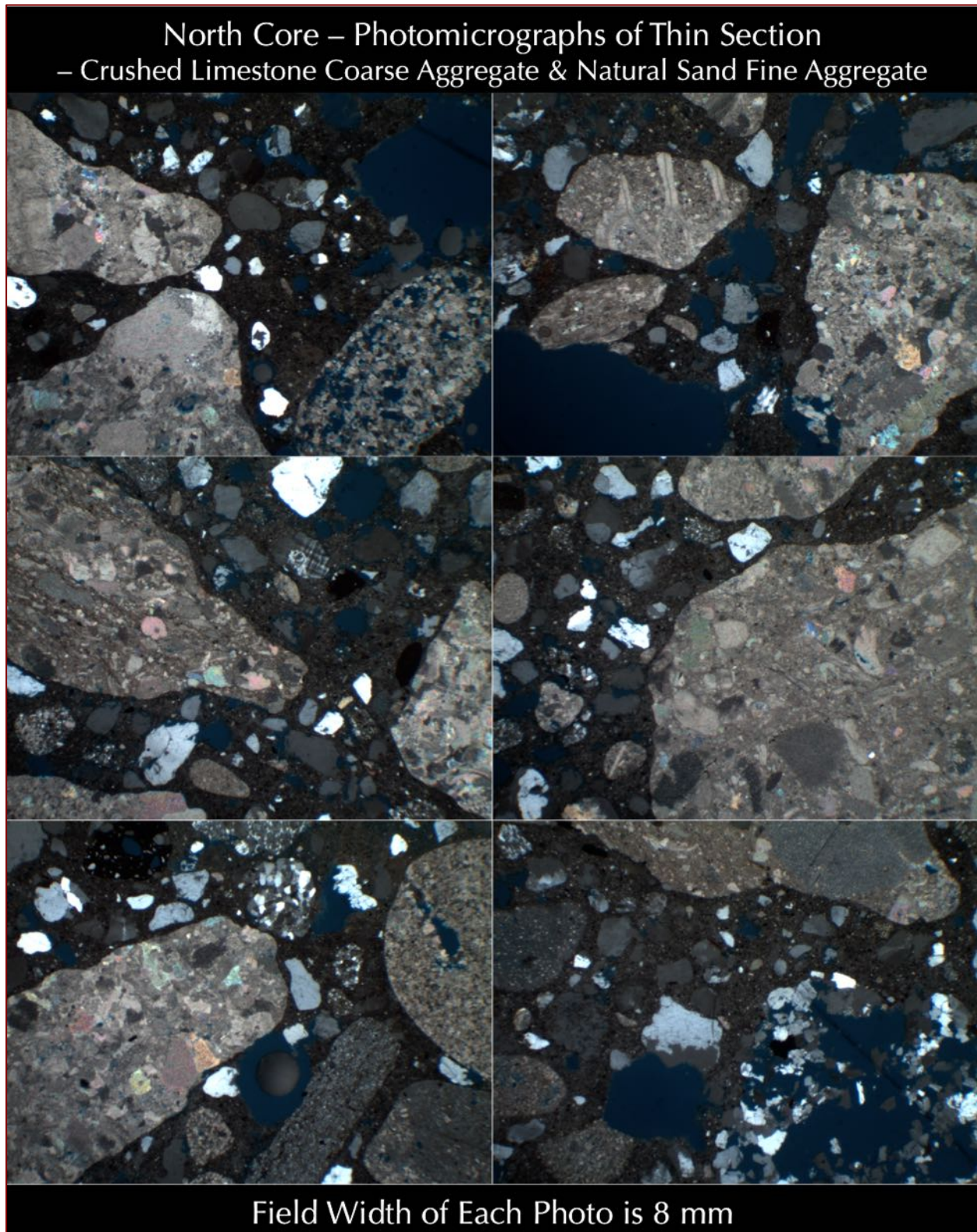
Figure 14: Photomicrographs of blue dye-mixed epoxy-impregnated thin section of concrete in 'south' core taken with a reflected-light Stereozoom microscope showing crushed limestone coarse aggregate and natural siliceous-calcareous sand fine aggregate containing quartz, quartzite, feldspar, sandstone, shale, limestone, and dolomite particles in fine aggregate.
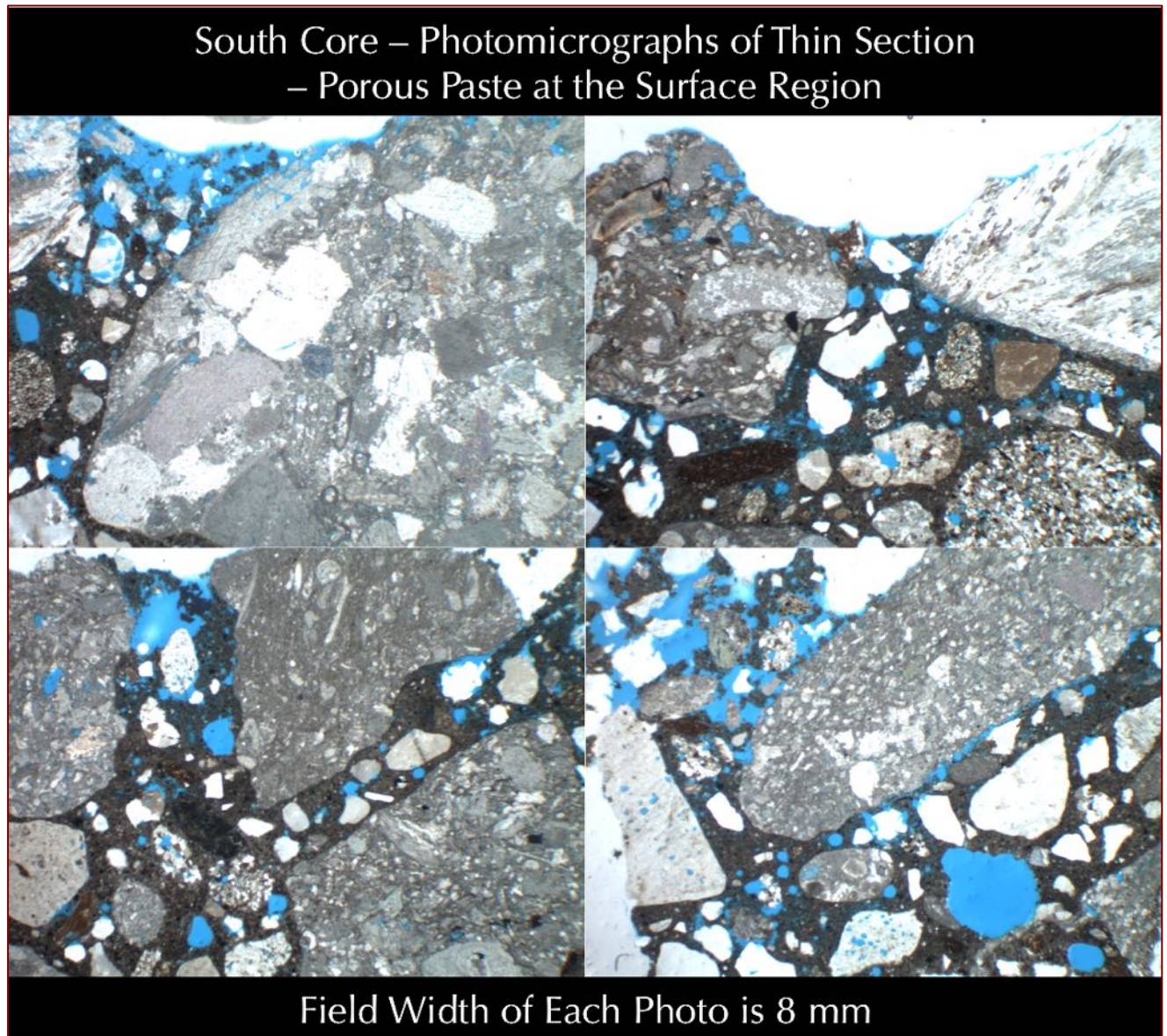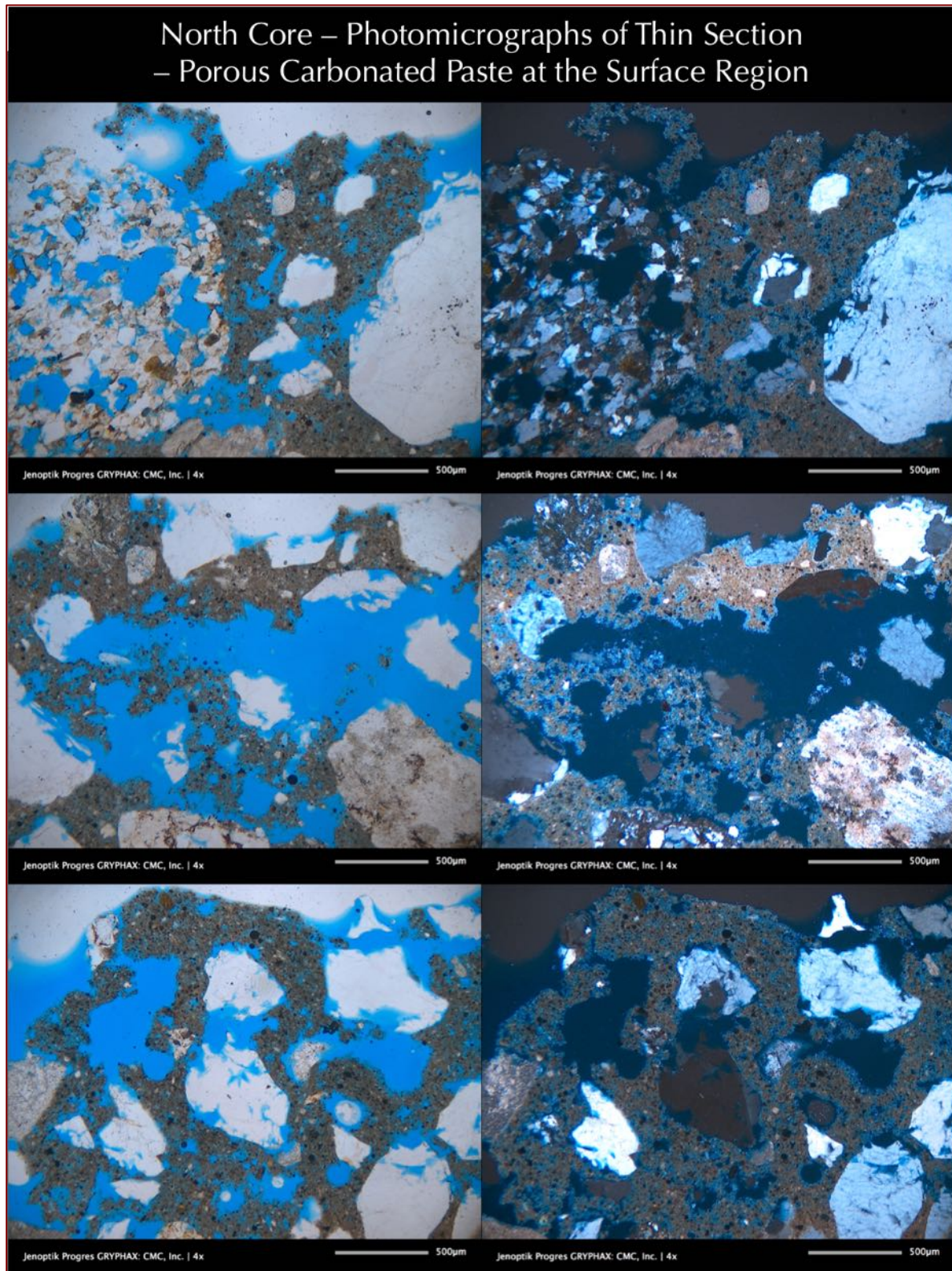
Figure 15: Photomicrographs of blue dye-mixed epoxy-impregnated thin section of concrete in 'north' core taken with a petrographic microscope showing porous, carbonated paste at the scaled surface region.
