

### Swimming Pool Plaster Discoloration – A Case Study From Field & Laboratory-Cured Plasters



Primera Stone Sapphire Treasure & Blue Ocean



CONSTRUCTION MATERIALS CONSULTANTS, INC.

### Swimming Pool Plaster Discoloration

### **Table Of Contents**

Executive Summary	1
Introduction	5
Background Information	5
Field Photographs	5
Discolored Field Plasters	5
Plaster Kits, Cements, And Pigments	5
Purpose Of Present Investigation	5
Methodologies	7
Optical Microscopy	7
Scanning Electron Microscopy And X-Ray Microanalyses	8
X-Ray Diffraction	9
X-Ray Fluorescence Spectroscopy	10
Discolored Pool Plasters	11
Petrographic Examinations	12
Discoloration Of The Exposed Plaster Surfaces In Contact With Pool Water	12
Plaster Discoloration Due To Interactions With Pool Water	20
SEM-EDS Studies Of Pool-Plaster Interactions	22
Plaster Kits, Cement, And Pigments	
Laboratory-Cured Hardened Plasters With And Without CaCl <sub>2</sub> Immersed In Aggrassive And Balanced Waters	31
Discussions	34
Theories On Causes Of Discoloration Of Pool Plaster	34
Plaster Discoloration	35
Primera Stone Pool Plaster – Sapphire Treasure	36
Primera Stone Pool Plaster – Blue Ocean	
Evidence Of Leaching And Increased Paste Porosity	
Evidence Of Leaching Of Pigment	
Shrinkage Microcracking Of Pool Plaster	
Calcium Carbonate Scale And Near-Surface Precipitation	38
Primera Stone Plaster Kits, Cement, And Pigments	
Laboratory-Cured Plasters With And Without Calcium Chloride Addition	41
References	43
Appendix	44
Appendix 1Primera Stone Brochure, Safety Data Sheet, Field Photos Of Sapphire Treasure & Blue Ocean Pools	62
Appendix 2 Primera Stone Sapphire Treasure Sun Shelf & Blue Ocean Spa Field Plaster Samples	68
Appendix 3 Primera Stone Plaster Kits, Cements, And Pigments	138
Appendix 4 Primera Stone Laboratory-Cured Plasters & Experiments In Water	168
Appendix 5 Swimming Pool Plaster Deterioration – Overview And Case Studies	200



### **EXECUTIVE SUMMARY**

Primera Stone pool plaster is an engineered mix of a variety of specialty aggregates, white Portland cement, and various iron oxide-based pigment dyes, with or without a calcium chloride accelerator, which is first hard troweled, then a light water wand wash is applied for curing, which is subsequently removed by polishing to create a dense terrazzo-like shine with the added benefit of an advertised dense surface resistant to algae, staining, and a long-term durability.

1

Reported discoloration of two Primera Stone products, i.e., a *Sapphire Treasure* plaster, and, a *Blue Ocean* plaster has initiated this investigation. As a result, representative samples of both plaster types were provided, i.e., Sapphire Treasure plaster from the sun shelf area, and Blue Ocean plaster from the spa area of pool, both of which showed the typical discolored surfaces after contact with the pool water during service.

Two types of discoloration are seen on the exposed surfaces of both Sapphire Treasure and Blue Ocean plasters, which are seen in the field photos as well as in the two plaster samples received. These are classified as: (a) darker to lighter faded blue discoloration of plaster, which occupies the majority of the interstitial spaces between the exposed aggregate particles, and, (b) more localized, medium gray to beige discolored patches of plaster mostly occurring at the edges of many exposed aggregate particles. Both types have created blotchy discoloration of plaster surfaces, irrespective of the plaster types.

In addition to the two field plasters, three different dry, pre-packaged plaster kits identified as Kit# 1830, 1831, and 1835 were provided. Kit# 1830 reportedly represents the Sapphire Treasure plaster, which consists of (in a 5 lbs. kit) 2.81 lbs. aggregate, 2.20 lbs. white Portland cement, an iron oxide (Mediterranean) pigment, mix water having a water-cement ratio (w/c) between 0.42 to 0.50 with an optional flake calcium chloride accelerator addition in the mix water depending on weather conditions at a dosage of 0.044 lbs. per 5 lbs. kit. Kit# 1831 and 1835 are representative of Blue Ocean plasters having crushed dark gray aggregates (as opposed to lighter, variable-colored aggregates of Sapphire Treasure), similar white Portland cement, water mixed with or without calcium chloride accelerator at a similar w/c of 0.42 to 0.50, and, a pigment component as the Sapphire Treasure plaster but with a different aggregate type (crushed basalt as opposed to crushed glass, marble, seashell in Sapphire Treasure), and a different iron-chromium (Midnight) pigment. Laboratory examinations of these three kits showed the presence of a limestone fine microfiller component in the binder at subordinate amounts compared to the major white Portland cement component in kits 1830 and 1831 and in minor amount in kit# 1835, which have given an overall appearance of a masonry cement binder (possibly with some hydrated lime added as well). Additionally, a Lehigh blended cement (#1834) was provided, which is reportedly used at the jobsite, which contains major amount of white Portland cement, and subordinate amounts of limestone fines having the fineness of Portland cement, thus compositionally similar to the binders found in kit# 1830 or 1831. White Portland cement, the main cementitious component in all plaster kits and in the two field samples contains major amounts of alite (tricalcium silicate,  $C_3S$ ), which is the main cementitious phase of cement, subordinate belite (dicalcium silicate,  $C_2S$ ), minor calcium aluminates, negligible to no ferrite phase, trace amounts of gypsum for set control, and occasional free lime components. Also provided were two different pigment dyes, #1832 and #1833, where the former is found to contain iron oxide and a minor barium sulfate stabilizer, whereas, the latter contains iron-chromium oxides and minor barium sulfate stabilizers. Both field plaster samples were reportedly prepared with flake calcium chloride set accelerating admixture added to the mix waters. A flake calcium chlorite sample was also provided, which showed sinjarite (CaCl<sub>2</sub>. 2H<sub>2</sub>O) composition from the XRD pattern.

All these plaster kits, raw ingredients, cement, pigments, accelerator, etc. as well as the two field plaster samples were studied extensively by a variety of laboratory techniques, including: (a) optical microscopy for detailed compositional and textural investigations often by preparing thin i.e., light-transparent sections of all the materials received after encapsulating or impregnating with an epoxy resin medium; (b) scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS) of thin sections or solid samples for microstructural and microanalytical investigations; (c) X-ray diffraction for mineralogical compositions of plaster kits and components, and, (d) X-ray fluorescence for major element oxide compositions of plaster kits and components, and, (d) X-ray fluorescence for major element, along with laboratory-cured hardened products of three plaster kits have provided a good background information needed for detailed investigation of all possible reasons for the observed discoloration of two Primera Stone plaster products. For the two field plasters, the exposed discolored surfaces as well as the vertical cross sections were examined by optical microscopy and SEM-EDS to observe the extent and depth of discoloration and associated alterations of plasters.

A number of theories have been proposed for various mechanisms of discoloration of pool plasters, which can be classified into three categories, e.g., according to the roles of: (a) plaster components, (b) installation practices, and, (c) complex interactions of plaster with the pool water. Amongst the *plaster components* that can introduce discoloration are: (1) variable *w*/c's of plaster mix creating corresponding variations in color tones of finished plasters; (2) addition of calcium chloride accelerator, which (2a)



being inherently highly soluble in pool water (whether balanced or aggressive) can be readily dissolved out (by as much as one fourth of the added amount) to create a soft, porous, and hence lighter faded paste, which can also (2b) delay the hydration of ferrite phase, if present, to develop a blotchy or mottled discoloration of plaster, and, (2c) can increase frequency of shrinkage microcracking in paste to allow deeper penetration of pool water; (3) addition of organic or inorganic pigment dyes in plaster mix, where the former is cheaper and more soluble than the latter but even inorganic dyes can be leached out in an aggressive water, or, even during normal lime and calcium chloride leaching from a balanced water; organic pigments can be bleached by the presence of chlorine or other oxidizers, or even by the sun; (4) contaminants in sand, e.g., iron sulfide which can cause rust stains; (5) difference in moisture contents beneath the plaster surface and/or substrate; and (6) presence of ground granulated blast furnace slag as a cementitious component in plaster to cause bluish-green to beige/gray discoloration due to variable atmospheric oxidation of slag cement paste. Amongst the plaster installation that can introduce discoloration are: (7) late hard troweling, over-troweling (trowel burn), and/or, addition of water during trowel finishing to increase porosity of paste at the exposed surface, water troweling is a detrimental practice that severely weakens and creates undesirable surface porosity and shrinkage cracks; (8) prolonged presence of pool water at a low level after a partial drainage to develop a darker hue on the aerated portion and a lighter hue on the underwater portion; and (9) corrosion of steel reinforcement in the substrate to bring corrosion stains to the exposed plaster surface. Amongst the interaction of pool water with plaster that can introduce discoloration are: (10) out-of-balance pool water (e.g., an overly positive Langelier Saturation Index or LSI value), which can readily dissolve (leaching, etching) and precipitate plaster constituents as a uniform thin layer or crust (scaling) of calcium carbonate throughout the pool and whitens the pool; a scaled plaster is generally rough to the touch, which can be easily removed by scraping, sanding or acid wash; an etched porous plaster, however, cannot be restored due to the loss of materials creating increased porosity and, thereby, discoloration from lightening of color; and (11) aggressive pool water, which can dissolve calcium hydroxide component of cement hydration and calcium chloride accelerating admixture to increase porosity of paste at the exposed surface with a white discoloration; if the discoloration is smooth to the touch, manifests itself in streaks, blotches, or small spots, and if diluted acid does not quickly remove the white discoloration, then the problem is probably not calcium carbonate scaling but a porous surface instead that leads to rapid deteriorations.

All these above-mentioned theories along with any other possible explanations were evaluated during the course of this comprehensive investigation to pinpoint the mechanism(s) of discoloration of two Primera Stone plaster products. Both products, irrespective of their similarities, e.g., in use of white Portland cement binder, reportedly having similar water-cement ratios, mix proportions, and apparently similar installation processes, as well as their differences, e.g., different aggregate and pigment types developed similar blotchy appearance of discoloration characterized by: (a) the overwhelming darker-to-lighter blue fading of the interstitial paste portions between the exposed aggregates, and (b) localized beige or tan discoloration of paste preferentially at the margins of exposed aggregate particles.

The first major clue of the mechanism of development of both types of discoloration came from detailed examinations of the *exposed discolored surfaces of field plasters* in a scanning electron microscope (SEM) after doing a detailed *in-situ* X-ray microanalyses of three different color tones of paste on the exposed surfaces, i.e., from darker blue to lighter blue and eventually in the beige localized paste areas. SEM-EDS studies showed: (1) overall compositional similarities of darker-to-lighter blue toned paste areas, where the darker toned pastes showed more uniform i.e., restricted chemical compositions than a little more spread in compositions in the faded lighter blue toned areas (though still restricted compared to the beige toned paste), which, are distinctly different than (2) localized beige toned paste occurring mostly at the interfaces to exposed aggregate particles.

Compared to the darker-to-lighter blue plaster surfaces, the beige toned areas showed many distinct compositional differences, e.g., (1) the beige paste showed distinctly lower lime and higher silica and alumina than the darker-to-lighter blue pastes, which could be due to excessive leaching of paste at the beige areas leading to the loss of lime at the expense of silica and alumina compared to the ubiquitous darker-to-lighter faded blue paste; (2) the beige paste shows higher iron, silica, magnesia, and alumina than the darker-to-lighter blue pastes, which, again, could be due to excessive leaching of lime in the beige areas leading to enrichment of silica, alumina, iron, and alumina compared to the ubiquitous darker-to-lighter blue paste; and (c) the beige paste shows lower lime due to lime leaching but similar sulfate contents as the darker-to-lighter blue paste but overall higher silica and alumina and lower lime and magnesia than the darker-to-lighter blue pastes, which is again due to excessive leaching of lime in the beige areas leading to enrichment of silica, alumina it on magnesia than the darker-to-lighter blue pastes, which is again due to excessive leaching of lime in the beige areas leading to enrichment of silica, alumina, iron, and alumina, iron, and alumina (without necessarily changing the sulfate contents) compared to the ubiquitous darker-to-lighter blue paste.

These results are consistent with the conclusion that the darker-to-lighter blue color variations of plaster surface in the interstitial spaces between the exposed aggregate particles are more due to variations in underlying porosities of paste from denser/darker to porous/lighter blue areas as opposed to any noticeable variations in chemical compositions. The faded lighter blue areas are characteristically more porous hence reflected more light to appear in lighter hues than the adjacent denser and darker blue areas. These variations in darker-to-lighter blue areas are the results of variable leaching of inherent soluble calcium hydroxide

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### Swimming Pool Plaster Discoloration

and calcium chloride components of plaster to cause variations in near-surface porosities of paste and subsequent variations in hues. The more localized beige areas, however, showed excessive lime leaching to the point of depleting the lime at the expense of silica, alumina, and iron (without affecting the sulfate) compared to the ubiquitous darker-to-faded lighter blue interstitial areas of paste.

Results obtained from exposed surface of Sapphire Treasure plaster sample are consistent with the exposed surface of Blue Ocean plaster. Both samples showed the ubiquitous darker-to-faded lighter blue discoloration in the interstitial paste between exposed aggregate particles, as well as localized beige discoloration around exposed aggregates due to excessive leaching of lime at the expense of other elements. The only difference between the two plasters are in their aggregates, which are a mixed lime-sodium-silicate glass (dark blue), crushed dolomitic marble (medium brown), seashell (white to off-white), etc. as opposed to darker gray crushed basalt volcanic rocks in the Blue Ocean plaster, and, in compositions of pigments from iron oxide types in the Sapphire Treasure to iron-chromium oxide types in the Blue Ocean plaster.

Information obtained from chemical variations of exposed discolored surfaces are integrated with additional information obtained from *vertical cross sections of field plasters from the exposed surface regions to the interiors*. Both field plasters showed evidence of: (1) very thin (< 0.5 mm thickness) localized scales of secondary calcium carbonate precipitates on the exposed surface; (2) a leached porous zone of paste at the top 1 mm, which is characteristically depleted in lime than the interior paste; (3) secondary calcium precipitate beneath the leached zone at the interface between the leached porous surface region and denser interior; (4) increased porosity of paste at the surface region with soft, friable, porous paste situated immediately beneath the exposed surface; (5) fine, hairline, vertical, shallow-depth shrinkage microcracks at the surface region oriented perpendicular to the exposed surface and extended to depths of less than 1 to 1 mm; (6) and abundant fine, hairline shrinkage microcracks in the interior plaster, especially at locations devoid of aggregate and rich in paste fractions, which were judged to have formed from high paste fractions along with the presence of calcium chloride accelerator in the plasters. Evidences of near-surface leaching of lime, increased porosity of near-surface paste, thin scale on exposed surface are all present in both samples, which are the telltale evidence of interaction of plasters with the pool water.

Binder in Plaster Kit# 1830 has white Portland cement consisting of major amount of subhedral to anhedral alite, subordinate mostly isolated and a few clustered belite, and abundant limestone fine particles having the fineness of Portland cement. Binder in Plaster Kit# 1831 has similar composition as that in 1830 in having major amount of subhedral to anhedral alite, subordinate mostly isolated and a few clustered belite, and abundant limestone fine particles (though slightly lower than that in 1830) having the fineness of Portland cement. Binder in Plaster Kit# 1835 is different than the other two in having white Portland cement, but the cement has major amount of mostly isolated and a few clustered and a few clustered rounded belite, subordinate amount of subhedral to anhedral alite, and minor to negligible amount of limestone fine. Aggregate in the Kit# 1830 is similar to the one found in Sapphire Treasure plaster, and, the aggregate in Kit# 1831 is similar to the Blue Ocean plaster. Both field plasters have major amount of white Portland cement (having major alite and subordinate belite) and subordinate limestone fines. Based on the difference in binder mineralogy, Kit# 1835 was judged not used in either of the two examined field plasters.

Laboratory-cured hardened plaster samples prepared according to the recommended mix proportions from the three plaster kits (#1830, #1831, and #1835) mixed with tap water, or, water with addition of flake calcium chloride accelerating admixture at the recommended dosage showed a clear and distinct darkening of all three hardened plasters when calcium chloride accelerator was added to the mix water. The darkening is uniform, well-known, and happened all throughout the interior bodies of all three laboratory-cured hardened plaster kits with calcium chloride accelerator. Both sets of plasters with and without accelerator of all three kits were then completely immersed in beakers having tap water, and, in water mixed with calcium hypochlorite disinfectant solution for 7 days to observe any leaching and/or scaling of the plasters, and subsequent discoloration.

Three hardened plaster kits# 1830, 1831, and 1835 without CaCl<sub>2</sub> addition showed typical mineralogies of residual calcium silicates (alite and belite) from white Portland cement, and limestone fine microfillers (mostly for kit# 1830 and 1831) as seen in their dry microstructures except having an overwhelming matrix of calcium silicate hydrate hydration products of cement on which the residual cement grains are scattered, fine-grained short prismatic or lath-shaped grains of water-soluble calcium hydroxide component of cement hydration, sometimes appearing as coarsely crystalline laths in air voids. The hardened plasters without CaCl<sub>2</sub> addition after 7 days of immersion in tap water showed the *aggressive action of tap water* on all three plasters as dissolution of soluble component (calcium hydroxide component of cement hydration) from the plaster and its precipitation as coarsely crystalline dog tooth-shaped subhedral to euhedral grains of secondary calcite precipitates on the exposed surfaces of all three plasters. By contrast, immersion of all three hardened plasters without CaCl<sub>2</sub> addition in a calcium hydroxide the *balanced action of the solution* with localized dissolution of paste especially along the surface hairline microcracks, but no appearance of any secondary calcite scales on the exposed surfaces.



Addition of CaCl<sub>2</sub> accelerator in the mix water during preparation of hardened plasters showed no major difference in microstructures compared to their companion CaCl<sub>2</sub>-free ones. There is no evidence of any increase in the frequency of fine hairline drying shrinkage microcracks that are present in all hardened plasters irrespective of CaCl<sub>2</sub> addition. All three hardened plaster kits showed typical mineralogies of residual calcium silicates (alite and belite) from white Portland cement, and limestone fine microfillers (mostly for kit# 1830 and 1831) as seen in their dry microstructures except having an overwhelming matrix of calcium silicate hydrate hydration products of cement on which the residual cement grains are scattered, fine-grained short prismatic or lath-shaped grains of water-soluble calcium hydroxide component of cement hydration. Contrary to significant secondary calcite scales on the exposed surface for kits immersed in tap water without any CaCl<sub>2</sub> addition, the present three hardened plasters with CaCl<sub>2</sub> addition showed no scaling of precipitation of secondary calcite on the exposed surfaces of any kit. Apparently, CaCl<sub>2</sub> addition has prevented scaling in tap water. Micrographs of thin section of laboratory-cured hardened plaster kits with CaCl<sub>2</sub> accelerator and immersed in tap water for 7 days showed abundant residual alite grains, and subordinate limestone fines in paste with the cement hydration products overall giving an appearance of a masonry cement paste, along with some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. There are evidence of localized dissolution of paste, especially in near-surface region or along fine microcracks but no surface scaling. Kit# 1835 also showed no surface scaling on the exposed sides. Similar microstructures of localized dissolution but no surface scaling is found when the CaCl<sub>2</sub> doped kit was immersed in calcium hypochlorite disinfectant solution. Abundant coarse lath-shaped secondary calcium hydroxide deposits in air voids in all three kits indicates high solubility of this component of white Portland cement hydration.

Other than overall darkening of laboratory-cured plasters in the presence of calcium chloride accelerator in the mix water, there is no other evidence of patchy or blotchy discoloration or fading of darker to lighter blue color tone or localized beige discoloration of exposed surfaces of any of the three hardened plaster kits (1830, 1831, and 1835) found after 7 days of immersion in tap water or Ca-hypochlorite solution. This indicates either the time of laboratory exposure was short compared to the field exposure, and/or the field exposure condition was chemically more complex due to the unknown use of pool water chemicals and disinfectants than the present simpler laboratory experiment. Tap water immersion of hardened plasters showed the aggressive action of tap water in leaching of soluble components of plaster and precipitation (scaling) on the exposed surface as coarse, dog tooth-shaped euhedral, hexagonal secondary calcite crystals in all three plasters. Such dissolution and reprecipitation, however, did not develop any color fading of the exposed surface, except some common discoloration from the absorbed water (which disappeared after the immersed plasters were subsequently air-dried).

Therefore, based on extensive studies on two field plasters and subsequent experiments on three laboratory-cured hardened plaster kits with and without CaCl<sub>2</sub> accelerator addition in the mix water showed that the addition of calcium chloride accelerator in combination with pigment dyes have created an ideal environment for plaster discoloration, which may have been aggravated by the advertised light water wash after hard troweling, which, if not done properly, could have left a higher water-cement cream of paste at the surface to increase the paste porosity and thus enhanced pool water and plaster interactions from leaching and dissolution of soluble components of plaster to scaling and precipitation of components from supersaturated solution. The darker to lighter blue discoloration is more due to variable porosities of paste resulted from variable leaching of soluble components (e.g., calcium hydroxide component of white Portland cement hydration, and calcium chloride accelerator) than from any variations in chemical compositions, whereas the localized beige/gray discoloration of paste adjacent to exposed aggregate particles in two field plasters clearly represented severe leaching of lime to cause distinct chemical variations of depleted lime and enriched silica-alumina-iron-magnesia contents in those localized beige discolored areas compared to the overwhelming darker-to-lighter blue discolored pastes from variable paste porosities.

Combined use of a chloride-based accelerator and a pigment increases the risk of discoloration compared to use of nonpigmented colored exposed aggregate plaster, or a plaster without a soluble chloride-based accelerator. The situation gets complicated by superposition of the actions of chemicals added to the pool water, which may bring imbalance between the pool water chemistry (alkalinity, pH, calcium concentration, LSI, etc.) and plaster. High temperatures in the spa can also enhance the rate of dissolution of soluble components from plaster and some pigments along with it. Extensive long-term laboratory testing of mockup plasters as the present short-term laboratory experiments are needed to evaluate the potential for discoloration of plaster by using a chemically-doped water which is representative of the pool water in service.



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Swimming Pool Plaster Discoloration

### INTRODUCTION

Reported herein are the results of discoloration of two pool plasters identified as Sapphire Treasure plaster, and, a Blue Ocean plaster, both of which have shown blotchy discoloration of exposed surfaces from darker to faded lighter blue colors as well as localized gray/beige discoloration (Figure 1).

### BACKGROUND INFORMATION

Both Sapphire Treasure and Primera Stone plaster products are marked under Primera Stone plasters where a discolored sample of the former was collected from the sun shelf area and the latter from the spa area of the subject pool (Figure 1).

### FIELD PHOTOGRAPHS

Figure 1 and numerous additional Figures in the Appendix show field photos of swimming pool.

### DISCOLORED FIELD PLASTERS

Figure 1 and additional Figures in the Appendix show field photos of discoloration of pool plasters. The *Sapphire Treasure* plaster sample has: (a) an overall lighter blue color tone of the exposed surface with exposed aggregate particles that vary in colors from white to off-white, light gray, blue, etc., and (b) a darker blue color of cross section, whereas, the *Blue Ocean* plaster sample has: (a) an overall medium gray color tone on the exposed surface with exposed aggregate particles that are more uniform in color and mostly show medium gray colors, and, (b) dark blue tone on the vertical cross section. On close examinations of the exposed surfaces, both samples show: (1) fading of the overwhelming color of paste from darker to light blue in the interstitial spaces between the exposed aggregate particles, and, (2) localized gray/beige color tone of paste especially at the margins of exposed aggregate particles.

### PLASTER KITS, CEMENTS, AND PIGMENTS

Along with two field discolored plaster samples, some 5-lbs. buckets of dry plaster mixes were provided (Kit# 1830, 1831, 1835) as well as a field applied blended cement (#1834), two pigment dyes (#1832 and #1833), and flake calcium chloride accelerator, which are all described in detail in the Appendix.

### PURPOSE OF PRESENT INVESTIGATION

Based on the background information provided along with field and as-received plaster photos of discoloration, the purposes of the present investigation are to determine the reasons for discoloration, e.g., leaching of plaster from pool water interactions, fading of the pigment dyes, scaling, role of calcium chloride accelerator, etc.





Figure 1: Field photos of Primera Stone Sapphire Treasure plaster at left and Blue Ocean plaster at right along with corresponding blotchy discoloration of exposed surfaces of plasters from respective pools in the bottom row. The Sapphire Treasure plaster has an overall blue color with exposed light gray, white, and blue color aggregates, and patchy discoloration of darker to lighter shade or fading of blue color and beige gray discoloration of paste around exposed aggregate particles. The Blue Ocean plaster has an overall gray color tone of exposed surface with dark gray exposed aggregate particles, and patchy discoloration of darker to lighter shade or fading of color and beige gray discoloration of paste around beige gray discoloration of paste around exposed aggregate particles.



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Swimming Pool Plaster Discoloration

### METHODOLOGIES

### **OPTICAL MICROSCOPY**

All samples from two discolored field plasters to multiple plaster kits, cement, dyes, etc. as well as laboratory-cured hardened plaster prepared from the kits were examined by detailed 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 (2006).

The steps of petrographic examinations include (Jana 2006):

- i. Visual examinations of the samples, as received;
- ii. Low-power stereo-microscopical examinations of as-received, saw-cut and freshly fractured sections, and lapped cross sections of samples for evaluation of textures, and compositions;
- iii. Low-power stereo-microscopical examinations of air contents and air-void systems in the samples;
- 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 samples 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 sections and thin sections of samples taken with stereomicroscope and petrographic microscope, respectively to provide detailed compositional and mineralogical information of concrete.



Figure 2: The optical microscopy laboratory at CMC, which used various microscopes for this study.



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### Swimming Pool Plaster Discoloration

### SCANNING ELECTRON MICROSCOPY AND X-RAY MICROANALYSES



Figure 3: CamScan Series 2 scanning electron microscope used for examination of pool plaster compositions.

After optical microscopy, thin section examination was further carried out in a CamScan Series 2 scanning electron microscope (Figure 3) to determine the compositions of aggregates and discolored pastes on the exposed surfaces of field plasters, as well as chemical variations of paste from the exposed surface to interior. The microscope is equipped with a high-resolution column 40Å tungsten, 40 kV electron optics zoom condenser 75° focusing lens operating at 20 kV, equipped with a variable geometry secondary electron detector, backscatter electron detector, EDS detector for observations of microstructures at high-resolution, compositional analysis, and quantitative determinations of major element oxides from various areas of interest, respectively. Revolution 4Pi software is used for digital storage of secondary electron and backscatter electron images, elemental mapping, and analysis along a line, a point, or an area of interest. Numerous 50 mm × 75 mm thin sections of field, dry plaster mix, and laboratory prepared plaster samples were polished, coated with a gold-palladium alloy, and used with a custom-made aluminum sample holder in the large multiported chamber with the eucentric 50 × 100 mm motorized stage.

#### X-RAY DIFFRACTION

Representative portions of plaster kits, pigments, and hardened plaster samples were pulverized to finer than 44micron (US 325 sieve) particle size for X-ray diffraction studies. The purpose of this study is to detect the mineralogical compositions of samples.

X-ray diffraction was carried out in a Bruker D2 Phaser (2nd Generation, Figure 4) benchtop Powder diffractometer Bragg-Brentano geometry) employing a Cu X-ray tube (Cu k-alpha radiation of 1.54 angstroms), a primary slit of 1 mm, a receiving slit of 3 mm, a position sensitive 1D Lynxeye XE-T detector. Generator settings used are 30 kV and 10mA (300 watt). Sample was placed in a zero background sample holder which is an optically polished 111 plane of silicon wafer attached to a stainless steel sample holder for use in the 6-position sample stage of D2 Phaser. Tests were scanned at 20 from 8° to  $64^{\circ}$ with a step of 0.05° 20 integrated at 0.05 sec. step<sup>-1</sup> dwell time.

The resulting diffraction patterns were collected by Bruker's Diffrac.Measurement software.



Figure 4: Bruker's D2 Phaser (2<sup>nd</sup> generation) benchtop X-ray powder diffractometer with Lynxeye 1D position sensitive detector used in X-ray diffraction studies of plaster samples.

Phase identification was done with Bruker's Diffrac.EVA software with the search-match database from Crystallographic Open Database (COD). Additional phase identification, and Rietveld quantitative analyses were carried out with Match! software.

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### X-RAY FLUORESCENCE SPECTROSCOPY

Representative portions of plaster kits, pigments, and hardened plaster samples were also analyzed by X-ray

fluorescence (XRF) to determine the major element oxide compositions of samples.

A series of standards from Portland cements, lime, gypsum to various rocks, and masonry mortars of certified compositions (e.g., from USGS, GSA, NIST, CCRL, Brammer, or measured by ICP) are used to calibrate the instrument for various oxides and empirical calculations are done from such calibrations to determine oxide compositions of concretes.

An energy-dispersive bench-top X-ray fluorescence unit from Rigaku Americas Corporation (NEX-CG) was used (Figure 5). Rigaku NEX CG delivers rapid <complex-block>

 Rigenker

 Rigenker

Figure 5: Rigaku NEX-CG in CMC, which can perform analyses of 9 pressed pellet or fused bead of sample. Samples are prepared either as pressed pellet (usually the one already prepared for XRD) or can also accommodate fused bead with proper calibration of standard beads.

qualitative and quantitative determination of major and minor atomic elements in a wide variety of sample types with minimal standards. Unlike conventional EDXRF analyzers, the NEX CG was engineered with a unique close-coupled Cartesian Geometry (CG) optical kernel that dramatically increases signal-to-noise. By using monochromatic secondary target excitation, instead of conventional direct excitation, sensitivity is further improved. The resulting dramatic reduction in background noise, and simultaneous increase in element peaks, result in a spectrometer capable of routine trace element analysis even in difficult sample types. The instrument is calibrated by using various certified (CCRL, NIST, GSA, and Brammer) reference standards of cements and rocks.



### **DISCOLORED POOL PLASTERS**



Figure 6: Shown are: (a) Primera Stone Sapphire Treasure plaster from Sun Shelf area at left with blotchy discoloration of exposed surface consisting of (i) fading of blue color from darker to lighter blue, and, (ii) beige gray discoloration of paste especially around the light gray, white, off-white, and blue crushed exposed aggregate particles, and, (b) Blue Ocean plaster from Spa area at right with blotchy discoloration of exposed surface consisting of (i) fading of color from darker to lighter blue along with (ii) beige gray discoloration of paste especially around the dark gray crushed exposed aggregate particles. Lines 1 through 4 in each plaster sample were sectioned vertically for through-depth variations in plaster compositions after interaction with pool water, and areas A and B were sectioned for observations of exposed discolored surfaces that were in contact with pool water by optical microscopy and SEM-EDS. See Appendix for more photos.



### PETROGRAPHIC EXAMINATIONS

### DISCOLORATION OF THE EXPOSED PLASTER SURFACES IN CONTACT WITH POOL WATER



Figure 7: Stereomicrographs (top row), and thin section micrographs (middle and bottom rows) of the exposed discolored plaster surface of Primera Stone Sapphire Treasure showing blotchy discoloration of exposed surface consisting of (i) fading of blue color from darker to lighter blue (marked with dashed red arrows), and (ii) extreme fading to beige gray discoloration of paste mostly around light gray, white, off-white, and blue crushed exposed particles aggregate (marked with yellow arrows). Thin section show micrographs numerous fine hairline shrinkage microcracks (marked with white arrows, common in many plasters containing calcium chloride accelerator, many containing secondary calcite precipitates from pool water migration and evaporation through the microcracks), and darker to lighter blue paste from differences in paste porosities from differential leaching of paste by the pool water. See Appendix for more photos.





Figure 8: Exposed discolored surface of Sapphire Treasure plaster that was in contact with pool water and subsequently developed three color tones – a darker blue tone, which has faded into a lighter blue tone, and a beige tone of localized paste especially in contact with aggregate particles.

SEM-EDS analyses were done on all three paste color tones and correspondingly color coded by the oxide variations of discolored pastes measured at the tips of callouts and in boxed areas across the photo.

Results are given in the Table below, which shows overall compositional similarities of darker and lighter blue paste indicating color variations due to difference in porosities of pastes (lighter paste is more porous than the darker blue paste) than any compositional variaitons.

The beige paste at Probe# 1, 3, and 6 to 10, however, are very different than the dark or light blue pastes, which is shown in the subsequent compositional plots of oxide variation diagrams of all three paste color tones.





Figure 9: Exposed discolored surface of Sapphire Treasure plaster that was in contact with pool water and subsequently developed three color tones – a darker blue tone, which has faded into a lighter blue tone, and a beige tone of localized paste especially in contact with aggregate particles.

Oxide variation diagrams of darker and lighter blue pastes and localized beige toned pastes at aggregate surfaces show overall compositional similarities of darker to lighter faded blue pastes where darker paste at the locations of Probe# 2, 5, 11, 12, and 15 are more compositionally homogeneous than the lighter faded blue paste at the locations of Probe# 4, 13, 14, 16, and 17 (faded paste shows a slightly more spread) in the lime, alumina, and silica plots.

The beige paste at Probe# 1, 3, and 6 to 10, however, shows a distinctly different composition of lower lime and higher silica and alumina than the darker-to-lighter faded blue pastes, which could be due to excessive leaching of paste at the beige areas leading to loss of lime at the expense of silica and alumina compared to the ubiquitous darker-to-lighter faded blue paste.





