CONSTRUCTION MATERIALS CONSULTANTS, INC.

Laboratory Analyses of A Stain From A Concrete Slab Surface

SMC Distribution Center-Noblesville, IN
10650 SMC Boulevard
Noblesville, IN 46060

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CMC 0219104

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LABORATORY ANALYSES OF A STAIN FROM A CONCRETE SLAB SURFACE

ABSTRACT

An off-white to light gray, soft, powdery sample reportedly of a stain on the trowel-finished surface of a concrete slab located at SMC Distribution Center at 10650 SMC Boulevard, Noblesville, Indiana was provided for determination of its composition, and if it contains one or both of two surface treatments reportedly applied on the trowel-finished surface, e.g., Speedhide interior Dry-Fog vinyl acrylic latex mixture containing kaolin (≧20 to ≦50%), limestone (≧1.0 to ≦5.0%), diatomaceous earth (≧1.0 to ≦5.0%), and titanium dioxide (≧1.0 to ≦5.0%), and, SpecChem E-Cure water-based concrete curing agent of sodium silicate composition (Sodium Silicate N <50%). Field photographs showed white stains, reportedly appeared within 2 weeks of hard trowel finish, either as long trails or as isolated patches that is soft, dusty and easily rubbed into fingers.

Low-power stereomicroscopical examinations of as-received powder shows its soft, dusty, particulate nature with occasional very fine (less than 0.5 mm) sand grains, probably from concrete sand mixed in other off-white to light gray components. No fibers, metals, bituminous materials, grease or other contaminants are found. Subsequent microscopical examinations of thin section of a clear epoxy-encapsulated powder in a petrographic microscope determined the presence of very fine particles of calcite and dolomite, quartz, and occasional trace feldspar all in a cloudy mass of intermixed clay and cement hydration products. The stain, therefore is similar in appearance to a dried out cream of dissolved matter from the concrete surface that contains some common usual components of concrete surface, e.g., calcite, quartz, and cement paste. Organic matter, if present, e.g., the reported vinyl acrylic-based and sodium silicate-based surface treatments and curing agents cannot be determined from optical microcopy. No contaminant or potentially deleterious salts were found, nor was the typical calcium carbonate composition of surface deposit that is a common efflorescence deposit on concrete surface formed by atmospheric carbonation of precipitate brought to the surface by moisture from within the concrete.

SEM-EDS analyses showed overall silica-rich particulate matters, which is consistent with optical microscopical determination of fine quartz and ultrafine clay, isolated particulate matters rich in aluminum (Al) from clay and feldspar, isolated particules rich in calcium from calcite and dolomite, fine particles of dolomite rich in magnesium, isolated spots rich in titanium, which is consistent with reported presence of titanium dixoide in the Speedhide interior Dry-Fog vinyl acrylic latex mixture. Alkalies are from concrete along with reported sodium silicate surface treatment.

Mineralogical and chemical compositions of surface deposits are determined from X-ray diffraction (XRD), and X-ray fluorescence spectroscopy (XRF), respectively. XRD analysis showed dominant 57% dolomite, 17.9% calcite, 21.4% quartz and 3.7% kaolinite clay as the recognizable crystalline materials. XRF showed high lime and magnesium from dolomite and calcite found in XRD, silica is from quartz, clay, and reported sodium silicate surface treatments, and alumina is from clay. High titanium is from titanium dioxide present in Speedhide interior Dry-Fog vinyl acrylic latex mixture. Of particular interest are high alkalis, especially sodium from reported sodium silicate surface treatment along with alkalis from concrete.

Ion chromatography of water-soluble salts in surface deposit showed 0.003% chloride and 0.234% sulphate with no major concentration of any potentially deleterious salts. Chloride result is typical of an indoor concrete containing negligible chloride, not exposed to chloride from the environment, and has no chloride-containing set accelerating admixture. Sulfate result is typical of surface deposit on a Portland cement concrete slab where sulfate was derived from cement sulfate after hydration and moisture migration through the slab.

FTIR analyses showed no detectable epoxy or acrylic as reported in surface treatments except calcite and clay from particulate (crystalline) matters on the surface, which were already diagnosed in XRD. Absence of organics indicate possible washing away of organics by sweeping action on the surface.

Thermal analyses showed most pronounced peaks from dehydroxylation of clays at 110ºC and decarbonation of carbonates at 759.5ºC. DSC curve shows polymorphic transition from alpha to beta form of quartz from silica (quartz) sand.

Comprehensive laboratory examination of surface deposits from optical and electron microscopy and microanalysis to determination of mineralogical and chemical compositions by XRD and XRF, water-soluble salts from ion chromatography, organics from FTIR, and hydrates/organics/sulfates/carbonates from thermal analysis confirmed a typical surface deposit of concrete as off-white, soft, powdery dried out cream of surface treatments having signatures of reported applications of surface treatments, e.g., from high alkalis and silicate from sodium silicate treatments of curing agent to titanium dioxide in chemical composition and clay in XRD and FTIR from reported application of Dry-Fog mixture. The deposit does not match with a typical calcium carbonate based efflorescence deposit found in many concrete slab surfaces but rather a dried out cream of concrete slab surface that has clear evidence of application of the reported surface treatments including the sodium silicate-based curing agent.

INTRODUCTION

A powder of off-white to light gray stain on the trowel-finished surface of a concrete slab located at SMC Distribution Center at 10650 SMC Boulevard, Noblesville, Indiana was provided for examination. The floor surface was reportedly treated with (a) Speedhide interior Dry-Fog vinyl acrylic latex mixture containing kaolin (≧ 20 to ≦50%), limestone (≧1.0 to ≦5.0%), diatomaceous earth (≧1.0 to ≦5.0%), and titanium dioxide (≧1.0 to ≦5.0%), and, (b) SpecChem E-Cure water-based concrete curing agent of sodium silicate composition (Sodium Silicate N <50%). Field photographs (Figure 1) showed white stains, reportedly appeared within 2 weeks of hard trowel finish, either as long trails or as isolated patches that is soft, dusty and easily rubbed into fingers. The purpose of laboraotry testing is to identify the stain and its composition.