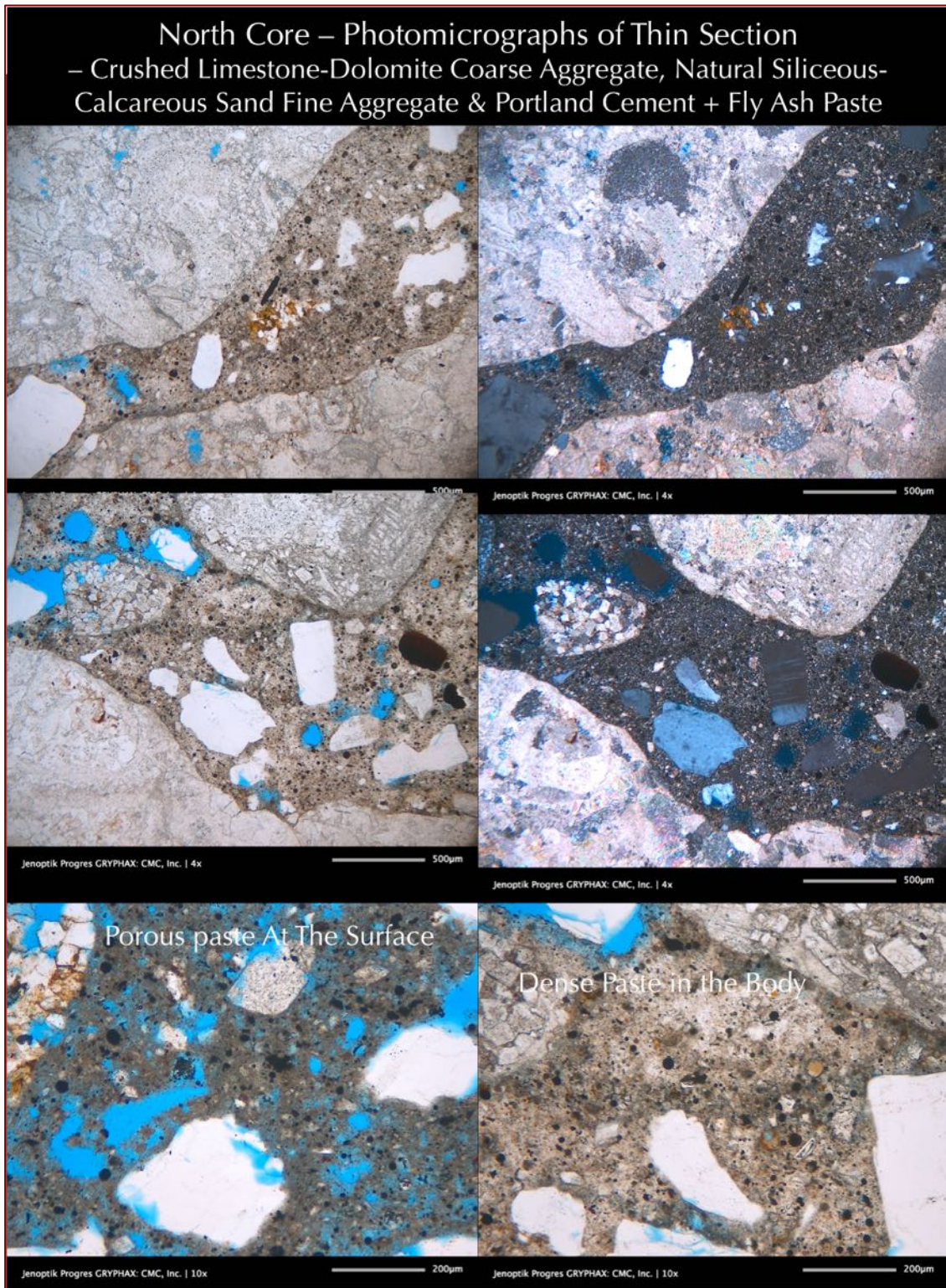
Figure 16: Photomicrographs of blue dye-mixed epoxy-impregnated thin section of concrete in 'north' core taken with a petrographic microscope showing crushed limestone coarse aggregate, natural siliceous-calcareous sand fine aggregate, and non-air-entrained concrete (top and middle rows), dense paste in the body (top and middle row), and contrasting paste porosities between porous paste at the surface versus denser paste in the body (bottom row). Notice spherical fly ash particles in paste (bottom right photo).
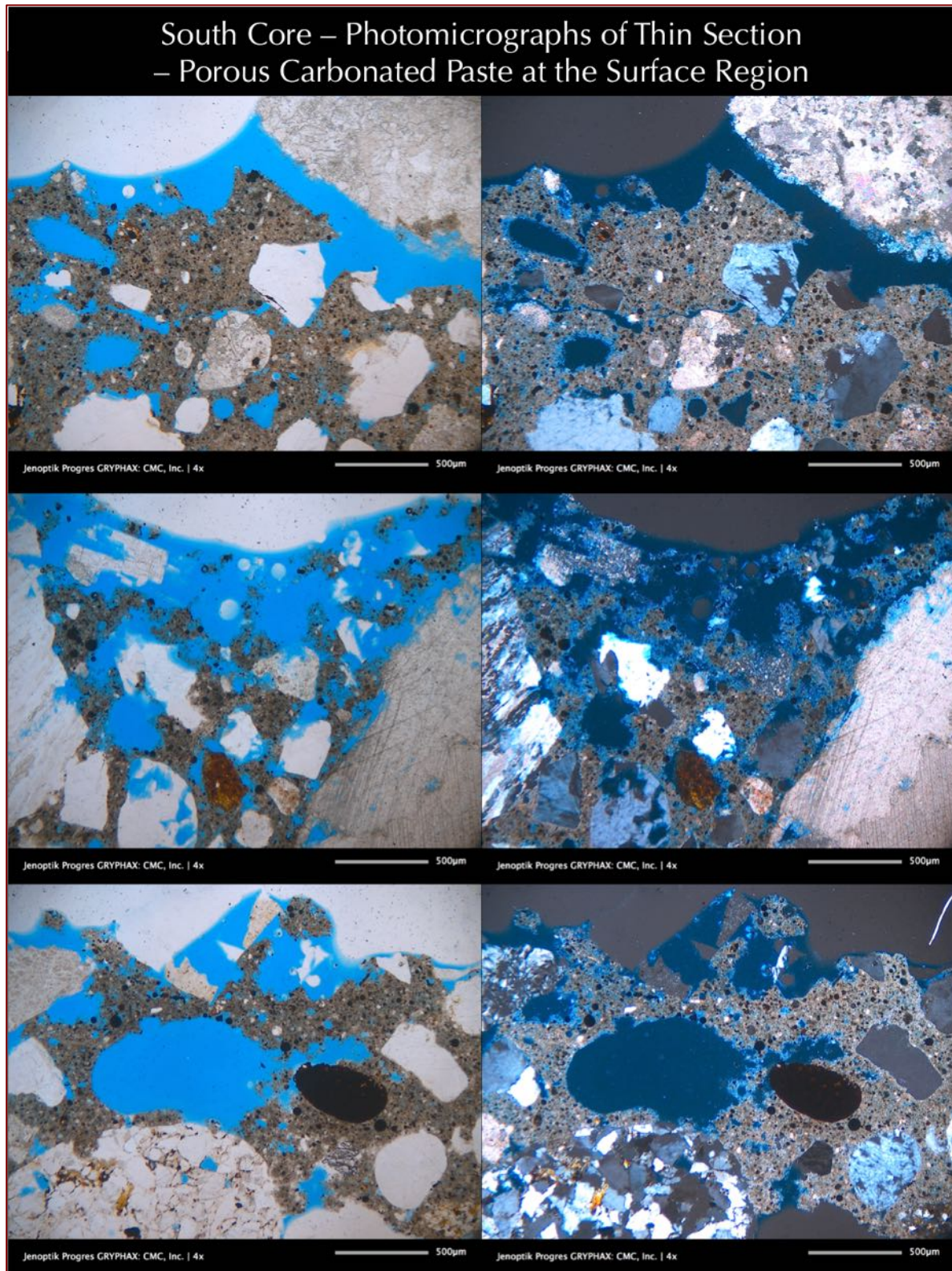
Figure 17: Photomicrographs of blue dye-mixed epoxy-impregnated thin section of concrete in 'south' core taken with a petrographic microscope showing porous, carbonated paste at the scaled surface region.