Figure 10: Exposed discolored surface of Sapphire Treasure plaster that was in contact with pool water and subsequently developed three color tones – a darker blue tone, which has faded into a lighter blue tone, and a beige tone of localized paste especially in contact with aggregate particles.

Oxide variation diagrams of darker and lighter blue pastes and localized beige toned pastes at aggregate surfaces show overall compositional similarities of darker to lighter faded blue pastes where darker paste at the locations of Probe# 2, 5, 11, 12, and 15 are more compositionally homogeneous than the lighter faded blue paste at the locations of Probe# 4, 13, 14, 16, and 17 (faded paste shows a slightly more spread) in the lime, alumina, and silica plots.

The beige paste at Probe# 1, 3, and 6 to 10, however, shows a distinctly different composition of higher iron, silica, magnesia, and alumina than the darkerto-lighter faded blue pastes, which could be due to excessive leaching of lime in the beige areas leading to enrichment of silica, alumina, and iron compared to the ubiquitous darker-to-lighter faded blue paste.





Figure 11: Exposed discolored surface of Sapphire Treasure plaster that was in contact with pool water and subsequently developed three color tones – a darker blue tone, which has faded into a lighter blue tone, and a beige tone of localized paste especially in contact with aggregate particles.

Oxide variation diagrams of darker and lighter blue pastes and localized beige toned pastes at aggregate surfaces show overall compositional similarities of darker to lighter faded blue pastes where darker paste at the locations of Probe# 2, 5, 11, 12, and 15 are more compositionally homogeneous than the lighter faded blue paste at the locations of Probe# 4, 13, 14, 16, and 17 (faded paste shows a slightly more spread) in the lime, alumina, and silica plots.

The beige paste at Probe# 1, 3, and 6 to 10, however, shows a distinctly different composition of lower lime due to lime leaching but similar sulfate contents as the darker-to-lighter blue paste but overall higher silica and alumina and lower lime and magnesia than the darker-to-lighter faded blue pastes, which are again due to excessive leaching of lime in the beige areas leading to enrichment of silica, alumina, and iron (without necessarily changing the sulfate contents) compared to the ubiquitous darker-to-lighter faded blue paste.





Figure 12: Exposed discolored surface of Sapphire Treasure plaster that was in contact with pool water and subsequently developed three color tones – a darker blue tone, which has faded into a lighter blue tone, and a beige tone of localized paste especially in contact with aggregate particles. In this Figure, chemical compositions of various aggregate particles are determined from SEM-EDS. Particles are lime-sodium-silicate glass, which is mostly dark blue in color, crushed dolomitic marble which are light to medium brown, and calcareous seashell particles, which are white to off-white. Contrary to these variations in aggregate compositions in the Sapphire Treasure sample, plaster in the Blue Ocean sample contains more uniform crushed basalt volcanic rocks. See Appendix for more photos.





Figure 13: Grainsize distribution of exposed aggregate particles on the discolored surfaces of Sapphire Treasure (left) and Blue Ocean (right) plasters where aggregate particles in the former are lighter colored (white, off-white, brown, blue, light gray) crushed marble, seashell, quartz, quartzite, chert, and glass, whereas in the Blue Ocean plaster, aggregate particles are darker gray mostly basalt volcanic rocks and trace seashell particles. Grain size distribution plots of aggregates show relatively finer size and better grading of particles in the Blue Ocean plaster.





White Arrows = Shrinkage Microcracks, Crushed Basalt Aggregate

Figure 14: Stereo-micrographs (top row), and thin section micrographs (middle and bottom rows) of the exposed discolored plaster surface of Primera Stone Blue Ocean showing blotchy discoloration of exposed surface consisting of (i) fading of blue color from darker to lighter blue (marked in dashed red arrows), and (ii) extreme fading to beige gray discoloration of paste mostly around light gray, white, off-white, and blue crushed exposed aggregate particles (marked in yellow arrows). Thin section micrographs show numerous fine hairline shrinkage microcracks (marked in white arrows, common in many plasters containing calcium chloride accelerator, many containing secondary calcite precipitates from pool water migration and evaporation through the microcracks), and darker to lighter blue paste from differences in paste porosities resulted from differential leaching of paste by the pool water. See Appendix for more photos.



### PLASTER DISCOLORATION DUE TO INTERACTIONS WITH POOL WATER



Figure 15: Stereo-micrographs (top row), and thin section micrographs (middle and bottom rows) of vertical cross section of Primera Stone Sapphire Treasure showing soft, crumbly, and noticeably porous paste at the top 2 to 3 mm (within the boxed area in the top row) due to leaching of calcium hydroxide component of Portland cement hydration and calcium chloride accelerator added in the plaster. Corresponding thin section micrographs in the middle and bottom rows show noticeably porous paste at the surface region (above the white dashed lines) compared to variably dense paste in the interior, and some fine, hairline vertical shrinkage microcracks marked with yellow or white arrows (common in many plasters containing calcium chloride accelerator), and darker to lighter blue paste from differences in paste porosities resulted from differential leaching of paste by the pool water. See Appendix for more photos.





Figure 16: Stereo-micrographs (top row), and thin section micrographs (middle and bottom rows) of vertical cross section of Primera Stone Blue Ocean showing soft, crumbly, and noticeably porous paste at the top 1 to 2 mm (within the boxed area in the top row) due to leaching of calcium hydroxide component of Portland cement hydration and calcium chloride accelerator added in the plaster. Corresponding thin section micrographs in the middle and bottom rows show noticeably altered paste at the surface region (marked as carbonated zone at '1' and underlying leached zone at '2' then carbonated and porous paste at '3' above white dashed line separating surface altered and porous paste from interior), and some fine, hairline vertical shrinkage microcracks marked with yellow or white arrows (common in many plasters containing calcium chloride accelerator), and darker to lighter blue paste from differences in paste porosities resulted from differential leaching of paste by the pool water. See Appendix for more photos.



### SEM-EDS STUDIES OF POOL-PLASTER INTERACTIONS



Figure 17: Backscatter electron (BSE) images and X-ray microanalyses of paste at the vertical cross sections of Primera Stone Blue Ocean plaster from the discolored exposed surface at the top ends of the images through depth to the interior to determine the compositional variations of plaster pastes from interactions with the pool water. Compositions of pastes are analyzed at the tips of callouts and in boxed areas, and, results are provided as major element oxide variations in the Tables beneath the images. In the BSE images, variations in paste porosities and compositions are portrayed by corresponding variations in gray scales of images. Notice the darker paste appearance at the very top exposed surface ends due to leaching of calcium hydroxide and calcium chloride from the paste by the pool water that has increased the paste porosities as we have seen in the optical micrographs. A layer of secondary calcite precipitate formed either on the exposed surface at the very top as a thin (< 1 mm thick) scale (not seen in these images, but shown in many other images in the Appendix), or, immediately beneath the leached surface as a thin carbonate layer shown in the left and middle BSE images. Right BSE image shows a leached paste at the top surface region where it appeared dark gray compared to denser brighter gray paste in the interior. Compositional variations show loss of CaO with an increase of  $SiO_2$  due to leaching, along with a loss of sulfate (as  $SO_3$ ) from the leached zone and magnesia, where the last two components were derived more from the pigments used than from cement hydration products. Therefore, leaching of not only paste to increase paste porosity but also of pigment components is seen at the leached surface zones of plaster. Similar features are seen in the Sapphire Treasure plaster at the exposed surface ends. The next Table and compositional plots show variations in plaster paste compositions due to interaction with the pool water. As opposed to a homogeneous composition of the paste without any pool water interactions, paste from the exposed leached surface region to interior show linear or other compositional variations of oxide compositions due to pool water interactions.



Compositional Variations of Paste In Sapphire Treasure &												
Blue Ocean Plaster - From Exposed Surface to Interior												
		ceun	i ias		1011		0500	ourr	ace	0 1110	error	
		CaO	SiO2	AI2O3	Na2O	MgO	SO3	K2O	TiO2	FeO	P2O5	Total
Sapphire	Surface	39.53	38.01	17.34	0.42	2.95	0.43	0.13	0.30	0.89	0.00	100
Sapphire	Surface	65.10	22.86	4.23	0.24	4.85	0.84	0.03	0.23	1.64	0.00	100
Sapphire	Surface	37.55	41.44	6.54	0.62	13.16	0.32	0.06	0.09	0.22	0.00	100
Sapphire	Interior	22.85	56.06	7.87	0.46	9.79	2.27	0.12	0.20	0.40	0.00	100
Sapphire	Interior	37.97	41.74	7.31	0.48	9.39	2.54	0.03	0.01	0.53	0.00	100
Sapphire	Interior	43.85	36.15	6.55	0.49	9.02	2.40	0.03	0.00	1.51	0.00	100
Sapphire	Interior	43.98	36.08	6.38	0.53	8.79	3.09	0.10	0.19	0.87	0.00	100
Blue Ocean	Surface	43.57	36.94	8.90	0.00	5.84	0.41	0.00	0.27	1.34	-	98.1
Blue Ocean	Surface	64.96	22.34	3.85	0.78	3.15	0.90	0.08	0.07	3.15	-	100
Blue Ocean	Surface	48.62	37.76	5.90	0.61	5.85	0.47	0.09	0.00	0.69	-	100
Blue Ocean	Surface	18.14	48.92	12.56	0.57	17.02	0.12	0.03	0.22	2.42	0.00	100
Blue Ocean	Surface	31.47	43.17	9.44	0.35	12.55	0.77	0.06	0.81	0.89	0.49	100
Blue Ocean	Surface	15.55	54.11	12.05	0.70	16.64	0.00	0.00	0.04	0.56	0.36	100
Blue Ocean	Surface	33.02	44.15	8.01	0.48	13.07	0.57	0.01	0.00	0.44	0.25	100
Blue Ocean	Surface	29.58	43.40	8.56	0.61	15.09	1.02	0.00	0.48	1.00	0.26	100
Blue Ocean	Surface	5.25	65.19	11.60	0.44	14.97	1.25	0.02	0.21	0.66	0.41	100
Blue Ocean	Surface	47.40	30.47	4.52	0.50	15.32	0.80	0.00	0.07	0.73	0.19	100
Blue Ocean	Surface	79.28	12.37	1.05	0.17	5.56	0.90	0.00	0.10	0.27	0.00	100
Blue Ocean	Surface	29.60	42.27	7.25	0.37	17.87	1.39	0.10	0.20	0.95	0.01	100
Blue Ocean	Surface	31.68	43.72	8.04	0.29	13.29	1.52	0.09	0.19	1.14	0.03	100
Blue Ocean	Surface	32.59	39.44	6.22	0.47	19.92	0.60	0.00	0.03	0.73	0.00	100
Blue Ocean	Interior	79.29	12.80	1.36	0.34	2.57	1.19	0.00	0.06	0.94		100
Blue Ocean	Interior	70.53	17.86	2.21	0.44	4.25	1.24	0.01	0.30	2.31	-	100
Blue Ocean	Interior	35.19	42.58	6.01	0.61	11.59	2.55	0.03	0.22	1.03	-	100
Blue Ocean	Interior	34.10	42.56	5.87	0.44	13.52	2.39	0.16	0.37	0.44	-	100
Blue Ocean	Interior	37.49	41.40	5.41	0.58	12.02	2.25	0.06	0.36	0.00	-	100
Blue Ocean	Interior	45.94	29.54	10.00	0.96	1.28	11.36	0.16	0.04	0.71		100
Blue Ocean	Interior	42.34	39.02	5.74	0.40	7.38	3.87	0.08	0.11	1.00	-	100
Blue Ocean	Interior	48.59	37.83	6.27	1.05	2.85	2.54	0.16	0.26	0.31	-	100
Blue Ocean	Interior	61.49	27.20	5.08	1.34	2.44	1.80	0.00	0.20	0.42		100
Blue Ocean	Interior	51.13	27.35	3.13	0.31	15.09	0.84	0.00	0.13	1.43	0.58	100
Blue Ocean	Interior	35.21	37.98	3.57	0.09	21.79	0.40	0.00	0.23	0.62	0.10	100
Blue Ocean	Interior	22.76	45.77	6.04	0.01	23.29	0.61	0.00	0.02	1.34	0.15	100
Blue Ocean	Interior	36.04	32.17	5.57	0.05	15.38	5.04	0.00	1.80	0.81	0.00	96.9
Blue Ocean	Interior	38.70	37.56	3.60	0.38	18.08	0.93	0.01	0.18	0.44	0.13	100
Blue Ocean	Interior	11.37	56.31	5.93	0.00	25.80	0.31	0.01	0.00	0.12	0.16	100
Blue Ocean	Interior	26.10	47.43	6.87	0.22	16.94	0.89	0.00	0.07	1.41	0.06	100
Blue Ocean	Interior	58.41	27.75	4.83	0.54	1.59	5.77	0.06	0.23	0.65	0.17	100
Blue Ocean	Interior	55.13	28.05	5.18	0.85	3.41	6.19	0.00	0.07	0.75	0.38	100
Blue Ocean	Interior	70.85	18.14	2.38	0.38	1.19	4.84	0.00	0.06	1.88	0.29	100
Blue Ocean	Interior	61.78	21.71	4.03	0.38	0.89	9.95	0.00	0.00	0.98	0.27	100

Figure 18: Oxide compositional variations of plaster paste at the surface regions to the interior of Sapphire Treasure and Blue Ocean plasters due to interaction with pool water. Components marked in colors are most susceptible to variations due to pool water interactions.





Figure 19: Oxide compositional variations of plaster paste at the surface regions to the interior of Sapphire Treasure and Blue Ocean plasters due to interaction with pool water. The linear trend at the top and large spread at the bottom plots are indicative of strong interactions of pool water with plaster, without which paste compositions would have been homogenous i.e., without any trend or spread.





Figure 20: Oxide compositional variations of plaster paste at the surface regions to the interior of Sapphire Treasure and Blue Ocean plasters due to interaction with pool water. The linear trend at the top and large spread at the bottom plots are indicative of strong interactions of pool water with plaster, without which paste compositions would have been homogenous i.e., without any trend or spread.



### PLASTER KITS, CEMENT, AND PIGMENTS

Thin Section of Plaster Kit 1830 – Dry Powder Components That Make Up Primera Sapphire Treasure Crushed Marble, Chert, Quartzite, Glass in Blended Cement



Figure 21: Optical and scanning electron (backscatter electron, BSE) micrographs of epoxyencapsulated thin section (30 micron thickness) of 1830 Plaster kit consisting of crushed aggregate of marble, seashell, sodium-calcium-silicate glass, chert, quartzite, quartz, etc. and white Portland cement binder containing abundant alite, subordinate belite, free lime, and trace gypsum components some of which are analyzed at the tips of callouts in the BSE image and shown in the Table beneath. The boxed area on one crushed glass aggregate showed the composition in Probe# 1.

The plaster kit reportedly contains in a 5 lbs. bucket, 2.81 lbs. aggregate, 2.2 lbs. white Portland cement, to which water is added at water-to-cement ratio of 0.42 to 0.50 by mass, and calcium chloride flake accelerator is added (during cold weather plastering) to the water at 0.044 pounds for 5-pound kit.



Thin Section of Plaster Kit 1831 – Dry Powder Components That Make Up Primera Blue Ocean Crushed Basalt in Blended Cement



Plaster Kit 1831 Primera Blue Ocean

1 4 7 Basalt												
CMC, Inc. 20.0 KV EM Mag 170X Captured by Dipayan Jana			BSE Image & EDS Compositional At The Tips of Callouts & In The B					l Analy Boxed	/ses Areas	200nm		
Probe	CaO	SiO2	Al2O3	Na2O	MgO	503	K20	TiO2	FeO	Mn2O3	Total	Phase
1	65.11	32.70	0.68	0.00	1.11	0.06	0.00	0.04	0.16	0.14	100.0	Alite
2	78.12	13.96	6.06	0.00	1.08	0.00	0.01	80.0	0.41	0.28	100.0	Alite
3	76.91	20.08	1.22	0.17	1.13	0.24	0.00	0.15	0.11	0.00	100.0	Alite
4	40.37	0.00	0.00	0.24	0.00	59.22	0.05	0.05	0.08	0.00	100.0	Gypsum
5	76.93	20.77	0.57	0.08	0.87	0.15	0.12	0.24	0.08	0.19	100.0	Alite
6	56.92	37.76	2.41	0.21	0.76	1.15	0.37	0.29	0.12	0.00	100.0	Alite
( <b>7</b> )	10.81	53.72	17.27	4.18	4.84	0.00	1.79	2.27	4.94	0.18	100.0	Basalt

#1831 Patch Kit – In 5 lbs. kit: Aggregate 2.81 lbs., White PC 2.20 lbs., Add to the patch kit Calcium Chloride 0.044 lbs., Water-cement ratio 0.42 to 0.50 Figure 22: Optical and scanning electron (backscatter electron, BSE) micrographs of epoxyencapsulated thin section (30 micron thickness) of 1831 Plaster kit consisting of crushed basalt aggregate containing anhedral to subhedral pyroxene (augite, diopside), subhedral lath-shaped plagioclase (albite, oligoclase), anhedral dark iron-titanium oxide interstitial glass grains, in porphyritic texture arrangement typical of basalt, and, white Portland cement binder having abundant alite, subordinate belite, and trace gypsum components some of which are analyzed at the tips of callouts in the BSE image and shown in the Table beneath. The boxed area on one crushed basalt aggregate showed the composition in Probe# 7.

The plaster kit reportedly contains in a 5 lbs. bucket, 2.81 lbs. aggregate, 2.2 lbs. white Portland cement, to which water is added at water-to-cement ratio of 0.42 to 0.50 by mass, and calcium chloride flake accelerator is added (during cold weather plastering) to the water at 0.044 pounds for 5pound kit.







Figure 23: Optical and scanning electron (backscatter electron, BSE) micrographs of epoxyencapsulated thin section (30 micron thickness) of 1835 Plaster kit consisting of crushed basalt aggregate containing anhedral to subhedral pyroxene (augite, diopside), subhedral lath-shaped plagioclase (albite, oligoclase), nepheline (determined from XRD), anhedral dark iron-titanium oxide grains, interstitial glass in porphyritic texture arrangement typical of basalt, and, white Portland cement binder having abundant alite, subordinate belite, and trace gypsum components some of which are analyzed at the tips of callouts in the BSE image and shown in the Table beneath. The boxed area on one crushed basalt aggregate showed the composition in Probe# 5.

The plaster kit reportedly contains in a 5 lbs. bucket, 2.81 lbs. aggregate, 2.2 lbs. white Portland cement, to which water is added at water-to-cement ratio of 0.42 to 0.50 by mass, and calcium chloride flake accelerator is added (during cold weather plastering) to the water at 0.044 pounds for 5-pound kit.



98.95

0.37

0.00

0.11

0.09

0.36

0.00

Swimming Pool Plaster Discoloration

#### Thin Section of 1834 - Dry Powder Lehigh Blended Cement Added At Jobsite WPC+LF Plaster Cement 1834 Lehigh Blended Cement CMC, Inc. 20.0 KV EM Mag 740X Captured by Dise **BSE Image & EDS Compositional Analyses** 200nm At The Tips of Callouts & In The Boxed Areas by Dipavan Jana SHO2 AI2O3 Mn2O3 Na2O TiO2 Total CaO MgO SOB 120 FeO Phase 1 79.09 19.33 0.87 0.00 0.63 0.01 0.00 0.07 0.00 0.00 100.0 Alite 2 68.82 25.40 3.64 0.00 0.30 1.47 0.04 0.12 0.07 0.15 100.0 Alite 3 70.51 27.30 0.64 0.02 0.64 0.21 0.00 0.00 0.42 0.25 100.0 Alite 4 Alite 75.96 19.30 0.00 0.96 0.00 0.05 0.19 100.0 3.24 0.10 0.19 5 81.12 17.80 0.35 0.00 0.56 0.00 0.00 0.00 0.09 0.07 100.0 Alite 6 58.50 37.99 1.58 0.20 0.44 0.95 0.29 0.05 0.00 0.00 100.0 Alite 66.03 21.45 0.70 1.99 6.55 0.39 0.32 0.27 1.03 100.0 Alite 1.26

0.03

0.00

0.10 100.0 Lst. Fine

Figure 24: Optical and scanning electron (backscatter electron, BSE) micrographs of epoxyencapsulated thin section (30 micron thickness) of 1834 Lehigh blended cement reportedly added at the jobsite, which consists of white Portland cement binder abundant having alite. subordinate belite, and trace gypsum components, and some limestone fine components having the fineness of Portland cement, some of which are analyzed at the tips of callouts and in boxed areas in the BSE image and shown in the Table beneath.



CONSTRUCTION MATERIALS CONSULTANTS, INC.

Swimming Pool Plaster Discoloration



Figure 25: Backscatter electron micrographs (top) of the Mediterranean Pigment (left) and Midnight Pigment (right) showing the presence of barium sulfate as a major component and source of sulfate, along with iron oxide-based composition of Mediterranean Pigment in 1832 as opposed to iron-chromium oxide-based composition of Midnight Pigment in 1833.



# LABORATORY-CURED HARDENED PLASTERS WITH AND WITHOUT CACL<sub>2</sub> IMMERSED IN AGGRASSIVE AND BALANCED WATERS



Figure 26: Laboratory-cured hardened plaster kits 1831, 1831, and 1835 prepared with and without calcium chloride set accelerator addition to the mix water, which were subsequently immersed in aggressive (tap) water and balanced (calcium hypochlorite) waters for 7 days. Shown are the solid sections in the middle and thin sections in PPL and XPL modes at left and right, respectively.





Figure 27: Micrographs of thin sections of hardened pastes of three plaster kits *without* CaCl<sub>2</sub> addition and after immersion in tap water and calcium hypochlorite disinfectant solution showing the following:

- a. Three hardened plaster kits# 1830, 1831, and 1835 without CaCl<sub>2</sub> addition (top row) showed typical mineralogies of residual calcium silicates (alite and belite) from white Portland cement, and limestone fine microfillers (mostly for kit# 1830 and 1831) as seen in their dry microstructures except having an overwhelming matrix of calcium silicate hydrate hydration products of cement on which the residual cement grains are scattered, fine-grained short prismatic or lath-shaped grains of water-soluble calcium hydroxide component of cement hydration, sometimes appearing as coarsely crystalline laths in air voids.
- b. The same three hardened plaster kits# 1830, 1831, and 1835 without CaCl<sub>2</sub> addition after 7 days of immersion in tap water (middle row) showed the *aggressive nature and action of tap water* on all three plasters as dissolution of soluble component (calcium hydroxide component of cement hydration) from the plaster and its precipitation as coarsely crystalline dog tooth-shaped subhedral to euhedral grains of secondary calcite precipitates on the exposed surfaces of all three plasters.
- c. By contrast, immersion of three hardened plasters without CaCl<sub>2</sub> addition in a calcium hypochlorite disinfectant solution (bottom row) showed the **balanced action of the solution** with localized dissolution of paste especially along the surface hairline microcracks but no appearance of any secondary calcite scales on the exposed surfaces.





Figure 28: Micrographs of thin sections of hardened pastes of three plaster kits *with* CaCl<sub>2</sub> addition and after immersion in tap water and calcium hypochlorite disinfectant solution showing the following:

- a. Addition of CaCl<sub>2</sub> accelerator in the mix water during preparation of hardened plasters from kit# 1830, 1831, and 1835 showed no major difference in microstructure compared to the companion CaCl<sub>2</sub>-free ones. There is no evidence of any increase in the frequency of fine hairline drying shrinkage microcracks that are present in all hardened plasters irrespective of CaCl<sub>2</sub> addition. All three hardened plaster kits showed typical mineralogies of residual calcium silicates (alite and belite) from white Portland cement, and limestone fine microfillers (mostly for kit# 1830 and 1831) as seen in their dry microstructures except having an overwhelming matrix of calcium silicate hydrate hydration products of cement on which the residual cement grains are scattered, fine-grained short prismatic or lath-shaped grains of water-soluble calcium hydroxide component of cement hydration.
- b. Contrary to significant secondary calcite scales on the exposed surface for kits immersed in tap water without any CaCl<sub>2</sub> addition, the present three hardened plasters with CaCl<sub>2</sub> addition showed no scaling of precipitation of secondary calcite on the exposed surfaces of any kit. Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 and 1831 with calcium chloride accelerator immersed in tap water for 7 days showed abundant residual alite grains, and subordinate limestone fines in paste with the cement hydration products overall giving an appearance of a masonry cement paste, along with some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. There are evidence of localized dissolution of paste, especially in near-surface region or along fine microcracks but no surface scaling. Kit# 1835 also showed no surface scaling on the exposed sides.
- c. Similar microstructures of localized dissolution but no surface scaling is found when the CaCl<sub>2</sub> doped kit were immersed in calcium hypochlorite disinfectant solution. Abundant coarse lath-shaped secondary calcium hydroxide deposits in air voids in all three kits indicates high solubility of this component of white Portland cement hydration.



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Swimming Pool Plaster Discoloration

### DISCUSSIONS

### THEORIES ON CAUSES OF DISCOLORATION OF POOL PLASTER

Potenti	al Cause	d For Discoloration of Swimming Pool Plaster
Plaster Materials	1. 2. 3. 4. 5.	High water-cement ratio (w/c) of plaster mix which increases porosity and permeability of paste; variation in w/c can cause color variations of finished plaster Addition of calcium chloride accelerator, which (a) is soluble in pool water (whether balanced or aggressive) and can dissolve out (as much as one forth of the added amount) to create a porous paste, (b) can delay hydration of ferrite phase to develop blotchy or mottled discoloration, and (c) can increase shrinkage microcracking in paste. Addition of organic or inorganic pigment dyes in plaster mix where former is cheaper and more soluble than latter but even inorganic dyes can leach out in aggressive water, or, during normal lime and calcium chloride leaching from a balanced water. Organic pigments can be bleached by the presence of chlorine or other oxidizers, and even by the sun. Pigments are usually recommended not to be added especially when calcium chloride is added. Contaminants in sand, e.g., iron sulfide which can cause rust stains Difference in moisture contents beneath the plaster surface and/or substrate
Plaster Finishing, Curing, Maintenance	6. 7. 8. 9.	The presence of ground granulated blast furnace slag as a cementitious component in plaster can cause bluish green to beige/gray discoloration due to differentiation oxidation of slag cement paste Late hard troweling, over-troweling (trowel burn), and/or, addition of water during trowel finishing can increase porosity of paste at the exposed surface. Avoid overly late hard troweling and having to add lots of water to the surface to make it more pliable for troweling. Water troweling is a detrimental practice that severely weakens and creates undesirable surface porosity and shrinkage cracks. Prolonged presence of pool water at a low level after a partial drainage to develop a darker hue on the aerated portion and a lighter hue on the underwater portion Corrosion of steel reinforcement in the substrate to bring corrosion stains to the exposed plaster surface
Pool Water Chemistry	10.	Out-of-balance water (an overly positive Langelier Saturation Index or LSI value) can dissolve (leaching, etching) and precipitate plaster constituents as a uniform thin layer or crust (scaling) of calcium carbonate throughout the pool and whitens the pool. A scaled plaster is generally rough to the touch, which can be easily removed by scraping, sanding or acid wash. An etched porous plaster, however, cannot be restored due to the loss of materials creating increased porosity and, thereby, discoloration from lightening of color. Aggressive pool water can dissolve calcium hydroxide component of cement hydration and calcium chloride accelerating admixture to increase porosity of paste at the exposed surface with a white discoloration. If the discoloration is smooth to the touch, manifests itself in streaks, blotches, or small spots, and if diluted acid does not quickly remove the white discoloration, then the problem is probably not calcium carbonate scaling but a porous surface instead that leads to rapid deteriorations.

Figure 29: Various theories on causes of discoloraiton of pool plaster that are broadly classified into three categories of discoloraiton due to plaster ingredients, installation practices, and, interactions with pool water (water chemistry). All these theories were evaluated for investigation of plaster discoloration in the present case.


Swimming Pool Plaster Discoloration

#### PLASTER DISCOLORATION

Two types of discoloration of exposed surfaces of plaster samples are seen in both Primera Stone Sapphire Treasure and Blue Ocean samples. These are:

- a. Darker to faded lighter blue discoloration of plaster, which occupies the majority of the interstitial spaces between the exposed aggregate particles, and,
- b. More localized medium gray to beige discolored patches of plaster mostly occurring at the edges of many exposed aggregate particles.

SEM-EDS analyses of all three color tones of exposed plaster surfaces from (a) darker blue hue to (b) faded lighter blue hue, and (c) more localized beige toned paste in the Sapphire Treasure plaster showed:

- a. Overall compositional similarities of darker-to-faded lighter blue toned paste where the darker toned plaster showed more uniform i.e., restricted chemical composition than a little more spread in compositions in the faded blue toned areas (though still restricted compared to the beige toned paste), which, are, however, distinctly different than
- b. Localized beige toned paste occurring mostly at the surfaces of exposed aggregate particles.

Compared to the darker-to-faded lighter blue plaster surfaces, the beige toned areas show the following compositional differences, which are depicted in Figures 9, 10, and 11:

- a. The beige paste shows lower lime and higher silica and alumina than the darker-to-lighter blue pastes, which could be due to excessive leaching of paste at the beige areas leading to loss of lime at the expense of silica and alumina compared to the ubiquitous darker-to-lighter blue paste.
- b. The beige paste shows higher iron, silica, magnesia, and alumina than the darker-to-lighter blue pastes, which could be due to excessive leaching of lime in the beige areas leading to enrichment of silica, alumina, and iron compared to the ubiquitous darker-to-lighter blue paste.
- c. The beige paste shows lower lime due to lime leaching but similar sulfate contents as the darker-to-lighter blue paste but overall higher silica and alumina and lower lime and magnesia than the darker-to-lighter blue pastes, which is again due to excessive leaching of lime in the beige areas leading to enrichment of silica, iron, and alumina (without necessarily changing the sulfate contents) compared to the ubiquitous darker-to-lighter blue paste.

These results are consistent with the conclusion that the darker-to-lighter blue color variations of plaster surface in the interstitial spaces between the exposed aggregate particles are more due to variations in underlying porosities of paste from darker to lighter blue areas as opposed to any noticeable variation in chemical compositions. The lighter blue areas are more porous hence reflected more light to appear in lighter hues than the denser and darker blue areas. These variations in darker-to-lighter blue areas are the results of differential leaching of inherent calcium



hydroxide and calcium chloride components of plaster to cause variations in near-surface porosities of paste and subsequent variations in hues. The more localized beige areas, however, show excessive lime leaching to the point of depleting the lime at the expense of silica, alumina, and iron (without affecting the sulfate) compared to the ubiquitous darker-to-faded lighter blue interstitial areas of paste.

Results obtained from exposed surface of Sapphire Treasure plaster sample are consistent with the exposed surface of Blue Ocean plaster. Both field samples showed the ubiquitous darker-to-lighter blue discoloration in the interstitial paste between the exposed aggregate particles, as well as localized beige discoloration around exposed aggregates due to excessive leaching of lime at the expense of other elements. The only difference between the two plasters is in their aggregates, which are a mixed lime-sodium-silica glass (dark blue), crushed dolomitic marble (medium brown), seashell (white to off-white), etc. which are shown in Figures 7, 8, and 11, and many of which are determined by SEM-EDS in Figure 12, whereas aggregate in Blue Ocean plaster is more uniform i.e., crushed basalt volcanic rocks, which are shown in Figures 14 and 16.

#### PRIMERA STONE POOL PLASTER – SAPPHIRE TREASURE

The Sapphire Treasure field plaster sample consists of: (a) crushed aggregates of light brown to off-white marble, white to off-white seashell, light gray crushed quartz, quartzite and chert, and blue sodium-calcium-silicate glass (Figures 6, 12, and 13); (b) a hardened paste consisting of major amount of white Portland cement, and subordinate limestone fines having the fineness of Portland cement, which appear in similar mineralogy and microstructure to a masonry cement paste (possibly with some hydrated lime as well); (c) a reported Mediterranean iron oxide pigment; and (d) calcium chloride accelerator reportedly added to the mix water. Aggregate particles are nominal 4.75 mm in size (finer than US Sieve No. 4, longest dimension is 6 mm), poorly graded but well sorted due to the dominance of certain grain sizes, well-distributed in most vertical cross sections and present in sound conditions. The blue color crushed sodium-calcium-silicate glass particles in the aggregate are found to be present in sound condition without any evidence of any potentially deleterious alkali-silica reaction. Figures 7, 8, and 15 show optical micrographs of field sample of Sapphire Treasure. Appendix Figures A 12 to A 17 provide numerous optical micrographs (stereo-micrographs and thin section micrographs) of discolored exposed surface of Sapphire Treasure plaster, and, Figures A 31 to A 38 provide optical micrographs (stereo-micrographs and thin section micrographs (stereo-micrographs of discolored Sapphire Treasure plaster.