Figure 1: White stain on a trowel-finished concrete surface at SMC Distribution Center in Noblesville, Indiana.

Figure 2 shows the off-white to light gray powder, as received in a plasic ziploc bag, as well as after removing a portion of it on a petri dish, and its apprarance while viewed through a low-power stereomicroscope.

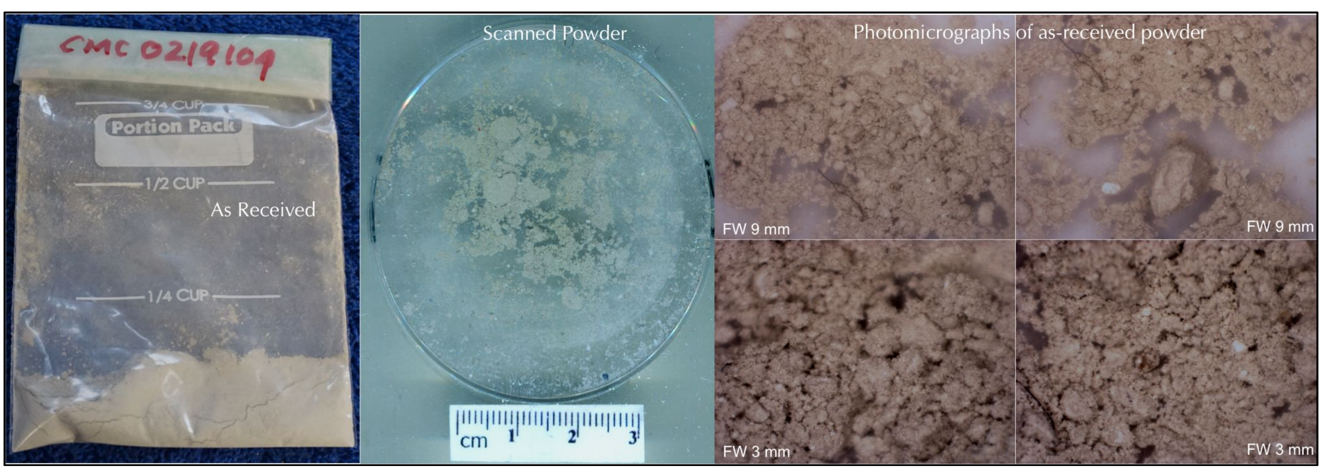


Figure 2: Off-white to light gray stain sample as received, and viewed through a low-power stereomicroscope.

METHODOLOGIES

Optical Microscopy

The powder was first examined by optical microscopes of the as-received sample as shown in the photomicrographs in Figures 2 and 3, followed by thoroughly mixing some powder in a clear epoxy to prepare a hardened epoxy-encapsulated block of powder to prepare a polished thin section of epoxy-encapsulated powder (down to 25 to 30 micron in thickness to transmit polarized light through it) to be viewed in a transmitted-light polarizing (petrographic) microscope (Figures 4 and 5). The main purposes of optical microscopy are to determine the mineral particulates present in the powder as well as any cement hydration and carbonation products from the concrete surface, salts, and other contaminants on the surface that could be recognized by their optical properties (*a la* ASTM C 856, C1324, Jana 2006).

Scanning Electron Microscopy & Microanalysis by Energy-Dispersive X-ray Spectroscopy (SEM-EDS)

Following optical microscopy, polished thin section was viewed in a CamScan scanning electron microscope to determine chemical (elemental) composition of overall powder including all inorganic and possible organic components. Surface deposit was examined in SEM-EDS by: (a) secondary electron imaging (SEI) to determine the microstructure and morphology of components in stain, (b) backscatter electron (BSE) imaging to determine compositions of various phases from various shades of darkness/grayness/brightness from average atomic numbers of phases from the darkest pore spaces to brightest minerals in stain, and (c) X-ray elemental mapping (dot mapping) of an area of interest to differentiate various phases (*a la* ASTM C 1723).

X-ray Diffraction (XRD)

X-ray diffraction (XRD) of powder is done on Siemens D 5000 diffractometer, which is perhaps the most important test to determine all crystalline/mineralogical components present in the deposit. Particles like quartz, calcite, clay, salts, etc. present on the concrete surface could be easily detected by XRD by their characteristic diffraction peaks.

X-ray Fluorescence (XRF)

X-ray fluorescence (XRF) is done on Rigaku NEX-CG for determining major element oxide compositions of stain, where any unusual composition compared to a normal composition of a Portland cement concrete, e.g., elevated alkali levels etc. would indicate the presence of surface treatments, e.g., residues of reported sodium silicate-based curing agent, or an elevated sulfate level to indicate moisture migration, etc.

Fourier Transform Infra-red Spectroscopy (FT-IR)

Fourier-transform infrared spectroscopy (FT-IR) was done of the powder in a Perkin Elmer Spectrum 100 FT-IR spectrophotometer running with Spectrum 10 software, using attenuated total reflection (ATR) on a single bounce diamond/ZnSe ATR crystal, and measured between a frequency range of 4000 to 650 cm^{-1}. Organics are best detected by this method.

Ion Chromatography

Ion chromatography of water-soluble filtrate from the stain was done to determine the presence of any water-soluble salts, e.g., of chloride, sulfates, etc. in the stain.

Thermal Analysis

Thermogravimetric analysis (TGA and DTG) and differential scanning calorimetry (DSC) of powder were done on a Mettler Toledo TGA/DSC1 unit to determine various hydrous, sulfate, and carbonate phases from their characteristic decomposition temperatures.

RESULTS

Optical Microscopy

Low-power stereomicroscopical examinations of as-received powder shows its soft, dusty, particulate nature with occasional very fine (less than 0.5 mm) sand grains, probably from concrete sand mixed in other off-white to light gray components. No fibers, metals, bituminous materials, grease or other contaminants are found.