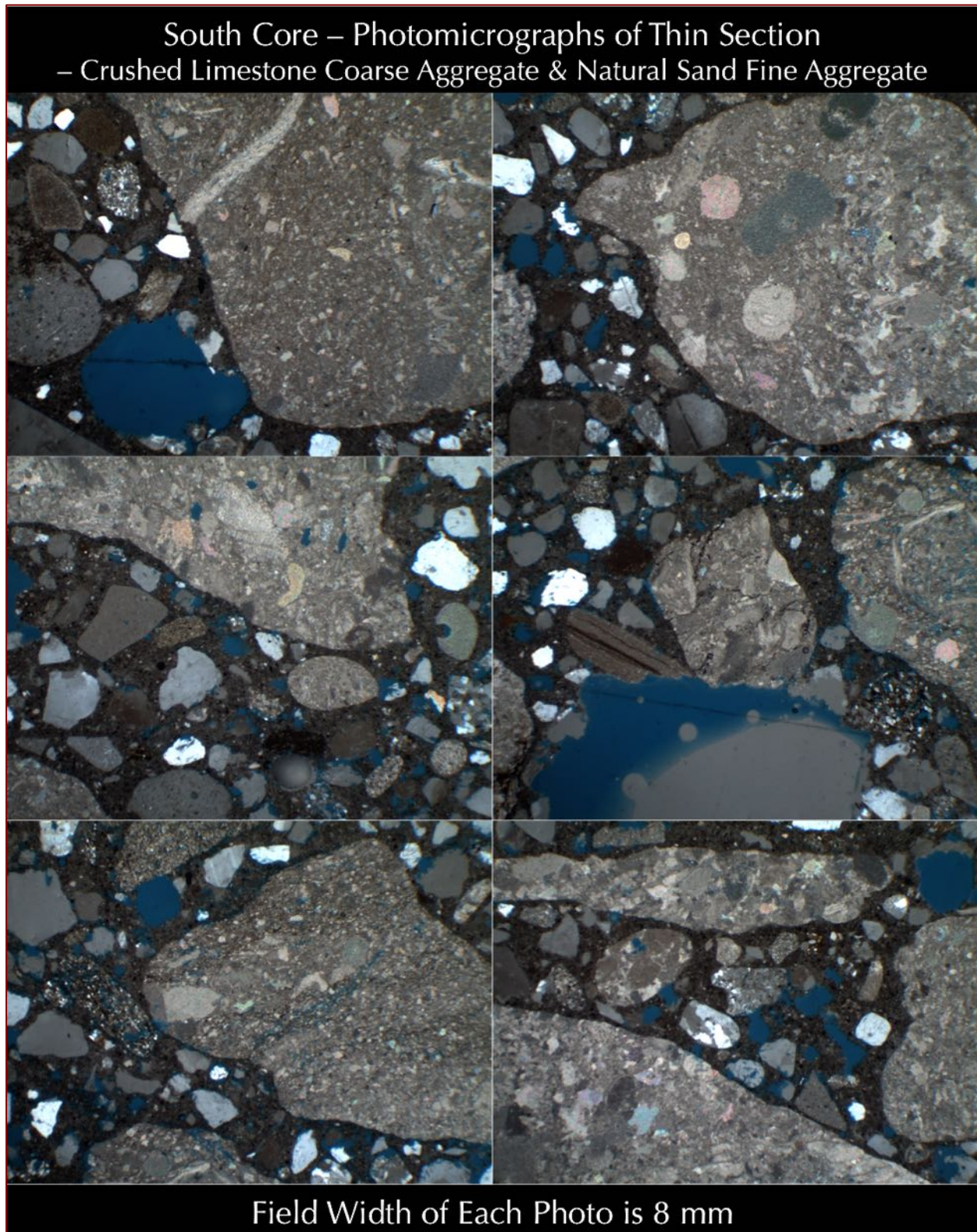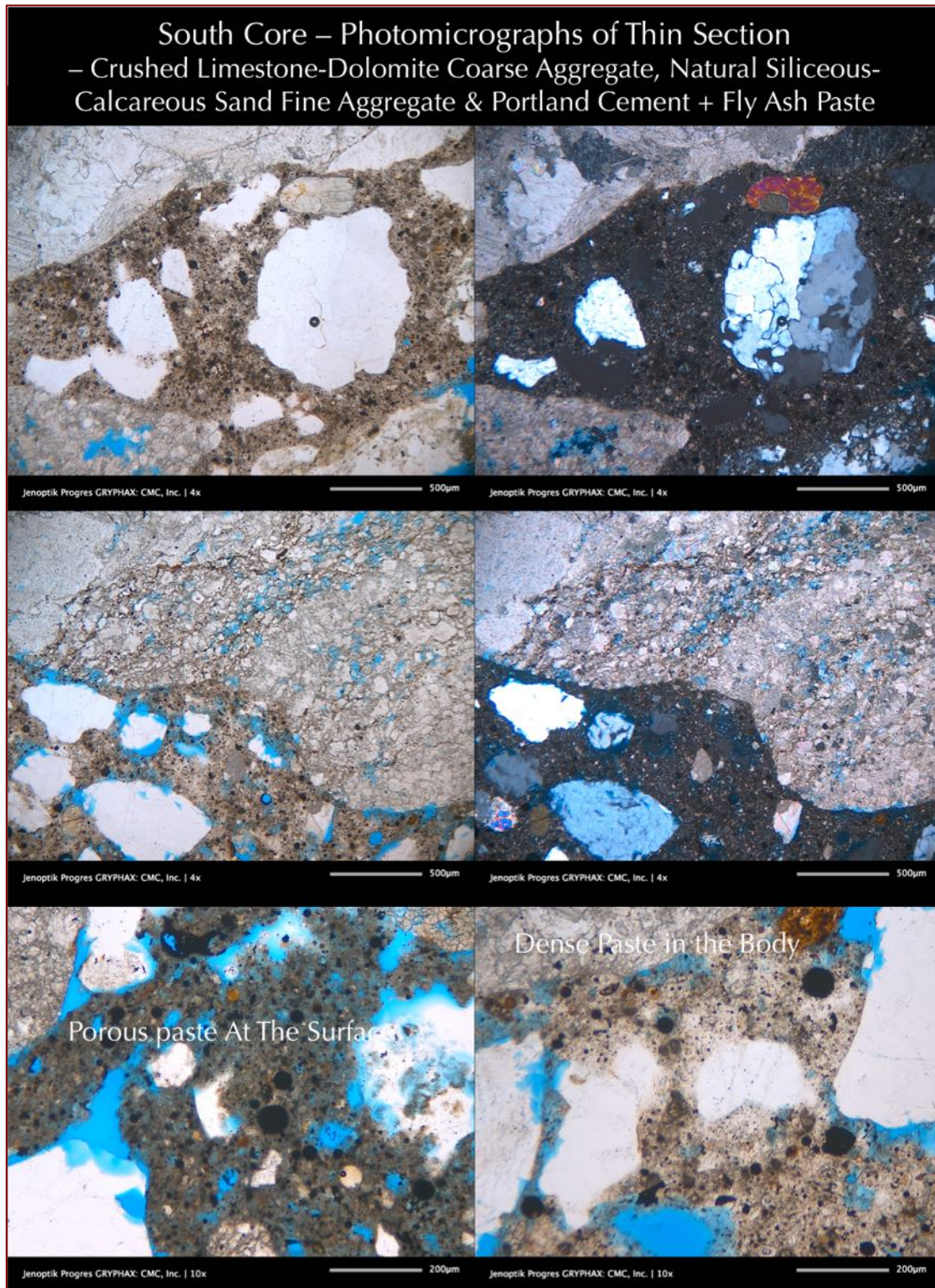
Figure 18: Photomicrographs of blue dye-mixed epoxy-impregnated thin section of concrete in 'south' core taken with a petrographic microscope showing crushed limestone coarse aggregate, natural siliceous-calcareous sand fine aggregate, and non-air-entrained concrete (top and middle rows), dense paste in the body (top and middle row), and contrasting paste porosities between porous paste at the surface versus denser paste in the body (bottom row). Notice spherical fly ash particles in paste (bottom right photo).