#### PRIMERA STONE POOL PLASTER – BLUE OCEAN

The Blue Ocean field plaster sample consists of: (a) medium gray crushed basalt volcanic rock containing anhedral to subhedral pyroxene (augite, diopside), lath-shaped subhedral grains of plagioclase, anhedral dark iron-titanium oxide, and interstitial glass in a porphyritic texture, and a trace amount of seashell (Figures 6 and 13); (b) a hardened paste consisting of major amount of white Portland cement, and subordinate limestone fines having the fineness of Portland cement, which appear in similar mineralogy and microstructure to a masonry cement paste (possibly with



some hydrated lime as well) as well as the paste found in the Sapphire Treasure field plaster and in plaster kits# 1830 and 1831; (c) a reported Midnight iron-chromium oxide pigment; and (d) calcium chloride accelerator reportedly added to the mix water. Aggregate particles are nominal 4.75 mm in size (finer than US Sieve No. 4, longest dimension is 6 mm), relatively better graded than the aggregates in Sapphire Treasure plaster (Figure 6) due to better spread in size ranges of particles encountered, well-distributed in most vertical cross sections, and present in sound conditions. Figures 14 and 16 show optical micrographs of field sample of Blue Ocean. Appendix Figures A 45 to A 51 provide numerous optical micrographs (stereo-micrographs and thin section micrographs) of discolored exposed surface of Blue Ocean plaster, and, Figures A 59 to A 66 provide optical micrographs (stereo-micrographs and thin section micrographs) of vertical cross sections of discolored Blue Ocean plaster.

#### EVIDENCE OF LEACHING AND INCREASED PASTE POROSITY

Exposed discolored surfaces of both field plasters as well as their vertical cross sections show evidence of leaching of paste (e.g., of calcium hydroxide component of white Portland cement hydration, and calcium chloride accelerator) resulting in localized beige discoloration of paste on the exposed surfaces as well as increased porosity from the loss of mass on the vertical cross sections immediately beneath the exposed surfaces.

Figures 8 to 11 show evidence of leaching of lime in the beige discolored areas of exposed surface of Sapphire Treasure plaster in the oxide variation diagrams where depleted lime and enriched silica, alumina, and iron in the localized beige discolored areas compared to the overwhelming darker to lighter blue areas of paste are clear. Similar trends are present in the beige discolored areas on the exposed surface of Blue Ocean plaster (Figure 14).

Figures 15 and 16 show stereo-micrographs and thin section micrographs of vertical cross sections of Sapphire Treasure and Blue Ocean plasters, respectively where the surface regions of both field plaster show clear evidence of (a) increased porosity due to loss of materials by the pool water, and (b) a lighter fading of the plaster color tone at the leached zone from the interior plaster. Appendix Figures A 31 to A 33 (stereo-micrographs), and A 35 (thin section micrograph) show vertical cross sections of Sapphire Treasure where leaching of paste at the surface and increased paste porosity are shown. Appendix Figures A 59 to A 61 (stereo-micrographs) and A 63 to A 66 (thin section micrographs) show similar microstructures of increased porosity of paste on cross sections of Blue Ocean plaster with zoned alterations of near-surface paste from carbonated to leached to interior carbonated zones.

Backscatter electron images and microanalyses of paste in vertical cross sections of plasters in Figure 17 show various surface alterations of plaster paste compositions compared to the interior, e.g., from leaching of lime to precipitation of lime beneath the leached zone as a narrow band of secondary calcite precipitate or on the exposed surface as a thin film (scale). Appendix Figure A 39 shows leaching at the surface region whereas A 40 to A 42 show precipitation of thin secondary calcite layer (scale) on the exposed surface of Sapphire Treasure. Figures A 67 to A 72 show leaching and precipitation of secondary calcite beneath the leached surface region on vertical cross section of Blue Ocean plaster.



Swimming Pool Plaster Discoloration

#### EVIDENCE OF LEACHING OF PIGMENT

Since barium sulfate is found to be present as a stabilizer in both pigment samples (#1832 and #1833) provided (Figure 25), the high sulfate contents in the pastes found in both field plaster samples i.e., higher than the sulfate contributed from white Portland cement is determined to be from the pigments where the large spread in the sulfate contents of paste in Figure 19 compositional plot of pastes on vertical cross sections of both plasters from the leached surface regions to the interiors are testaments of leaching of pigments along with paste. Addition of calcium chloride accelerator is commonly known to enhance leaching of pigments, which is noted in both plasters from large spread of sulfate variations across the vertical cross sections as well as relatively lower sulfate results at the leached zones of plasters than the interiors.

#### SHRINKAGE MICROCRACKING OF POOL PLASTER

Extensive fine hairline shrinkage microcracks are found on the exposed discolored surfaces as well as vertical cross sections of both plasters. Numerous stereo-micrographs of solid surfaces, thin section micrographs, and electron micrographs in the Appendix of exposed surfaces and vertical cross sections of field plasters show those microcracks. *Addition of calcium chloride accelerating admixture is commonly known to increase the frequency of microcracking in pool plaster above and beyond the microcracks form from drying of cement paste prior to the pool water immersion, which, however, is not found in the present study of laboratory-cured hardened plasters with or without CaCl<sub>2</sub> addition.* 

#### CALCIUM CARBONATE SCALE AND NEAR-SURFACE PRECIPITATION

The Blue Ocean plaster showed localized thin film of secondary calcium carbonate precipitate on the exposed surface as scale, which is a testament of aggressive action of the water at this plaster. Both field plasters show near-surface secondary calcium precipitate beneath the leached zone at the intersection between the porous leached zone and interior dense zone. These deposits are *testaments of interaction of plaster with the pool water that has caused dissolution of soluble components (calcium hydroxide, calcium chloride) of plaster followed by precipitation from the water either on the exposed surface or beneath the near-surface leached zone.* 

#### PRIMERA STONE PLASTER KITS, CEMENT, AND PIGMENTS

Plaster Kit# 1830 is reportedly representative of Sapphire Treasure plaster, which consists of (in a 5-lb. kit) 2.81 lbs. of crushed glass, marble, seashell aggregate, 2.21 lbs. of white Portland cement, Mediterranean blue iron oxide pigment, mix water having a water-to-cement mass ratio ranging from 0.42 to 0.50, and optional weather-required calcium chloride set accelerator addition to the mix water at a dosage of 0.044 lbs. per 5 lb. plaster.

Plaster Kit# 1831 and 1835 are reportedly representative of Blue Ocean plaster, which consists of (in a 5-lb. kit) 2.81 lbs. of crushed basalt volcanic rock aggregate, 2.21 lbs. of white Portland cement, Midnight blue iron-



#### Swimming Pool Plaster Discoloration

chromium oxide pigment, mix water having a water-to-cement mass ratio ranging from 0.42 to 0.50, and optional weather-required calcium chloride set accelerator addition to the mix water at a dosage of 0.044 lbs. per 5 lb. plaster.

The Lehigh blended cement #1834 is reportedly a field applied cement containing major amount of white Portland cement and subordinate amounts of limestone fines having the fineness of Portland cement.

The two pigment dyes #1832 and #1833 are iron-oxide and iron-chromium oxide, respectively, added to plaster kits 1830 and 1831/1835, respectively. Both pigments have a barium sulfate extender.

The following Table summarizes chemical compositions of all these plaster ingredients provide by energy-dispersive X-ray fluorescence spectroscopy (EDXRF).

	1830 Kit	1831 Kit	1835 Kit	1834 Kit
Oxides	Sapphire Treasure	Blue Ocean	Blue Ocean	Lehigh White Portland Cement
SiO <sub>2</sub>	32.7	29.9	32.3	18.1
Al <sub>2</sub> O <sub>3</sub>	2.94	9.14	9.28	4.24
CaO	49.1	41.9	37.4	70.5
MgO	1.6	5.91	6.94	1.22
Na <sub>2</sub> O	2.44	2.98	3.14	ND
K <sub>2</sub> O	0.213	0.934	0.971	0.213
Fe <sub>2</sub> O <sub>3</sub>	0.8	8.1	9.01	0.483
TiO <sub>2</sub>	0.0238	2.85	3.3	ND
$P_2O_5$	0.0383	0.288	0.321	0.0415
SO <sub>3</sub>	2.74	2.48	2.35	3.53
Balance	7.42	<0.0001	< 0.0001	1.69
Total	100	104	105	100

XRF analyses of binder phases of plaster kits# 1830 and 1831 and Lehigh white cement showed overall compositional similarity to each other and to the binder found in the Blue Ocean and Sapphire Treasure plasters, but have different compositions from the Sapphire Treasure's 1830 kit in having higher alumna, magnesia, iron, and titanium, and slightly lower silica and lime in the Blue Ocean kits. These chemical variations are judged to be mainly from the difference in aggregate compositions of two plaster types where crushed basalt aggregate in the Blue Ocean plaster kits (#1831 and 1835) has increased the iron-magnesium oxide contents from the iron-magnesium minerals (e.g., pyroxene) and titanium oxide content from iron-titanium oxide grains in basalt. Sulfate contents of all three plaster kits are similar (2.5 to 2.75%), and despite having pigments where barium sulfate found in the Lehigh blended cement (#1834).

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#### Swimming Pool Plaster Discoloration

The following details are provided in the Appendix section of Figures of dry and hardened plaster components that were received with the two field plasters.

- a. Thin section micrographs of Plaster Kit# 1830 showed the presence of crushed marble, glass, seashell, and chert particles in dry white Portland cement (WPC) where the interstitial dry binder shows masonry cement-like appearance in mineralogy and microstructure having major amount of white Portland cement and subordinate amount of limestone fines (Appendix Figures A 79 and A 80, possibly with some hydrated lime as well). SEM-EDS studies (Appendix Figures A 81 to A 83) of aggregates showed marble, Na-Ca-silicate glass, seashell, etc. and binder showed calcium silicates (alite, belite), sulfate (gypsum), and free lime. XRD studies (Appendix Figure A 84) showed major phases of alite, calcite, and quartz from binder and aggregates.
- b. Thin section micrographs of Plaster Kit# 1831 showed the presence of crushed basalt volcanic rock in dry white Portland cement (WPC) where the interstitial dry binder shows similar masonry cement-like appearance in mineralogy and microstructure as seen in kit# 1830 in having major amount of white Portland cement and subordinate amount of limestone fines (Appendix Figures A 85 and A 86, possibly with some hydrated lime as well). SEM-EDS studies (Appendix Figure A87) of aggregates showed the typical basaltic composition, and binder showed calcium silicates (alite, belite), and sulfate (gypsum). XRD studies (Appendix Figure A88) showed major phases of alite from binder, and pyroxene (augite, diopside), plagioclase (oligoclase, albite), and iron oxide opaques from crushed basalt aggregate.
- c. Backscatter electron image (BSE) and corresponding X-ray microanalyses of 1832 Mediterranean pigment dye used for Primera Stone Sapphire Treasure plaster showed the presence of a barium sulfate extender, which has appeared as bright spots in BSE image and is responsible for the higher sulfate content of paste in the field plaster samples compared to the sulfate contributed from hydration of Portland cement. The dye showed iron oxide as the main component (Appendix Figure A 89 and A90 for SEM-EDS and A91 for XRD) along with variable other components present in minor amounts.
- d. Backscatter electron image (BSE) and corresponding X-ray microanalyses of 1833 Midnight pigment dye used for Primera Stone Blue Ocean plaster showed the presence of a barium sulfate extender, which appeared as bright spots and is responsible for the higher sulfate content of paste in the field plaster samples compared to the sulfate contributed from hydration of Portland cement. The dye showed iron-chromium oxide as the main component (Appendix Figures A92 and A93 for SEM-EDS and A94 for XRD) along with variable other components present in minor amounts.
- e. Thin section micrographs of Lehigh blended cement (Appendix Figure A95) shows a mixture of major amount of white Portland cement (WPC) and limestone fine particles (LF), having overall mineralogies and microstructures similar to that of a masonry cement made using white Portland cement, and limestone fines (possibly with some hydrated lime as well) which are seen for the binders used in kit# 1830 and 1831. SEM-EDS studies (Appendix Figure A 96) showed calcium silicates (e.g., alite) as the major phase in binder, and calcite as subordinate phase in binder as microfiller, which are also confirmed by the XRD studies (Appendix Figure A 97).

#### Swimming Pool Plaster Discoloration

- f. Thin section micrographs of Plaster Kit# 1835 (Appendix Figure A 98 and A 99) showed the presence of crushed basalt particles (containing anhedral to subhedral pyroxene, subhedral lath-shaped plagioclase, nepheline, and dark opaque grains in porphyritic texture) as seen in kit# 1831 which are dispersed in dry white Portland cement (WPC), but higher amount of rounded belite grains in cement and noticeably negligible amount of limestone fine than the binder in kit# 1830 and 1831. SEM-EDS studies (Appendix Figure A 100) showed calcium silicates (e.g., alite) as the major phase in binder, and typical basaltic composition of aggregate (Appendix Figure A 101), which are also confirmed by the XRD studies (Appendix Figure A 102) showing major phases of alite from white Portland cement, and pyroxene (augite, diopside), plagioclase (albite, oligoclase), and nepheline in basalt aggregate.
- g. XRD pattern (Appendix Figure A 103) of the dry flakes of calcium chloride set accelerator received showed the diffraction patterns of sinjarite (CaCl<sub>2</sub>. 2H<sub>2</sub>O).

#### LABORATORY-CURED PLASTERS WITH AND WITHOUT CALCIUM CHLORIDE ADDITION

The following steps were followed during preparation of laboratory-cured hardened plasters from the three plaster kits with and without calcium chloride (CaCl<sub>2</sub>) accelerating admixtures added. Kits were immersed in tap water and calcium hypochlorite solution.

- a. For laboratory-cured hardened plasters, the three dry plaster kits# 1830, 1831, and 1835 were mixed with water (without or without calcium chloride accelerator), in a laboratory mixer and poured in three layers in 2 in. size cube molds (Appendix Figure A 104).
- b. A mix proportion consisting of 400 grams of plaster, 80 grams of tap water, at a plaster-to-water mass ratio of 0.20 was used. Two sets were prepared, one with tap water only, and the second batch where 80 grams of water was mixed with 17.6 grams of calcium chloride flake.
- c. Plasters with and without set accelerator were cured at 100 percent humidity in the ambient temperature of laboratory for 1 day (Appendix Figure A 105), then demolded, then cured for an additional 7 days (Appendix Figure A 106).
- d. Samples thus prepared were then submerged in tap water and water with calcium hypochlorite disinfectant solutions (Appendix Figure A 107) to observe the discoloration of plasters prepared with and without calcium chloride accelerators.
- e. Finally, thin sections were prepared (Appendix Figure A 108 to A 110, A 114, A 115, A 119, A 120, A 124, and A 125) of lab-cured plaster kits with and without calcium chloride accelerator immersed in tap water and hypochlorite solution.
- f. Micrographs of these thin sections are shown in detail in Appendix Figures A 109 through A 128.

The first main observation came from lab-cured hardened plasters is the *clear and distinct darkening of all three hardened plaster kits in the presence of calcium chloride accelerating admixture in the mix water*. Irrespective of

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#### Swimming Pool Plaster Discoloration

the plaster composition, addition of calcium chloride accelerator has darkened the plaster which is shown in the Appendix Figure A 106.

Second, the tap water immersion has shown some patchy discoloration of exposed surfaces of hardened plasters with or without calcium chloride accelerator which is judged to be from absorbed moisture by the plaster.

- d. Three hardened plaster kits# 1830, 1831, and 1835 without CaCl<sub>2</sub> addition (Appendix Figures A 111 to A 113) showed typical mineralogies of residual calcium silicates (alite and belite) from white Portland cement, and limestone fine microfillers (mostly for kit# 1830 and 1831) as seen in their dry microstructures except having an overwhelming matrix of calcium silicate hydrate hydration products of cement on which the residual cement grains are scattered, fine-grained short prismatic or lath-shaped grains of water-soluble calcium hydroxide component of cement hydration, sometimes appearing as coarsely crystalline laths in air voids.
- e. The same three hardened plaster kits# 1830, 1831, and 1835 without CaCl<sub>2</sub> addition after 7 days of immersion in tap water (Appendix Figures A 114 to A 118) showed the *aggressive nature and action of tap water* on all three plasters as dissolution of soluble component (calcium hydroxide component of cement hydration) from the plaster and its precipitation as coarsely crystalline dog tooth-shaped subhedral to euhedral grains of secondary calcite precipitates on the exposed surfaces of all three plasters.
- f. By contrast, immersion of three hardened plasters without CaCl<sub>2</sub> addition in a calcium hypochlorite disinfectant solution showed (Appendix Figures A 119 to A 123) the *balanced action of the solution* with localized dissolution of paste especially along the surface hairline microcracks but no appearance of any secondary calcite scales on the exposed surfaces.
- g. Addition of CaCl<sub>2</sub> accelerator in the mix water during preparation of hardened plasters from kit# 1830, 1831, and 1835 (Appendix Figures A 124 to A 128) showed *no major difference in microstructure compared to the companion CaCl<sub>2</sub>-free ones*. There is *no evidence of any increase in the frequency of fine hairline drying shrinkage microcracks that are present in all hardened plasters irrespective of CaCl<sub>2</sub> addition*. All three hardened plaster kits showed typical mineralogies of residual calcium silicates (alite and belite) from white Portland cement, and limestone fine microfillers (mostly for kit# 1830 and 1831) as seen in their dry microstructures except having an overwhelming matrix of calcium silicate hydrate hydration products of cement on which the residual cement grains are scattered, fine-grained short prismatic or lath-shaped grains of water-soluble calcium hydroxide component of cement hydration, sometimes appearing as coarsely crystalline laths in air voids.
- h. Contrary to significant secondary calcite scales on the exposed surface for kits immersed in tap water without any CaCl<sub>2</sub> addition, the present three hardened plasters with CaCl<sub>2</sub> addition showed no scaling of precipitation of secondary calcite on the exposed surfaces of any kit. Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 and 1831 with calcium chloride accelerator immersed in tap water for 7 days (Appendix Figure A 129 and A 130) showed abundant residual alite grains, and subordinate



limestone fines in paste with the cement hydration products overall giving an appearance of a masonry cement paste, along with some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. There are evidence of localized dissolution of paste, especially in near-surface region or along fine microcracks but no surface scaling. Kit 1835 (Figure A 131) also showed no surface scaling on the exposed sides.

i. Similar microstructures of localized dissolution but no surface scaling is found when the CaCl<sub>2</sub> doped kits were immersed in calcium hypochlorite disinfectant solution (Appendix Figures A 132 to A 134). Abundant coarse lath-shaped secondary calcium hydroxide deposits in air voids in all three kits indicates high solubility of this component of white Portland cement hydration.

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The above conclusions are based solely on the information and samples provided at the time of this investigation. The conclusion may expand or modify upon receipt of further information, field evidence, or samples. Samples will be disposed after submission of the report as requested. All reports are the confidential property of clients, and information contained herein may not be published or reproduced pending our written approval. Neither CMC nor its employees assume any obligation or liability for damages, including, but not limited to, consequential damages arising out of, or, in conjunction with the use, or inability to use this resulting information.



# APPENDIX

Swimming Pool Plaster Discoloration

Fig. A 1: Literature on Primera Stone pool plaster	63
Fig. A 2: Safety data sheet of Primera Stone pool plaster	64
Fig. A 3: Safety data sheet of pigment dyes showing 100 percent black iron oxide composition	65
Fig. A 4: Field photo of swimming pool portion where Primera Stone Sapphire Treasure plaster was installed	66
Fig. A 5: Field photo of swimming pool portion where Primera Stone Blue Ocean plaster was installed	67
Fig. A 6: Two field plaster samples provided from Primera Stone Sapphire Treasure from Sun Shelf (left) and Primera	
Stone Blue Ocean from Spa (right)	69
Fig. A 7: Blotchy discoloration (mottling) of exposed surfaces of Primera Stone Sapphire Treasure (top) and Primera	
Stone Blue Ocean (bottom) plasters from the field	70
Fig. A 8: Blotchy discoloration (mottling) of exposed surface of Primera Stone Sapphire Treasure plaster.	71
Fig. A 9: Blotchy discoloration (mottling) of exposed surface of Primera Stone Blue Ocean plaster	72
Fig. A 10: Portions selected for sectioning through the two field plasters from Primera Stone Sapphire Treasure (left) and	
Blue Ocean (right). Each plaster was sectioned vertically into four strips (1 to 4) from one end to the other for four vertical	
cross sections, as well as two sections at A and B for examinations of discolored exposed surfaces in optical and electron	
microscopy and X-ray microanalyses	73
Fig. A 11: Vertical cross sections of Primera Stone Sapphire Treasure and Blue Ocean showing size, shape, angularity,	
distribution of aggregates, color tones of paste, color variations or uniformity through depths, and overall consolidated	
natures of plaster in both samples. Locations of Sections 1 through 4 in each sample is shown in the previous Figure	74
Fig. A 12: Micrographs of exposed discolored surface of Primera Stone Sapphire Treasure pool plaster that was in contact	
with the pool water from the Sun Shelf area showing blotchy appearance of plaster consisting of: (a) beige gray	
discolored plaster patches marked with yellow arrows and (b) fading of darker to lighter blue colors of plaster marked	
by the dashed red arrows. Both the beige and lighter blue fading of color are the result of interaction of plaster and pool	
water. The micrographs were taken with a stereo-microscope	75
Fig. A 13: More micrographs of exposed discolored surface of Primera Stone Sapphire Treasure pool plaster that was in	
contact with the pool water from the Sun Shelf area showing blotchy appearance of plaster consisting of: (a) beige gray	
discolored plaster patches marked with yellow arrows and (b) fading of darker to lighter blue colors of plaster marked	
by the dashed red arrows. Both the beige and lighter blue fading of color are the result of interaction of plaster and pool	
water. The micrographs were taken with a stereo-microscope	76
Fig. A 14: Blue dye-mixed epoxy-impregnated thin section (30 micron thickness) of exposed discolored surface of	
Primera Stone Sapphire Treasure pool plaster that was in contact with the pool water from the Sun Shelf area. The thin	
section was scanned on a flatbed film scanner with a polarizing filter to create plane polarized light (PPL) view at the	
top image, and then sandwiched between two polarizing filters at perpendicular positions to create crossed polarized	
light (XPL) view at the bottom. The PPL image shows difference in porosities of paste from variations in the degree of	
absorption of blue epoxy used for preparation of thin section, where porous areas absorbed more blue dye to appear	
brighter blue whereas denser areas absorb less blue epoxy to appear darker. The XPL image shows the different aggregate	



#### Swimming Pool Plaster Discoloration

types used, which showed major amounts of crushed marble and seashell carbonate particles and minor amounts of Fig. A 15: Micrographs of thin section of exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) crushed marble (C), quartz (Qtz), alkali-silicate glass (G), strained quartzite, and seashell particles in aggregate; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to Fig. A 16: Micrographs of thin section of exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) crushed marble (M), alkali-silicate glass (G), and seashell particles in aggregate; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades due to variations in paste porosities; (d) secondary calcite (SC) precipitates from dissolution and re-precipitation of dissolved constituents Fig. A 17: Micrographs of thin section of exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) crushed marble (M), and seashell particles in aggregate; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades due to variations in paste porosities; (d) secondary calcite (SC) precipitates from dissolution and re-precipitation of dissolved constituents from plaster by the Fig. A 18: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts on the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) calcite and dolomite grains from crushed marble and carbonate deposits (probed at Nos. 1, 7, and 10); (b) residual alite grains from white Portland cement (which appear in lighter shades of small grains Probed at Nos. 3 and 5); and (c) interstitial calcium silicate hydrate and calcium hydroxide components of white Portland cement paste (Probed at Nos. 4, 8, 9, 11, and 12). Each component is showing its characteristic chemical composition. Sulfate contents in the paste in Probe# 4, 6, 8, 9, 11, and 12 are highly variable Fig. A 19: Secondary electron (SE) image (top) and corresponding backscatter electron (BSE) image (bottom) of the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) extensive fine, hairline shrinkage microcracks in the plaster, which are distinct in the SE image at the top; and (b) different shades of lighter and darker gray areas of paste due to leaching and dissolution of cement hydration products and calcium chloride accelerator from Fig. A 20: X-ray elemental maps of different elements showing compositional variations of the exposed discolored surface of Primera Stone Sapphire Treasure plaster, where paste is showing overall calcium enrichment from white Portland cement paste, with patches enriched in magnesium as shown in the Mg map indicating a potential source of Fig. A 21: Secondary electron (SE) image (top) and corresponding backscatter electron (BSE) image (bottom) of the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing different shades of lighter and darker gray areas of paste due to leaching and dissolution of cement hydration products and calcium chloride accelerator from



the plaster by the pool water that are distinct in both images. In the BSE image, variations in different shades of gray Fig. A 22: Secondary electron (SE) image (top) and X-ray microanalyses at the tips of callouts on the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) calcite grains from crushed marble and carbonate deposits (probed at Nos. 1, 3, 4, and 5); (b) a quartz sand particle Probed at No. 9; and (c) interstitial calcium silicate hydrate and calcium hydroxide components of white Portland cement paste (Probed at Nos. 2, 6, 7, and 8). Each component is showing its characteristic chemical composition. Sulfate contents in the paste in Probe# 2, and 6 to 8 are Fig. A 23: X-ray elemental maps of different elements showing compositional variations of the exposed discolored surface of Primera Stone Sapphire Treasure plaster, where paste is showing patchy areas of calcium enrichment in Camap from differential dissolution of white Portland cement paste, with patches enriched in magnesium in the Mg map indicating a potential source of magnesium besides the Portland cement, which could come from the reported addition of the pigment dyes. Overall silica enrichment is from calcium silicate hydrate component of paste where silicon was Fig. A 24: Secondary electron (SE) image (top) and corresponding backscatter electron (BSE) image (bottom) of the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing different shades of lighter and darker gray areas of paste due to leaching and dissolution of cement hydration products and calcium chloride accelerator from the plaster by the pool water that are distinct in both images. Also shown are fine hairline shrinkage microcracks in paste which are more distinct in the SE image. Notice a marble aggregate at the bottom and a darker gray paste Fig. A 25: Secondary electron (SE) image (top) and X-ray microanalyses at the boxed areas on the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing the typical characteristic calcium silicate hydrate and calcium hydroxide components of white Portland cement paste. The next Figure shows a line scan along the arrow to Fig. A 26: X-ray elemental analysis along the line traversing from darker to lighter gray area of paste showing the compositional variations in the paste due to variations in inherent porosities that has caused the blotchy appearance of Fig. A 27: Backscatter electron (BSE) image (top) and corresponding secondary electron (SE) image (bottom) of the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing different shades of lighter and darker gray areas of paste due to variations in chemical compositions of aggregates and interstitial paste where the latter shows numerous fine hairline shrinkage microcracks in the middle separated from the aggregate particles by dashed lines. Fig. A 28: Backscatter electron (BSE) image (top) and X-ray microanalyses at the boxed areas on the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) calcite grain in marble (probed at No. 1); (b) an alkalisilicate glass (Probed at No. 6); and (c) interstitial calcium silicate hydrate and calcium hydroxide components of white Portland cement paste (Probed at Nos. 2 to 5). Each component is showing its characteristic chemical composition.



#### Swimming Pool Plaster Discoloration

Fig. A 31: Micrographs of vertical cross section of Primera Stone Sapphire Treasure pool plaster where the top edge in each photo was in contact with the pool water showing evidence of leaching and dissolution of paste with increased paste porosity due to dissolution within the boxed areas at the surface regions in all photos. Arrows show vertical, shallow-depth shrinkage microcracks. Fading of darker interior to lighter blue colors of plaster at the surface region is Fig. A 32: Micrographs of vertical cross section of Primera Stone Sapphire Treasure pool plaster where the top edges in the top row photos were in contact with the pool water showing evidence of leaching and dissolution of paste with increased paste porosity due to dissolution within the boxed areas at the surface regions. Yellow arrows in the top row show vertical, shallow-depth shrinkage microcracks. Red arrows in the middle and bottom row photos of interior plaster Fig. A 33: Micrographs of vertical cross section of Primera Stone Sapphire Treasure pool plaster where the top edges in the top row photos were in contact with the pool water showing evidence of leaching and dissolution of paste with increased paste porosity due to dissolution within the boxed areas at the surface regions. Yellow arrows show vertical, Fig. A 34: Blue dye-mixed epoxy-impregnated thin section (30 micron thickness) of vertical cross sections of Primera Stone Sapphire Treasure pool plaster from the Sun Shelf area. The thin section was scanned on a flatbed film scanner with a polarizing filter to create plane polarized light (PPL) view at the top image, and then sandwiched between two polarizing filters at perpendicular positions to create crossed polarized light (XPL) view at the bottom. The PPL image shows difference in porosities of paste from variations in the degree of absorption of blue epoxy used for preparation of thin section where porous areas absorbed more blue dye to appear brighter blue whereas denser areas absorb less blue epoxy to appear darker. The XPL image shows the different aggregate types used, which showed major amounts of Fig. A 35: Micrographs of thin section of vertical cross section of Primera Stone Sapphire Treasure plaster showing: (a) crushed seashell (SS) particles in aggregate; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from lighter (more porous) shade at the surface region and darker (denser) shade in



Fig. A 38: Micrographs of thin section of vertical cross section of Primera Stone Sapphire Treasure plaster from the interior showing: (a) crushed quartz (Q) and seashell (SS) particles in aggregate; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from lighter (more porous) shade and darker (denser) shade; and (d) fine, hairline shrinkage microcracks in paste (arrows) many of which are filled with secondary calcium carbonate deposits.

Fig. A 39: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts on the vertical cross section of Primera Stone Sapphire Treasure plaster showing: (a) secondary calcium precipitate in the near-surface region of paste (e.g., Probe# 4, 5, 6) having noticeably higher calcium oxide than silica compared to paste at the surface region (Probe# 1, 2, 3) or in the interior (Probe# 7, 8, 11, 12). Paste in the interior (Probe# 7, 8, 11, 12) shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate extender present in the pigment dyes used in the plaster. Sulfate at the surface region of paste at Probe# 1, 2, and 3 are noticeably lower Fig. A 40: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts on the vertical cross section of Primera Stone Sapphire Treasure plaster showing: (a) a thin film of secondary calcium precipitate at the exposed surface (Probe# 1, 2, and 3) due to localized scaling. Paste in the interior (Probe# 4 to 7, then 9 to 11, then 13 to 17) shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate Fig. A 41: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts on the vertical cross section of Primera Stone Sapphire Treasure plaster showing: (a) a thin film of secondary calcium precipitate at the



exposed surface (Probe# 1, and 2) due to localized scaling. Paste in the interior (Probe# 10 to 21) shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate extender present Fig. A 42: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts on the vertical cross section of Primera Stone Sapphire Treasure plaster showing: (a) a thin film of secondary calcium precipitate at the exposed surface (Probe# 1, and 2) due to localized scaling. Paste in the interior (Probe# 5 to 12) shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate extender present Fig. A 43: Backscatter electron (BSE) image (top) and corresponding secondary electron (SE) image (bottom) of the vertical cross section of Primera Stone Sapphire Treasure plaster showing different shades of lighter and darker gray areas of paste due to variations in chemical compositions of aggregates and interstitial paste where the latter shows numerous fine hairline shrinkage microcracks that are distinct in the SE image. Boxed areas are analyzed in the next Fig. A 44: Backscatter electron (BSE) image (top) and X-ray microanalyses at the boxed areas on the vertical cross section

Fig. A 47: Blue dye-mixed epoxy-impregnated thin section (30 micron thickness) of exposed discolored surface of Primera Stone Blue Ocean pool plaster that was in contact with the pool water from the Spa area. The thin section was scanned on a flatbed film scanner with a polarizing filter to create plane polarized light (PPL) view at the top image, and then sandwiched between two polarizing filters at perpendicular positions to create crossed polarized light (XPL) view at the bottom. The PPL image shows difference in porosities of paste from variations in the degree of absorption of blue epoxy used for preparation of thin section where porous areas absorbed more blue dye to appear brighter blue whereas denser areas absorb less blue epoxy to appear darker. The XPL image shows the different aggregate types used,



#### Swimming Pool Plaster Discoloration

which showed major amounts of crushed basalt particles and trace amounts of siliceous (guartz sand) and calcareous Fig. A 48: Micrographs of thin section of exposed discolored surface of Primera Stone Blue Ocean plaster showing: (a) crushed basalt particles in aggregate consisting of anhedral to subhedral pyroxene, subhedral plagioclase laths, and dark opaque grains arranged in a porphyritic texture; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades; and (d) secondary calcite precipitates in some Fig. A 49: Micrographs of thin section of exposed discolored surface of Primera Stone Blue Ocean plaster showing: (a) crushed basalt particles in aggregate consisting of anhedral to subhedral pyroxene, subhedral plagioclase laths, and dark opaque grains arranged in a porphyritic texture; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades; (d) fine, hairline shrinkage microcracks in paste; and (e) secondary calcite precipitates in some voids due to dissolution and re-precipitation of paste by the pool water Fig. A 50: Micrographs of thin section of exposed discolored surface of Primera Stone Blue Ocean plaster showing: (a) crushed basalt particles in aggregate consisting of anhedral to subhedral pyroxene, subhedral plagioclase laths, and dark opaque grains arranged in a porphyritic texture; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades; (d) fine, hairline shrinkage microcracks in paste; and (e) secondary calcite precipitates in some voids due to dissolution and re-precipitation of paste by the pool water Fig. A 51: Micrographs of thin section of exposed discolored surface of Primera Stone Blue Ocean plaster showing: (a)

Fig. A 53: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts and in boxed areas on the exposed discolored surface of Primera Stone Blue Ocean plaster showing crushed basalt aggregate particles (where bright spots within the particles are from iron-titanium oxide opaque grains in basalt) and interstitial paste. Paste was



porosity due to dissolution within the boxed areas at the surface regions in all photos. Arrows show vertical, shallow-



Fig. A 64: Micrographs of thin section of vertical cross sections of Primera Stone Blue Ocean plaster showing: (a) crushed basalt particles in aggregate consisting of anhedral to subhedral pyroxene, subhedral plagioclase laths, and dark opaque grains arranged in a porphyritic texture; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades; (d) fine, vertical, hairline shrinkage microcracks in paste (arrows in the left column photos); and (e) zones of chemical alterations of exposed surface region due to pool water interactions that are marked in Photos 2, 4, and 6 as carbonated zone at the very top surface (#1), a darker intermediate zone beneath (#2), and interior paste (#3).