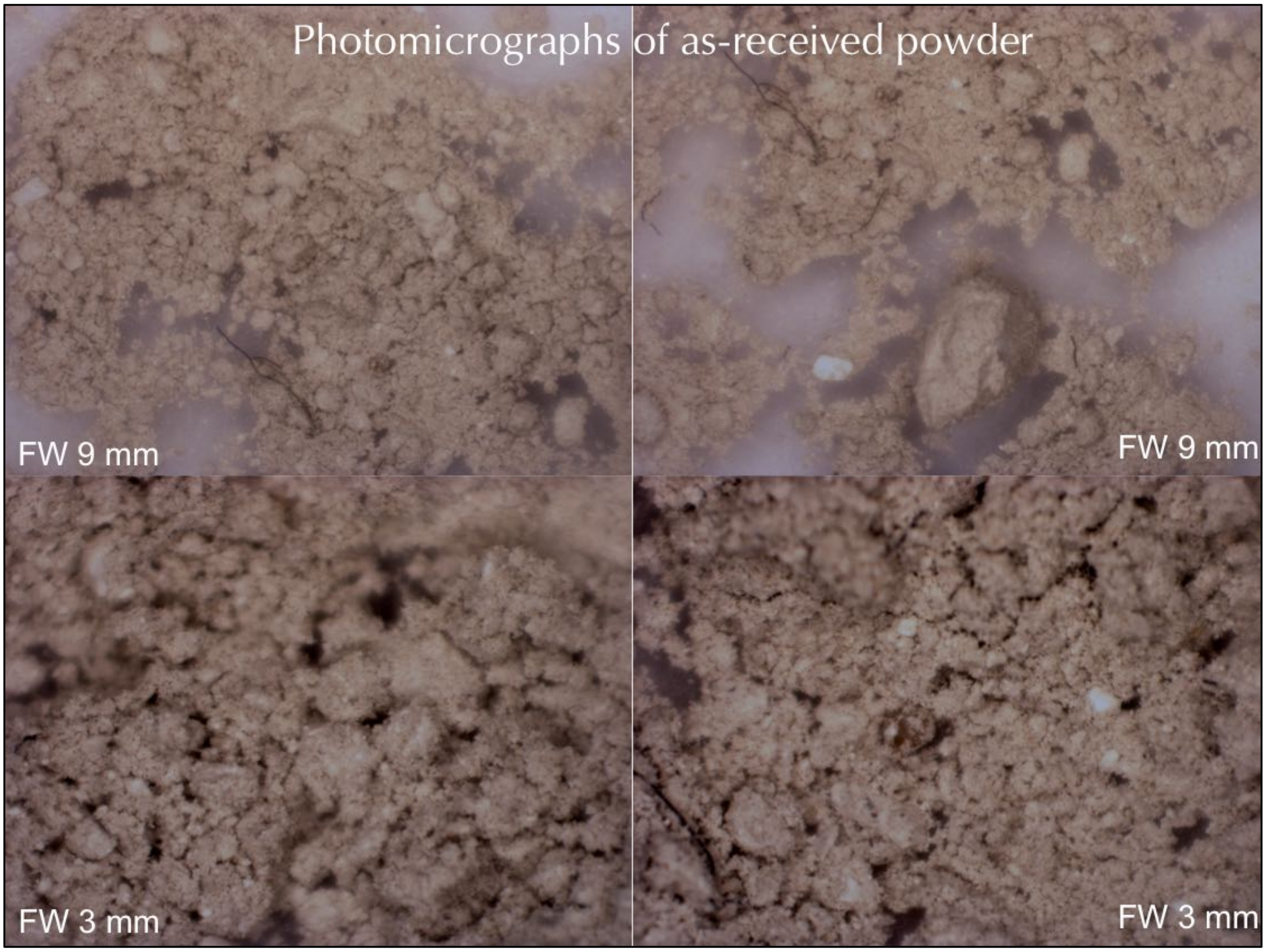


Figure 3: Photomicrographs of as-received powder.

Subsequent examinations of thin section of powder in a petrographic microscope determined the presence of very fine particles of: (a) **calcite and dolomite** (some coarser ones are marked as 'C' in Figures 4 and 5), (b) **quartz** (some are marked as 'Q' in Figures 4 and 5), and (c) occasional trace **feldspar** (marked as 'F' in Figure 5) – all in a cloudy mass of **intermixed clay and cement hydration products**. The stain, therefore is similar in appearance to a dried out cream of dissolved matter from the concrete surface that contains some common usual components of concrete surface, e.g., calcite, quartz, and cement paste. Organic matter, if present, e.g., the reported vinyl acrylic-based and sodium silicate-based surface treatments and curing agents cannot be determined from optical microcopy. No contaminant or potentially deleterious salts were found, nor was the typical calcium carbonate composition of surface deposit that is a common efflorescence deposit on concrete surface formed by atmospheric carbonation of precipitate brought to the surface by moisture from within the concrete.