COARSE AGGREGATES

Coarse aggregates are compositionally similar crushed limestone having nominal maximum sizes of $^1/_2$ in. (12.5 mm). Particles are medium to dark gray, dense, hard, angular, massive textured, equidimensional to elongated, unaltered, uncoated, and uncracked. Coarse aggregate particles are well-graded and well-distributed. There is no evidence of alkali-aggregate reactions of coarse aggregate particles in the cores. Coarse aggregate particles have been sound during their service in the concrete and did not contribute to the surface distress.

FINE AGGREGATES

Fine aggregates are compositionally similar natural siliceous-calcareous sands having major amounts of siliceous components (quartz, quartzite, feldspar, chert, siltstone, sandstone), subordinate amounts of calcareous components (limestone, dolomite), and minor amounts of argillaceous and ferruginous components (shale, ferruginous siltstone). Fine aggregates have nominal maximum sizes of $^3/_8$ in. (9.5 mm). Particles are variably colored, rounded to subangular, dense, hard, equidimensional to elongated, unaltered, uncoated, and uncracked. Fine aggregate particles are well-graded and well-distributed. There is no evidence of alkali-aggregate reaction of fine aggregate particles. Fine aggregate particles have been sound during their service in the concrete.

The following Table summarizes properties of coarse and fine aggregates.

Properties and Compositions of Aggregates	North and South Cores
Coarse Aggregate	
Types	Crushed Limestone
Nominal maximum size (in.)	$^1/_2$ in. (12.5 mm)
Rock Types	Limestone
Angularity, Density, Hardness, Color, Texture, Sphericity	Angular, dense, hard, dark gray, massive textured, equidimensional to elongated
Cracking, Alteration, Coating	Unaltered, Uncoated, and Uncracked
Grading & Distribution	Well-graded and Well-distributed
Soundness	Sound
Alkali-Aggregate Reactivity	None
Fine Aggregate	
Types	Natural siliceous-calcareous sand
Nominal maximum size (in.)	$^3/_8$ in. (9.5 mm)
Rock Types	Major amounts of siliceous components (quartz, quartzite, feldspar, chert, siltstone), subordinate amounts of calcareous components (limestone, dolomite), and minor amount of argillaceous and ferruginous components (shale, ferruginous siltstone)
Cracking, Alteration, Coating	Variably colored, rounded to subangular, dense, hard, equidimensional to

Properties and Compositions of Aggregates	North and South Cores
	elongated
Grading & Distribution	Well-graded and Well-distributed
Soundness	Sound
Alkali-Aggregate Reactivity	None

Table 1: Properties of coarse and fine aggregates of concrete.

PASTE

Properties and composition of hardened cement paste are summarized in Table 2. Paste in both cores is light gray and noticeably porous at the top 1 to 2 mm of scaled surface (Figures 8 to 11, 13, 15, and 17) but medium to dark gray and denser in the interior bodies (Figures 8, 9, 16, and 18). Paste is dense and hard; freshly fractured surfaces of interior paste have subvitreous lusters and subconchoidal textures. Residual and relict Portland cement particles are present and estimated to constitute 6 to 8 percent of the paste volumes. Hydration of Portland cement is normal. Distributed throughout the paste are fine, clear to dark brown spherical glassy particles of fly ash having the fineness of Portland cement (Figures 16 and 18).

Properties and Compositions of Paste	North and South Cores
Color, Hardness, Porosity, Luster	Light gray and noticeably porous at the top 1 to 2 mm of scaled surface (Figures 8 to 11, 13, 15, and 17) but medium to dark gray and denser in the interior bodies (Figures 8, 9, 16, and 18)
Residual Portland Cement Particles	Normal, 6 to 8 percent by paste volume
Calcium hydroxide from cement hydration	Normal, 10 to 14 percent by paste volume
Pozzolans, Slag, etc.	Distributed throughout the paste are fine, clear to dark brown spherical glassy particles of fly ash having the fineness of Portland cement (Figures 16 and 18)
Water-cementitious materials ratio (*w/cm*), estimated	0.40 to 0.44 in the body but 0.44 to 0.50 at the scaled surface region
Cement Content (bags per cubic yard)	8 to $8^{1}/_{2}$ of which 15 to 20 percent is estimated to be fly ash
Secondary Deposits	None
Depth of Carbonation, mm	1 to 2 mm at the scaled surface region
Microcracking	None except for some near-surface microcracking that are judged to be related to the scaling distress (Figure 8).
Aggregate-paste Bond	Tight
Bleeding, Tempering	None
Chemical deterioration	None

Table 2: Proportions and composition of hardened cement paste.

The textural and compositional features of the paste are indicative of Portland cement contents similar in both cores and estimated to be equivalent to 8 to $8^{1}/_{2}$ bags of Portland cement per cubic yard of which 15 to 20

percent is estimated to be fly ash, and, water-cementitious materials ratio (*w/cm*) estimated to be 0.40 to 0.44 in the body but 0.44 to 0.50 at the scaled surface region.

There is no evidence of any deleterious deposits found in the cores. Carbonation is shallow 1 to 2 mm, which does not represent the true depth due to loss of the original finished surface. Bonds between the coarse and fine aggregate particles and paste are tight. There is no evidence of microcracking due to deleterious reactions, except for some near-surface microcracking that are judged to be related to the scaling distress (Figure 8).

The overall quality and condition of the concrete in the interior bodies of the cores i.e. beneath the scaled surface are judged to be dense, well-consolidated with no evidence of any physical or chemical deterioration. However, due to the observed non-air-entrained nature of the concrete in both cores (Figures 8 and 9), as described below, freeze-thaw durability of concrete is found to be low and responsible for the surface scaling.

AIR

Air occurs as a few coarse, near-spherical and irregularly shaped voids of sizes coarser than 1 mm that are characteristic of entrapped air. Air-void system of concrete in both cores is suggestive of no intentional addition of an air-entraining agent in the mix. Concretes in both cores are found to be non-air-entrained.

Air contents are estimated from petrographic examinations to be 2 to 3 percent in 'north' core and 3 to 4 percent in 'south' core. Figures 8 and 9 show overall air-void systems of concrete in both cores.

CHEMICAL PROFILES

POTENTIOMETRIC TITRATION (WATER-SOLUBLE CHLORIDE)

Water-soluble chloride contents were determined at the top scaled surface region (within the top 0.5 in.), at mid-depth location (at 1.75 to 2 in. depth), and bottom end of the cores (at 3 to 3.25 in. depth), as shown in Figures 19 and 20. Table 3 summarizes results of water-soluble chloride contents, where first column shows the sample identification, second column shows the depth in inches from where sections for chloride analyses were taken, third column shows the raw chloride content data as percent chloride in the concrete by mass of the sample, forth column represents percent chloride content in the sample by mass of cement by assuming 15 percent Portland cement content in the concrete and normal-weight concrete (i.e. by dividing the raw chloride contents by mass of 'concrete' by 0.15 to obtain chloride contents by mass of 'cement'), fifth column converts the raw chloride content in concrete from weight percent to ppm by multiplying the third column data by 10,000, and the last column is only applicable if the chloride found in concrete is obtained not from the external environment but from the use of flake (anhydrous) calcium chloride as a set-accelerating admixture in solution, in which case the data in the last column represents equivalent flake calcium chloride added to the mix as an accelerating

admixture. This last column data can be discarded if there is no evidence of addition of a chloride-containing set-accelerating admixture in the concrete, as appeared to be the case here.