Fig. A 66: Micrographs of thin section of vertical cross sections of Primera Stone Blue Ocean plaster showing: (a) crushed basalt particles in aggregate consisting of anhedral to subhedral pyroxene, subhedral plagioclase laths, and dark opaque grains arranged in a porphyritic texture; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades; (d) fine, vertical, hairline shrinkage microcracks in paste; and (e) zones of chemical alterations of exposed surface region due to pool water interactions that are marked in Photos 2, 4, and 6 as carbonated zone at the very top surface (#1), a darker intermediate zone beneath (#2), and interior paste

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fine vertical hairline shrinkage microcracks. The tips of callouts in the BSE image were analyzed in the previous Figure.



Fig. A 70: Backscatter electron (BSE) image (top) and corresponding secondary electron (SE) image (bottom) of the vertical cross section of Primera Stone Blue Ocean plaster showing different shades of lighter and darker gray areas of paste due to variations in chemical compositions of aggregates and interstitial paste where the latter shows numerous fine vertical hairline shrinkage microcracks. The tips of callouts in the BSE image were analyzed in the previous Figure.



Fig. A 78: Clear epoxy-encapsulated thin sections (30 micron thickness) of various plaster kits including the kits for both field plaster types, as well as the blended cement, and two pigment dyes prepared for examinations in a petrographic Fig. A 79: Thin section micrographs of Plaster Kit# 1830 for Primera Stone Sapphire Treasure showing the presence of crushed marble, glass, and chert particles in dry white Portland cement (WPC), which are all encapsulated in a clear epoxy medium. Notice the masonry cement-like appearance (in mineralogy and microstructure) of the interstitial dry binder component, which shows major amount of white Portland cement and subordinate amount of limestone fines.. 143 Fig. A 80: Thin section micrographs of Plaster Kit# 1830 for Primera Stone Sapphire Treasure showing the presence of crushed seashell particles in dry white Portland cement (WPC), which are all encapsulated in a clear epoxy medium. Notice the overall mineralogies and microstructures of the binder in the plaster kit# 1830 are similar to that of a masonry Fig. A 81: Backscatter electron image (BSE) and corresponding X-ray microanalyses of aggregates dispersed in white Portland cement in Plaster Kit# 1830 for Primera Stone Sapphire Treasure......145 Fig. A 82: X-ray elemental maps in SEM of aggregates dispersed in white Portland cement in Plaster Kit# 1830 for Primera Fig. A 83: Backscatter electron image (BSE) and corresponding X-ray microanalyses of aggregates and alite particles, free lime, and gypsum in white Portland cement, and a sodium silicate glass aggregate particle in Plaster Kit# 1830 for Fig. A 84: X-ray diffraction pattern of Plaster Kit# 1830 for Primera Stone Sapphire Treasure showing the presence of Fig. A 85: Thin section micrographs of Plaster Kit# 1831 for Primera Stone Blue Ocean showing the presence of crushed basalt particles (containing anhedral to subhedral pyroxene, subhedral lath-shaped plagioclase, and dark opaque grains in porphyritic texture) dispersed in dry white Portland cement (WPC), which are all encapsulated in a clear epoxy medium. Notice the interstitial dry binder shows similarity to the binder in kit# 1830 in having a masonry cement-like appearance in mineralogy and microstructure containing major amount of white Portland cement and subordinate Fig. A 86: Thin section micrographs of Plaster Kit# 1831 for Primera Stone Blue Ocean showing the presence of crushed basalt particles (containing anhedral to subhedral pyroxene, subhedral lath-shaped plagioclase, and dark opaque grains in porphyritic texture) dispersed in dry white Portland cement (WPC), which are all encapsulated in a clear epoxy medium. Notice the overall mineralogies and microstructures of the binder in the plaster kit# 1831 are similar to that of kit# 1830, which are similar to that of a masonry cement made using white Portland cement, and limestone fines Fig. A 87: Backscatter electron image (BSE) and corresponding X-ray microanalyses of aggregates and alite particles in Fig. A 88: X-ray diffraction pattern of Plaster Kit# 1830 for Primera Stone Blue Ocean showing the presence of alite from 



Fig. A 92: Backscatter electron image (BSE) and corresponding X-ray microanalyses of 1833 Midnight pigment dye used for Primera Stone Blue Ocean plaster. The dye showed the presence of a barium sulfate extender, which appeared as bright spots in this image all over the dye, which is responsible for the higher sulfate content of paste in the field plaster samples compared to the sulfate contributed from hydration of Portland cement. The dye showed iron-chromium oxide Fig. A 93: Backscatter electron image (BSE) and corresponding X-ray microanalyses of 1833 Midnight pigment dye used for Primera Stone Blue Ocean plaster. The dye showed the presence of a barium sulfate extender (Probe# 1 and 2), which appeared as bright spots in this image all over the dye, which is responsible for the higher sulfate content of paste in the field plaster samples compared to the sulfate contributed from hydration of Portland cement. The dye showed Fig. A 95: Thin section micrographs of Lehigh blended cement which is a mixture of major amount of white Portland cement (WPC) and limestone fine particles (LF), which are all encapsulated in a clear epoxy medium. Notice the overall mineralogies and microstructures of the blended cement binder in 1834 are similar to that of a masonry cement made using white Portland cement, and limestone fines (possibly with some hydrated lime as well), which are seen for the Fig. A 96: Backscatter electron image (BSE) and corresponding X-ray microanalyses of Lehigh blended cement showing alite from white Portland cement (WPC) in Probe# 1 to 7 and limestone fine particles (LF) in Probe# 8...... 160 Fig. A 97: X-ray diffraction pattern of Lehigh blended cement showing alite from white Portland cement and calcite from

Fig. A 98: Thin section micrographs of Plaster Kit# 1835 for Primera Stone Blue Ocean showing the presence of crushed basalt particles (containing anhedral to subhedral pyroxene, subhedral lath-shaped plagioclase, nepheline, and dark opaque grains in porphyritic texture) dispersed in dry white Portland cement (WPC), which are all encapsulated in a clear epoxy medium. Notice the overall mineralogies and microstructures of the binder in the plaster kit #1835 are



slightly different from that in kits# 1830 and 1831, in having overall lesser amount of limestone fine, if any, and higher amount of rounded belite grains in white Portland cement......162 Fig. A 99: Thin section micrographs of Plaster Kit# 1835 for Primera Stone Blue Ocean showing the presence of crushed basalt particles (containing anhedral to subhedral pyroxene, subhedral lath-shaped plagioclase, nepheline, and dark opaque grains in porphyritic texture) dispersed in dry white Portland cement (WPC), which are all encapsulated in a clear epoxy medium. Notice the overall mineralogies and microstructures of the binder in the plaster kit #1835 are slightly different from that in kits# 1830 and 1831, in having overall lesser amount of limestone fine, if any, and higher Fig. A 100: Backscatter electron image (BSE) and corresponding X-ray microanalyses of basalt aggregate (Probe# 5) and alite and belite particles in white Portland cement (Probe# 1 to 4) in Plaster Kit# 1835 for Primera Stone Blue Ocean... 164 Fig. A 101: X- ray elemental maps of Plaster Kit# 1835 for Primera Stone Blue Ocean showing basalt aggregate particles Fig. A 102: X-ray diffraction pattern of Plaster Kit# 1835 for Primera Stone Blue Ocean showing alite from white Portland Fig. A 103: X-ray diffraction pattern of calcium chloride set accelerator (flake-type) showing the diffraction pattern of Fig. A 104: Preparation of 2 in. size cubes of plaster from three kits 1830, 1831, and 1835 used for field plaster samples. 



Fig. A 111: Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 without calcium chloride accelerator showing abundant subhedral to anhedral alite, subordinate rounded belite, and limestone fines (a few are marked with arrows) in paste. Notice the overall mineralogies and microstructures of the binder in the hardened plaster kit# 1830 are similar to that of a masonry cement paste made using white Portland cement, and limestone fines (possibly Fig. A 112: Micrographs of thin section of laboratory-cured hardened plaster kit# 1831 without calcium chloride accelerator showing abundant subhedral to anhedral alite, subordinate rounded belite, and limestone fines (a few are marked with arrows) in paste. Notice the overall mineralogies and microstructures of the binder in the hardened plaster kit# 1831 are similar to that of kit# 1830, which are similar to that of a masonry cement paste made using white Portland cement, and limestone fines (possibly with some hydrated lime as well)...... 177 Fig. A 113: Micrographs of thin section of laboratory-cured hardened plaster kit# 1835 without calcium chloride accelerator showing abundant rounded belite, subordinate subhedral to anhedral alite, and minor limestone fines (a few are marked with arrows) in paste. Notice the overall mineralogies and microstructures of the binder in the hardened plaster kit# 1835 are slightly different from that in kits# 1830 and 1831, in having overall lesser amount of limestone Fig. A 114: Thin section of three lab-cured plasters (7 days of moist curing) without calcium chloride accelerator addition to mix water after immersing the plasters in tap water for 7 days to observe dissolution of paste - shown in PPL image.. 179 Fig. A 115: Thin section of three lab-cured plasters (7 days of moist curing) without calcium chloride accelerator addition to mix water after immersing the plasters in tap water for 7 days to observe dissolution of paste - shown in XPL image. 180 Fig. A 116: Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 without calcium chloride accelerator after 7 days of immersion in tap water showing aggressive action of tap water by dissolution of soluble Fig. A 117: Micrographs of thin section of laboratory-cured hardened plaster kit# 1831 without calcium chloride accelerator after 7 days of immersion in tap water showing aggressive action of tap water by dissolution of soluble Fig. A 118: Micrographs of thin section of laboratory-cured hardened plaster kit# 1835 without calcium chloride accelerator after 7 days of immersion in tap water showing aggressive action of tap water by dissolution of soluble Fig. A 119: Thin section of three lab-cured plasters (7 days of moist curing) without calcium chloride accelerator addition to mix water after immersing the plasters in calcium hypochlorite disinfectant solution for 7 days to observe dissolution Fig. A 120: Thin section of three lab-cured plasters (7 days of moist curing) without calcium chloride accelerator addition to mix water after immersing the plasters in calcium hypochlorite disinfectant solution for 7 days to observe dissolution 



#### Swimming Pool Plaster Discoloration

Fig. A 121: Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 without calcium chloride accelerator after 7 days of immersion in calcium hypochlorite solution showing balanced nature of solution due to lack Fig. A 122: Micrographs of thin section of laboratory-cured hardened plaster kit# 1831 without calcium chloride accelerator after 7 days of immersion in calcium hypochlorite solution showing balanced nature of solution due to lack Fig. A 123: Micrographs of thin section of laboratory-cured hardened plaster kit# 1835 without calcium chloride accelerator after 7 days of immersion in calcium hypochlorite solution showing balanced nature of solution due to lack Fig. A 124: Thin section of three lab-cured plasters (7 days of moist curing) with calcium chloride accelerator addition Fig. A 125: Thin section of three lab-cured plasters (7 days of moist curing) with calcium chloride accelerator addition Fig. A 126: Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 with calcium chloride accelerator showing abundant subhedral to anhedral alite, subordinate rounded belite, and limestone fines (a few are marked with Fig. A 127: Micrographs of thin section of laboratory-cured hardened plaster kit# 1831 with calcium chloride accelerator showing abundant subhedral to anhedral alite, subordinate rounded belite, and limestone fines (a few are marked with arrows) in paste. Notice some coarsely crystalline secondary calcium hydroxide crystals in an air void in the bottom Fig. A 128: Micrographs of thin section of laboratory-cured hardened plaster kit# 1835 with calcium chloride accelerator showing abundant rounded belite, subordinate subhedral to anhedral alite, and minor limestone fines in paste. Notice some coarsely crystalline secondary calcium hydroxide crystals in an air void in the middle row indicating high solubility Fig. A 129: Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 with calcium chloride accelerator immersed in tap water for 7 days, showing abundant residual alite grains, and subordinate limestone fines in paste. Notice some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. Notice the lack of surface scaling of Fig. A 130: Micrographs of thin section of laboratory-cured hardened plaster kit# 1831 with calcium chloride accelerator immersed in tap water for 7 days, showing abundant residual alite grains, and subordinate limestone fines in paste. Notice some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. Notice the lack of surface scaling of Fig. A 131: Micrographs of thin section of laboratory-cured hardened plaster kit# 1835 with calcium chloride accelerator immersed in tap water for 7 days, showing abundant residual belite grains, subordinate alite, and negligible limestone



#### Swimming Pool Plaster Discoloration

fines in paste. Notice some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. Notice the lack of Fig. A 132: Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 with calcium chloride accelerator immersed in calcium hypochlorite disinfectant solution for 7 days, showing abundant residual alite grains, and subordinate limestone fines in paste. Notice some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. Fig. A 133: Micrographs of thin section of laboratory-cured hardened plaster kit# 1831 with calcium chloride accelerator immersed in calcium hypochlorite disinfectant solution for 7 days, showing abundant residual alite grains, and subordinate limestone fines in paste. Notice some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. Fig. A 134: Micrographs of thin section of laboratory-cured hardened plaster kit# 1835 with calcium chloride accelerator immersed in calcium hypochlorite disinfectant solution for 7 days, showing abundant residual belite grains, subordinate alite, and negligible limestone fines in paste. Notice some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in 



**APPENDIX 1** 

## PRIMERA STONE BROCHURE, SAFETY DATA SHEET, & FIELD PHOTOS OF SAPPHIRE TREASURE AND BLUE OCEAN POOLS



#### Swimming Pool Plaster Discoloration



Fig. A 1: Literature on Primera Stone pool plaster.

Primera	
Stone	

Possessing both the coveted architectural beauty of a pebble surface combined with the desired smooth texture of a hand-polished finish, Primera Stone® is our elite designer selection. In addition to elegant aesthetics and preferred feel, Primera Stone® provides durability and longevity that is second to none. The added value of the Primera Stone® is its renewability. If the surface becomes dull or stained due to water chemistry issues, it can be re-polished and given a new look at a fraction of the cost to re-plaster.

#### COMPONENT BENEFITS

Specialty pebble apgregates are combined with the engineered admixture Pebble Edge\*, which fortifies standard cement and creates a stronger bond to the pebbles, increases the flexural strength, and reduces the formation of calcium hydroxide. Primera Stone<sup>®</sup> is installed by a unique installation process; first hard troweled, then a light water wand wash to initiate the exposure process that leaves a slight bit of cream on the surface that will be removed during the polishing phase.

The polishing begins as soon as the finish has cured, which usually is the next day. The top porous cementitious layer is then removed by hand with the high-powered Primera Stone" polishing tool using diamond abrasive discs exposing the beautiful pebbles. The polishing process produces a smooth non-slip surface that has a similar characteristic to a Terrazzo floor seen in many arports

and hospitals. In addition to the visual aesthetic beauty of a polished finish, the consumer also receives the additional benefit of an extremely dense surface that resists algae and staining.

#### BEAUTY

BEAUTY Swimming pool designs and construction methods have advanced over the years. Simple rectangular pools have evolved into complex architectural projects that can range from a backward resort to inspired works of art that integrate the natural elements surrounding the pool. Today's pools must meet the needs and demands of both a fun family near works of a wear-orund water feature. play area as well as a year-round water feature.

Primera Stone® satisfies the consumer's desire for a smooth touch while remaining pleasurable to the eye. This finish offers a pallet of color selections ranging from dark and mysterious to light and lively. Some Primers Stone® selections incorporate colored glass and ocean shells into the mix that bring life and movement to the water. There is sure to be a selection that complements the design and the pool's environment

#### QUALITY ASSURANCE

Wet Edge Technologies" is the only pool finish manufacturer to own and operate quaries both internationally and domestically, placing Wet Edge Technologies" in a unique position to control all aspects of production from the sourcing, harvesting, processing, and sizing to applicator certification, Wet Edge Technologies" ensures that every stage of production. produces a long-lasting pool finish for the consumer.

Our commitment to quality drives us to exceed our customer's expectations and to pursue new products that surpass their dreams.



4322 South 80th Street Mesa, AZ 86212 wetedgetechnologies.com 877-964-4687

Primera Stans" Limited Warranty Coverage: ▶ 15 years on Residential Pools & Spas • 7 years on Commercial Pools & Spas





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ECTION 1 - P	RODUCT AND	COMPA	NY IDENTI	FICATION					
PRODUCT NAME:	Primera Stone				MANUFACTURER: Turley Internatio	nal Resources, LLC.			
PRODUCT USE: P	<b>Nool Interior Finish</b>				4322 South 80*	Street			
SUPPLIER: Wet E	dge Technologies				Mesa, A2 85212	- USA			
3					TEL: 844-786-63	33 E: Info@wetedge.com			
EMERGENCY: CH	EMTREC P: 703-527-	3887 F: 703	1-527-3887 (Int	ternational)	MEDICAL: 3E Company P: 800-451-834	V6 F: 760-602-8856 (International)			
ECTION 2 - H	AZARDS IDEN	TIFICATI	ON						
LASSIFICATION O	IF THE SUBSTANCE	MIXTURE:	Laurean	215		81.00X			
Acute Toxicity, O	TAZAND CLASS		CATEGORY 4	Harmful if s	HAZAND STATEM	ENTS			
Acute Toxicity, Dermal			5	May be har	May be harmful in contact with skin				
Skin corrosion / irritation			1	Causes seve	Causes severe skin burns and eye damage				
Carcinopenicity	age / Eye initiation		28	Hazardous	ous eye damage in case of inhalation				
Specific target or	gan toxicity, single e	sposure	3	May cause	respiratory irritation				
Specific target or exposure	gan toxicity, repeat	d	1	Causes dam inhalation.	tage to lungs and respiratory system, thro Causes damage to kidney and liver throug	ugh prolonged or repeated exposure by h prolonged or repeated exposure.			
OSHA HAZARD CI	OMMUNICATION ST	ANDARD:	This product 1910.1200.	is a "Hazardou	s Chemical" as defined by the OSHA Haza	rd Communication Standard, 29 CFR			
RECAUTIONARY S HEADING	TATEMENTS: OSHA Ref. #				Instructions				
	P201	Obta	in special instr	uction before a	ne.				
	P202 P281	Don	ot handle until personal prote	I all safety preci ctive environmen	autions have been read and understood.				
BREITER TICH	P271	Use	only outdoors	or in a well-ven	cilated area.				
DEFUENTION	0160	Don	ot breathe dus	its or mists.		Do not breathe dusts or mists.			
PREVENTION:	P200	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Do not eat, drink, and smoke when using this product.						
PREVENTION	P200 P270 P280	Wea	ot eat, drink, a r protective ak	nd smoke whe oves/ protective	n using this product. e clothing / eve protection/ face protectio	n.			
PREVENTION	P280 P270 P280 P264	Wea	ot eat, drink, a r protective gk h exposed area	nd smoke whe oves/ protective a with plenty of	n using this product. e clothing / eye protection/ face protectio water and soap thoroughly after handling	ei. I-			
PREVENTION	P260 P270 P280 P264 P301 + P330 + P	Wea Was 312 IF 5V	ot eat, drink, a r protective gk h exposed area VALLOWED: Ri	nd smoke whe oves/ protective a with plenty of nse mouth. Cal	n using this product. e clothing / eye protection/ face protectio water and soap thoroughly after handling I a POISON CENTER or physician if you fee	n. I- Lonwell.			
PREVENTION	P270 P280 P264 P301 + P330 + P. P331 P303 + 9351 + 9	Wea Was 312 IF SW Do n	ot eat, drink, a r protective gk h exposed area VALLOWED: Ri ot induce vom	nd smoke whe oves/ protective a with plenty of nse mouth. Call iting.	n using this product. e clothing / eye protection/ face protectio water and soap thoroughly after handling a POISON CENTER or physician if you fee off immediately all contaminanted clothic	n. I. I unwell. e Rince chin with water/showers			
PREVENTION	P260 P270 P280 P264 P301 + P330 + P. P331 P303 + P361 + P. P363	Wea Was 312 IF SW Do n 353 IF Ot Was	ot eat, drink, a r protective gk h exposed area VALLOWED: Ri ot induce vom N SKIN (or hair) h contaminate	nd smoke whe oves/ protective a with plenty of nse mouth. Call iting. I: Remove/Take d clothing befo	n using this product. e clothing / eye protection/ face protectio water and scap thoroughly after handling a POISON CENTER or physician if you fee off immediately all contaminated clothin re reuse.	n. I. I unwell. g. Rinse skin with water/shower.			
RESPONSE:	P280 P270 P280 P264 P301 + P330 + P. P331 P303 + P361 + P. P363 P304 + P340 + P.	Wea Wasi 312 IF SW Do n 353 IF Ot Wasi 310 IF IN a PO	ot eat, drink, a r protective gk h exposed area VALLOWED: Ri ot induce vom N SKIN (or hair) h contaminate HALED: Remov ISON CENTER (	nd smoke whe oves/ protective a with plenty of nse mouth. Call iting.  : Remove/Take d clothing before victim to fres- or doctor/ phys-	n using this product. e clothing / eye protection/ face protectio water and soap thoroughly after handling la POISON CENTER or physician if you feel off immediately all contaminated clothin re reuse. In air and keep at rest in a position comfo ician	n. I- I unwell. g. Rinse skin with water/shower. rtable for breathing. Immediately call			
RESPONSE:	P200 P270 P280 P264 P301 + P330 + P P303 + P361 + P P303 + P361 + P P305 + P340 + P P305 + P351 + P3	Usin           Wea           Wasi           312         IF SW           Don           353         IF ON           310         IF IN           38         IF IN           Cont         Cont	ot eat, drink, a r protective glu h exposed area vALLOWED: Ri ot induce vom s SKIN (or hair) h Contaminate HALED: Remon ISON CENTER ( EYES: Rinse ca Inue rinsing.	ind smoke whe over,/ protective a with plenty of nise mouth. Call iting. I: Remove/Take d clothing before e victim to free er doctor/ phys utiously with w	n using this product. e clothing / eye protection/ face protectio water and soap thoroughly after handling a POISON CENTER or physician if you fee off immediately all contaminated clothin re reuse. In eir and keep at rest in a position comfor ician water for several minutes. Remove contact	n, }. umwell. g. Rinse skin with water/shower. rtable for breathing, Immediately call Llenses, if present and easy to do.			
RESPONSE:	P280 P270 P280 P301 + P330 + P P301 + P330 + P P303 + P361 + P P363 P304 + P340 + P P305 + P351 + P3 P310	Usea           Wea           Wasi           312         IF SW           Don           353         IF ON           Wasi         Wasi           310         IF IN           338         IF IN           Imm         Imm	ot ead, drink, a r protective glu h exposed area VALLOWED: Ri ot induce vom N SKIN (or hair) h contaminate HALED: Remos ISON CENTER o EYES: Rinse ca inue rinsing, ediately call a gased o	ind smoke whe swes/ protective with plenty of nee mouth. Call iting. I: Remove/Take d clothing before e victim to frea or doctor/ phys utiously with w PDISON CENTE PDISON CENTE	n using this product. e clothing / eye protection/ face protectio water and soap thoroughly after handling a POISON CENTER or physician if you feel r off immediately all contaminated clothin re reuse. In eir and keep at rest in a position comfor- ician water for several minutes. Remove contact R or doctor/ physician.	n, }- g. Rinse skin with water/shower. rtable for breathing, Immediately call lenses, if present and easy to do.			
RESPONSE:	P200 P270 P280 P264 P301 + P330 + P P303 + P361 + P P305 + P363 P304 + P340 + P P305 + P351 + P3 P310 P306 + P313 P401 + P235 + P	Wea Weas 312 IF SW Don 353 IF Of Wasi 310 IF IN 310 a PO 388 IF IN Cont Imm IF ex 405 Stere	ot ead, drink, a r protective gh r exposed area VALLOWED: Ri ot induce vom N SKIN (or hair) h contaminate HALED: Remov HALED: Remov ISON CENTER of EVES: Rinse ca inue rinsing, ediately call a posed or concu-	ind smoke whe sweld protective with plenty of new mouth. Call iting. I: Remove/Take d clothing before withing before or doctor/ phys utiously with w POISON CENTE: erned: Get med tighted place. Y	n using this product. e clothing / eye protection/ face protectio water and soap thoroughly after handling a POISON CENTER or physician if you feel i off immediately all contaminated clothin re reuse. their and keep at rest in a position comfor- ician water for several minutes. Remove contact R or doctor/ physician. lical advice/attention. wo cond. Store Locked Un	n, 8- 9- 9. Rinse skin with water/shower. rtable for breathing, Immediately call 1 lenses, if present and easy to do.			
RESPONSE: STORAGE: DISPOSAL:	P300 P270 P280 P301 + P330 + P P331 P303 + P351 + P P363 P304 + P340 + P P305 + P351 + P3 P306 + P313 P403 + P235 + P P501	Wasi Wasi 312 IF SV Don 353 IF O Wasi 310 IF IN 310 IF IN 318 IF IN 318 IF IN 318 IF IN 319 IF IN 319 IF IN 319 IF IN 310 IF I	ot eac, drink, a in protective glu- nexposed area VALLOWED: Ri- tot induce vom statinduce vom statinduce vom statingen induce vom SON CENTER a EVES: Rinse ca isoue rinsing, ediately call a ispased or conce is in a weil-verri ose of contents	ind smoke whe over/ protective a with plenty of nise mouth. Call liting. [: Remove/Take d clothing before e victim to free or doctor/ phys utiously with w POISON CENTE erned: Get med tiloted place. Ke s/container to 1	n using this product. e clothing / eye protection/ face protectio water and soap thoroughly after handling a PDISON CENTER or physician if you feel i off immediately all contaminated clothin re reuse. In air and keep at rest in a position comfor- ician water for serveral minutes. Remove contact R or doctor/ physician. Ical advice/attention. sep cool. Store Locked Up hazardous or special waste collection poin nal regulations	et. 6- 1 unwell. g. Rinse skin with water/shower. rtable for breathing. Immediately call clenses, if present and easy to do.			
RESPONSE: STORAGE: DISPOSAL: ECTION 3 – C	P200 P270 P280 P264 P301 + P330 + P P303 + P361 + P P305 + P363 P304 + P340 + P P305 + P351 + P3 P306 + P313 P403 + P235 + P P501 COMPOSITION	Wasi Wasi B12 IF SW Don S53 IF ON Wasi B10 a PO a PO a PO a PO a PO a PO b P b P b P b P b P b P b P b P b P b P	ot eac, drink, a protective gh h exposed area VALLOWED: Ri dt induce vom N SKIN (or hair) h contaminate HALED: Remon SON CENTER 4 EYES: Rinse ca linue rinsing, ediately call a posed or concu- e in a well-vent one of content /regional/hatk MATION C	ind smoke when over/ protective a with plenty of nise mouth. Call king. I: Remove/Take d clothing before victim to frest or doctor/ phys autiously with w POISON CENTE erned: Get med tilated place. Kn on al/internation	n using this product. e clothing / eye protection/ face protectio water and soap thoroughly after handling a POISON CENTER or physician if you feel r off immediately all contaminated clothin re reuse. In air and keep at rest in a position comfor- ician water for several minutes. Remove contact R or doctor/ physician. IIcal advice/ottention. sep cool. Store Locked Up hazardous or special waste collection poin nal regulations IENTS	n, 8- 9- 9. Rinse skin with water/shower. rtable for breathing. Immediately call 1 lenses, if present and easy to do. 1 in accordance with			
RESPONSE: STORAGE: DISPOSAL: ECTION 3 – C Componen	P200 P270 P280 P264 P301 + P330 + P P303 + P361 + P P308 + P361 + P P306 + P340 + P P306 + P351 + P3 P306 + P351 + P3 P306 + P313 P403 + P235 + P P501	Wasi Wasi 312 IF SW Don 353 IF OU Wasi 310 IF IN 330 IF IN 330 IF IN 331 IF IN 330 IF IN 555 Storn 0isp. 10cal 10c	ot eac, drink, a protective gh h exposed area VALLOWED: Ri dt induce vom N SKIN (or hair) h contaminate HALED: Remon SON CENTER & EYES: Rinse ca linue rinsing, ediately call a posed or concu- ie of content /regional/hatik MATION C CAS #	ind smoke when over/ protective a with plenty of new mouth. Call king. I: Remove/Take d clothing before victim to free or doctor/ phys uutiously with w POISON CENTE erned: Get med tilated place. Kin scientariar to to onal/internation DN INGRED	n using this product. e clothing / eye protection/ face protectio water and soap thoroughly after handling a POISON CENTER or physician if you feel r off immediately all contaminated clothin re reuse. In air and keep at rest in a position comfor- ician nater for several minutes. Remove contact R or doctor/ physician. IIcal advice/ottention. sep cool. Store Locked Up naardous or special waste collection poin nal regulations IENTS EC #	n, l- umwell. g. Rinse skin with water/shower. rtable for breathing. Immediately call lenses, if present and easy to do. f in accordance with Concentration, %			
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RESPONSE: STORAGE: DISPOSAL: ECTION 3 – C Componen Attapulgite ( Polypropelene	P200 P220 P280 P264 P301 + P330 + P P331 P303 + P351 + P P363 P304 + P340 + P P305 + P351 + P P305 + P351 + P2 P306 + P313 P403 + P235 + P P501 COMPOSITION as Clay phot based	Wasi Wasi 312 IF SW Don 353 IF OD 330 IF IN 330 IF IN 331 IF IN 330 IF IN 331 IF IN 332 IF SW 330 IF IN 333 IF OD 10 334 IF IN 335 IF IN 336 IF IN 337 IF IN 338 IF IN 337 IF IN 338 IF IN 338 IF IN 338 IF IN 338 IF IN 339 IF IN 330 IF IN	ot eak, drink, a protective gh h exposed area VALLOWED: Ri dt induce vom SKIN (or hair) HALED: Remon SON CENTER ( EVES: Rinse ca inue rinsing, ediately call a posed or conci: in a well-vent /regional/hatik MATION C CAS # 4808-60-7 7631-86-9 9002-83-5 9003-07-0	ind smoke whe over/ protective a with plenty of nise mouth. Call liting. (: Remove/Take d clothing before victim to free or doctor/ phys utiously with w POISON CENTE erned: Get med tilated place. Ke s/container to s/ on al/internatio ON INGRED	n using this product. e clothing / eye protection/ face protectio water and soap thoroughly after handling a POISON CENTER or physician if you feel r off immediately all contaminated clothin re nuse. In air and keep at rest in a position comfor- ician ater for serveral minutes. Remove contact R or doctor/ physician. Ical advice/ottention. seep cool. Store Locked Up hazardous or special waste collection poin rait regulations IENTS EC # N/A N/A N/A	et. 6- 1 unwell. g. Rinse skin with water/shower. rtable for breathing. Immediately call lenses, if present and easy to do. it in accordance with Concentration, % <5% <15% <10% <10%			
RESPONSE: STORAGE: DISPOSAL: ECTION 3 – C Componen Attapulgie ( Polypropelene fiber Calpione Site	P200 P270 P280 P264 P301 + P330 + P P331 P303 + P361 + P P365 P304 + P340 + P P305 + P351 + P2 P305 + P351 + P2 P306 + P313 P403 + P235 + P P501 COMPOSITION as Clay based are	Wasi Wasi 312 IF SW Don 353 IF ON 330 IF IN 330 IF IN 331 IF IN 330 IF IN 331 IF ON 332 IF SW Disput Incal 4 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	ot eak, drink, a protective gh h exposed area VALLOWED: Ri ot induce vom 4 SKIN (or hair) HALED: Remon SON CENTER ( EVES: Rinse ca EVES: Rinse ca EVES: Rinse ca eliately call a posed or conce in a well-vem /regional/hatk <b>MATION C</b> CAS # 4808-60-7 7631-86-9 9002-83-5 9003-07-0 1844.95-3	ind smoke whe over/ protective a with plenty of nise mouth. Call liting. (: Remove/Take d clothing before victim to free or doctor/ phys utiously with w POISON CENTE erned: Get med tilated place. Ke s/container to on al/intermatico ON INGRED	n using this product. e clothing / eye protection/ face protectio water and soap thoroughly after handling a POISON CENTER or physician if you feel r off immediately all contaminated clothin re nuse. In air and keep at rest in a position comfor- ician ater for serveral minutes. Remove contact R or doctor/ physician. Ical advice/ottention. See pool. Store Locked Up hazardous or special waste collection poin nair regulations IENTS EC # N/A N/A N/A N/A N/A N/A	et. 6- 1 unwell. g. Rinse skin with water/shower. rtable for breathing. Immediately call lenses, if present and easy to do. it in accordance with Concentration, % <5% <13% <10% <10% <10%			
RESPONSE: STORAGE: DISPOSAL: ECTION 3 – C Componen Attapulgite ( Polypingi Alo Polypingi Alo Polypingi Alo	P200 P20 P280 P284 P301+P330+P P331 P303+P361+P P365 P304+P340+P P305+P351+P3 P306+P313 P403+P235+P P501 COMPOSITION Its Clay phol based ate	Wasi Wasi 312 IF SW Don 353 IF ON 330 IF IN 330 IF IN 331 IF IN 330 IF IN 331 IF IN 332 IF SW 05 STORE 0 IS 10 CON 10	ot eak, drink, a r protective gh to exposed area VALLOWED: Ri ot induce vom SKIN (or hair) HALED: Remonister HALED: Remonister HALED: Remonister HALED: Remonister PYES: Rinse ca posed or conce in a well-vem vregional/hatik <b>MATION C</b> CAS # 4808-60-7 7631-86-9 3002-83-5 3003-07-0 1344-95-2 1344-95-2	ind smoke whe over/ protective a with plenty of nise mouth. Call liting. (: Remove/Take d clothing before victim to free or doctor/ phys autiously with w POISON CENTE erned: Get med tilated place. Ko s/container to on al/intermatico ON INGRED	n using this product. e clothing / eye protection/ face protectio water and soap thoroughly after handling a PDISON CENTER or physician if you feel i off immediately all contaminated clothin re nuse. In air and keep at rest in a position comfor- ician ater for serveral minutes. Remove contact R or doctor/ physician. Ical advice/ottention. Sep cool. Store Locked Up hazardous or special waste collection poin nal regulations IENTS EC # N/A N/A N/A N/A N/A N/A N/A	et. - - - - - - - - - - - - -			

Fig. A 2: Safety data sheet of Primera Stone pool plaster.