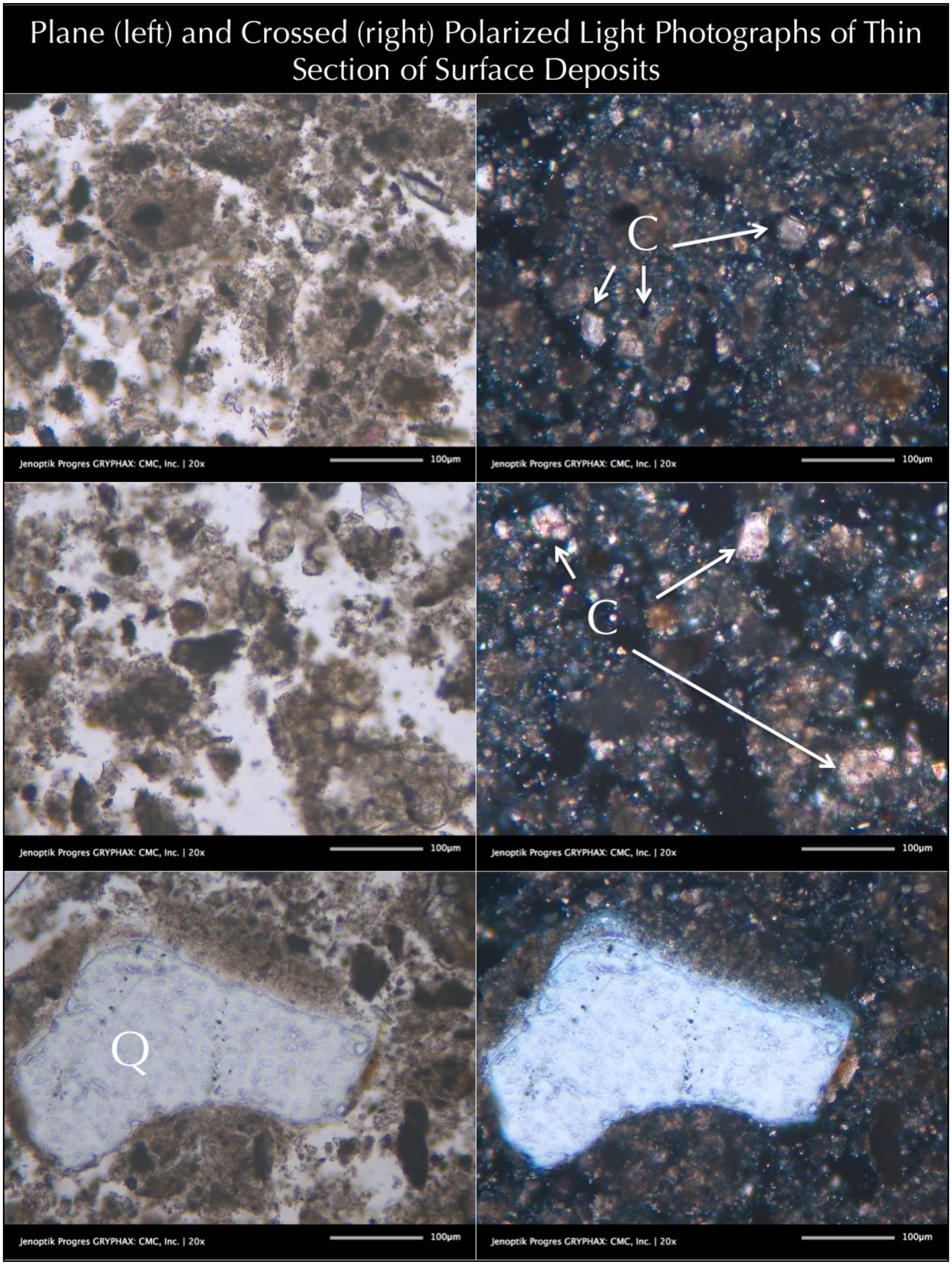


Figure 4: Photomicrographs of thin section of surface deposit showing abundant particulate matters consisting of carbonates (calcite and dolomite grains, some are marked as 'C'), quartz (largest particle is marked as 'Q'), and cloudy mixture of Portland cement paste and ultrafine particles of clay.