Sample ID	Location (inches from top surface)	Percent Acid Soluble Chloride by Mass of Sample	Percent Acid Soluble Chloride by Mass of Cement[1] (% Chloride by Mass of Sample/0.15)	Percent Acid Soluble Chloride PPM (% Chloride by Mass of Sample x 10000)	Equivalent Flake Calcium Chloride (% Chloride by Mass of Cement x 2.07)
North Core	0.50	0.0154	0.73	1105	1.51
	1.75	0.0037	0.20	301	0.41
	3.0	0.0108	0.60	898	1.24
South Core	0.50	0.0811	0.73	1105	1.51
	2.0	0.0071	0.20	301	0.41
	3.25	0.0248	0.60	898	1.24

Table 3: Water-soluble chloride contents from the top, mid-depth, and bottom locations of cores. [1]Assuming a cementitious materials content of 15 percent by mass of a normal-weight concrete.

ION CHROMATOGRAPHY (WATER-SOLUBLE ANIONS AND CATIONS)

Water-soluble anions and cations from the top, mid-depth, and bottom ends of cores are shown in Figures 21 and 22 and in the following Table 4. Results show noticeable enrichments of sulfates, sodium, and calcium at the scaled surface regions of both cores compared to their interiors, which are judged to be due to chemical contamination of the exposed surface regions of concrete during service.

Sample ID	Location (inches from top surface)	Percent by weight of concrete of water-soluble anions from Ion Chromatography			Ppm-by weight of concrete of water-soluble anions from Ion Chromatography		
		Chloride	Nitrate	Sulfate	Sodium	Potassium	Calcium
North Core	0.50	0.012	0.003	0.221	464.2	403.8	679.2
	1.75	0.007	0.003	0.031	201.0	919.8	5.7
	3.0	0.011	0.003	0.010	106.7	402.6	98.3
South Core	0.50	0.057	0.008	0.185	400.1	263.1	848.1
	2.0	0.006	0.004	0.007	179.1	871.5	25.5
	3.25	0.030	0.011	0.014	140.1	376.2	171.5

Table 4: Water-soluble anions and cations from the top, mid-depth, and bottom locations of cores determined from ion chromatography. Results in red show noticeable enrichment at the exposed surface regions compared to the interiors of cores.

Figure 19: The potentiometric titration curves of chloride analyses from the top (top right), mid-depth location (middle right), and bottom end (bottom right) of 'north core' (left column). In all titration curves, the equivalent point of titration is marked with a dot and circle. Chloride content is shown both in the data from the Metrohm Titrator as well as in red. Notice slightly higher chloride at the scaled surface region compared to mid-depth location, but not high enough to indicate exposure to a chloride-containing deicing chemical.
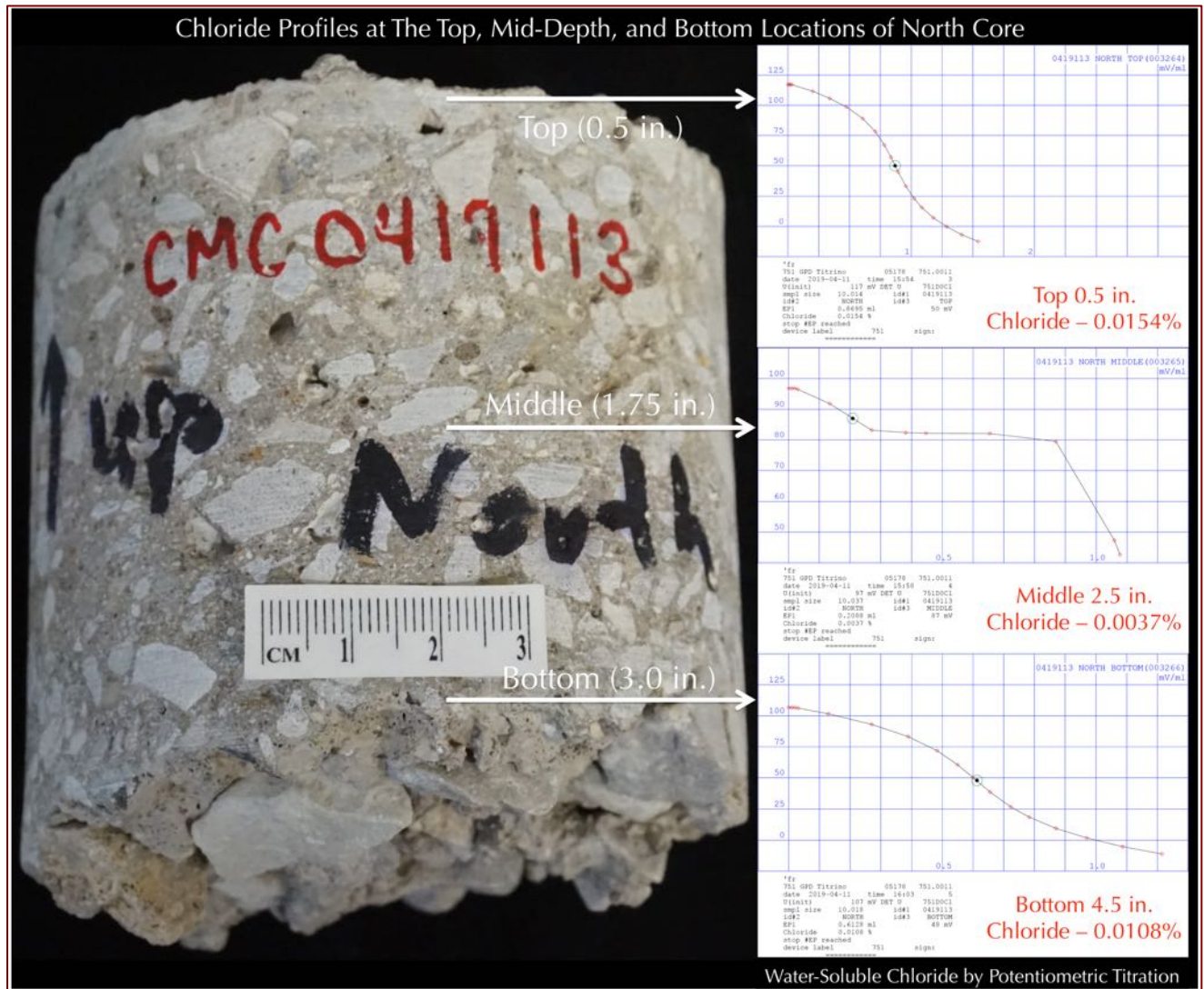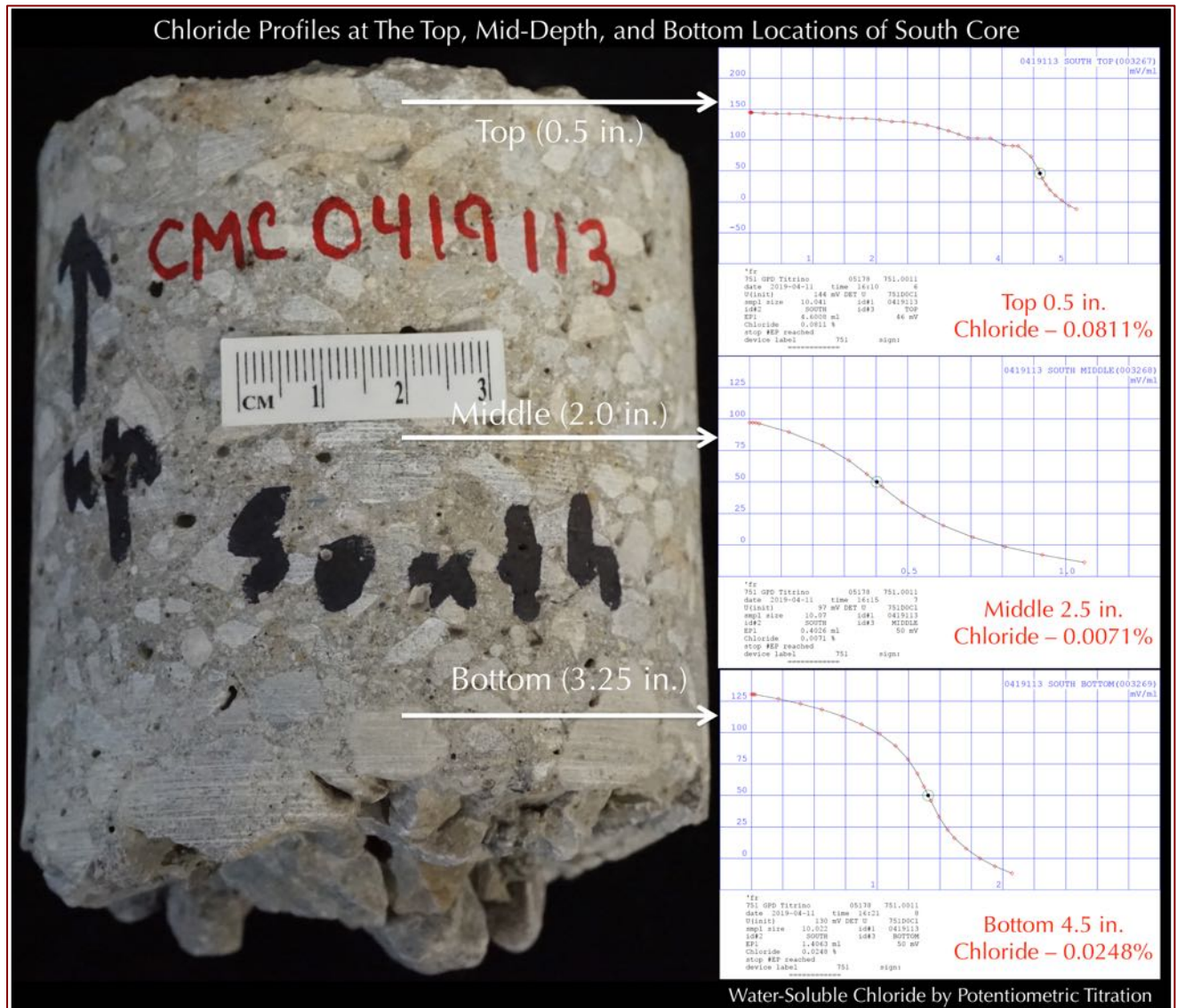
Figure 20: The potentiometric titration curves of chloride analyses from the top (top right), mid-depth location (middle right), and bottom end (bottom right) of 'south core' (left column). In all titration curves, the equivalent point of titration is marked with a dot and circle. Chloride content is shown both in the data from the Metrohm Titrator as well as in red. Notice higher chloride at the scaled surface region compared to mid-depth and bottom location, but not high enough to indicate exposure to a chloride-containing deicing chemical.