Swimming Pool Plaster Discoloration

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SECTION 1 - PRODUCT AND CO	ACDANIX IDCANT	FICATION			
PRODUCT NAME: Pigment Dve	MPANT IDENTI	FICATION	MANUFACTURER: Turley Inte	mational Resources, LLC.	
PRODUCT USE: Pool Interior Finish Dye			4322 South	1 80 <sup>th</sup> Street	
SUPPLIER: Wet Edge Technologies			Mesa, AZ 8	5212 - USA	
			TEL: 844-71	86-6333 E: Info@wetedge.com	
EMERGENCY: CHEMTREC P: 703-527-388	7 F:703-527-3887 (Inti	ernational)	MEDICAL: 3E Company P: 800-43	51-8346 F: 760-602-8856 (Internatio	(lene
SECTION 2 – HAZARDS IDENTIF	ICATION		1297		
CLASSIFICATION OF THE SUBSTANCE MIXT HAZARD CLASS	CATEGORY	G 94	HAZARD ST	ATEMENTS	
Acute Toxicity, Oral	N/A	Not Class	ified		
Acute Toxicity, Dermal Skin corrector / Irritation	N/A N/A	Not Class	ified		
Serious eye damage / Eye irritation	N/A	Not Class	ified		
Carcinogenicity Specific target organ toxicity, single even	N/A N/A	Not Class	ified		
Specific target organ toxicity, repeated	N/A	Not Class	ified		
exposure	20 S	5-30			
SECTION 3 - COMPOSITION / II	NFORMATION C	INGRE	DIENTS		
Components					_
Black from oxide	CAS 1317-6 RES	A EYES: In minutes, SKIN: W treatme treatme	EC# n/a mediately flush eye thoroughly with including under lids, to remove all pa sch skin with cool water and pil-nes at if irritation or inflammation dev it in the event of burns. TON: demonstration process in frach air if it	Concentration, N 100% water. Continue Rushing eye for a rticles. Call physician immediately. tral scop or a mild detergent. See elops or persists. Seek immediate explose is difficult actenisister on	it least 1 ik medic e medic
Black from oxide	CAS 1317-6 RES	# EYES: in minutes, SRM: W treatme treatme treatme iNHALA breathin not subs	EC# n/a mediately flush eye thoroughly with including under lids, to remove all pa ash skin with cool water and pH-nes at if irritation or inflammation dev nt in the event of burns. IDM: Remove parson to frush air. If b g, give artificial respiration. Seek med de. Inshalstor of large amounts of pro OM: Do not induce vomiting. If conscie and menderately.	Concentration. 3 100% water. Continue flushing eye for a rticles. Call physician immediately. trai scap or a mild detergent. See elops or persists. Seek immediately ical help if coughing and other sym dicat requires immediate medical a sas, have victim drink plenty of wab	it least 1 ik medica e medica gen. If no sptoms d sttention, er and ca
Black Iron oride SECTION 4 – FIRST AID MEASUR EMERGENCY INFORMATION: SECTION 5 – FIREFIGHTING ME	ASURES	A EVES: In minutes, SKIN; W treatme treatme INHART INGESTIN aphysici	EC # n/a mediately flush eye thoroughly with , including under lids, to remove all pa ash skin with cool water and pit-nes et if initation or inflammation devi it in the event of burns. (DM): Remove parson to finish air. If b g, give artificial respiration. Seek med- ide. Inhalation of large amounts of pro DN: Do not induce vomiting. If conscie an immediately.	Concentration, N 100% water. Continue flushing eye for a rticles. Call physician immediately. trai soap or a mild detergent. See elops or persists. Seek immediat reathing is difficult, administer oxy lical help if coughing and other sym pduct requires immediate medical a sea, have victim drink plenty of wab	et least 1 ek medica e medica gen. If no aptoms d ttention, er and ca
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Fig. A 3: Safety data sheet of pigment dyes showing 100 percent black iron oxide composition.



Swimming Pool Plaster Discoloration



Fig. A 4: Field photo of swimming pool portion where Primera Stone Sapphire Treasure plaster was installed.



Swimming Pool Plaster Discoloration



Fig. A 5: Field photo of swimming pool portion where Primera Stone Blue Ocean plaster was installed.



## **APPENDIX 2**

## **PRIMERA STONE**

### **SAPPHIRE TREASURE SUN SHELF**

&

## **BLUE OCEAN SPA**

**FIELD PLASTER SAMPLES** 





Fig. A 6: Two field plaster samples provided from Primera Stone Sapphire Treasure from Sun Shelf (left) and Primera Stone Blue Ocean from Spa (right).





Fig. A 7: Blotchy discoloration (mottling) of exposed surfaces of Primera Stone Sapphire Treasure (top) and Primera Stone Blue Ocean (bottom) plasters from the field.




Fig. A 8: Blotchy discoloration (mottling) of exposed surface of Primera Stone Sapphire Treasure plaster.



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Fig. A 9: Blotchy discoloration (mottling) of exposed surface of Primera Stone Blue Ocean plaster.





Fig. A 10: Portions selected for sectioning through the two field plasters from Primera Stone Sapphire Treasure (left) and Blue Ocean (right). Each plaster was sectioned vertically into four strips (1 to 4) from one end to the other for four vertical cross sections, as well as two sections at A and B for examinations of discolored exposed surfaces in optical and electron microscopy and X-ray microanalyses.





Fig. A 11: Vertical cross sections of Primera Stone Sapphire Treasure and Blue Ocean showing size, shape, angularity, distribution of aggregates, color tones of paste, color variations or uniformity through depths, and overall consolidated natures of plaster in both samples. Locations of Sections 1 through 4 in each sample is shown in the previous Figure.



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Swimming Pool Plaster Discoloration



Multi-colored crushed aggregate – Blue glass, White quartz, quartzite, chert, Off-white marble, seashell, Gray marble, etc.

Fig. A 12: Micrographs of exposed discolored surface of Primera Stone Sapphire Treasure pool plaster that was in contact with the pool water from the Sun Shelf area showing blotchy appearance of plaster consisting of: (a) beige gray discolored plaster patches marked with yellow arrows and (b) fading of darker to lighter blue colors of plaster marked by the dashed red arrows. Both the beige and lighter blue fading of color are the result of interaction of plaster and pool water. The micrographs were taken with a stereo-microscope.









Yellow arrows – Re-precipitation as secondary carbonates after leaching and dissolution of cement hydration products in paste Red dashed arrows – Fading of original pigment from darker to lighter shades due to differential leaching of cement hydration products creating a blotchy appearance of denser and porous regions Multi-colored crushed aggregate – Blue glass, White quartz, quartzite, chert, Off-white marble, seashell, Gray marble, etc.

Fig. A 13: More micrographs of exposed discolored surface of Primera Stone Sapphire Treasure pool plaster that was in contact with the pool water from the Sun Shelf area showing blotchy appearance of plaster consisting of: (a) beige gray discolored plaster patches marked with yellow arrows and (b) fading of darker to lighter blue colors of plaster marked by the dashed red arrows. Both the beige and lighter blue fading of color are the result of interaction of plaster and pool water. The micrographs were taken with a stereo-microscope.





Fig. A 14: Blue dye-mixed epoxy-impregnated thin section (30 micron thickness) of exposed discolored surface of Primera Stone Sapphire Treasure pool plaster that was in contact with the pool water from the Sun Shelf area. The thin section was scanned on a flatbed film scanner with a polarizing filter to create plane polarized light (PPL) view at the top image, and then sandwiched between two polarizing filters at perpendicular positions to create crossed polarized light (XPL) view at the bottom. The PPL image shows difference in porosities of paste from variations in the degree of absorption of blue epoxy used for preparation of thin section, where porous areas absorbed more blue dye to appear brighter blue whereas denser areas absorb less blue epoxy to appear darker. The XPL image shows the different aggregate types used, which showed major amounts of crushed marble and seashell carbonate particles and minor amounts of siliceous (quartz, quartzite sand) components.





Fig. A 15: Micrographs of thin section of exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) crushed marble (C), quartz (Qtz), alkali-silicate glass (G), strained quartzite, and seashell particles in aggregate; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades due to variations in paste porosities;; and (d) fine, hairline shrinkage microcracks in paste (arrows).





Fig. A 16: Micrographs of thin section of exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) crushed marble (M), alkali-silicate glass (G), and seashell particles in aggregate; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades due to variations in paste porosities; (d) secondary calcite (SC) precipitates from dissolution and re-precipitation of dissolved constituents from plaster by the pool water; and (e) fine, hairline shrinkage microcracks in paste (arrows).





Fig. A 17: Micrographs of thin section of exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) crushed marble (M), and seashell particles in aggregate; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades due to variations in paste porosities; (d) secondary calcite (SC) precipitates from dissolution and re-precipitation of dissolved constituents from plaster by the pool water; and (e) fine, hairline shrinkage microcracks in paste (arrows).





Fig. A 18: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts on the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) calcite and dolomite grains from crushed marble and carbonate deposits (probed at Nos. 1, 7, and 10); (b) residual alite grains from white Portland cement (which appear in lighter shades of small grains Probed at Nos. 3 and 5); and (c) interstitial calcium silicate hydrate and calcium hydroxide components of white Portland cement paste (Probed at Nos. 4, 8, 9, 11, and 12). Each component is showing its characteristic chemical composition. Sulfate contents in the paste in Probe# 4, 6, 8, 9, 11, and 12 are highly variable due to differential leaching and dissolution by the pool water.





Fig. A 19: Secondary electron (SE) image (top) and corresponding backscatter electron (BSE) image (bottom) of the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) extensive fine, hairline shrinkage microcracks in the plaster, which are distinct in the SE image at the top; and (b) different shades of lighter and darker gray areas of paste due to leaching and dissolution of cement hydration products and calcium chloride accelerator from the plaster by the pool water that are separated by yellow dashed lines.





Fig. A 20: X-ray elemental maps of different elements showing compositional variations of the exposed discolored surface of Primera Stone Sapphire Treasure plaster, where paste is showing overall calcium enrichment from white Portland cement paste, with patches enriched in magnesium as shown in the Mg map indicating a potential source of magnesium besides the Portland cement, which could come from the reported addition of the pigment dyes.





Fig. A 21: Secondary electron (SE) image (top) and corresponding backscatter electron (BSE) image (bottom) of the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing different shades of lighter and darker gray areas of paste due to leaching and dissolution of cement hydration products and calcium chloride accelerator from the plaster by the pool water that are distinct in both images. In the BSE image, variations in different shades of gray indicates a variation in chemical compositions and/or porosities of paste.





Fig. A 22: Secondary electron (SE) image (top) and X-ray microanalyses at the tips of callouts on the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) calcite grains from crushed marble and carbonate deposits (probed at Nos. 1, 3, 4, and 5); (b) a quartz sand particle Probed at No. 9; and (c) interstitial calcium silicate hydrate and calcium hydroxide components of white Portland cement paste (Probed at Nos. 2, 6, 7, and 8). Each component is showing its characteristic chemical composition. Sulfate contents in the paste in Probe# 2, and 6 to 8 are negligible to none due to leaching and dissolution by the pool water.





Fig. A 23: X-ray elemental maps of different elements showing compositional variations of the exposed discolored surface of Primera Stone Sapphire Treasure plaster, where paste is showing patchy areas of calcium enrichment in Ca-map from differential dissolution of white Portland cement paste, with patches enriched in magnesium in the Mg map indicating a potential source of magnesium besides the Portland cement, which could come from the reported addition of the pigment dyes. Overall silica enrichment is from calcium silicate hydrate component of paste where silicon was left behind whereas calcium was leached out at various patches.





Fig. A 24: Secondary electron (SE) image (top) and corresponding backscatter electron (BSE) image (bottom) of the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing different shades of lighter and darker gray areas of paste due to leaching and dissolution of cement hydration products and calcium chloride accelerator from the plaster by the pool water that are distinct in both images. Also shown are fine hairline shrinkage microcracks in paste which are more distinct in the SE image. Notice a marble aggregate at the bottom and a darker gray paste immediately around the aggregate.



CONSTRUCTION MATERIALS CONSULTANTS, INC.

Swimming Pool Plaster Discoloration

3

4

56.53 29.76

57.83 29.60



Fig. A 25: Secondary electron (SE) image (top) and X-ray microanalyses at the boxed areas on the exposed discolored
surface of Primera Stone Sapphire Treasure plaster showing the typical characteristic calcium silicate hydrate and
calcium hydroxide components of white Portland cement paste. The next Figure shows a line scan along the arrow
to show chemical variations from darker to lighter gray area of paste.

4.35

4.49

0.02

0.04

0.15

0.05

0.52

0.75

0.00 100.0

0.00 99.98

Paste

Paste

0.63

0.75

1.77

1.72

6.27

4.75





Fig. A 26: X-ray elemental analysis along the line traversing from darker to lighter gray area of paste showing the compositional variations in the paste due to variations in inherent porosities that has caused the blotchy appearance of paste due to differential dissolution of plaster by the pool water.





Fig. A 27: Backscatter electron (BSE) image (top) and corresponding secondary electron (SE) image (bottom) of the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing different shades of lighter and darker gray areas of paste due to variations in chemical compositions of aggregates and interstitial paste where the latter shows numerous fine hairline shrinkage microcracks in the middle separated from the aggregate particles by dashed lines. Boxed areas are analyzed in the next Figure.





Fig. A 28: Backscatter electron (BSE) image (top) and X-ray microanalyses at the boxed areas on the exposed discolored surface of Primera Stone Sapphire Treasure plaster showing: (a) calcite grain in marble (probed at No. 1); (b) an alkali-silicate glass (Probed at No. 6); and (c) interstitial calcium silicate hydrate and calcium hydroxide components of white Portland cement paste (Probed at Nos. 2 to 5). Each component is showing its characteristic chemical composition. Sulfate contents in the paste are higher than that contributed from Portland cement, which is found to be from the barium sulfate extender present in the pigment dyes.





Fig. A 29: X-ray elemental maps of different elements showing compositional variations of the exposed discolored surface of Primera Stone Sapphire Treasure plaster where paste is showing: (a) characteristic calcium enrichment from calcium silicate hydrate and calcium hydroxide composition of cement hydration, and distinguished from (b) sodium silicate glass at the right edge having enriched Na and Si in the respective maps. Notice excessive fine hairline shrinkage microcracks in the paste portion that are prominent in the SE image.





Fig. A 30: Secondary electron image of the exposed discolored surface of Primera Stone Sapphire Treasure plaster where paste is showing a network of numerous fine, hairline shrinkage microcracks. Also shown at the center is a fiber, which is analyzed by EDS to determine the potassium aluminum silicate composition indicating a possible mica flake in the paste.





- 1. Chemical Alterations and associated discoloration of paste
- 2. Thin Scale on Exposed Surface
- 3. Dissolution and Increased Porosity of Plaster Immediately Beneath the Exposed Surface
- 4. Vertical and Horizontal Near-Surface Shallow depth Fine Shrinkage Microcracking

Fig. A 31: Micrographs of vertical cross section of Primera Stone Sapphire Treasure pool plaster where the top edge in each photo was in contact with the pool water showing evidence of leaching and dissolution of paste with increased paste porosity due to dissolution within the boxed areas at the surface regions in all photos. Arrows show vertical, shallow-depth shrinkage microcracks. Fading of darker interior to lighter blue colors of plaster at the surface region is seen from the interior to the boxed areas at the surface. The micrographs were taken with a stereomicroscope.





- Top Side of Each Micrograph to Interior Plaster Towards the Bottom Sides Showing: 1. Chemical Alterations and associated discoloration of paste
- 2. Thin Scale on Exposed Surface
- 3. Dissolution and Increased Porosity of Plaster Immediately Beneath the Exposed Surface
- 4. Vertical and Horizontal Near-Surface Shallow depth Fine Shrinkage Microcracking

Fig. A 32: Micrographs of vertical cross section of Primera Stone Sapphire Treasure pool plaster where the top edges in the top row photos were in contact with the pool water showing evidence of leaching and dissolution of paste with increased paste porosity due to dissolution within the boxed areas at the surface regions. Yellow arrows in the top row show vertical, shallow-depth shrinkage microcracks. Red arrows in the middle and bottom row photos of interior plaster mark fine hairline shrinkage microcracks in paste. The micrographs were taken with a stereomicroscope.





Fig. A 33: Micrographs of vertical cross section of Primera Stone Sapphire Treasure pool plaster where the top edges in the top row photos were in contact with the pool water showing evidence of leaching and dissolution of paste with increased paste porosity due to dissolution within the boxed areas at the surface regions. Yellow arrows show vertical, shallow-depth shrinkage microcracks. The micrographs were taken with a stereo-microscope.





Fig. A 34: Blue dye-mixed epoxy-impregnated thin section (30 micron thickness) of vertical cross sections of Primera Stone Sapphire Treasure pool plaster from the Sun Shelf area. The thin section was scanned on a flatbed film scanner with a polarizing filter to create plane polarized light (PPL) view at the top image, and then sandwiched between two polarizing filters at perpendicular positions to create crossed polarized light (XPL) view at the bottom. The PPL image shows difference in porosities of paste from variations in the degree of absorption of blue epoxy used for preparation of thin section where porous areas absorbed more blue dye to appear brighter blue whereas denser areas absorb less blue epoxy to appear darker. The XPL image shows the different aggregate types used, which showed major amounts of crushed marble and seashell carbonate particles and minor amounts of siliceous (quartz sand) components.





Fig. A 35: Micrographs of thin section of vertical cross section of Primera Stone Sapphire Treasure plaster showing: (a) crushed seashell (SS) particles in aggregate; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from lighter (more porous) shade at the surface region and darker (denser) shade in the interior separated by white dashed lines; and (d) fine, hairline shrinkage microcracks in paste (arrows). The top and middle left photos show increased paste porosity above the dashed lines due to dissolution of cement hydration products by the pool water. Down arrows in the right column show thin films of secondary calcium carbonate precipitation on the exposed surface of plaster.





Fig. A 36: Micrographs of thin section of vertical cross section of Primera Stone Sapphire Treasure plaster showing: (a) crushed marble (M), glass (G), and seashell (SS) particles in aggregate; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from lighter (more porous) shade at the surface region and darker (denser) shade in the interior; and (d) shrinkage microcracks in paste that are filled with secondary calcium carbonate and sulfate deposits (arrows). Down arrows in the top right photo show a thin film of secondary calcium carbonate precipitation on the exposed surface of plaster.





Fig. A 37: Micrographs of thin section of vertical cross section of Primera Stone Sapphire Treasure plaster from the interior showing: (a) crushed marble (M) and glass (G) particles in aggregate; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from lighter (more porous) shade and darker (denser) shade; and (d) fine, hairline shrinkage microcracks in paste (arrows) many of which are filled with secondary calcium carbonate deposits.





Fig. A 38: Micrographs of thin section of vertical cross section of Primera Stone Sapphire Treasure plaster from the interior showing: (a) crushed quartz (Q) and seashell (SS) particles in aggregate; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from lighter (more porous) shade and darker (denser) shade; and (d) fine, hairline shrinkage microcracks in paste (arrows) many of which are filled with secondary calcium carbonate deposits.





Fig. A 39: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts on the vertical cross section of Primera Stone Sapphire Treasure plaster showing: (a) secondary calcium precipitate in the near-surface region of paste (e.g., Probe# 4, 5, 6) having noticeably higher calcium oxide than silica compared to paste at the surface region (Probe# 1, 2, 3) or in the interior (Probe# 7, 8, 11, 12). Paste in the interior (Probe# 7, 8, 11, 12) shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate extender present in the pigment dyes used in the plaster. Sulfate at the surface region of paste at Probe# 1, 2, and 3 are noticeably lower than the interior due to dissolution of sulfate at the surface by pool water.





Fig. A 40: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts on the vertical cross section of Primera Stone Sapphire Treasure plaster showing: (a) a thin film of secondary calcium precipitate at the exposed surface (Probe# 1, 2, and 3) due to localized scaling. Paste in the interior (Probe# 4 to 7, then 9 to 11, then 13 to 17) shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate extender present in the pigment dyes used in the plaster.





Fig. A 41: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts on the vertical cross section of Primera Stone Sapphire Treasure plaster showing: (a) a thin film of secondary calcium precipitate at the exposed surface (Probe# 1, and 2) due to localized scaling. Paste in the interior (Probe# 10 to 21) shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate extender present in the pigment dyes used in the plaster. Sulfate content is variable due to dissolution of plaster by pool water.





Fig. A 42: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts on the vertical cross section of Primera Stone Sapphire Treasure plaster showing: (a) a thin film of secondary calcium precipitate at the exposed surface (Probe# 1, and 2) due to localized scaling. Paste in the interior (Probe# 5 to 12) shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate extender present in the pigment dyes used in the plaster. Sulfate content is variable due to dissolution of plaster by pool water.





Fig. A 43: Backscatter electron (BSE) image (top) and corresponding secondary electron (SE) image (bottom) of the vertical cross section of Primera Stone Sapphire Treasure plaster showing different shades of lighter and darker gray areas of paste due to variations in chemical compositions of aggregates and interstitial paste where the latter shows numerous fine hairline shrinkage microcracks that are distinct in the SE image. Boxed areas are analyzed in the next Figure.




Fig. A 44: Backscatter electron (BSE) image (top) and X-ray microanalyses at the boxed areas on the vertical cross section of Primera Stone Sapphire Treasure plaster showing compositional variations of paste (Probe# 1 and 4), silica sand (Probe# 2), and calcium in marble (Probe# 3). Notice many fine hairline shrinkage microcracks that appear as dark lines in the image.





Fig. A 45: Micrographs of exposed discolored surface of Primera Stone Blue Ocean pool plaster that was in contact with the pool water from the Spa area showing blotchy appearance of plaster consisting of: (a) beige gray discolored plaster patches marked with yellow arrows and (b) fading of darker to lighter blue colors of plaster marked by the dashed red arrows. Both the beige and lighter blue fading of color are the result of interaction of plaster and pool water. The micrographs were taken with a stereo-microscope.





Fig. A 46: Micrographs of exposed discolored surface of Primera Stone Blue Ocean pool plaster that was in contact with the pool water from the Spa area showing blotchy appearance of plaster consisting of: (a) beige gray discolored plaster patches marked with yellow arrows and (b) fading of darker to lighter blue colors of plaster marked by the dashed red arrows. Both the beige and lighter blue fading of color are the result of interaction of plaster and pool water. The micrographs were taken with a stereo-microscope.





Fig. A 47: Blue dye-mixed epoxy-impregnated thin section (30 micron thickness) of exposed discolored surface of Primera Stone Blue Ocean pool plaster that was in contact with the pool water from the Spa area. The thin section was scanned on a flatbed film scanner with a polarizing filter to create plane polarized light (PPL) view at the top image, and then sandwiched between two polarizing filters at perpendicular positions to create crossed polarized light (XPL) view at the bottom. The PPL image shows difference in porosities of paste from variations in the degree of absorption of blue epoxy used for preparation of thin section where porous areas absorbed more blue dye to appear brighter blue whereas denser areas absorb less blue epoxy to appear darker. The XPL image shows the different aggregate types used, which showed major amounts of crushed basalt particles and trace amounts of siliceous (quartz sand) and calcareous (seashell) components.





Fig. A 48: Micrographs of thin section of exposed discolored surface of Primera Stone Blue Ocean plaster showing: (a) crushed basalt particles in aggregate consisting of anhedral to subhedral pyroxene, subhedral plagioclase laths, and dark opaque grains arranged in a porphyritic texture; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades; and (d) secondary calcite precipitates in some voids due to dissolution and re-precipitation of paste by the pool water (arrows).





Fig. A 49: Micrographs of thin section of exposed discolored surface of Primera Stone Blue Ocean plaster showing: (a) crushed basalt particles in aggregate consisting of anhedral to subhedral pyroxene, subhedral plagioclase laths, and dark opaque grains arranged in a porphyritic texture; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades; (d) fine, hairline shrinkage microcracks in paste; and (e) secondary calcite precipitates in some voids due to dissolution and re-precipitation of paste by the pool water (arrow in middle right photo).





Fig. A 50: Micrographs of thin section of exposed discolored surface of Primera Stone Blue Ocean plaster showing: (a) crushed basalt particles in aggregate consisting of anhedral to subhedral pyroxene, subhedral plagioclase laths, and dark opaque grains arranged in a porphyritic texture; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades; (d) fine, hairline shrinkage microcracks in paste; and (e) secondary calcite precipitates in some voids due to dissolution and re-precipitation of paste by the pool water (arrows).





Fig. A 51: Micrographs of thin section of exposed discolored surface of Primera Stone Blue Ocean plaster showing: (a) crushed basalt particles in aggregate consisting of anhedral to subhedral pyroxene, subhedral plagioclase laths, and dark opaque grains arranged in a porphyritic texture; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades; (d) fine, hairline shrinkage microcracks in paste; and (e) secondary calcite precipitates in some voids due to dissolution and re-precipitation of paste by the pool water (arrows).





Fig. A 52: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts and in boxed areas on the exposed discolored surface of Primera Stone Blue Ocean plaster showing crushed basalt aggregate particles (where bright spots within the particles are from iron-titanium oxide opaque grains in basalt) and interstitial paste. Paste was analyzed at various locations from Probe# 1 to 13, and 15 whereas an overall composition of basalt is determined at Probe# 14. Paste shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate extender present in the pigment dyes used in the plaster. Sulfate content is variable due to dissolution of plaster by pool water.





Fig. A 53: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts and in boxed areas on the exposed discolored surface of Primera Stone Blue Ocean plaster showing crushed basalt aggregate particles (where bright spots within the particles are from iron-titanium oxide opaque grains in basalt) and interstitial paste. Paste was analyzed at various locations from Probe# 1 to 10, whereas an overall composition of basalt is determined at Probe# 11. Paste shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate extender present in the pigment dyes used in the plaster. Sulfate content is variable due to dissolution of plaster by pool water.





Fig. A 54: Backscatter electron (BSE) image (top) and corresponding secondary electron (SE) image (bottom) of the exposed discolored surface of Primera Stone Blue Ocean plaster showing different shades of lighter and darker gray areas of paste due to variations in chemical compositions of aggregates and interstitial paste where the latter shows numerous fine hairline shrinkage microcracks that are distinct in the SE image. Boxed areas and tips of callouts are analyzed in the next Figure.





Fig. A 55: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts and in boxed areas on the exposed discolored surface of Primera Stone Blue Ocean plaster showing crushed basalt aggregate particles (where bright spots within the particles are from iron-titanium oxide opaque grains in basalt) and interstitial paste. Paste was analyzed at various locations from Probe# 1 to 10. Paste shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate extender present in the pigment dyes used in the plaster. Sulfate content is variable due to dissolution of plaster by pool water.





Fig. A 56: Secondary electron (SE) image (top) and corresponding backscatter electron (BSE) image (bottom) of the exposed discolored surface of Primera Stone Blue Ocean plaster showing different shades of lighter and darker gray areas of paste due to variations in chemical compositions of aggregates and interstitial paste where the latter shows numerous fine hairline shrinkage microcracks that are distinct in the SE image.





Fig. A 57: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts and in boxed areas on the exposed discolored surface of Primera Stone Blue Ocean plaster showing crushed basalt aggregate particles (where bright spots within the particles are from iron-titanium oxide opaque grains in basalt) and interstitial paste. Paste was analyzed at various locations from Probe# 1 to 13. Paste shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate extender present in the pigment dyes used in the plaster. Sulfate content is variable due to dissolution of plaster by pool water.





Fig. A 58: Backscatter electron (BSE) image (top) and corresponding secondary electron (SE) image (bottom) of the exposed discolored surface of Primera Stone Blue Ocean plaster showing different shades of lighter and darker gray areas of paste due to variations in chemical compositions of aggregates and interstitial paste where the latter shows numerous fine hairline shrinkage microcracks that are distinct in the SE image.





Vertical Cross Sections Through Plaster From The Exposed Surface In Contact with Pool Water At the Top Side of Each Micrograph to Interior Plaster Towards the Bottom Sides Showing: 1. Chemical Alterations and associated discoloration of paste

- 2. Thin Scale on Exposed Surface
- 3. Dissolution and Increased Porosity of Plaster Immediately Beneath the Exposed Surface
- 4. Vertical and Horizontal Near-Surface Shallow depth Fine Shrinkage Microcracking

Fig. A 59: Micrographs of vertical cross section of Primera Stone Blue Ocean pool plaster where the top edge in each photo was in contact with the pool water showing evidence of leaching and dissolution of paste with increased paste porosity due to dissolution within the boxed areas at the surface regions in all photos. Arrows show vertical, shallow-depth shrinkage microcracks. Fading of darker interior to lighter blue colors of plaster at the surface region is seen from the interior to the boxed areas at the surface. The micrographs were taken with a stereo-microscope.





4. Vertical and Horizontal Near-Surface Shallow depth Fine Shrinkage Microcracking

Fig. A 60: Micrographs of vertical cross section of Primera Stone Blue Ocean pool plaster where the top edge in each photo was in contact with the pool water showing evidence of leaching and dissolution of paste with increased paste porosity due to dissolution within the boxed areas at the surface regions in all photos. Arrows show vertical, shallow-depth shrinkage microcracks. Fading of darker interior to lighter blue colors of plaster at the surface region is seen from the interior to the boxed areas at the surface. The micrographs were taken with a stereo-microscope.





Fig. A 61: Micrographs of vertical cross section of Primera Stone Blue Ocean pool plaster where the top edges in the top and middle row photos were in contact with the pool water showing evidence of leaching and dissolution of paste with increased paste porosity due to dissolution within the boxed areas at the surface regions. Yellow arrows in the top and middle rows show vertical, shallow-depth shrinkage microcracks. Red arrows in the middle and bottom row photos of interior plaster mark fine hairline shrinkage microcracks in paste. The micrographs were taken with a stereo-microscope.





Fig. A 62: Blue dye-mixed epoxy-impregnated thin section (30 micron thickness) of vertical cross sections of Primera Stone Blue Ocean pool plaster from the Spa area. The thin section was scanned on a flatbed film scanner with a polarizing filter to create plane polarized light (PPL) view at the top image, and then sandwiched between two polarizing filters at perpendicular positions to create crossed polarized light (XPL) view at the bottom. The PPL image shows difference in porosities of paste from variations in the degree of absorption of blue epoxy used for preparation of thin section where porous areas absorbed more blue dye to appear brighter blue whereas denser areas absorb less blue epoxy to appear darker. The XPL image shows the different aggregate types used, which showed major amounts of crushed basalt and trace amounts of siliceous (quartz sand) and carbonate (seashell) components.





Fig. A 63: Micrographs of thin section of vertical cross sections of Primera Stone Blue Ocean plaster showing: (a) crushed basalt particles in aggregate consisting of anhedral to subhedral pyroxene, subhedral plagioclase laths, and dark opaque grains arranged in a porphyritic texture; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades; (d) fine, hairline shrinkage microcracks in paste (arrows in the top row); and (e) zones of chemical alterations of exposed surface region due to pool water interactions that are marked in Photo 6 as carbonated zone at the very top surface (#1), a darker intermediate zone beneath (#2), and interior paste (#3).





Fig. A 64: Micrographs of thin section of vertical cross sections of Primera Stone Blue Ocean plaster showing: (a) crushed basalt particles in aggregate consisting of anhedral to subhedral pyroxene, subhedral plagioclase laths, and dark opaque grains arranged in a porphyritic texture; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades; (d) fine, vertical, hairline shrinkage microcracks in paste (arrows in the left column photos); and (e) zones of chemical alterations of exposed surface region due to pool water interactions that are marked in Photos 2, 4, and 6 as carbonated zone at the very top surface (#1), a darker intermediate zone beneath (#2), and interior paste (#3).





Fig. A 65: Micrographs of thin section of vertical cross sections of Primera Stone Blue Ocean plaster showing: (a) crushed basalt particles in aggregate consisting of anhedral to subhedral pyroxene, subhedral plagioclase laths, and dark opaque grains arranged in a porphyritic texture; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades; (d) fine, vertical, hairline shrinkage microcracks in paste (arrows in the top left photo); and (e) zones of chemical alterations of exposed surface region due to pool water interactions that are marked in Photos 2, 4, and 6 as carbonated zone at the very top surface (#1), a darker intermediate zone beneath (#2), and interior paste (#3). Yellow arrow in Photo 6 marks a secondary calcite precipitate in an air void immediately beneath the surface.