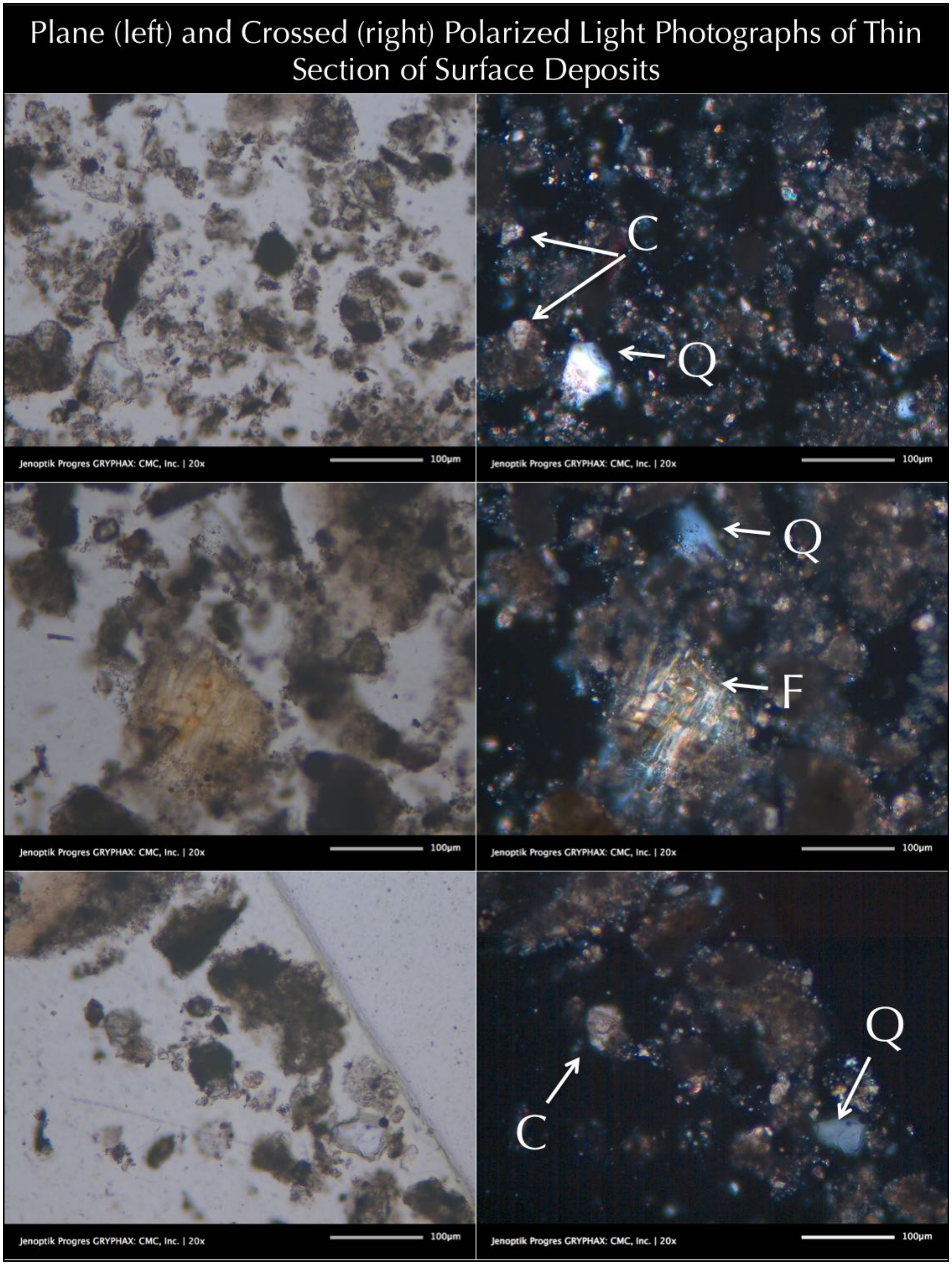


Figure 5: Photomicrographs of thin section of surface deposit showing abundant particulate matters consisting of carbonates (calcite and dolomite grains, some are marked as ‘C’), quartz (largest particle is marked as ‘Q’), feldspar (marked as ‘F’), and cloudy mixture of Portland cement paste and ultrafine particles of clay.

Electron Microscopy

Figure 6 shows secondary electron image (SED), backscatter electron image (BSE) and X-ray elemental maps of thin section of surface deposit showing

(a) Overall silica-rich particulate matters highlighted in silicon (Si) map, which is consistent with optical microscopical determination of fine quartz and ultrafine clay,

(b) Isolated pariculate matters rich in aluminum (Al) from clay and feldspar,

(c) Isolated particules rich in calcium as seen in Ca-map from calcite and dolomite,

(d) Fine particles of dolomite rich in magnesium as seen in Mg-map,

(e) Isolated spots rich in titanium in Ti-map, which is consistent with reported presence of titanium dixoide in the Speedhide interior Dry-Fog vinyl acrylic latex mixture.

(f) Alkalies are from concrete along with reported sodium silicate surface treatment.

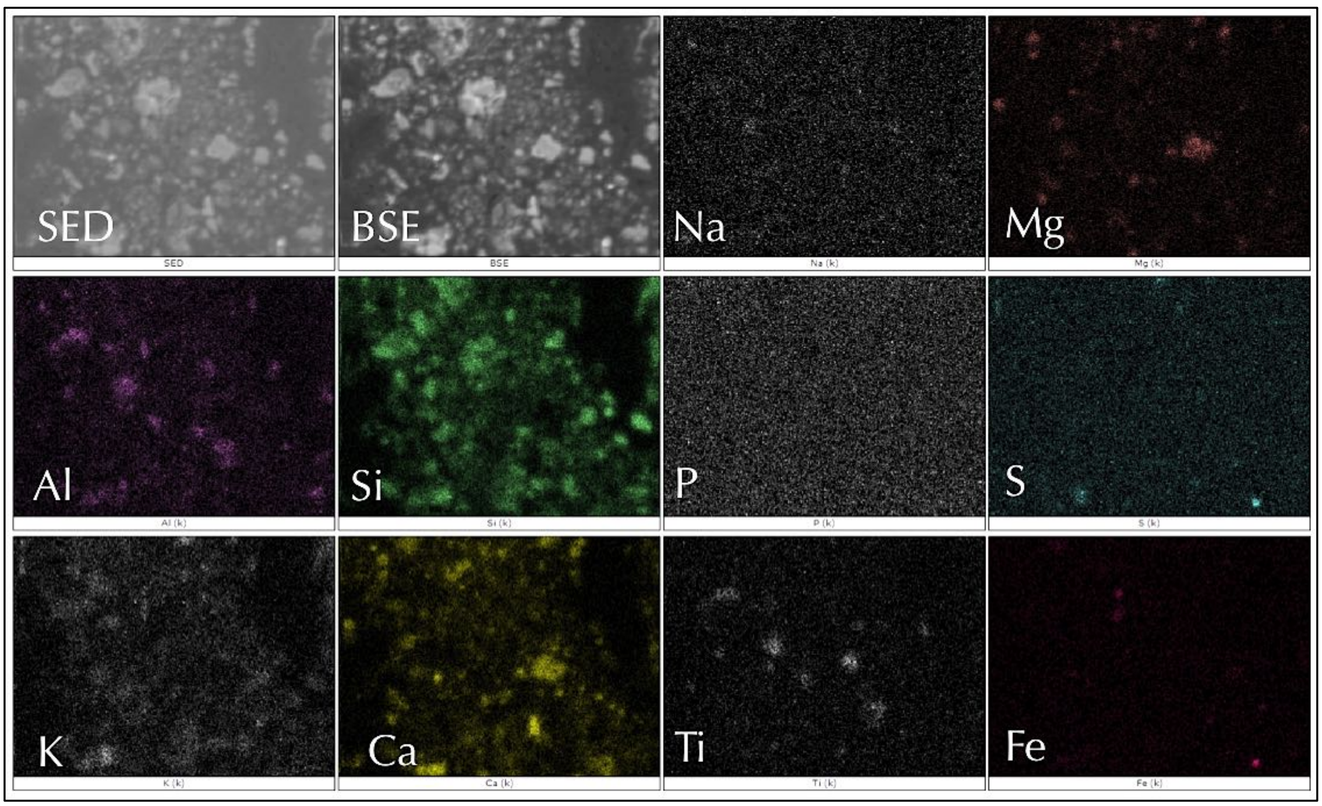
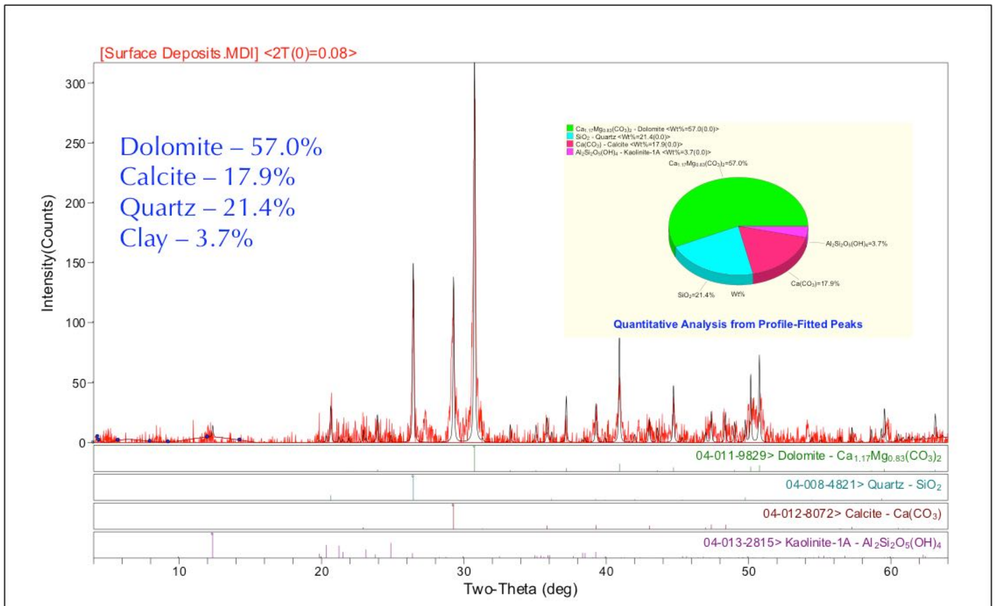