Chemical Profiles at The Top, Mid-Depth, and Bottom Locations of North Core

	Number	Ident						Analysis	Legend	Display
1	... 1	S1 - CMC 0419113 Core Noth Top	...	...	1.	1.	...	Anions		on
2	... 2	S2 - CMC 0419113 Core North Middle	...	...	1.	1.	...	Anions		on
3	... 3	S3 - CMC 0219107 Core 1 Bottom	...	...	1.	1.	...	Anions		on

Metrohm 881 Professional IC and 858 Sample Processor, in-vial dilution method, Sodium carbonate-bicarbonate eluent			
Depth	Chloride (%)	Nitrate (%)	Sulfate (%)
Top	0.012	0.003	0.221
Middle	0.007	0.003	0.031
Bottom	0.011	0.003	0.010

Anion % Weight in the Table = [(In-vial concentration from IC including Dilution Factor shown by curves, ppm) × (Original Filtrate Volume, mL)] ÷ [(Sample Weight, g) × (10,000 for ppm to wt.% conversion)]

Comment

		Ident					Method	Analysis	Legend	Display
1	... ...	CMC 0419113 Core North Top	...	...	1.	1.	CMC Cations	CMC Cations		on
2	... ...	CMC 0419113 Core North Middle	...	...	1.	1.	CMC Cations	CMC Cations		on
3	... ...	CMC 0419113 Core North Bottom	...	...	1.	1.	CMC Cations	CMC Cations		on

Metrohm 861 Advanced Compact IC and 788 Sample Processor, Nitric/Dipicolinic Acid eluent			
Depth	Na, ppm	K, ppm	Ca, ppm
Top	464.2	403.8	679.2
Middle	201.0	919.8	5.7
Bottom	106.7	402.6	98.3