Fig. A 66: Micrographs of thin section of vertical cross sections of Primera Stone Blue Ocean plaster showing: (a) crushed basalt particles in aggregate consisting of anhedral to subhedral pyroxene, subhedral plagioclase laths, and dark opaque grains arranged in a porphyritic texture; (b) dense interstitial paste consisting of white Portland cement; (c) blotchy or patchy discoloration of plaster from darker to lighter shades; (d) fine, vertical, hairline shrinkage microcracks in paste; and (e) zones of chemical alterations of exposed surface region due to pool water interactions that are marked in Photos 2, 4, and 6 as carbonated zone at the very top surface (#1), a darker intermediate zone beneath (#2), and interior paste (#3).





Fig. A 67: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts on the vertical cross section of Primera Stone Blue Ocean plaster showing: (a) secondary calcium precipitate in the near-surface region of paste (e.g., Probe# 5) having noticeably higher calcium oxide than silica compared to paste at the surface region (Probe# 1, 2, 3, 4) or in the interior (Probe# 6 to 14). Paste in the interior (Probe# 6 to 14) shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate extender present in the pigment dyes used in the plaster. Sulfate at the surface region of paste at Probe# 1 to 3 are noticeably lower than the interior due to dissolution of sulfate at the surface by pool water.





Fig. A 68: Backscatter electron (BSE) image (top) and corresponding secondary electron (SE) image (bottom) of the vertical cross section of Primera Stone Blue Ocean plaster showing different shades of lighter and darker gray areas of paste due to variations in chemical compositions of aggregates and interstitial paste where the latter shows numerous fine vertical hairline shrinkage microcracks. The tips of callouts in the BSE image were analyzed in the previous Figure.





Fig. A 69: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts on the vertical cross section of Primera Stone Blue Ocean plaster showing: (a) secondary calcium precipitate in the near-surface region of paste (e.g., Probe# 5 to 9) having noticeably higher calcium oxide than silica compared to paste at the surface region (Probe# 1, 2, 3, 4) or in the interior (Probe# 11 to 16). Paste in the interior (Probe# 11 to 16) shows typical compositions of calcium silicate hydrate and calcium hydroxide components of cement hydration products except higher sulfate than that contributed from Portland cement, which is found to be from the barium sulfate extender present in the pigment dyes used in the plaster. Sulfate at the surface region of paste at Probe# 1 to 4 are lower than the interior due to dissolution of sulfate at the surface by pool water.





Fig. A 70: Backscatter electron (BSE) image (top) and corresponding secondary electron (SE) image (bottom) of the vertical cross section of Primera Stone Blue Ocean plaster showing different shades of lighter and darker gray areas of paste due to variations in chemical compositions of aggregates and interstitial paste where the latter shows numerous fine vertical hairline shrinkage microcracks. The tips of callouts in the BSE image were analyzed in the previous Figure.





Fig. A 71: Backscatter electron (BSE) image (top) and X-ray microanalyses at the tips of callouts and in boxed areas on the vertical cross section of Primera Stone Blue Ocean plaster showing compositional variations of paste from the exposed surface region (Probe# 1 to 4) to interior (Probe# 8 to 11) due to interaction of plaster with pool water. Dissolution of paste by pool water is seen from variations in sulfate contents from the low sulfate in the dissolved paste at the top (Probe# 1 to 4) compared to higher sulfate in the interior paste in Probe# 8 to 11. The fine light gray particles in paste are residual alite. Two basalt particles in aggregate are seen at left and right edges. Paste shows network of fine shrinkage microcracks.





Fig. A 72: Backscatter electron (BSE) image (top) and corresponding secondary electron (SE) image (bottom) of the vertical cross section of Primera Stone Blue Ocean plaster showing different shades of lighter and darker gray areas of paste due to variations in chemical compositions of aggregates and interstitial paste where the latter shows numerous fine vertical hairline shrinkage microcracks. The tips of callouts and boxed areas in the BSE image are analyzed in the previous Figure. Notice the paste color variations in SE image due to dissolution of paste by pool water that has created a darker gray paste at the surface region in both images.





Fig. A 73: Secondary electron (SE) image (top) and corresponding backscatter electron (BSE) image (bottom) of the vertical cross section of Primera Stone Blue Ocean plaster from the interior region of plaster showing a central region of paste having numerous fine shrinkage microcracks and basalt aggregate particles. The boxed area in the paste in SE image is analyzed below which showed typical calcium silicate hydrate and calcium hydroxide compositions of cement hydration products except higher sulfate than that contributed from Portland cement due to dissolution of some sulfate from barium sulfate extender present in the pigment dyes.



Swimming Pool Plaster Discoloration



Fig. A 74: Secondary electron (SE) image (top) and corresponding backscatter electron (BSE) image (bottom) of the vertical cross section of Primera Stone Blue Ocean plaster from the interior region of plaster showing a central region of paste having numerous fine shrinkage microcracks and a basalt aggregate at the right side. The boxed area in the paste in SE image is analyzed below which showed typical calcium silicate hydrate and calcium hydroxide compositions of cement hydration products except higher sulfate than that contributed from Portland cement due to dissolution of some sulfate from barium sulfate extender present in the pigment dyes.



## **APPENDIX 3**

## PRIMERA STONE PLASTER KITS, CEMENTS, AND PIGMENTS



## Swimming Pool Plaster Discoloration

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Attn: Dipayan Jana				
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#1831 – Patch Kit – Co #1832 – Mediterrane	omponents that r an Pigment used	to make up Primera Blue to make up Sapphire T	reasure SAMPLE 1	
#1833 – Midnight Pig	ment used to ma	ke up Blue Ocean SAM	PLE 2 ite per batch formu	la
Our pool finish produ formulas. The applica that installed these tw	cts are compone itors add their ov vo finishes used i nt according to t	nt mixed at the jobsite wn white portland cerr Lehigh Blended Cemer he website contains n	<ul> <li>Applicators follow eent at the jobsite.</li> <li>ht.</li> <li>hore lime than their</li> </ul>	v our batch The applicator standard white
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Fig. A 75: Information provided for various plaster kits, cement, and pigment dyes provided along with the field plaster samples. The mix proportions of both field plaster types and corresponding kits are provided.



Swimming Pool Plaster Discoloration

Fig. A 76: Shown are the various plaster kits including the kits for both field plaster types, as well as two pigment dyes provided.



**Pool Plaster Dry Ingredients** & Pigments Received (MCO221105 1834 Lehigh Blended Cement (MC0221105 1833 CMC0221105 CM(022/105 CNO221105 MC0221105 1831 18.30 Blue Ocean Blue Ocean Sapphire Treasure 1830 Patch Kit - SAMPLE 1 1831 Patch Kit - SAMPLE 2 Components that make Primera Stone Sapphire Treasure Complete weight of patch kit is 5 lbs Aggregate weight 2.81 lbs rimera Stone Blue Ocean Primera Blue Ocean with omplete weight of patch kit is 5 lbs Aggregate weight 2.81 lbs White Portland cement weight 2.20 lbs Standard White Portland White Portland coment weight 2.20 lbs Add to the patch kit Calcium Chloride .044 lb Cement Add to the patch kit Calcium Chloride .044 lb Add Percentage of water is .42 to .50 Add Percentage of water is A2 to .50

Fig. A 77: Shown are the various plaster kits including the kits for both field plaster types, as well as a blended cement and two pigment dyes provided.





Fig. A 78: Clear epoxy-encapsulated thin sections (30 micron thickness) of various plaster kits including the kits for both field plaster types, as well as the blended cement, and two pigment dyes prepared for examinations in a petrographic microscope and in SEM.




Fig. A 79: Thin section micrographs of Plaster Kit# 1830 for Primera Stone Sapphire Treasure showing the presence of crushed marble, glass, and chert particles in dry white Portland cement (WPC), which are all encapsulated in a clear epoxy medium. Notice the masonry cement-like appearance (in mineralogy and microstructure) of the interstitial dry binder component, which shows major amount of white Portland cement and subordinate amount of limestone fines.





Fig. A 80: Thin section micrographs of Plaster Kit# 1830 for Primera Stone Sapphire Treasure showing the presence of crushed seashell particles in dry white Portland cement (WPC), which are all encapsulated in a clear epoxy medium. Notice the overall mineralogies and microstructures of the binder in the plaster kit# 1830 are similar to that of a masonry cement made using white Portland cement, and limestone fines (possibly with some hydrated lime as well).





Fig. A 81: Backscatter electron image (BSE) and corresponding X-ray microanalyses of aggregates dispersed in white Portland cement in Plaster Kit# 1830 for Primera Stone Sapphire Treasure.





#1830 Patch Kit – In 5 lbs. kit: Aggregate 2.81 lbs., White PC 2.20 lbs., Add to the patch kit Calcium Chloride 0.044 lbs., Water-cement ratio 0.42 to 0.50.

Fig. A 82: X-ray elemental maps in SEM of aggregates dispersed in white Portland cement in Plaster Kit# 1830 for Primera Stone Sapphire Treasure.





Fig. A 83: Backscatter electron image (BSE) and corresponding X-ray microanalyses of aggregates and alite particles, free lime, and gypsum in white Portland cement, and a sodium silicate glass aggregate particle in Plaster Kit# 1830 for Primera Stone Sapphire Treasure.





Fig. A 84: X-ray diffraction pattern of Plaster Kit# 1830 for Primera Stone Sapphire Treasure showing the presence of alite from white Portland cement, and calcite and quartz from aggregate particles.

148





Fig. A 85: Thin section micrographs of Plaster Kit# 1831 for Primera Stone Blue Ocean showing the presence of crushed basalt particles (containing anhedral to subhedral pyroxene, subhedral lath-shaped plagioclase, and dark opaque grains in porphyritic texture) dispersed in dry white Portland cement (WPC), which are all encapsulated in a clear epoxy medium. Notice the interstitial dry binder shows similarity to the binder in kit# 1830 in having a masonry cement-like appearance in mineralogy and microstructure containing major amount of white Portland cement and subordinate amount of limestone fines (possibly with some hydrated lime as well).





Fig. A 86: Thin section micrographs of Plaster Kit# 1831 for Primera Stone Blue Ocean showing the presence of crushed basalt particles (containing anhedral to subhedral pyroxene, subhedral lath-shaped plagioclase, and dark opaque grains in porphyritic texture) dispersed in dry white Portland cement (WPC), which are all encapsulated in a clear epoxy medium. Notice the overall mineralogies and microstructures of the binder in the plaster kit# 1831 are similar to that of kit# 1830, which are similar to that of a masonry cement made using white Portland cement, and limestone fines (possibly with some hydrated lime as well).





Fig. A 87: Backscatter electron image (BSE) and corresponding X-ray microanalyses of aggregates and alite particles in white Portland cement and a basalt aggregate particle in Plaster Kit# 1831 for Primera Stone Blue Ocean.





Fig. A 88: X-ray diffraction pattern of Plaster Kit# 1830 for Primera Stone Blue Ocean showing the presence of alite from white Portland cement and pyroxene (augite, diopside), and plagioclase (albite, oligoclase) in basalt aggregate.





Fig. A 89: Backscatter electron image (BSE) and corresponding X-ray microanalyses of 1832 Mediterranean pigment dye used for Primera Stone Sapphire Treasure plaster. The dye showed the presence of a barium sulfate extender (Probe# 1 and 2), which appeared as bright spots in this image all over the dye, which is responsible for the higher sulfate content of paste in the field plaster samples compared to the sulfate contributed from hydration of Portland cement. The dye showed iron oxide as the main component along with variable other components present in minor amounts.





Fig. A 90: Backscatter electron image (BSE) and corresponding X-ray microanalyses of 1832 Mediterranean pigment dye used for Primera Stone Sapphire Treasure plaster. The dye showed the presence of a barium sulfate extender (Probe# 10), which appeared as bright spots in this image all over the dye, which is responsible for the higher sulfate content of paste in the field plaster samples compared to the sulfate contributed from hydration of Portland cement. The dye showed iron oxide as the main component along with variable other components present in minor amounts.





Fig. A 91: X-ray diffraction pattern of 1832 Mediterranean pigment dye used for Primera Stone Sapphire Treasure plaster.





Fig. A 92: Backscatter electron image (BSE) and corresponding X-ray microanalyses of 1833 Midnight pigment dye used for Primera Stone Blue Ocean plaster. The dye showed the presence of a barium sulfate extender, which appeared as bright spots in this image all over the dye, which is responsible for the higher sulfate content of paste in the field plaster samples compared to the sulfate contributed from hydration of Portland cement. The dye showed iron-chromium oxide as the main component along with variable other components present in minor amounts.





Fig. A 93: Backscatter electron image (BSE) and corresponding X-ray microanalyses of 1833 Midnight pigment dye used for Primera Stone Blue Ocean plaster. The dye showed the presence of a barium sulfate extender (Probe# 1 and 2), which appeared as bright spots in this image all over the dye, which is responsible for the higher sulfate content of paste in the field plaster samples compared to the sulfate contributed from hydration of Portland cement. The dye showed iron-chromium oxide as the main component along with variable other components present in minor amounts.





Fig. A 94: X-ray diffraction pattern of 1833 Midnight pigment dye used for Primera Stone Blue Ocean plaster.



Swimming Pool Plaster Discoloration



Fig. A 95: Thin section micrographs of Lehigh blended cement which is a mixture of major amount of white Portland cement (WPC) and limestone fine particles (LF), which are all encapsulated in a clear epoxy medium. Notice the overall mineralogies and microstructures of the blended cement binder in 1834 are similar to that of a masonry cement made using white Portland cement, and limestone fines (possibly with some hydrated lime as well), which are seen for the binders used in kit# 1830 and 1831.





Fig. A 96: Backscatter electron image (BSE) and corresponding X-ray microanalyses of Lehigh blended cement showing alite from white Portland cement (WPC) in Probe# 1 to 7 and limestone fine particles (LF) in Probe# 8.





Fig. A 97: X-ray diffraction pattern of Lehigh blended cement showing alite from white Portland cement and calcite from limestone fines.

161





Fig. A 98: Thin section micrographs of Plaster Kit# 1835 for Primera Stone Blue Ocean showing the presence of crushed basalt particles (containing anhedral to subhedral pyroxene, subhedral lath-shaped plagioclase, nepheline, and dark opaque grains in porphyritic texture) dispersed in dry white Portland cement (WPC), which are all encapsulated in a clear epoxy medium. Notice the overall mineralogies and microstructures of the binder in the plaster kit #1835 are slightly different from that in kits# 1830 and 1831, in having overall lesser amount of limestone fine, if any, and higher amount of rounded belite grains in white Portland cement.





Fig. A 99: Thin section micrographs of Plaster Kit# 1835 for Primera Stone Blue Ocean showing the presence of crushed basalt particles (containing anhedral to subhedral pyroxene, subhedral lath-shaped plagioclase, nepheline, and dark opaque grains in porphyritic texture) dispersed in dry white Portland cement (WPC), which are all encapsulated in a clear epoxy medium. Notice the overall mineralogies and microstructures of the binder in the plaster kit #1835 are slightly different from that in kits# 1830 and 1831, in having overall lesser amount of limestone fine, if any, and higher amount of rounded belite grains in white Portland cement.





Fig. A 100: Backscatter electron image (BSE) and corresponding X-ray microanalyses of basalt aggregate (Probe# 5) and alite and belite particles in white Portland cement (Probe# 1 to 4) in Plaster Kit# 1835 for Primera Stone Blue Ocean.



Swimming Pool Plaster Discoloration



Fig. A 101: X- ray elemental maps of Plaster Kit# 1835 for Primera Stone Blue Ocean showing basalt aggregate particles highlighted in Ca and Al maps and interstitial white Portland cement paste highlighted in Ca map.



Swimming Pool Plaster Discoloration



Fig. A 102: X-ray diffraction pattern of Plaster Kit# 1835 for Primera Stone Blue Ocean showing alite from white Portland cement, and pyroxene (augite, diopside), plagioclase (albite, oligoclase), and nepheline in basalt aggregate.

166



Swimming Pool Plaster Discoloration



Fig. A 103: X-ray diffraction pattern of calcium chloride set accelerator (flake-type) showing the diffraction pattern of mineral sinjarite of composition CaCl<sub>2</sub>.2H<sub>2</sub>O.

167



# **APPENDIX 4**

# **PRIMERA STONE**

## **LABORATORY-CURED PLASTERS**

&

## **EXPERIMENTS IN WATER**



#### Preparation of Plaster Cubes From Three Kits With & Without Calcium Chloride Accelerator



Plaster 400 grams, Water 80 grams, CaCl<sub>2</sub> 17.6 grams, Plaster-to-Water Mass Ratio 0.20 (Water-to-Cement Ratio of 0.50) Calcium Chloride-to-Plaster Mass Ratio 0.044 (Flake CaCl<sub>2</sub> Added to water before mixing)

Fig. A 104: Preparation of 2 in. size cubes of plaster from three kits 1830, 1831, and 1835 used for field plaster samples.

A mix proportion consisting of 400 grams of plaster, 80 grams of tap water, at a plaster-to-water mass ratio of 0.20 was used.

Two sets were prepared, one with tap water only, and the second batch where 80 grams of water was mixed with 17.6 grams of calcium chloride flake.

Plasters with and without set accelerator were cured at 100 percent humidity in the ambient temperature of laboratory for 1 day, then demolded, then cured for an additional 7 days.

Samples thus prepared were then submerged in tap water and water with calcium hypochlorite disinfectant solutions to observe the discoloration of plasters prepared with and without calcium chloride accelerators.

Finally, thin sections were prepared of lab-cured plaster kits with and without calcium chloride accelerator immersed in tap water and hypochlorite solution.





Fig. A 105: Cubes demolded after one day of mixing, and subsequently enclosed in a box that has water at the bottom (not touching the cubes) and a moist towel placed on top of the cubes to create 100 percent humidity.





### CaCl<sub>2</sub> Has Darkened All Three Plaster Kits

Fig. A 106: Darkening of all three lab-cured hardened plaster kits due to addition of flake calcium chloride accelerating admixture in the mix water. The photos were taken prior to the immersion of samples in tap water or hypochlorite solution.



### Laboratory-Prepared 2 in. Cubes of Three Plaster Kits With & Without Calcium Chloride Accelerator

### Plaster Immersed in Calcium Hypochlorite Solution



Plaster Immersed in Tap Water

This above batch is for plaster samples prepared without adding a flake calcium chloride accelerator in the mix water. The second batch of three kits prepared with flake calcium chloride accelerator added to the mix water were also completely immersed in tap water and calcium hypochlorite disinfectant solution for 7 days as above.

Fig. A 107: Laboratory-cured plaster samples immersed in tap water and a calcium hypochlorite solution to observe the surface discoloration, especially for the batch prepared with calcium chloride accelerator.





Fig. A 108: Thin sections of all components of plasters received from: (a) the dry plaster kits (1830, 1831, 1835), Lehigh blended cement (1834), and two pigments (1832 and 1833) at the very top to (b) Laboratory-cured hardened plasters from kits 1830, 1831, and 1835 prepared with calcium chloride accelerator addition to the mix water shown in the 2<sup>nd</sup> row left photo to the ones prepared straight with tap water without any accelerator in the 2<sup>nd</sup> row, right; to (c) effects after immersion of both sets of hardened plasters to the aggressive tap water in the 3<sup>rd</sup> row, and (d) immersion to more balanced solution of water mixed with calcium hypochlorite solution at the bottom row. Micrographs of these thin sections are all shown in the following Figures.





Fig. A 109: Thin section of three lab-cured plasters (7 days of moist curing) without calcium chloride accelerator addition to mix water shown in PPL image.





Fig. A 110: Thin section of three lab-cured plasters (7 days of moist curing) without calcium chloride accelerator addition to mix water shown in XPL image.





Fig. A 111: Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 without calcium chloride accelerator showing abundant subhedral to anhedral alite, subordinate rounded belite, and limestone fines (a few are marked with arrows) in paste. Notice the overall mineralogies and microstructures of the binder in the hardened plaster kit# 1830 are similar to that of a masonry cement paste made using white Portland cement, and limestone fines (possibly with some hydrated lime as well).





Fig. A 112: Micrographs of thin section of laboratory-cured hardened plaster kit# 1831 without calcium chloride accelerator showing abundant subhedral to anhedral alite, subordinate rounded belite, and limestone fines (a few are marked with arrows) in paste. Notice the overall mineralogies and microstructures of the binder in the hardened plaster kit# 1831 are similar to that of kit# 1830, which are similar to that of a masonry cement paste made using white Portland cement, and limestone fines (possibly with some hydrated lime as well).





Fig. A 113: Micrographs of thin section of laboratory-cured hardened plaster kit# 1835 without calcium chloride accelerator showing abundant rounded belite, subordinate subhedral to anhedral alite, and minor limestone fines (a few are marked with arrows) in paste. Notice the overall mineralogies and microstructures of the binder in the hardened plaster kit# 1835 are slightly different from that in kits# 1830 and 1831, in having overall lesser amount of limestone fine, if any, and higher amount of rounded belite grains in white Portland cement.


### Thin Section of Laboratory-Prepared 2 in. Cubes of Three Plaster Kits Without Calcium Chloride Accelerator Immersed in Tap water For 7 Days – PPL Image



Fig. A 114: Thin section of three lab-cured plasters (7 days of moist curing) without calcium chloride accelerator addition to mix water after immersing the plasters in tap water for 7 days to observe dissolution of paste - shown in PPL image.







Fig. A 115: Thin section of three lab-cured plasters (7 days of moist curing) without calcium chloride accelerator addition to mix water after immersing the plasters in tap water for 7 days to observe dissolution of paste - shown in XPL image.





Fig. A 116: Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 without calcium chloride accelerator after 7 days of immersion in tap water showing aggressive action of tap water by dissolution of soluble components of paste and precipitation as dog tooth-shaped secondary calcite precipitates on exposed surfaces.





Fig. A 117: Micrographs of thin section of laboratory-cured hardened plaster kit# 1831 without calcium chloride accelerator after 7 days of immersion in tap water showing aggressive action of tap water by dissolution of soluble components of paste and precipitation as dog tooth-shaped secondary calcite precipitates on exposed surfaces.





Fig. A 118: Micrographs of thin section of laboratory-cured hardened plaster kit# 1835 without calcium chloride accelerator after 7 days of immersion in tap water showing aggressive action of tap water by dissolution of soluble components of paste and precipitation as dog tooth-shaped secondary calcite precipitates on exposed surfaces.







Fig. A 119: Thin section of three lab-cured plasters (7 days of moist curing) without calcium chloride accelerator addition to mix water after immersing the plasters in calcium hypochlorite disinfectant solution for 7 days to observe dissolution of paste - shown in PPL image.



Thin Section of Laboratory-Prepared 2 in. Cubes of Three Plaster Kits Without Calcium Chloride Accelerator Immersed in Ca-Hypochlorite Solution For 7 Days – XPL Image



Fig. A 120: Thin section of three lab-cured plasters (7 days of moist curing) without calcium chloride accelerator addition to mix water after immersing the plasters in calcium hypochlorite disinfectant solution for 7 days to observe dissolution of paste - shown in XPL image.





Fig. A 121: Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 without calcium chloride accelerator after 7 days of immersion in calcium hypochlorite solution showing balanced nature of solution due to lack of scaling or secondary calcite precipitate on exposed surface which was seen in tap water immersion.

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Fig. A 122: Micrographs of thin section of laboratory-cured hardened plaster kit# 1831 without calcium chloride accelerator after 7 days of immersion in calcium hypochlorite solution showing balanced nature of solution due to lack of scaling or secondary calcite precipitate on exposed surface which was seen in tap water immersion.





Fig. A 123: Micrographs of thin section of laboratory-cured hardened plaster kit# 1835 without calcium chloride accelerator after 7 days of immersion in calcium hypochlorite solution showing balanced nature of solution due to lack of scaling or secondary calcite precipitate on exposed surface which was seen in tap water immersion.





Fig. A 124: Thin section of three lab-cured plasters (7 days of moist curing) with calcium chloride accelerator addition to mix water shown in PPL image.





Fig. A 125: Thin section of three lab-cured plasters (7 days of moist curing) with calcium chloride accelerator addition to mix water shown in XPL image.





Fig. A 126: Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 with calcium chloride accelerator showing abundant subhedral to anhedral alite, subordinate rounded belite, and limestone fines (a few are marked with arrows) in paste.





Fig. A 127: Micrographs of thin section of laboratory-cured hardened plaster kit# 1831 with calcium chloride accelerator showing abundant subhedral to anhedral alite, subordinate rounded belite, and limestone fines (a few are marked with arrows) in paste. Notice some coarsely crystalline secondary calcium hydroxide crystals in an air void in the bottom row indicating high solubility of finely crystalline calcium hydroxide component of cement hydration.





Fig. A 128: Micrographs of thin section of laboratory-cured hardened plaster kit# 1835 with calcium chloride accelerator showing abundant rounded belite, subordinate subhedral to anhedral alite, and minor limestone fines in paste. Notice some coarsely crystalline secondary calcium hydroxide crystals in an air void in the middle row indicating high solubility of finely crystalline calcium hydroxide component of cement hydration.





Fig. A 129: Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 with calcium chloride accelerator immersed in tap water for 7 days, showing abundant residual alite grains, and subordinate limestone fines in paste. Notice some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. Notice the lack of surface scaling of secondary calcite.





Fig. A 130: Micrographs of thin section of laboratory-cured hardened plaster kit# 1831 with calcium chloride accelerator immersed in tap water for 7 days, showing abundant residual alite grains, and subordinate limestone fines in paste. Notice some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. Notice the lack of surface scaling of secondary calcite.





Fig. A 131: Micrographs of thin section of laboratory-cured hardened plaster kit# 1835 with calcium chloride accelerator immersed in tap water for 7 days, showing abundant residual belite grains, subordinate alite, and negligible limestone fines in paste. Notice some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. Notice the lack of surface scaling of secondary calcite.





No Scaling or precipitation of coarse dog tooth-shaped secondary calcite on the exposed surface as found in plasters without CaCl<sub>2</sub> addition

Fig. A 132: Micrographs of thin section of laboratory-cured hardened plaster kit# 1830 with calcium chloride accelerator immersed in calcium hypochlorite disinfectant solution for 7 days, showing abundant residual alite grains, and subordinate limestone fines in paste. Notice some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. Notice the lack of surface scaling of secondary calcite.





Fig. A 133: Micrographs of thin section of laboratory-cured hardened plaster kit# 1831 with calcium chloride accelerator immersed in calcium hypochlorite disinfectant solution for 7 days, showing abundant residual alite grains, and subordinate limestone fines in paste. Notice some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. Notice the lack of surface scaling of secondary calcite.





No Scaling or precipitation of coarse dog tooth-shaped secondary calcite on the exposed surface as found in plasters without CaCl<sub>2</sub> addition

Fig. A 134: Micrographs of thin section of laboratory-cured hardened plaster kit# 1835 with calcium chloride accelerator immersed in calcium hypochlorite disinfectant solution for 7 days, showing abundant residual belite grains, subordinate alite, and negligible limestone fines in paste. Notice some coarsely crystalline lath-shaped secondary calcium hydroxide crystals in air voids indicating high solubility of finely crystalline calcium hydroxide component of cement hydration in water. Notice the lack of surface scaling of secondary calcite.



**APPENDIX 5** 

# SWIMMING POOL PLASTER DETERIORATION

## **– OVERVIEW AND CASE STUDIES**

PROCEEDINGS OF THE THIRTIETH CONFERENCE ON CEMENT MICROSCOPY, APRIL 20 TO 24, RENO, NEVADA, USA 2008

### **SWIMMING POOL PLASTER DETERIORATION - OVERVIEW & CASE STUDIES**

Dipayan Jana

Applied Petrographic Services, Inc., and Construction Materials Consultants, Inc. Greensburg, PA, USA

### AB\$TRACT

Deterioration of swimming pool's cementitious coating (plaster) is a complex process involving interactions of four closely related systems – (a) the pool water containing water-treatment and other chemicals, (b) the plaster, (c) the shotcrete or concrete substrate on which the plaster is applied, and, (d) the environments in which the plaster was placed and is in service. Common forms of pool plaster deterioration include: (a) cracking of pool plaster by various mechanisms, such as shrinkage prior to water immersion, structural movement of pool such as settlement of substrate, or, expansive chemical reactions within the substrate putting the plaster in tension; (b) softening of plaster due to the use of inferior plaster materials or mix, improper placement temperature and practices, and interactions with aggressive pool water; (c) debonding of plaster from substrate, or debonding of one coat of plaster from its undercoat; (d) sporadic mottled or blotchy gray-hued abnormal discoloration of plaster surface; (e) staining discoloration from various sources; (f) dissolution of plaster (leaching) and associated etching by aggressive acid water, (g) scaling or precipitation of secondary deposits on plaster surface by alkaline water chemistry; (h) combined aggressive chemical attacks by alternating acidic and basic pool water chemistries on the plaster surface and associated etching and staining; (i) spot alterations from aggressive water attack and/or improper plastering processes; (j) plaster surface popout and local staining by unsound or reactive sand particles in plaster; and (k) freezing and thawing damage of plaster surface prior to water immersion, or of portions not immersed in water, etc.

Petrographic examinations (optical and scanning electron microscopy) and chemical analyses of plaster samples from damaged pools are often helpful to diagnose the cause(s) of plaster deterioration and its extent. Case studies presented herein are of samples received to our laboratory from various pools at different degrees and types of deterioration. Studies discussed include: (a) cracking of pool plasters by excessive shrinkage of plaster and deleterious alkali-silica reaction of aggregates in the concrete substrate, (b) plaster debonding and blistering, (c) plaster etching and scaling by imbalanced pool water, (d) mottled discoloration of plaster, (e) staining by brick masonry copings, and (f) spot alterations and associated spot staining of plaster.

### INTRODUCTION

Swimming pool plaster is a relatively thin [thickness 9.5 to 19 mm (<sup>3</sup>/s to <sup>3</sup>/4 in.)] layer of dense cementitious coating containing a mixture of white portland cement (or pigmented cement), aggregate (commonly calcium carbonate aggregate such as limestone or marble chips, or siliceous aggregate), and water, with or without other admixtures that when mixed thoroughly, placed properly over the shotcrete or concrete substrate, and finished and cured accordingly, forms a decorative, maintainable, and near water-tight finish. Plaster containing white portland cement and marble chip aggregate has been one of the most commonly applied pool finishes used over the past 40 years. Deterioration of swimming pool plaster, prior to its anticipated service life, has been a growing concern of not only the pool owners but also of plasterers, service and chlorine industries, and other professionals in the pool and spa industry. Concerns commonly raised for plaster deterioration include inferior plaster materials and plaster quality, improper proportioning (e.g., excessive addition of calcium chloride admixture), improper finishing, substrate expansion or settlement, aggressive pool water attacks, etc. Increasing use of various water treatment chemicals multiplies the complexity of interactions of pool water with its cementitious coating and sometimes contributes to the plaster problems. This paper provides an overview and case studies of various pool plaster deterioration.

202

PROCEEDINGS OF THE THIRTIETH CONFERENCE ON CEMENT MICROSCOPY, APRIL 20 TO 24, RENO, NEVADA, USA 2008

### TYPE\$ OF \$WIMMING POOL PLASTER DETERIORATION

The Technical Manual of National Plasterers Council (NPC) provides a good overview of various deterioration of swimming pool plaster [1], which is summarized below. Many of these distress mechanisms are manifestations of one or a combination of the following:

- (a) Interactions between the swimming pool water and the plaster (the imbalance of the pool water chemistry and its deleterious effects on the plaster causing leaching/etching, or staining/scaling type deteriorations);
- (b) Use of improper plaster materials, mix (e.g., improper amounts of sand, cement, or calcium chloride admixture), or construction practices (improper finishing, inadequate curing and rapid drying of freshly placed plaster, placement in subfreezing temperatures, placement on improper substrate surface, etc.) causing plaster softening, debonding, and discoloration;
- (c) Effect of unstable substrate on plaster (expansion, settlement, source for plaster staining, etc.) causing plaster cracking or staining;
- (d) Improper design of pool; and,
- (e) Improper pool maintenance (e.g., excessive dosage of some water-treatment chemicals).

A comprehensive list of pool plaster deterioration includes [1]:

- (a) Plaster **cracking**, either by plaster shrinkage prior to immersion in water, or by structural movement, subgrade settlement, or, soil/substrate expansion putting plaster in tension;
- (b) Plaster **softening**, due to use of improper plaster mix, materials, or proportions, interaction with aggressive pool water, or placement in subfreezing temperatures;
- (c) Plaster **debonding**, either debonding between the coats of plaster, or of plaster from substrate, incipient delamination (e.g., blisters, buckles), and spalls;
- (d) Plaster discoloration as sporadic shaded, gray-hued areas of excessive mottling, blotchiness;
- (e) Plaster staining at isolated small localized areas having colors distinct from the rest;
- (f) Plaster etching by aggressive chemical attack;
- (g) Plaster scaling, efflorescence, and salt crystallization by imbalanced alkaline water;
- (h) **Spot alteration** (i.e., spot staining, soft spots, spot leaching, spot etching) as isolated dimesized whitened or lightened (sometimes stained) spots on smooth plaster surface;
- (i) **Surface pitting**, popout, and stain by unsound or reactive sand aggregate in plaster;
- (j) **Freezing and thawing damage** of plaster, especially prior to immersion in water, or in portions above water; and,
- (k) Aggravated surface mottling of hard-troweled plaster due to carbonation prior to immersion in water, or dissolution of carbonated plaster as water-soluble bicarbonate by water having a low carbonate alkalinity.