Figure 6: Secondary electron image (SED), backscatter electron image (BSE) and X-ray elemental maps of thin section of surface deposit.

Mineralogy and Chemical Composition from XRD and XRF

Figure 7 shows mineralogical and chemical compositions of surface deposits as determined from X-ray diffraction (XRD), and X-ray fluorescence spectroscopy (XRF), respectively. XRD pattern of surface deposit, and quantitative analysis (Rietveld) of major mineralogical compositions show dominant 57% dolomite, 17.9% calcite, 21.4% quartz and 3.7% kaolinite clay as the recognizable crystalline materials. XRF showed high lime and magnesium from dolomite and calcite found in XRD, silica is from quartz, clay, and reported sodium silicate surface treatments, and alumina is from clay. High titanium is from titanium dioxide present in Speedhide interior Dry-Fog vinyl acrylic latex mixture. Of particular interest are high alkalis, especially sodium from reported sodium silicate surface treatment along with alkalis from concrete.



Mortar Composition	Values	Methods
Silica - SiO_2	47.7	XRF
Alumina - Al_2O_3	3.76	XRF
Iron - Fe_2O_3	1.6	XRF
Lime - CaO	13.9	XRF
Magnesia - MgO	6.63	XRF
Sodium - Na_2O	3.39	XRF
Potassium - K_2O	5.71	XRF
Titanium - TiO_2	3.16	XRF
Phosphorus - P_2O_5	0.033	XRF
Sulfate - SO_3	1.79	XRF
Balance	12.4	XRF
Total	100	XRF

Figure 7: XRD (top) and XRF (bottom) analyses of surface deposits showing mineralogical and chemical compositions, respectively.

Ion Chromatography

Figure 8 shows chromatogram of water-soluble salts in surface deposit after digesting a gram of pulverized deposit in distilled water for 30 minutes at a temperature below boiling, followed by continued digestion in water at the ambient laboratory condition for 24 hours. The filtrate was analyze by ion chromatography. Results showed 0.003% chloride and 0.234% sulphate with no major concentration of any potentially deleterious salts. Chloride result is typical of an indoor concrete containing negligible chloride, not exposed to chloride from the environment, and has no chloride-containing set accelerating admixture. Sulfate result is typical of surface deposit on a Portland cement concrete slab where sulfate was derived from cement sulfate after hydration and moisture migration through the slab.