Cation-ppm in the Table = [(In-vial concentration from IC including Dilution Factor shown by curves, ppm) × (Original Filtrate Volume, mL)] ÷ [(Sample Weight, g)]
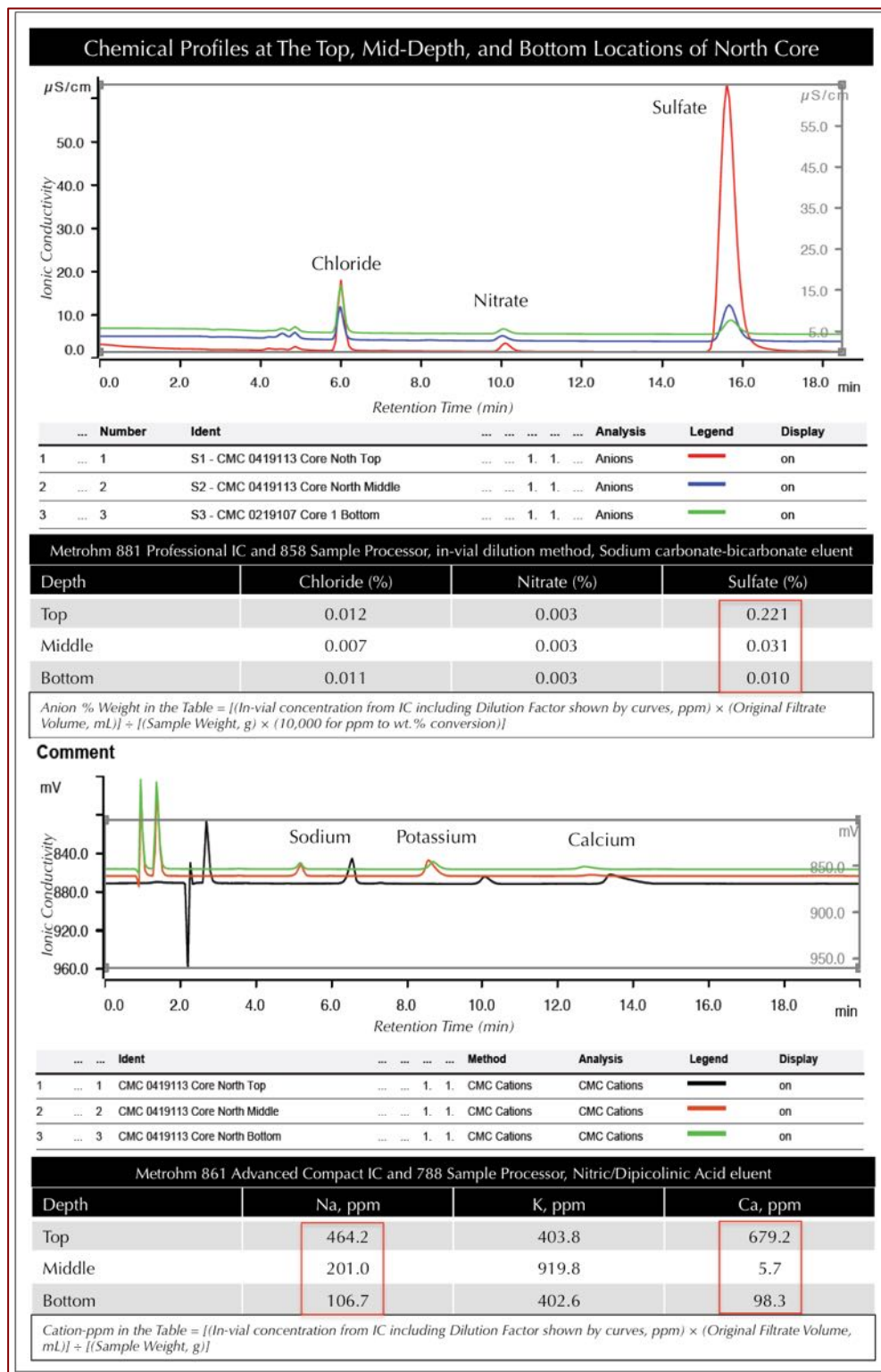
Figure 21: Results of ion chromatography of water-soluble anions (chloride, nitrate, sulfate) at the top, and, water-soluble cations (sodium, potassium, and calcium) at the bottom of deionized water-digested pulverized concrete from the top, mid-depth, and bottom locations of 'north' core showing noticeable enrichment of sulfate, sodium and calcium at the scaled surface region compared to interior. Tables beneath ion chromatograms show results as percent by mass of concrete for anions and ppm-concentration by mass of concrete for cations.
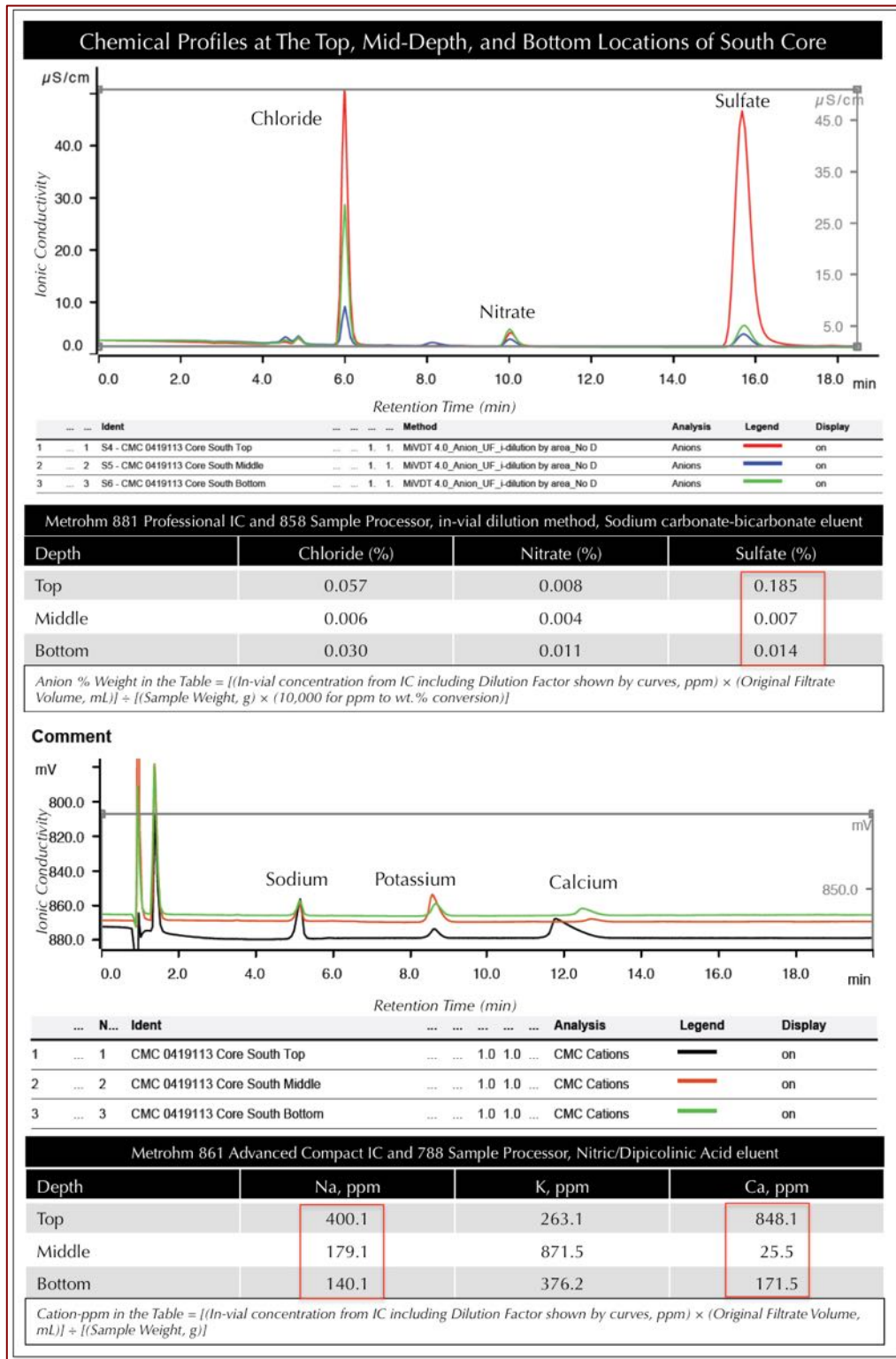
Figure 22: Results of ion chromatography of water-soluble anions (chloride, nitrate, sulfate) at the top, and, water-soluble cations (sodium, potassium, and calcium) at the bottom of deionized water-digested pulverized concrete from the top, mid-depth, and bottom locations of 'north' core showing noticeable enrichment of sulfate, sodium and calcium at the scaled surface region compared to interior. Tables beneath ion chromatograms show results as percent by mass of concrete for anions and ppm-concentration by mass of concrete for cations.
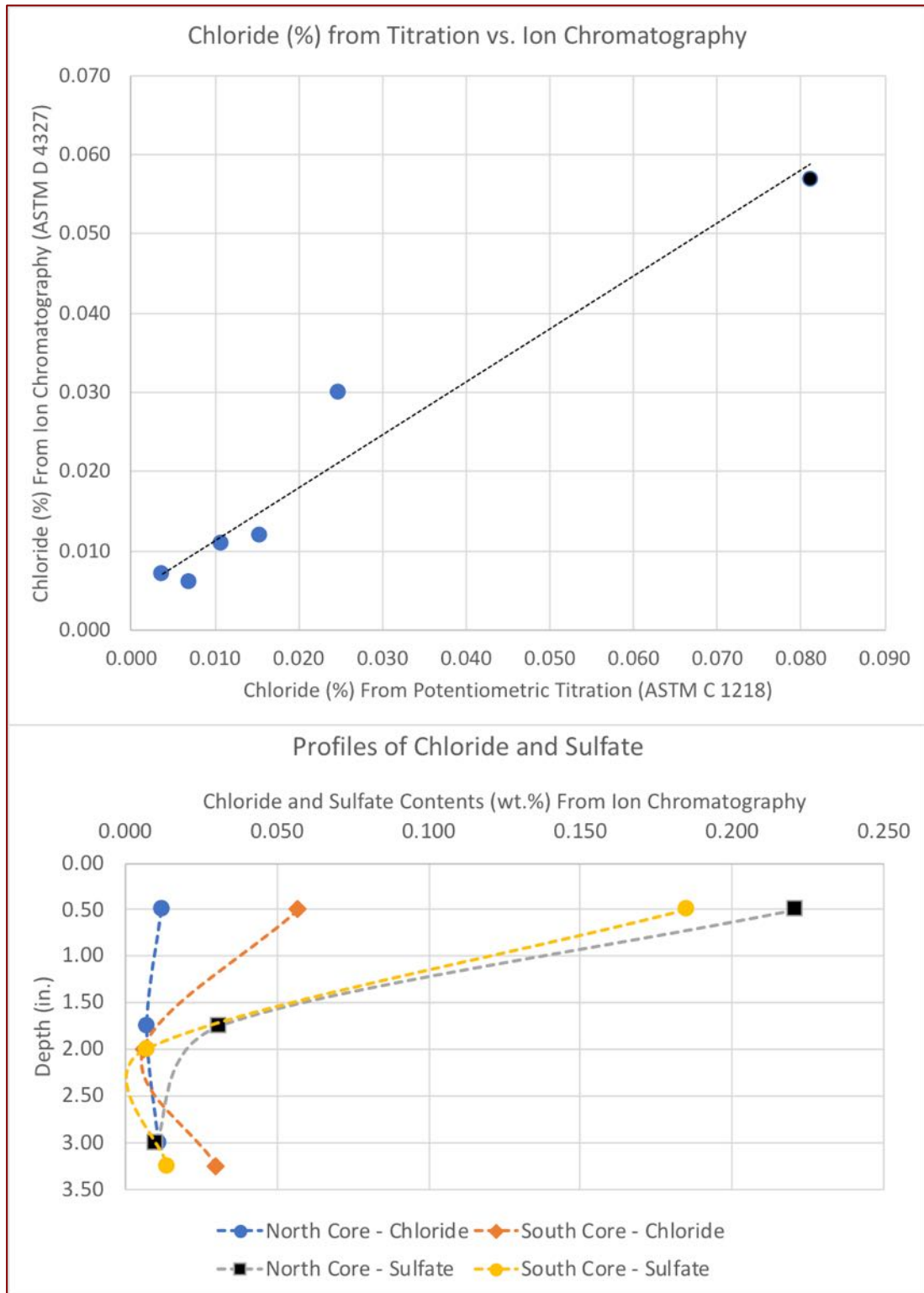
Figure 23: Top: Correlations between chloride contents from potentiometric titration (ASTM C 1218) and ion chromatography (ASTM D 4327) from the top, mid-depth, and bottom locations of 'north' and 'south' cores. Bottom: Profiles of chloride and sulfate from top, mid-depth, and bottom locations of 'north' and 'south' cores as obtained from ion chromatography.

DISCUSSIONS

The following paragraphs discuss various factors that are important for investigation of concrete surface scaling at the Project location.

AIR CONTENTS AND AIR-VOID SYSTEMS

Concrete in the examined cores showed lack of an air-entraining agent to have only 2 to 4 percent estimated air contents, as opposed to common industry-recommended air contents of 4.5 to 7.5 percent and air entrainment of concrete for exposures to similar environment conditions as the present cores. Lack of air entrainment in both cores show serious deviations from common industry recommendations, which is judged to be the primary factor for observed and reported scaling of concrete due to cyclic freezing and thawing of a non-air-entrained concrete at critically saturated conditions.

AGGREGATES

The crushed limestone coarse aggregates and natural sand fine aggregates are present in sound conditions and did not contribute to the observed surface issues.