The common types of plaster deterioration, which the author has frequently encountered, are: plaster cracking, delamination, discoloration, staining, etching, scaling, surface pitting, and spot alteration.

The primary focus of the paper is to demonstrate the role of various laboratory investigative methods in diagnosing the cause(s) and extents of these plaster problems. Fifteen case studies are presented discussing a multitude of plaster problems from cracking to debonding to discoloration/staining to etching/scaling, and their causes. An elaborate discussion of spot alteration of plaster is given.

### METHODS OF LABORATORY INVESTIGATION OF PLASTER DETERIORATION

Due to the nature and complexity of various deterioration mechanisms in a swimming pool plaster, appropriate sampling and comprehensive examination of plaster samples in the laboratory are essential. Samples should be collected from areas of plaster surface showing visible deterioration, as well as, sometimes from less damaged or sound areas. Sample thickness should encompass not only the plaster but also portions of concrete or shotcrete substrate. Usually 3 to 4 in. diameter drilled core, or at least 4 to 10 in. size square or rectangular saw-cut samples are collected. Information needed with samples include but are not limited to photographs of plaster surface showing damage and of sample locations, project specification, pool plaster and substrate mix designs, placement environment and weather, specified coating thickness, plaster materials' (cement, sand, admixture) specifications, raw plaster cement and sand for separate examinations (in specific cases of investigation of sources of staining discoloration), etc.

Methods of laboratory investigation of pool plaster deterioration include:

- (a) Petrographic examinations a la ASTM C 856 and ASTM C 1324 [2] by using the methods of optical microscopy (reflected and transmitted light observations of as received, fractured, lapped, thin sectioned, or polished samples), scanning electron microscopy (backscatter and secondary electron imaging), and associated energy-dispersive x-ray microanalysis. Optical microscopy is helpful to identify composition, mineralogy, and microstructure of aggregates and cement paste in the plaster and substrate, evidence of deterioration on plaster surface from scaling and etching, and evidence of deterioration in the substrate. Scanning electron microscopy and x-ray microanalysis can investigate plaster deterioration in a great detail and determine compositions of scales, stains, leached paste, depth of deterioration, etc.;
- (b) X-ray diffraction analysis of plaster can detect stain-forming minerals or metals, and any unusual compositions of plaster and substrate;
- (c) Acid-soluble chloride analysis (a la ASTM C 1152 [3]) of bulk plaster can estimate dosage of calcium chloride admixture, and any over-dosage or related plaster problems (such estimate, however, must consider chlorides from the pool water and the age of the plaster);
- (d) X-ray fluorescence (XRF), atomic absorption spectroscopy (AAS), or inductively-coupled plasma spectroscopy (ICP) can determine composition of hardened plaster and its ingredients;
- (e) Chemical analysis (pH, alkalinity, calcium hardness, etc.) of pool water containing watertreatment and other chemicals is helpful to determine the balanced versus aggressive chemistry and influence of pool water on plaster properties and performance; and,
- (f) Supplementary physical tests of plaster properties are helpful to access plaster quality, e.g., tests of absorption, specific gravity, volume of permeable voids (*a la* ASTM C 642 [4]), compressive strength (*a la* ASTM C 109 [5]), and water tightness.

Although author's laboratories are well-equipped to perform all these analyses, the methods that the author most commonly use are optical and scanning electron microscopy, and acid-soluble chloride content analysis, which are usually adequate to diagnose reasons for plaster deterioration.

No laboratory method, however, can provide a comprehensive diagnosis without considering all background information related to a project.

Experiments designed with controlled variables of: (a) pool water chemistry (pH, total alkalinity, calcium hardness), (b) dosages of water-treatment chemicals (sanitizers, stabilizers), (c) plaster design (cement factor, water-cement ratio, cement/sand ratio, calcium chloride dosage), (d) finishing techniques (troweled vs. formed surface, over-troweling, re-tempered surface), and (e) other relevant project-specific variables, and their evolution with time are sometimes essential to understand mechanisms of plaster deterioration in the more complex systems of pools in the field.

PROCEEDINGS OF THE THIRTIETH CONFERENCE ON CEMENT MICROSCOPY, APRIL 20 TO 24, RENO, NEVADA, USA 2008

### **PLASTER CRACKING**

Cracking in swimming pool plaster can be one or a combination of the following types [1]:

- (a) Closed Shrinkage Cracks Development of normal shrinkage cracks (also called check cracks) on a freshly set and hardened plaster surface is not uncommon prior to their immersion in water. They form due to normal moisture loss from plaster as it sets and dries prior to water immersion. These are small hair-like microcracks, usually autogenically sealed by the cement hydration process within days underwater. These cracks are more noticeable during wetting after drying, on smooth hard troweled finishes, and could remain visible if dirt or dust becomes trapped within the cracks prior to sealing by cement hydration products.
- (b) Open Shrinkage Cracks Shrinkage cracks wider than normal check cracks, however, can stay open underwater, and, therefore, require repair. They occur by excessive moisture loss from plaster during drying and setting, and can penetrate from as shallow as <sup>1</sup>/s in. to the entire thickness of plaster. Open shrinkage cracks can form by: (i) excessive evaporation of water from plaster surface, (ii) water loss from plaster to an absorptive substrate, (iii) water loss from plaster due to placement in hot, windy, dry weather, (iv) excessive addition of water in plaster (over-tempering), (v) use of excessive water during finishing, (vi) finishing with excess water on plaster state (plastic shrinkage), (viii) excessive water loss while the plaster is in a plastic or semi-plaster state (plastic shrinkage), (viii) use of excess cement, (ix) use of excess calcium chloride admixture in mix<sup>1</sup> (i.e., in excess of the usual limit of 2 percent calcium chloride dihydrate by weight of cementitious materials), (x) delayed filling of pool with water after plastering, and (xi) some combination of all.
- (c) Structural Movement Cracks Structural cracks form due to: (i) substrate or soil expansion and/or settlement, (ii) use of thin plaster coating that cannot withstand stresses related to movement, (iii) improper substrate surface preparation, or, (iv) improper structural design.
- (d) Tensile Stress Cracks Form due to expansion of substrate, such as by alkali-aggregate reactions or other deleterious expansive processes within the substrate (e.g., cyclic freezing, sulfate attack, etc.) putting the outer plaster coat in tension.

Of all the types of pool plaster deterioration that the author has investigated, cracking is, perhaps, the most common, which has caused either minor cosmetic repair or, in worst cases, removal or replastering of the plaster. Of all the types of author's plaster cracking projects, the ones related to expansion of substrate by expansive deleterious alkali-silica aggregate reactions, excessive plaster shrinkage at the early age, and substrate settlement are found to be the most common.

Prior to the initiation of a plaster cracking investigation, detailed background information related to the specified plaster composition, components, and mix design, the specified plaster thickness, substrate composition and mix design, plaster placement temperature and weather condition, and other relevant project information are needed. Field photographs showing the type of plaster cracking (e.g., closed polygonal-shaped, random, or longitudinal/transverse, etc.) are essential. Samples should be collected from over the cracks, encompassing the plaster and substrate components.

<sup>&</sup>lt;sup>1</sup> Addition of calcium chloride within 1 to 2 percent by weight of cement usually increases early strength of plaster by increased rate of cement hydration, especially at cold weather, and thereby may be beneficial (along with increased density, reduced porosity, and increased water tightness). Excessive addition, however, is detrimental as it reduces long-term strength, increases plaster porosity and shrinkage, and imparts darker gray hue on plaster.



#### Case Study 1 — Plaster Cracking due to Drying Shrinkage of An Excessively Thick Application



Figure 1 – A pool plaster showing random cracks on the steps.

The steps and floor of a swimming pool show extensive closed, polygonal-shaped cracks, many of which are up to 2 mm in surface width, and reported to be "early cracks," i.e., formed prior to the immersion of plaster underwater.

A 4-in. diameter core sample, taken from cracked plaster showed application of a plaster thicker than the usual industry-practice of  $^{3}/_{8}$  to  $^{3}/_{4}$  in. thick plaster, measuring up to  $1^{1}/_{4}$  in. in maximum thickness, applied in two  $^{1}/_{2}$  to  $^{3}/_{4}$  in. thick coats, which were intimately bonded to each other; the bottom coat was intimately bonded to a concrete substrate.

The plaster is non-air-entrained (< 2 percent air) and made using fine, angular, marble chip aggregate having a nominal size of 2 mm, and a white portland cement paste having an estimated watercement ratio of 0.35 to 0.40. Plaster is dense, well consolidated, and free of internal microcracks from any deleterious chemical reactions. Many air voids are lined or filler with fine, fibrous, acicular deposits of secondary ettringite, consistent with the prolonged moisture-saturated condition of the plaster. The plaster does not contain any unsound or reactive aggregate. Surface region of the plaster surface shows carbonation to a depth of 3 to 4 mm.

Acid-soluble chloride content of the plaster, determined in accordance with ASTM C 1152, was 0.71 percent chloride, by mass of the bulk plaster, which corresponds to 3.69 percent calcium chloride addition, by mass of cement<sup>2</sup>, in excess of the recommended maximum limit of 2 percent calcium chloride (assuming minimal contribution of chlorides from the pool water due to young age of plaster).

<sup>&</sup>lt;sup>2</sup> Converting percent chloride in hardened plaster (Cl, as determined from ASTM C 1152) to percent calcium chloride admixture addition by mass of cement – If the acid-soluble chloride content of plaster is 'A' percent, by mass of plaster (as determined from ASTM C 1152), then it is equivalent to 'A/0.B' percent chloride, by mass of cement (assuming that the plaster contains 'B' percent cement, which is usually around 40 percent by mass of plaster but can be determined from ASTM C 114) = This is equivalent to 1.56 (A/0.B) percent anhydrous CaCl<sub>2</sub>, by mass of cement, or, 2.08 (A/0.B) percent flake CaCl<sub>2</sub> [i.e., dihydrate, CaCl<sub>2</sub>.2H<sub>2</sub>O] addition. Usually, 2% flake CaCl<sub>2</sub> is equivalent to 1.5% anhydrous CaCl<sub>2</sub>. Usual amount of calcium chloride (i.e., dihydrate) addition is between 1 and 2 percent, by mass of cement. The cement content of a hardened plaster can be determined from ASTM C 114 or ASTM C 1084 by determining silica contents (as SiO<sub>2</sub>) of plaster (e.g., by XRF, AAS or wet chemistry), and cement (or, by assuming 21.0 percent silica as SiO<sub>2</sub> in white portland cement). The determined chloride



PROCEEDINGS OF THE THIRTIETH CONFERENCE ON CEMENT MICROSCOPY, APRIL 20 TO 24, RENO, NEVADA, USA 2008

The substrate was a  $6^{1/2}$  in. thick, dense, well-consolidated, crack-free, non-air-entrained concrete made using well-graded, well-distributed, sound, crushed, dark, argillaceous limestone and dolomite coarse aggregate having a nominal maximum size of  ${}^{3}/{}_{8}$  in., well-graded, sound, natural siliceous sand fine aggregate having a nominal maximum size of  ${}^{1}/{}_{4}$  in., a portland cement content estimated to be  $7^{1}/{}_{2}$  to 8 bags per cubic yard, a water-cement ratio estimated to be 0.44 to 0.48, and an air content estimated to be 2 to 3 percent. There is no evidence of alkali-aggregate reaction of either coarse or fine aggregate in the concrete. Lining the walls of many irregularly-shaped air voids in concrete are profuse fibrous secondary ettringite deposits, indicating prolonged moist condition of concrete.

There is no evidence of any deleterious chemical or physical reactions, either in the plaster or in the concrete substrate. Despite the non-air-entrained nature of plaster or substrate and occurrence of pool in an environment of cyclic freezing and thawing, there was no evidence of freezing-related distress in plaster or substrate.



Figure 2 – Left - Lapped cross section of a core from the pool shown in Figure 1. The section shows a thick plaster (comprising two  $^{1}/_{2}$  to  $^{3}/_{4}$  in. thick applications), which is intimately bonded to the concrete substrate. Middle = Thin section photomicrographs of plaster (top) and concrete substrate (bottom) showing marble aggregates in plaster and dolomite-quartz aggregates in concrete, and portland cement pastes. Right = Thin section photomicrographs of plaster showing marble aggregates in plaster (top), and an air void in concrete, which is filled with secondary ettringite deposits (bottom).

Based on the reported early occurrence of cracking, the observed absence of any deleterious reaction in the plaster or substrate, the intimate bond of plaster to substrate, and, most importantly, thicker-than-usual application of plaster (in two 1/2 to 3/4 in. coats), and excessive calcium chloride set-accelerating admixture addition (which is known to increase plaster shrinkage), the cracking was judged to have formed due to excessive early shrinkage of a thick plaster prior to immersion in water (steps commonly having thicker plaster than floor and filled at the end usually show more cracking).

content of a field plaster contains not only chloride added in the original plaster mix but also chloride from the pool water the latter can be higher than the former for an old plaster that has gone through prolonged interaction with pool water. ASTM C 1152 results, therefore, must be used with caution with a prior knowledge of the plaster age.





### Case Study 2 – Cracking due to Drying Shrinkage of a Plaster having an Excessive Dosage of Calcium Chloride Admixture

Figure 3 – A pool plaster surface showing closed polygonal-shaped check cracks.

The above photo shows a pool plaster having numerous fine, closed polygonal-shaped cracks. The plaster was approximately 1/2 in. in thickness and was applied on a concrete substrate. No evidence of any deleterious reaction was found in the plaster, or in the substrate. The plaster contained an excessive dosage of calcium chloride admixture, which is known to cause excessive shrinkage, and, as a result, development of these fine check cracks prior to the immersion of the plaster underwater. The cracks inside the body of the plaster have been partially sealed by cement hydration processes underwater, but were still open enough to be seen on the surface after being in service.

### Case Study 3 - Plaster Cracking due to Alkali-Silica Reaction in the Concrete Substrate

Of all the case studies of author related to plaster cracking, alkali-silica aggregate reaction of concrete or shotcrete substrate is found to be the most common, which had placed the plaster in tension, and, as a result, caused plaster cracking. Presented herein is a representative one, where a  $\frac{5}{16-in}$ . thick white plaster, intimately bonded to a concrete substrate showed extensive closed, polygonal-shaped cracks, similar in pattern to the one shown in the previous study (Case Study 1).

The concrete substrate, on which the plaster was applied, is non-air-entrained, contained  $\frac{3}{8}$  in. nominal maximum sized alkali-silica reactive crushed argillaceous siltstone coarse aggregate,  $\frac{1}{4}$  in. nominal maximum sized natural siliceous sand fine aggregate many of which contain severely strained potentially reactive quartz particles, a portland cement content estimated to be 7 to  $7^{1}/2$  bags per cubic yard, a water-cement ratio estimated to be 0.44 to 0.48, and an air content estimated to be 3 to 4 percent.



Figure 4 – Steps of a swimming pool showing cracks in plaster, mainly along the bases of the steps. Notice the radial pattern of cracks from the steps. Also shown is the location of the core presented for laboratory study (Case Study 3).

Concrete alkali-silica reaction (ASR) is evidenced by (see Figure 5):

- (a) Dark reaction rims around many reactive coarse aggregate particles; and, soft, white alkalisilica gel deposits on the fractured surfaces within the dark rims of such aggregates;
- (b) Microcracking extending from reactive coarse aggregate into paste; and,
- (c) Various forms of alkali-silica reaction gels in microcracks, entrapped voids, paste, and rims of reactive aggregates that are white porcelain-type, clear glassy and shiny type, light cream colored porcelain-type, layered birefringent-type, and massive isotropic type.

All forms of gel contained sodium, potassium, calcium, and silica (see Figure 5), where calcium in gel came from paste by cation-exchange with alkali; white gel deposits on the fresh fractured surfaces of dark-rimmed coarse aggregate particles, however, do not show calcium enrichment due to the absence of such cation exchange. Associated with ASR gel in many places are secondary ettringite deposits indicating prolonged presence of moisture in the concrete, a condition necessary for sustaining ASR.

Pool plaster was found dense (water-cement ratio estimated to be less than 0.40), made using good quality and well-proportioned, crushed marble chip aggregate and white portland cement. Plaster itself did not show ASR<sup>3</sup> or any other deterioration, and simply responded to the substrate expansion by cracking.

<sup>&</sup>lt;sup>3</sup> Pool plaster rarely shows alkali-silica reaction due to the near neutral environment of the pool water. Interior of the plaster, away from the near-neutral surface region, however, can develop ASR if reactive aggregates and high alkali-cements are used in the plaster mixes, which are seldom the case.

209



PROCEEDINGS OF THE THIRTIETH CONFERENCE ON CEMENT MICROSCOPY, APRIL 20 TO 24, RENO, NEVADA, USA 2008

Figure 5 – Top Row from Left = Top surface of a core showing plaster cracks; lapped cross section of the core showing the plaster intimately bonded to the concrete substrate, within the boxed area is a vertical crack that has extended through the entire plaster and a portion of the concrete substrate; fresh fractured surface of core showing white deposits of alkali-silica gel on the fractured aggregate surfaces in concrete that are surrounded by dark reaction rims; photomicrograph of fractured aggregate surfaces showing dark reaction rims and white powdery alkali-silica gel deposits on aggregate surface within the rims. Middle Row = Air voids in concrete lined with white alkali-silica gel; oil immersion mounts of white deposits in voids showing layered and birefringent gel deposits; the right photo shows immersion mount of acicular secondary ettringite deposits that are associated with ASR gel in many voids. Bottom Row = X-ray microanalyses of gel and secondary ettringite deposits in voids.

### Case Study 4 — Plaster Cracking due to Combined Cyclic Freezing and Alkali-Silica Reaction in the Concrete Substrate

The steps, wall, and floor of a pool plaster showed extensive closed polygonal-shaped cracking, as well as some long cracks. A core from over a plaster crack was received. The plaster was made using white portland cement and marble chip aggregate. The nominal thickness of plaster, as measured in the core, is 10 to 15 mm. The plaster is intimately bonded to a concrete substrate.

In this case, the concrete substrate, prior to plastering, has undergone deterioration by cyclic freezing and thawing at critically saturated conditions, and, alkali-aggregate reaction. The concrete substrate is dense, non-air-entrained, reasonably consolidated, and made using well-graded, well-distributed siliceous alkali-silica reactive pea-gravel coarse aggregate, natural siliceous sand fine aggregate  $(^1/_4-in.$  size) containing many potentially reactive particles as well, a portland cement content estimated to be from 6 to  $6^1/_2$  bags per cubic yard, a water-cement ratio variable within the sample, and estimated to be from as low as 0.40 in dark patches to 0.48 in lighter gray areas (due to inadequate mixing of batch or tempered water), and air content estimated to be from 1 to 2 percent.



Figure 6 - Photo showing severe polygonal-shaped cracking in a pool plaster.

Concrete and associated plaster cracking are determined to be due to alkali-silica reaction (ASR) in concrete, which is diagnosed by (see Figure 7):

- (a) Extensive microcracking in reactive chert and strained quartzite gravels in coarse aggregate that radiate out to the paste;
- (b) Light to dark brown reaction rims along the periphery of many of these particles; and,
- (c) Extensive development and migration of alkali-silica reaction gels forming within cracks, voids, paste, and margins of reactive particles.

Reactive particles, along with the use of a high-alkali cement and the moist environment in the concrete have triggered the deleterious reaction.

One of the major reasons for prolific development of ASR (more severe than that observed in Case Study 3) was determined to be due to the presence of numerous longitudinal and transverse long continuous cracks, not related to any specific reactive aggregate but were formed by bulk expansion during cyclic freezing and thawing of a non-air-entrained concrete at critically water-saturated conditions. Cracks formed by cyclic freezing have opened up channels for migration of water, an essential ingredient for sustaining ASR.

Expansion within the concrete substrate has placed the plaster in tension and created cracks that are wider at the trowel-finished plaster surface and taper inside.

The plaster itself was determined to be made using sound materials, following good plastering practice, did not contribute to the distress, but rather benignly responded to the internal expansion of concrete substrate by extensive cracking.

This case study indicates the importance of good quality control and assurance of not only the plaster but also the substrate on which the plaster is placed. In many case studies of plaster cracking by ASR in the substrate that the author was involved, plastering was done on substrate with no prior information about the quality and soundness of the substrate. Due to the proximity to a continuously moist environment, use of a dense, well consolidated concrete or substrate containing sound, nonreactive aggregate is essential.



Figure 7 – Top Row from Left = Top surface of a core showing cracks; fractured surface of concrete substrate showing alkali-silica reactive chert and quartzite aggregates (boxed) and alkali-silica gel deposits in voids (arrows); lapped section of concrete substrate showing parallel cracks formed due to cyclic freezing and thawing of concrete at critically saturated conditions. Middle Row from Left = Photomicrographs of lapped cross section of the core showing cracks in plaster that have originated from the concrete substrate; cracking of an alkali-silica reactive chert aggregate in concrete; right photo shows thin section of concrete where an elliptical reactive chert aggregate shows severe cracking due to alkali-silica reaction. Bottom = Photomicrographs of thin section of core showing microcracking due to alkali-silica reaction, many originated from the reactive particle and extended to the paste; also notice alkali-silica gel deposits lining the walls of the microcracks.

### Case Study 5 — Two additional Cases of Plaster Cracking due to Physical and Chemical Unsoundness in the Concrete Substrate

The following photos of plaster cracking, from two very similar case studies, show three superimposed deteriorations, all occurring in the concrete substrates that have caused cracking in polymer-modified white cement and quartz sand plasters: (a) physical unsoundness of crushed argillaceous limestone coarse aggregate particles in concrete causing expansion and fracturing, (b) alkali-silica reaction of severely strained quartz and quartzite particles in fine aggregate of substrate that have caused microcracking, reaction rims and alkali-silica gel formation in cracks and voids, and (c) cyclic freezing and thawing of concrete that was designed to be air-entrained but contained no air entraining agent. Crack patterns from these mechanisms were different but all continued to the plaster to show visible cracking. Clearly, durability of the substrate plays an important role in controlling plaster cracking. In both cases, plasters were sound and made using sound aggregates.





Figure 8 – Two separate pools showing cracking of pool plaster due to expansion of the underlying concrete substrate, which occurred due to unsoundness of argillaceous siltstone coarse aggregate and alkali-silica reaction of severely strained quartz-quartzite particles in fine aggregate in the concrete substrate. The right photo shows white ASR gel deposits on fresh fractured surfaces of reactive aggregates and dark reaction rims; unsound siltstone and reactive quartz particles in aggregate, white gel deposits lining the walls of voids, oil immersion mounts of gel showing its layered type birefringent nature, and EDS composition of gel having Na, K, Ca, and Si.

### PLASTER DEBONDING AND DELAMINATION

Plaster debonding and delamination can occur by bond failure of: (i) the plaster from the substrate; or (ii) one coat of plaster from the undercoat [1]. Both can occur by the following reasons:

- (a) Surface carbonation of substrate or undercoat preventing development of a mechanical interlocking or bond between the two systems (plaster-substrate), or coats of plaster;
- (b) Surface efflorescence or laitance acting as a bond breaker between two components;
- (c) Too smooth and/or dense substrate or undercoat surface preventing mechanical interlocking;
- (d) Rapid drying and premature stiffening of substrate or undercoat surface;
- (e) Overly wet or water-saturated substrate or undercoat surface having water-filled pore spaces, which could otherwise be filled with finish coat or plaster for good interlocking and bond;
- (f) Rapid drying of a thin coat, especially if applied over an absorptive substrate;
- (g) The absence of a bond coat between the two plaster coats;
- (h) Delayed application of the top coat to the undercoat, or, application of a too thin top coat;
- (i) Plaster placement in a subfreezing temperature, or on a frozen substrate;
- (j) High shrinkage potential of an excessively thick coat (or excessive addition of calcium chloride in a mix) causing cracking and debonding;
- (k) The presence of oil, dirt, loose debris, acid, form-release argent, or other contaminants on a substrate or undercoat surface preventing a good contact between two components;
- (I) Improperly scratched, scored, notched or finished undercoat surface; and,
- (m)Over-troweling the finish coat of a plaster, or, troweling beyond the final set can cause delamination of the top <sup>1</sup>/s in. of plaster.

Most of these reasons of plaster delamination can be readily diagnosed by the laboratory methods discussed in this paper.



PROCEEDINGS OF THE THIRTIETH CONFERENCE ON CEMENT MICROSCOPY, APRIL 20 TO 24, RENO, NEVADA, USA 2008

Three terms usually referred to in connection with plaster debonding are buckles, blisters, and spalls [1]. Buckles are debonded bulges on plaster surface where coating is partially separated from undercoat or substrate but have not yet lifted off, usually due to failure of one coat to bond to the undercoat or substrate. Blisters are small round bumps on plaster surface, due to partial separation within the finish coat by trapped air during finishing, or over-troweling or other reasons. Spalls are upper layer delamination due to failure to immerse plaster underwater and/or maintain immersion after placement, abrasion, aggressive pool water attack on plaster, etc.

### Case Study 6 — Debonding of Plaster Coats Due to the Absence of a Bond Coat between the Two Plaster Coats



Figure 9 – Incipient and Complete Delamination of Pool Plaster.

The above photo shows an incipient and a complete delamination of the top plaster coat from the undercoat due to the absence of a bond coat between the two. A latex-modified, white portland cement plus fine sand-based pre-packaged bond coat was specified for application in between the two plaster coats, but was missed. As a result, the top coat showed "incipient delamination" (i.e., lifted off but not lost) over several broad areas (as large as 4 feet in diameter, similar to the top left corner in the photo within the dashed line), as well as "complete delamination" (i.e., lost) at isolated areas due to foot pressure (similar to the area within the circle in the middle of the photo). Moreover, the top coat applied was too thin (less than 1/4 in. as opposed to 3/8 to 3/4 in.), which did not provide a sufficient bond strength to the undercoat. No bond coat and thin top coat – both contributed to the problem.

### Case Study 7 – Debonding of Plaster Coat Due to Premature Stiffening of a Thin Top Coat

An approximately 15-year old pool was re-plastered during a renovation project, and within months of re-plastering showed various areas of delamination. Received by our laboratory were some loose pieces of debonded new plaster from the pool floor that were reportedly delaminated from the old plaster coat. The exposed surface of the new plaster showed etching and greenish discoloration from copper staining (Figure 10). The underside (i.e., the delaminated surface) showed relatively clean striated appearance, free of any contaminants, and no trace of the old plaster, indicating a clean separation of the new plaster from the old one.



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The delaminated new plaster was too thin, only <sup>1</sup>/<sub>8</sub> in. in nominal thickness, which showed evidence of rapid drying and restricted hydration of portland cement particles. The plaster was made using marble chips and white portland cement. Acid-soluble chloride analysis showed 0.126 percent chloride, by mass of plaster, which is indicative of less than one percent calcium chloride addition by mass of cement, well within the normal range, or of no addition, where chloride came from interactions with pool water. Thin section photomicrographs of plaster show surface-parallel microcracking from shrinkage and abundant residual portland cement particles and high capillary porosity in the paste in the body of the thin plaster (Figure 11), indicating premature drying prior to the immersion of plaster underwater. Debonding was judged to be due to premature stiffening and rapid drying of a thin plaster coat, which was probably overly wet and exposed to a dry or windy weather condition.



Figure 10 – Loose samples of a de-bonded plaster that was delaminated from an old plaster coat, after a replastering project. Notice the light green copper stain on the exposed surfaces of plaster pieces.



Surface parallel microcracks

Excess abundance of residual portland cement particles and high capillary porosity of paste

Figure 11 – Thin section photomicrographs showing microstructure of loose, debonded plaster samples. The left photo shows surface-parallel microcracks and porous paste in plaster. The right photo shows excess abundances of residual portland cement particles and capillary pores in the paste. Both features indicate premature stiffening and rapid curing of plaster.




Case Study 8 - Plaster Blistering Due to Delayed Application of the Top Coat

Figure 12 - Blistering on Plaster Surface.

Contrary to the previous case study of plaster coat delamination due to the absence of a bond coat (Case Study 6), in the present case, a latex-modified white portland cement based bond coat was applied but remained exposed to air for two weeks prior to the application of the top coat, which has changed the characteristics of the bond coat from bonding to release (usually, the top coat is recommended to be applied within 2 to 3 days of application of the bond coat). Radial cracking at the incipient blister on the left in the photo indicates an expansion of the underlying bond coat, which may have related to the release characteristics of the bond coat due to the extended delay in application of the top coat. No evidence of any potentially expansive chemical reaction was detected in the coats.

# **PLASTER SOFTENING**

Portland cement plaster materials, and handling, mixing, and placement procedures should be in accordance with specifications and guidelines mentioned in ASTM C 926 and ACI 524. Performance and durability of plaster depends strongly on the use of proper materials, mix, placement, finishing, and curing techniques, and proper preparation of the substrate surface. Deviation from such guidelines could adversely affect the finish and performance of plaster. Possible reasons for a weak or soft plaster coating include:

(a) Excess sand in the mix without a sufficient cement binder<sup>4</sup>;

<sup>&</sup>lt;sup>4</sup> Pool plaster mixes usually contain: (a) a minimum 1 part cementitious materials for every 2 parts of aggregate by mass (commonly 4:6 cement/sand mass ratio); (b) mix water content is governed by weather condition, substrate water absorption, and plaster workability, tempered water is added for facilitating placement, finishing, and curing of plaster; (c) cementitious materials to be used should meet or exceed requirements of ASTM C 150, or C 1157 for white portland cement, ASTM C 595 for blended cement, ASTM C 618 for pozzolans, and ASTM C 1240 for silica fume; and (d) calcium chloride set accelerating admixture, at approximately 1 to 2 percent by mass of cementitious materials is commonly added in liquid, flake, or granular form [calcium chloride dihydrate, CaCl<sub>2</sub>.2H<sub>2</sub>O], fully dissolved in mix water prior to adding with cement. The uses of calcium chloride accelerator and supplemental water during troweling are common practices to prevent premature drying of rich mixes of thin plasters prior to set.

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- (b) Improper sand gradation, e.g., too much fines in sand can increase the water demand and cracking potential of plaster; too much coarse in sand can reduce bond to substrate and can lower the workability;
- (c) Impurities in the sand, or, in mixing water not in conformance to the industry guidelines;
- (d) Excess mixing water;
- (e) High water-cementitious materials ratio from high water and/or low cement contents;
- (f) Addition of lime in mix, which can increase laitance and cause lime leaching in pool water;
- (g) Improper or excessive use of certain admixtures (e.g., excess calcium chloride);
- (h) Aggressive chemical attacks causing leaching and progressive weakening of plaster; and,
- (i) Placement in a subfreezing temperature, or on a frozen substrate, causing bond failure, restricted cement hydration and the resultant soft or weakened plaster.

All these above possible reasons of plaster softening<sup>5</sup> can be readily diagnosed by detailed petrographic examinations, and supplemental chemical (e.g., chloride) analysis of a field sample of softened plaster. Excess sand, improper sand gradation, and impurities in sand are often best diagnosed by optical microscopy. Lime, or excess water additions are also detected by examining the textural and compositional properties of plaster paste during petrographic examinations. Acid-soluble chloride analysis of bulk plaster (ASTM C 1152) determines calcium chloride dosage and its influence on plaster characteristics. Softening by severe etching or leaching, as well as the depth of deterioration is best observed by optical and/or scanning electron microscopy. Freezing at the plastic or semi-plastic state of plaster is also best diagnosed by characteristic plastic freezing microstructures in the plaster paste in an optical microscopical examination.

#### ATTACK BY AGGRASSIVE POOL WATER – LEACHING, ETCHING AND SCALING

The ANSI/NSPI Standards [6] recommend the balanced pool water to have the following parameters:

Parameter;	Minimum	Ideal	Maximum
Free Chlorine (ppm) <sup>1</sup>	1.0	2.0-4.0	10.0
pH <sup>2</sup>	7.2	7.4-7.6	7.8
Total Alkalinity <sup>3</sup> (ppm, as CaCO <sub>3</sub> )	60	80-120	180
Calcium hardness <sup>4</sup> (ppm, as CaCO <sub>3</sub> )	150	200-400	1000
Total Dissolved Solids <sup>5</sup> (ppm)	300	1000-2000	2400

<sup>1</sup>Free chlorine is the active form of chlorine that is able to destroy potentially harmful organisms in water, which is total chlorine minus combined chlorine that was used up and thus no longer has the ability to disinfect; <sup>2</sup>pH is the acidity/alkalinity index of water, high value makes water alkaline, produces scale and reduces sanitizing capacity of chlorine, whereas low value makes water acidic/aggrassive, and causes etching; <sup>3</sup>Measure of water's resistance to change in pH, equates to the amount of alkaline substance, e.g., hydroxides, carbonates, and bicarbonates in water; <sup>4</sup>Measure of dissolved calcium salts in water; <sup>5</sup>The amount of total dissolved matter in water from all sources.