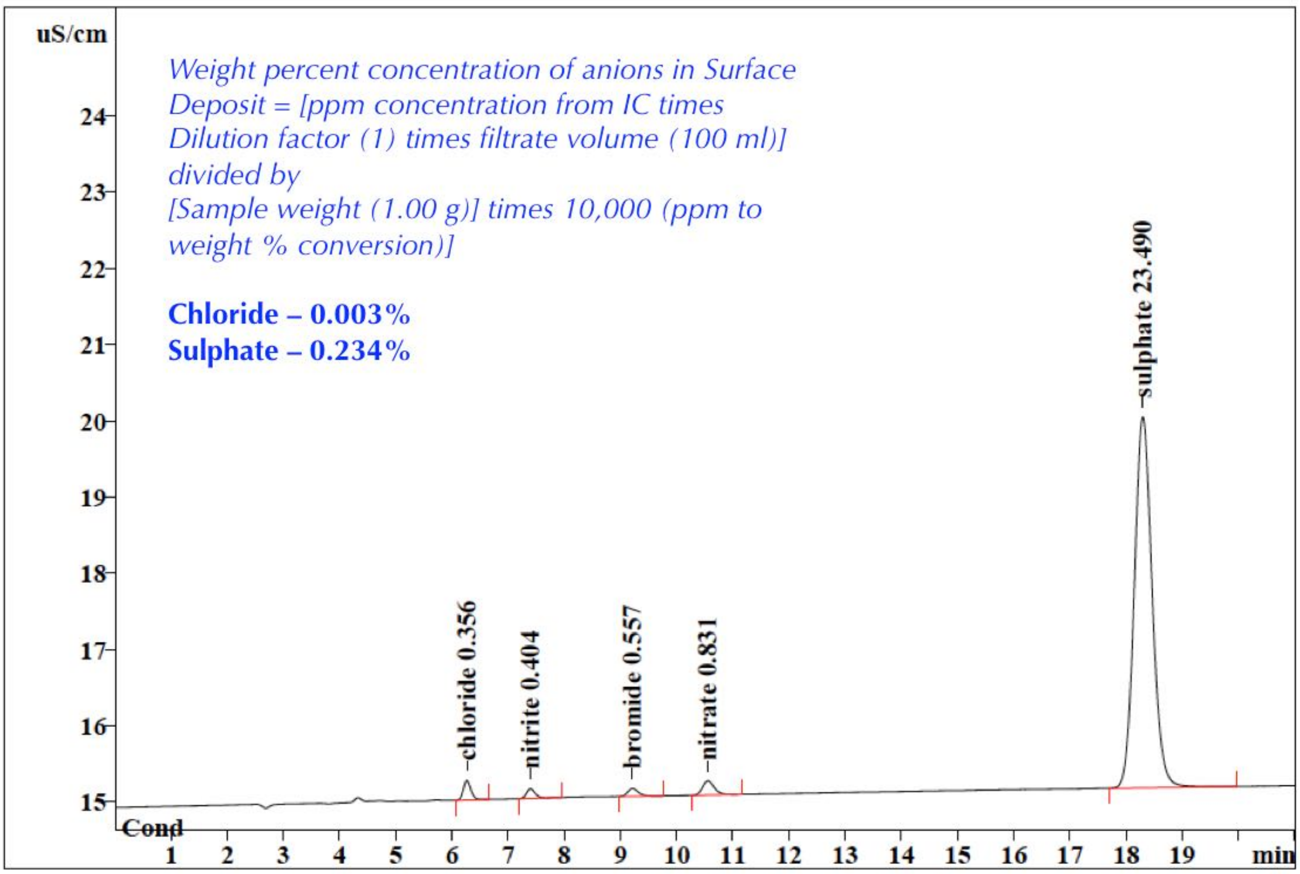
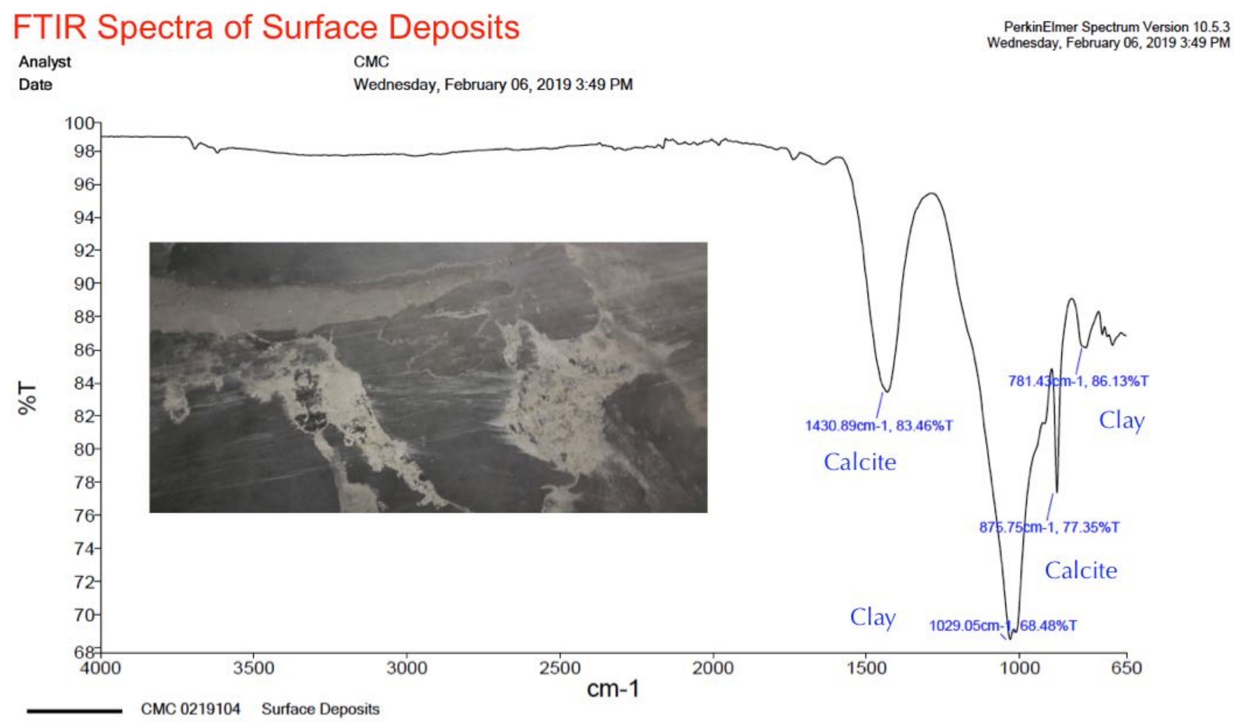


Figure 8: Ion chromatogram of water-soluble filtrate of surface deposit showing chloride and sulfate typical of an indoor Portland cement concrete slab with no indication of any deletrious salts or contaminant.

FTIR Analysis

Figure 9 shows FTIR spectrum of surface deposit obtained from a Perkin Elmer FTIR spectrometer with an Universal ATR module where the powder as received was directly analyzed in the ATR module. Spectrum showed no detectable epoxy or acrylic as reported in surface treatments except calcite and clay from particulate (crystalline) matters on the surface, which were already diagnosed in XRD. Absence of organics indicate possible washing away of organics by sweeping action on the surface.