PLACEMENT, FINISHING, AND CURING

A non-air-entrained concrete bleeds more and longer than an air-entrained concrete and thus increases the potential for bleed water accumulation beneath the finished surface if finishing operation starts prior to the cessation of bleeding. Such bleed water accumulation can cause sheet-like scaling of the finished surface due to the weak bond between the finished surface and the body, and/or a softer, porous, lighter toned paste at the surface from contamination and mixing of bleed water to the concrete as seen in both cores.

The interior concretes in both cores are dense and well-consolidated without any coarse voids or honeycombing, indicating adequate consolidation of concrete during placement. There is also no evidence of any segregation of aggregates during placement. There is, therefore, no evidence of any improper consolidation practice of slab at the locations of the examined cores.

Curing is essential for adequate cement hydration at the surface, and, thereby, development of the necessary strength of concrete at the surface by providing enough moisture and optimum temperature for cement hydration. The scaled surfaces of examined cores show no evidence of inadequate curing of concrete, e.g., no evidence of restricted cement hydration at the surfaces at least to cause the reported surface issues, however, cannot be examined properly due to the loss of the original finished surface.

COMPRESSIVE STRENGTH & CONCRETE MATURITY

The maturity of concrete is defined as: (i) a period of air drying and (ii) a compressive strength of at least 4000 psi – both prior to the first exposure of salts and snow so that the concrete does not contain any 'freezable' water in its capillary pores to freeze, expand, and thus cause distress (hence the importance of at least a period of air drying), and is strong enough to resist freezing-related stresses (hence the importance of adequate strength of at least 4500 psi) both prior to the first exposure of snow and salt (Jana 2004, Jana 2007).

A concrete is, therefore, needed to be 'matured' prior to the first exposure of freezing, especially during the winter weather constructions. Interior bodies of both cores are judged to have compressive strength of at least 4000 psi at the time of this investigation, which, however, does not indicate the strength during the first winter weather exposure after placement. If the strength prior to the first winter exposure was not at least 4000 psi then freezing of a concrete, especially of surface region prior to maturity can cause surface scaling.

WATER-CEMENTITIOUS MATERIALS RATIO AND DURABILITY

The estimated water-cementitious materials ratios (*w/cm*) of concrete at the surface regions of cores are higher than that in their interiors, which is indicative of a soft, porous paste at the surface region, perhaps due to finishing in the presence of bleed water at the surface and/or addition of water during finishing. Interior *w/cm* is within the common industry (e.g., ACI)-recommended maximum ratio of 0.45 (preferably 0.40) for an outdoor concrete exposed to freezing, salt, and snow.

Along with air entrainment, the primary defense of an outdoor concrete to stay durable in a moist environment of salt and snow it should also have the lowest possible *w/cm*, preferably around 0.40. The interior body of concrete in both cores is judged to have good *w/cm* but no entrained air, whereas surface region has no entrained air and high *w/cm* both of which have reduced the freeze-thaw durability of concrete at the exposed surface.

DEICING SALTS

Deicing salts, usually, do not cause surface scaling in a properly air-entrained concrete having a good air-void system that is made using sound aggregates, and has been placed, finished, cured, and matured properly (Jana 2004, 2007), *unless*: (i) salt is applied prior to the attainment of maturity of concrete, and/or (ii) a chemically aggressive (e.g., magnesium or ammonium sulphate or urea-based) salt is applied that can chemically decompose the paste (calcium silicate hydrate, the heart of concrete).

Premature exposures to salts i.e. prior to the attainment of maturity of concrete (i.e. a period of air drying and a compressive strength of at least 4000 psi before first exposure of salt and snow) can enhance surface scaling especially when finishing operations may have forced some water addition to improve workability of a sticky

unworkable high-air concrete mass. However, a well-designed concrete placed, finished, and cured properly should resist the deleterious action of salt unless salt was brought in too early and/or a chemically corrosive salt (magnesium sulfate or ammonium-based) was present that has caused chemical erosion of paste from the concrete surface.

Due to the lack of air entrainments in both cores deicing salts can aggravate surface scaling. Portions of slab placed in the winter month can cause scaling from premature applications of salts prior to the attainment of maturity.

Chemical profiles of cores showed no significant enrichment of chloride in the exposed surface regions of cores indicating perhaps a chloride-based deicer was not used. However, scaled surface regions of both cores showed noticeable enrichment in water-soluble sulfates, sodium, and calcium ions, indicating perhaps a sulfate-based salt was used that could have caused chemical and physical deterioration of surface region by chemical and/or physical salt attacks at the surface.

BENEFICIAL ASPECT OF A SURFACE SEALER

It is the concrete itself, i.e. an adequately air-entrained concrete made using 'optimum' air content and good air-void system, sound aggregates, good paste, placed, finished, and cured properly, and has been matured prior to the first exposure to freezing, salts, and snow, which should provide the necessary adequate durability. When all these basic factors are fulfilled from concrete materials to construction practices, having an additional surface sealer is not needed for protection. A surface sealer, however, does provide an additional protection, particularly when the inherent concrete quality and/or construction practices is/are questionable such as in this present case from the absence of air entrainment.

There are, however, many incidences of surface scaling in many outdoor slabs that did receive surface sealers, simply because sealer did not provide a long-term protection, and needed repeated applications. On the other hand, there are many incidences of perfectly sound outdoor slabs without any sealer that were exposed to freezing, salts, and snow but no distress at all simply because the concretes were made using sound durable materials and were constructed and matured properly. Therefore, having or not having a sealer is not the paramount factor for providing the first-hand protection against the environment. Sealer becomes more important when the inherent quality of concrete is questionable as here when concrete surface has poor scaling resistance. The examined cores examined showed no evidence of any sealer, which, however, is not possible to examine due to the total loss of the original finished surface in the scaled top of the cores received.

CONCLUSIONS

Based on detailed laboratory investigations, the reported surface scaling of concrete slab from field photographs to examined cores are judged to be due to a combination of one of several of the following factors:

a. **Lack of air entrainment in concrete**, which has affected the durability of concrete in a moist outdoor environment exposed to cyclic freezing and thawing at critically saturated conditions.

b. **Premature finishing prior to the evaporation of bleed water from the surface** that have created soft, porous, high *w/cm* paste at the top surface regions susceptible to scaling during freezing at critically saturated conditions.

c. **Potential exposures to non-chloride-containing deicing salts**, that might have caused the observed noticeable enrichment of water-soluble sulfate, sodium, and calcium ions at the scaled surface regions compared to the interiors of both cores, which could have caused chemical and/or physical salt attacks at the surfaces, probably aggravated by the lack of air entrainment of concrete to release any salt-related distress of concrete, especially if salts were applied at an early stage prior to the attainment of concrete maturity.

d. Due to the lack of air entrainment all throughout the depths of cores, **scaling will continue during future winter months of cyclic freezing and thawing at critically saturated conditions**.

REFERENCES

ACI Committee Report 201.2R, Guide to Durable Concrete, ACI Manual of Concrete Practice, Vol. 1, American Concrete Institute, 2008.

ASTM C 856 "Standard Practice for Petrographic Examination of Hardened Concrete," Vol. 4.02, ASTM International, West Conshohocken, PA, 2014.

ASTM C 1218 "Standard Test Method for Water-Soluble Chloride in Mortar and Concrete," Vol. 4.02, ASTM International, West Conshohocken, PA, 2014.

ASTM D 4327, "Standard Test Method for Anions in Water by Suppressed Ion Chromatography" Vol. 11.01, ASTM International, West Conshohocken, PA, 2014.

Jana, D., "Concrete, Construction or Salt – Which Causes Scaling? Part I: Importance of Air-void System in Concrete", *Concrete International*, American Concrete Institute, November 2004, pp. 31-38.

Jana, D., "Concrete, Construction or Salt – Which Causes Scaling? Part II: Importance of Finishing Practices", *Concrete International*, American Concrete Institute, December 2004, pp. 51-56.

Jana, D., Erlin, B., and Pistilli, M., "A Closer Look at Entrained Air in Concrete", *Concrete International*, American Concrete Institute, June 2005, pp. 31-38.

Jana, D., and Erlin, B., "Scaling Revisited", Letters, *Concrete International*, American Concrete Institute, September 2001, pp. 25-26.

Jana, D., "Petrography: A Powerful Tool for Solving Common Concrete Problems", *Civil Engineering NEWS*, March 1997, pp. 40-44.

Jana, D., and Cole, A.A., "Microscopy: A Practical Solution to Concrete Problems", *Bulletin of Concrete Industry Board*, September 1997, pp. 18-22.

Jana, D., Sample Preparation Techniques in Petrographic Examinations of Construction Materials: A State-of-the-art Review, Proceedings of the 28th Conference on Cement Microscopy, International Cement Microcopy Association, Denver, Colorado, pp. 23-70, 2006.

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END OF REPORT[1]

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[1] The CMC logo is made using a lapped polished section of a 1930's concrete from an underground tunnel in the U.S. Capitol.