Source Spectra Results	
Spectrum Name	**Number Of Peaks**
CMC 0219104	4

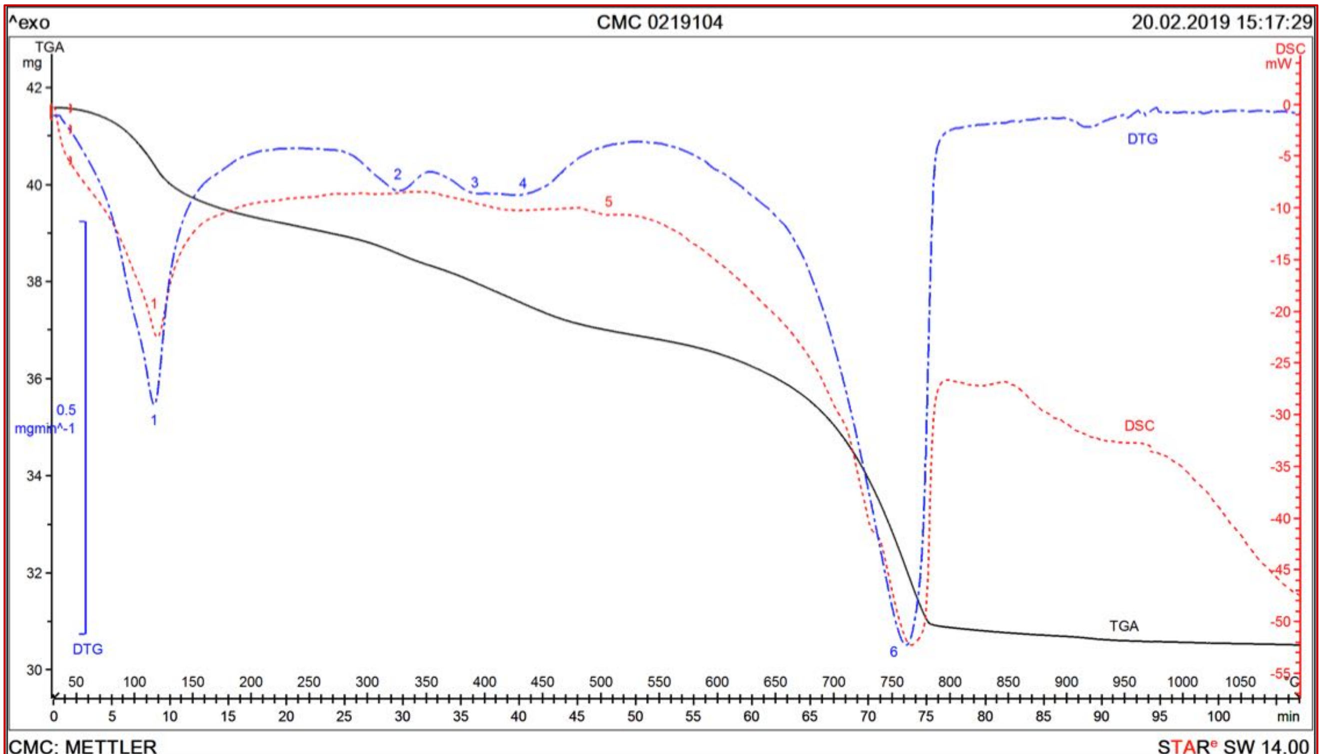
List of Peak Area/Height		
Peak Number	**X (cm-1)**	**Y (%T)**
1	1430.89	83.46
2	1029.05	68.48
3	875.75	77.35
4	781.43	86.13

Figure 9: FTIR Spetrum of surface deposits showing calcite and clay but no detectable organics.

Thermal Analyses

Figure 10 shows TGA (in bold black), DSC (in dotted red), and DTG (in dashed blue) curves of surface deposits showing losses in weight due to decompositions (loss of water and carbon dioxide) of various phases during controlled heating in a Mettler-Toledo's simultaneous TGA/DSC 1 unit from 30ºC to 1000ºC in a ceramic crucible (alumina 70µl, no lid) at a heating rate of 10ºC/min in a nitrogen purge at a rate of 75 mL/min. Dehydration and decarbonation reactions are marked as endothermic peaks in the DTG curve, whereas alpha to beta-form polymorphic transition of quartz is marked at the characteristic temperature of 573ºC in the DSC curve.

In the DTG curve, successive losses in weights are detected at Peaks 1, 2, 3, 4, and 6, of which the most pronounced peak is from dehydroxylation of clays at 110ºC and decarbonation of carbonates at 759.5ºC. DSC curve shows polymorphic transition from alpha to beta form of quartz at 503.7ºC from silica (quartz) sand (Peak# 5). Quantitative estimates of quartz and calcite are determined to be 16.3 and 25.33 percent, respectively.



Peak#	Peak Position (°C)	Phase	Amount (%)
1 (DTG)	110.81	Combined water from Clay	4.71
2 (DTG)	324.49	Dehyoxylation	1.17
3 (DTG)	386.96	Dehyoxylation	0.94
4 (DTG)	432.41	Portlandite, Epoxy	1.18
5 (DSC)	503.69	Quartz	16.3
6 (DTG)	759.55	Calcite	25.33

Figure 10: Thermal analysis of surface deposits.

DISCUSSIONS

Comprehensive laboratory examination of surface deposits from optical and electron microscopy and microanalysis to determination of mineralogical and chemical compositions by XRD and XRF, water-soluble salts from ion chromatography, organics from FTIR, and hydrates/organics/sulfates/carbonates from thermal analysis confirmed a typical surface deposit of concrete with signatures of reported surface treatments from high alkalis and silicate from sodium silicate treatments of curing agent to titanium dioxide in chemical composition and clay in XRD and FTIR from reported application of Dry-Fog mixture. The deposit does not match with a typical calcium carbonate based efflorescence deposit found in many concrete slab surfaces but rather a dried out cream of concrete slab surface that has evidence of application of reported surface treatments and curing agent.

REFERENCES

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ASTM C 1723, "Standard Guide for Examination of Hardened Concrete Using Scanning Electron Microscopy," In Annual Book of ASTM Standards, Section Four Construction, Vol. 04.02; ASTM Subcommittee C 9.65, 2017.

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]

[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.