Pool water having chemistries within these acceptable ranges is "balanced" in the sense that the water will not attack the cementitious coating. Pool water not in the range of above acceptable tolerance or balanced as in accordance with the ANSI/NSPI standards is detrimental to plaster. The term Langelier Saturation Index (LSI), after Wilfred Langelier, is widely used to determine thermodynamic potential for a water to dissolve or precipitate calcium carbonate [7]. LSI is a measure of saturation of water with respect to calcium carbonate incorporating: pH, total alkalinity (TA), calcium hardness (CH), total dissolved solids (TDS), and water temperature (WT) as the variables (LSI = pH+f<sub>WT</sub>+f<sub>CH</sub>+f<sub>TA</sub>-f<sub>TDS</sub>, where 'f' stands for factors for different variables shown in the table below, LSI for balanced water should be as close to zero as possible with an acceptable range from -0.3 to +0.3). Depending on LSI's variation in opposite directions of the recommended levels, the pool water may get cloudy and secondary deposits precipitate on plaster surface; or, causes leaching and etching of plaster surface. The LSI chart below provides factors for different variables, to determine the pool water chemistry:

<sup>&</sup>lt;sup>5</sup> Many pool professionals prefer the term "weak" plaster rather than "soft" plaster, which, in author's opinion, conveys different meanings, i.e., weak plaster refers to a low-strength plaster, whereas a 'soft" plaster can have excellent strength but have low scratch hardness on the surface.

Water Calcium Total **Total Dissolved** Hardness, Alkalinity Solids Temperature fcH °(F) fwt f<sub>TA</sub> f<sub>TD\$</sub> ppm ppn ppm 32 0.0 25 1.0 25 1.4 < 1000 12.1 ≥ **1000** 37 0.1 50 1.3 50 1.7 12.2 46 0.2 75 1.5 75 1.9 53 0.3 100 1.6 100 2.0 60 0.4 125 1.7 125 2.1 66 150 1.8 2.2 0.5 150 200 76 0.6 1.9 200 2.3 250 2.0 250 84 0.7 2.4 94 300 300 2.5 0.8 2.1 105 400 2.2 400 2.6 0.9 800 2.5 800 2.9

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Acidic water, i.e., water having a lower pH, lower calcium hardness, lower total dissolved solids, and lower total alkalinity than the minimum recommended limits, or soft water is *aggressive* to pool plaster, and causes plaster dissolution, leaching, and resultant *etching*<sup>6</sup> of the plaster surface [8].

Alkaline water, i.e., water having chemistries in the other extreme, water carrying water-soluble salts, dissolved sulfates, chlorides, and carbonates becomes cloudy and causes *scaling, salt precipitation, efflorescence,* and *staining* on plaster surface [8]. Excessive precipitation of salts out of the solution can severely roughen the plaster surface, requiring acid washing, scraping, or sanding the scaly surface. Precipitation of heavy metals causes stains, and of metallic salts (e.g., carbonates of calcium and/or magnesium) causes white deposits, or scales.

Often both scaling/staining/salt crystallization and leaching/etching-type deterioration can occur on the same pool plaster, as a thin layer of deposits (usually calcium carbonate, or a mixture of calcium and magnesium carbonate deposits precipitated out of pool water, or stains from soluble salts) at the surface as a thin layer over a soft, porous, and leached (decalcified) plaster paste. The surface region of many such plaster show a thin zone of highly porous plaster paste lacking calcium hydroxide component of portland cement hydration, which is overlain by a calcium carbonate-rich layer (see the case study below). Such microstructural feature indicates fluctuating pool water chemistries from acidic (causing leaching) to basic (causing scaling) extremes in relation to being in balance with the pool plaster.

Etching of pool plaster by aggressive water is a common and a well-known mechanism of plaster deterioration. Etching creates a softened, dusty, porous, *rough*, and chalky-textured plaster surface. Depending on the degree of aggressiveness of pool water, distress can vary from minor surface softening and etching to severe loss of the plaster thickness by mass dissolution.

<sup>&</sup>lt;sup>6</sup> "Leaching" is chemical dissolution of cement hydration products in paste or any water-soluble materials by water (not necessarily aggressive water). "Etching," on the other hand, refers to leaching or dissolution of paste by aggressive water, i.e., water having low pH, low alkalinity, low hardness, etc., which dissolves not only cement hydration products from paste but, depending on the degree of acidity, can also dissolve calcareous aggregates in plaster. This difference between the modes of dissolution of materials by any water (leaching) versus aggressive water (etching) is one of the reasons for the debate centered around the spot etching (vs. spot leaching) phenomenon. Leaching does not necessarily roughen the plaster surface but makes it porous and soft by loss of mass; etching, on the other hand, roughens the surface by aggressive water attack. Plasters (or areas in a plaster) having higher water-cementitious materials ratio and higher porosity of paste are more susceptible to leaching and etching than the denser plasters (or denser areas in a plaster) having a paste of lower water-cementitious materials ratio.



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During petrographic examinations, an etched plaster surface (i.e., attacked by aggressive water) appear as soft, dusty, rough, chalky-textured surface compared to the smooth sound finish, and shows increased porosity of paste and loss of cement hydration products (leaching of calcium hydroxide and decalcification of calcium silicate hydrate component of portland cement hydration) at the surface region of plaster. Carbonate aggregates near surface often show dissolution by acidic water attack. Damage by aggressive water can be best observed in a carefully prepared thin section of a plaster cross section by using a petrographic microscope, or a scanning electron microscope. Leaching (not necessarily by aggressive water) is evident by preferential dissolution of cement hydration products from near the exposed plaster surface without necessarily affecting the carbonate aggregates.

#### Case Study 9 - Evidence of Plaster Etching by Aggrassive Water

Due to the alkaline nature of the plaster, aggrassive pool water causes etching of plaster paste and carbonate aggregates. The depth and severity of etching depends on the aggressiveness of the water, the duration that the water remained aggrassive, and the quality of the plaster. The following case study shows an example, where plaster surface developed broad areas of etching (see Figure 13).



Figure 13 - Photographs of a swimming pool showing etching of plaster surface.

Core samples of plaster plus concrete substrate show evidence of plaster surface etching as darker patchy areas rich in carbonate aggregates (where the intervening paste in between the aggregate particles has been lost), and relatively lighter areas rich in leached and etched porous paste (see Figure 14). Plaster contained marble chip aggregate and white portland cement, acid-soluble chloride analysis indicated 2.6 percent calcium chloride addition.

Thin section photomicrographs of the plaster show clear evidence of loss of the paste and carbonate aggregates at the plaster surface, to a depth of 0.2 to 0.5 mm (Figure 15), and an overall porous nature of the plaster paste at the surface and down to a uniform depth of 3 to 4 mm. The total plaster thickness is 10 to 12 mm, where a denser region is present beneath the top porous region. The porous nature at the surface is clearly distinct in blue dye-mixed epoxy-impregnated thin section by a greater degree of blue dye absorption at the top 3 to 4 mm than the interior denser plaster body. Such a porous surface may indicate application of a finish coat having a higher water-cementitious materials ratio than the body, or, finishing in the presence of excess water at the surface, either of which has decreased the resistance of plaster to surface etching by the aggrassive water.



Figure 14 – Photograph of the top etched plaster surface in the core (left photo) taken from the pool shown in Figure 13, which, at a higher magnification (right photo) shows the loss of paste from around the aggregate particles, and loss of marble aggregate particles at the surface as well. The brown patchy areas are rich in aggregates and lighter gray areas are etched paste.



Figure 15 – Photomicrographs of blue dye-mixed epoxy-impregnated thin section of plaster showing etching of marble aggregates and paste on the plaster surface, loss of paste, and highly porous zone of paste at the top 0.2 to 0.5 mm. The porous nature of the paste at the surface region, beneath the etched plaster surface can be readily highlighted by the blue dye-mixed epoxy used for impregnating the sample prior to thin sectioning.



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# Case Study 10 — Secondary Calcite Precipitation on Plaster Surface — Evidence of Plaster Scaling by Alkaline Water

As the opposite extreme of etching, the following case study shows surface scaling, as secondary calcium carbonate precipitates on the plaster surface, due to the exposure of plaster to a pool water having a high pH, high alkalinity, high calcium hardness, and the presence of excess dissolved solids. The plaster surface showed dog-tooth shaped secondary calcite precipitates, 50 to 70 micron in thickness, some overlain by a relatively leached and porous paste.



Figure 16 – Photomicrographs of thin sections of plasters showing no scaling in the top left photo versus scaling and dog-tooth shaped secondary calcite precipitates on the plaster surface in the other photos. The bottom right photo shows leaching of paste beneath the calcite scales indicating effects of a fluctuating pool water chemistry from a low pH (caused leaching) to a high pH environment (caused scaling).

The top photomicrographs are thin sections of plaster cross sections showing appearance of a scaled plaster surface. Excessive development of secondary calcium carbonate scales on the surface requires acid washing or sanding – the extent of scaling or its removal after washing can be best diagnosed by examination of thin section of plaster in a petrographic microscope.



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# PLASTER DISCOLORATION – SPORADIC MOTTLED AND BLOTCHY SURFACE

Rarely, a white pool plaster (also called "marcite") is milky white in appearance; it is rather cloudy white with a normal color variation, or normal mottling, which generally has a uniform shading, blotchy or cloudy appearance across the plaster surface. Such a normal discoloration or mottled-shade variation is common and not usually considered as a failure or defect [1].

Abnormal discoloration [1], as sporadic shaded areas, excessive mottling, blotchiness, and smaller discolored, variably grayish hued areas, however, are different from normal uniform discoloration, can be a real aesthetic nightmare, and often require repair or re-plastering.

Discoloration can be due to one or more of the following reasons:

- (a) Contamination in sand, such as iron, which can cause rust stain;
- (b) Color pigment in a pigmented plaster, which is not mixed thoroughly;
- (c) Variations in water contents and water-cementitious materials ratio of the finish coat of plaster from batch to batch;
- (d) Excessive dry spots, wet spots, or uneven areas of moisture in the concrete or shotcrete substrate can affect the rate of plaster hydration, drying, and setting, and the resultant color of the plaster surface (which, depending on the area of dry or moist substrate, can show normal overall mottling, or, isolated plaster darkening, blotchiness or discoloration);
- (e) Trowel burn, either by over-troweling the finish near the final set of plaster, or troweling past the final set without supplemental moisture to lubricate the finish, can cause an aggravated form of mottling, or severe blotchiness. This discoloration is often in an arc or in the pattern that follows the trowel motion, and occurs by differential rate of squeezing mix water out of the surface by troweling pressure, and/or, from metal of the trowel being deposited onto the plaster surface;
- (f) Calcium chloride, commonly added as set accelerator and to improve plaster water tightness, early strength, and density, can alter the plaster surface coloration. Depending on the amount added, calcium chloride admixture can cause white plaster coating to exhibit a darker gray hue, and colored coating to exhibit blotchiness or mottling;
- (g) Large difference in plaster thickness can cause color variation; thicker areas are usually darker and thinner plaster appear lighter in color because thicker plaster tends to retain moisture longer, causing rate of cement hydration to be different from the rest; thinner plaster looses moisture fast, thereby affecting the rate of cement hydration and the resultant color;
- (h) Difference in moisture contents of concrete or shotcrete substrate can impart different shades of gray hues to a plaster surface, especially if the plaster is thin;
- (i) Splashing of rain or other water on a freshly placed plaster (especially in a colored plaster) that has reached the final set but has not yet been immersed in water can show color difference between the splashed area and other areas;
- (j) The presence of ground granulated blast-furnace slag as a cementitious material in the concrete or shotcrete substrate is known to impart a bluish grey to black discoloration on plaster, which can be reduced by a thick bond coat between the plaster and substrate;
- (k) Improper start-up of pool and failure to adequately brush the pool during the start-up period can impart discoloration on plaster;
- (1) Prolonged presence of pool water at a low level after a partial drainage can develop a darker hue on the aerated portion and a lighter hue on the underwater portion; and,
- (m) Corrosion of reinforcing steel in the substrate can generate rust stains, which can migrate through the substrate and plaster body to the surface of the plaster and appear as rust stains (from orange red to black) this type of plaster stain, as opposed to other stains on plaster surface precipitated or absorbed onto the surface, comes from within or below the plaster.



# Case Study 11 — Plaster Discoloration from Excessive Calcium Chloride Addition and High Iron Content in Plaster Cement



Figure 17 – Photograph of a swimming pool showing botchy or mottled grey-hued discoloration of pool plaster over a broad area.

In order to investigate the dark gray hued mottled or blotchy nature of discoloration of the abovepictured pool, a core sample was examined that contained a  $^{1}/_{2}$  in. thick plaster intimately bonded to a  $^{6}/_{2}$  in. thick shotcrete substrate. Acid-soluble chloride content of the plaster was 1.03 percent by mass of bulk plaster, which corresponds to a 5.3 percent addition of calcium chloride by mass of cement, well in excess of the standard limit of 2 percent. Calcium chloride admixture is known to impart a grayish hued discoloration on pool plaster, which was determined to have caused blotchy discoloration in the above pool as well. In addition, the white portland cement paste in the plaster showed an unusually high amount of ferrite phase, which also imparts a darker hue from delayed hydration of ferrite phase in the presence of excess calcium chloride (which explains the reported progressive darkening of the pool plaster with time). Discoloration reportedly occurred in a number of other pools as well, which were constructed with the present one by the same plasterer, after a change of the cement source. The evidence is consistent with the observed high iron content in the residual portland cement particles detected in the present sample being a possible reason for plaster discoloration. No evidence of leaching or etching of plaster paste was found, rather a thin layer of calcium carbonate deposit was noticed, as scale from alkaline pool water.

# Case Study 12 - Discoloration due to Prolonged Low Level of Pool Water

The following type of plaster discoloration (see Figure 18), from a uniform grey-hued top portion to a cloudy white bottom is very common in many pools, which is due to prolonged settling of pool water at a low level after a partial drainage (which was during the entire winter season in this case), where portions remained underwater appeared lighter in color than the aerated portion of the pool. The aerated portion, being drier than the underwater portion appeared as a darker shade.



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Figure 18 - Darker versus lighter gray discoloration of aerated and underwater portions of a pool.

# Case Study 13 - Discoloration due to Differential Moisture Contents of Plaster and/or Substrate



Figure 19 – Mottled Discoloration of Pool Plasters.

The left photo shows a gray pool plaster (prepared by using a normal grey Type I portland cement, black plaster sand, and a liquid dye), which developed normal early shrinkage cracks after application. The cracks remained open underwater, pool water entered through those cracks, caused leaching of paste from around the cracks, and as a result, increased paste porosity adjacent to the cracks. The porous areas of paste adjacent to the cracks appeared lighter grey in shade than the overall darker gray color of the denser plaster in areas away from the cracks. The right photo shows general overall mottled discoloration in a pool where the pool plaster has had an acceptable amount of calcium chloride admixture. The plaster was applied on a shotcrete substrate, which is usually more porous and absorptive than a concrete substrate. Differential moisture content of the plaster and/or substrate is mentioned by many pool professionals to be the reason to impart such a mottled appearance.



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# **STAINING DISCOLORATION**

Staining, as opposed to sporadic mottling or gray-hued blotchiness, commonly occur in localized areas, and is distinct in color from the rest of the plaster surface. Staining discoloration is caused by precipitation, leaching, or absorption onto a plaster surface by one or a combination of the following:

(a) Heavy metal minerals come out of pool water solution and precipitate on the plaster surface as inorganic stains; common examples of such stains and the source metals are [8]:

Metal	Sources	Stain on Plașter
Calcium	Plaster, grout, Mortar, Cal-hypo chlorine shock	White scales of calcite
Cobalt	Fiberglass shells	Red, blue, gray, black
Copper	Copper Algaecides, ionizers corrosion of copper and brass	Blue, green, blue/green, black,
	pipes, fittings, heat exchangers of pool heaters	dark red, teal
Iron	Well water, corrosion of iron pipe and fittings	Dark red, brown, black, gray,
		green
Manganese	Well water	Pink, red, black

- (b) Water spills or splashes after final set before immersion in pool water;
- (c) Stains by certain metal, mineral, organic or inorganic materials either after the final set prior to immersion in water, or, underwater by dissolution, oxidation, or other reactions with pool water and/or cementitious plaster;
- (d) Oils or dirt from human and/or pets;
- (e) Precipitation of calcium, iron, or some mineral (e.g., in fertilizers) or metals (e.g., in algaecides) shown in the above table;
- (f) Efflorescence, by migration of soluble salts from within the body of plaster underwater and deposition on plaster surface, especially noticeable on colored plaster surface;
- (g) Water, oil, or dirt drip lines that are not washed off from the cleaning of tile or pool deck; Drip stains from brick masonry coping around the plaster; and,
- (h) Organic deposits such as algae and bacteria can discolor pool water and precipitate on plaster surface as green, black, yellows, pink deposits, which are distinguished from metal/mineral stains in that they are on the surface and do not penetrate into the plaster.

Figure 10 shows characteristic green stain on pool plaster from copper (which comes from copper algaecides or degradation of copper pipes or heat exchanger in pool heater in a high chloride and/or low pH pool water).

# Case Study 14 - Staining of Brick Mortar Coping from Manganese in Bricks

The brick-masonry coping of a swimming pool showed dark gray to brown discoloration of jointing mortars, causing drip stains on plaster surface from the mortar joints. Brick units were brown, solid, clay-fired masonry, containing dark brown glassy aluminosilicate matrix, fine (< 1 mm size), angular quartz and feldspar grains, and dark brown to black grog of ferruginous materials. Jointing mortars are non-air-entrained and made using portland cement, sand, and a polymer binder. Elemental analyses of jointing mortars from stained areas show a marked enrichment of manganese in the stained mortars, having maximum concentration at darkest stained areas adjacent to bricks, an element, also detected in the adjacent bricks. Migration of manganese from bricks to the adjacent jointing mortar by splashing of the pool water has caused the stain. Manganese is common in many clay fired bricks that can cause similar staining in masonry coping or pool plaster.





Figure 20 – Dark brown stain on mortar joints (circled) from migration of manganese in bricks.



Figure 21 – The top row photos show the dark stain on jointing mortars, which have prompted the investigation. The bottom rows show manganese (Mn) enrichment in the stained mortar and its absence in the sound mortar, where Mn was derived from the adjacent bricks.



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# SPOT ALTERATION, SOFT (POROUS) SPOTS (SPOT LEACHING VS. ETCHING)

Beginning in the mid-1960s, and specially in the 1980s, a phenomenon then called "spot etching" received much attention in the pool industry and created significant debates among various pool professionals (e.g., NPC, onBalance, Arch Chemical<sup>7</sup>). Since then, there has been an increasing occurrence of this controversial and highly discussed type of plaster surface deterioration, which is reportedly characterized by:

- (a) Small, frequently round in shape, dime-sized spots (<sup>1</sup>/8 to <sup>3</sup>/4 in. in size, more commonly <sup>1</sup>/4 to <sup>1</sup>/2 in, size), much lighter or whitened in color than the surrounding areas of the plaster, sometimes as discolored stains (tan or aqua by absorbing dissolved iron or copper from solution);
- (b) Sometimes follows the edge of tile, troweled arcs, highlighting plaster cracks, or outlines low spots in the plaster;
- (c) Characterized by soft and porous but relatively smooth plaster surface at the spots (even though some spots show aggregates exposed); and,
- (d) Areas of plaster around the spots are smooth, dense, and intact.

According to the latest version (5<sup>th</sup> edition, 2005) of the technical manual of the National Plasterers Council, spot etching is a "slang" term originating in the swimming pool plastering trade that denotes a type of etching deterioration of the surface of a cementitious coating by chemical attack. Therefore, no separate discussion of spot etching is given, and rather included under the general "etching deterioration," indicating its origin from aggressive pool water attacks.

The term "spot etching," according to many professionals (e.g., onBalance, www.poolhelp.com [9]), is indeed a misnomer since the deterioration does not show any "etching," i.e., overall dissolution of plaster by aggressive water (which would be expected to be more widespread and uniform rather than localized spot-like manner), but can occur in a balanced water environment as well. Moreover, the spot surface appears as smooth in touch as in other areas, and areas away from spots are usually smooth and dense with no etching by aggressive water. Usually, there is some softening of paste with increased porosity at the discolored spots, for which, some prefer the term "soft spots" [9].

The term "spot alteration," in author's opinion, is broad, encompassing the "etching" versus "leaching/softening/staining" debate. The author prefers the term "spot alteration," or perhaps, "spot leaching" (and spot staining, if spots are stained).

The cause of spot alteration, therefore, has polarized pool and spa professionals for years [9, 10]:

- (a) The service and chlorine industries (including researchers of onBalance) believe materials (i.e., excess calcium chloride in plaster) and improper troweling techniques are at fault, while
- (b) Plasterers (including researchers at NPC) mention aggressive water chemistry as the culprit.

The polarization, in author's opinion, is guided more by debates from opposing professionals than by opposing science armed with valid sets of good data.

Researches in favor of materials and/or troweling improprieties (e.g., those conducted by onBalance, [9]) indicate no evidence of "etching" at the spots by aggressive water, or, more importantly, no etching in overall plaster or areas away from the spots, as would be expected if caused by aggressive water attack, but selective leaching, increased porosity, and softening of paste at local spots caused by a combination of improper plaster mix and over-troweling, in a sequence of events, i.e.:

(a) Use of excessive calcium chloride set-accelerating admixture in the plaster mix (almost all case studies of spot alteration by onBalance consultants reportedly contained excess calcium chlorides in plasters), which increases shrinkage potential, porosity, and microcracking in plaster paste, and subsequent weakening of aggregate-paste bonds by paste shrinkage;

<sup>&</sup>lt;sup>7</sup> See www.poolhelp.com for research conducted by onBalance, and www.npconline.org for research conducted by NPC.

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- (b) Over-troweling of surface, which brings plaster aggregates near surface, further weakens aggregate-paste bonds, and opens channels for water entrance;
- (c) Splashing of water during troweling, which increases water-cement ratio and porosity of paste at and around weakened near-surface aggregate-paste bonds, and, upon drying, deposits calcium hydroxide (readily soluble in pool water) in the porous zones;
- (d) Selective leaching of soft, porous paste underwater from areas of weakened near-surface aggregate-paste bonds (around aggregate tips) and its progressive increase of leaching laterally around the aggregates through porous paste as spots;
- (e) Eventually, continuation of similar process of increased paste porosity and thereby selective leaching and softening of paste in any other areas of local high water-cement ratio, or water entrance pathways, such as cracks, paste-plastic fitting, etc.;
- (f) Whitening of spots is due to increased porosity and softening of paste by selective leaching (and decalcification) of paste at the local spots (i.e., at and around the tips of exposed aggregates in spots, or at cracks) than at other areas; and,
- (g) Being more porous than elsewhere, spots are more receptive to form stain from absorption of metals on the soft surface than elsewhere, thereby sometime giving tan or aqua tint.

On the other hand, researches conducted by NPC (by California Polytechnic State University, Cal Poly, [10]) in the controlled pool plaster environments showed nearly 12 times more spot etching by aggressive water than that introduced by balanced water (which, in author's opinion, also indicate that balanced water also does cause spot alteration, which may have been aggravated by aggressive water). NPC/Cal Poly researchers did not document any significant effects of excess calcium chloride, hard troweling, and water supplementation on spot alteration. Questions have risen regarding whether their research documented (or addressed) general etching-type deterioration or special dimesized spot alteration-type deteriorations, and addressed reasons for spot-like nature of deterioration.

A recent experimental study of spot alteration by Rothstein et al. [11] funded by NPC (including Cal Poly researchers) showed deterioration by aggressive water attack (especially from excessive dosage of trichoride sanitizer), which started with the dissolution of calcium carbonate from the finished plaster surface, with progressive increase in the size and depth of areas of spots as pitting, discoloration, increased carbonation, and depth of calcium hydroxide depletion from the plaster paste, and eventual coalescence of large spots into broad areas of deterioration. Their work showed dissolution of calcium hydroxide component of cement hydration from the plaster paste by water, similar to regular etching, as well as etched aggregates on small spot-size scale, and, secondary calcium carbonate precipitation on etched aggregate and spot, indicating fluctuating water chemistries from acidic to alkaline. High chloride levels at their spots are indicative of possible chloride-induced increased rate of dissolution of calcium hydroxide from paste [11]. In their study, more spot alteration occurred in the plasters containing no CaCl<sub>2</sub> admixtures than the ones having CaCl<sub>2</sub> – indicating no influence of CaCl<sub>2</sub> addition in spot alteration<sup>8</sup> (see Table 1). Their SEM studies of field pool plaster samples of spot alteration show enriched copper (along with barium and phosphorus) deposits on the green discolored spots.

Pool	CaCl₂ Addition (%)	Trichlor Addition	Spot Alteration			
			Number	Size (microns)	Depth (microns)	Rank (Degree of Damage)
1	2	Balanced	0	0	0	1 (Least Damage)
3	0	Aggressive	7	3000	800	3 (Severe Damage)

Table 1 – A summery of the research done by Rothstein et al. [11] showing more spot alteration in the pool made using plaster containing no  $CaCl_2$  in the mix and exposed to aggressive trichlor dosage than the one having  $CaCl_2$  in the plaster mix and balanced trichlor dosage. The data indicates the influence of trichlor sanitizer dosage, and no influence of calcium chloride addition on spot alteration.

<sup>&</sup>lt;sup>8</sup> Excess CaCl<sub>2</sub> addition, however, could increase the potential for shrinkage cracking, and, thereby, provide pathways for entry of chemicals.



Research by Arch Chemical's Water Products division [12, see Figure 22] showed that high levels of cyanuric acid stabilizer can cause overstablization of pool water and shorten the life of plaster finishes, even in a balanced water pool<sup>9</sup>, and can generate spot deterioration. Their research shed new lights on spot alteration of pool plaster by specific localized high concentration of stabilizers in the pool water, their precipitation on plaster surface as local spots, and progressive development of spot leaching by localized high chlorine and acidic environments on the plaster surface, which increases rate of leaching of plaster on small spots.



Figure 22 – Arch Chemical's research [12] showing reaction of cyanuric acid with pool plaster, which increases with time in weeks, and dosage.

Both studies by Rothstein et al. [11] and Arch Chemical [12] show the influence of pool stabilizers (i.e., trichlor, CYA, which have high chloride and low pH characteristics) on spot alteration. Based on these studies, spot alteration may indicate an early stage of more advanced etching of pool plaster, if the pool water remains over-stabilized by excessive dosage of chemicals.

 $<sup>^{9}</sup>$  Various chlorine-based sanitizers/disinfectants that release hypochlorous acid (HOCI), the active sanitizing agent to kill harmful microorganisms in pool water are sodium hypochlorite (liquid, 10% chlorine), lithium hypochlorite (granular, 35% chlorine), calcium hypochlorite (granular, 65% chlorine), and trichlor (tablet or granular, 90% chlorine), etc. Trichlor is very acidic (pH 2.8), must be dispensed with a feeder, and is known to cause spot etching problem from cyanuric acid that it contains. Dichlor and trichlor are two granular stabilizers, fast and slow-dissolving, respectively, both of which contains chlorine and cyanuric acid. Cyanuric acid [CYA, (CNOH)<sub>3</sub>] is a stabilizer/conditioner used to resist chlorine loss in outdoor pools from UV-rays of sunlight by reacting with chlorine to produce dichloro CYA.





#### Case Study 15 - Spot Alteration (Spot Leaching, Pitting, and Staining)

Figure 23 – Photographs of a plaster sample showing spot alteration. The left photo shows 52 spots of different sizes (from  $1.5 \times 2$  mm to  $6 \times 9$  mm) over an area of  $110 \times 115$  mm. The right photo is an enlarged view showing spots having green stained cores and white rims.

All of the author's case studies on spot alteration in field plasters, including the one presented here (Figure 23), characteristically showed:

- (a) Overall smooth (on touch), soft, porous, and leached pastes at the spots, having sizes from less than <sup>1</sup>/<sub>8</sub> to <sup>1</sup>/<sub>2</sub> in.;
- (b) Common small pitting of the plaster surface preferentially inside the spots (Figure 24);
- (c) Dusty appearance of paste in between the aggregate particles on the spot (Figure 24);
- (d) Localized leaching of plaster paste beneath the spots, and no leaching of paste in areas in between the spots (Figures 26 and 27),
- (e) Microcracking in plaster, frequently associated with the leached paste beneath the spot (Figures 26 and 27);
- (f) Staining on spots for preferential heavy metal precipitation on porous paste (Figure 25);
- (g) Occurrences of spot etching on plasters containing normal dosages of calcium chloride admixtures; and,
- (h) Overall smooth appearance of plaster in areas away from the spots and no evidence of plaster etching (e.g., of aggregates) either on the spots or in areas away from the spots.

In the example shown here, 52 spots of shapes from circular to elliptical to irregular, and sizes from 1.5 × 2 mm to 6 × 9 mm are found on a 110 × 115 mm surface (Figure 23). Centers of the spots are stained green with copper and phosphorus enrichment, which are surrounded by white rims due to the porous nature of paste, and then normal dense, sound, smooth plaster (having no Cu or P signature) away from the spots. The green stains are from preferential absorption of copper and phosphate salts in pool water by the soft porous paste, where copper was introduced from copper algaecides. X-ray elemental analyses of spots, as shown in Figures 25 and 29, also indicated an enrichment of chlorine at many spots, which are not found in areas away from the spots (similar chlorine enrichment in spots was also mentioned by Rothstein et al., 11].



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No evidence of wide-scale etching deterioration by aggressive water attack (such as the one shown in Figures 13, 14, and 15) was noticed either on the spots, or, especially in other areas of smooth plaster away from spots. The spots, however, as mentioned, show distinct preferential pitting of soft paste surface, mainly on spots having sizes larger than 2 mm, as shown in Figure 24 below. The photos also show the dusty appearance of paste on the pitted spots and stained nature of the pitted and dusty surface, indicating leaching and pitting occurred prior to staining. Spot leaching may have preferentially occurred at the inherent porous locations within the surface of the plaster, or, leaching by an external chemical on small spots may have caused porous paste at the spots; preferential staining on soft spots has occurred from water carrying heavy metals and salts.

Acid-soluble chloride analysis of the bulk plaster showed 0.286 percent chloride by weight of plaster, or,  $\sim 1^{1}/_{2}$  percent CaCl<sub>2</sub> addition, which is well within the usual dosage of CaCl<sub>2</sub> admixture, indicating spot etching, in this case, was certainly not due to addition of excess CaCl<sub>2</sub>in the plaster mix. As mentioned, author's many other cases of spot alteration also showed no evidence of excess CaCl<sub>2</sub> addition.

Scanning electron microscopical examinations show evidence of leaching of calcium hydroxide from plaster beneath the spots, and precipitation of secondary calcium carbonate deposits on the surfaces of some samples by the fluctuating water chemistries. Scales, when found, however, occurred not only over the spots but in other areas as well, as thin (less than 50 micron in thickness) carbonate layers.



Figure 24 – Photomicrographs of plaster surface on and around the spots (taken by using a stereo microscope at a magnification of 10X) showing small surface pitting and leaching of paste on the spots, dusty appearance of paste around the aggregate particles on the spots, and greenish stains due to preferential enrichment of copper at the spots. Note the surface pitting at the spots are characteristic, occurred in almost all the spots and are not so evident in areas away from the spots.

231



PROCEEDINGS OF THE THIRTIETH CONFERENCE ON CEMENT MICROSCOPY, APRIL 20 TO 24, RENO, NEVADA, USA 2008

Figure 25 – The top left photo shows scanned image of a spot, where the green core, surrounded by a white rim are noticed. The two photomicrographs on the right show the spot at higher magnifications, where the green stain at the core is distinct. The lower three spectra are x-ray elemental analyses of the green core (marked as '1'), white rim (marked as '2'), and area away from the spot (marked as '3'), showing enrichment of copper, chlorine, and phosphorus at the spot. Copper stain at the spot is from copper algaecides used in this pool, where the porous paste beneath the spot absorbed copper from the pool water.

Two common sources of copper in the green spots in field plaster are: (a) copper algaecides, and (b) degradation of copper pipe or copper heat-exchangers of swimming pool heaters at the high chlorine and/or low pH (< 7.2) condition of pool water. The present one, as mentioned, was from copper algaecides.

The following two figures show thin section and polished section photos, where cross sections of plaster were made over multiple surface spots (two spots in the left column photos and three spots in the right column photos in Figures 26 and 27), by using a continuous rim ultrathin diamond blade in a low speed saw. Prior to sectioning, individual spots were oven-dried at  $60^{\circ}$ C, vacuum impregnated with a fluorescent dye-mixed very low viscosity epoxy, and sectioned surfaces were further dried and impregnated with the same epoxy. The sections, thus prepared, showed three characteristic microstructural features: (a) microcracking in plaster beneath the spots, oriented perpendicular to the plaster surface, (b) carbonation of plaster at the surface region, down to a depth of 1/8 to 3/16 in. and greater depth along the microcracks (creating V-shaped carbonation front along the crack paths, indicating preexisting nature of the microcracks and not an artifact of sample preparation), and (c) a small zone of leached and porous paste, immediately beneath the spot, within the carbonated zone, where the paste being more porous than the adjacent areas, is highlighted by the fluorescent dye.





Figure 26 – Photomicrographs of polished fluorescent dye-mixed epoxy-impregnated thick sections (~100 microns thick) of plaster and concrete in the core, cross-sectioned through the spots, showing: (a) carbonation of plaster at the surface region, down to a depth of <sup>1</sup>/s to <sup>3</sup>/16 in., where the carbonated paste at the surface being denser than the paste in the body showed a lower absorption of dyed epoxy than that in the body, a greater depth of carbonation along the vertical shrinkage microcracks than the areas in between the microcracks (creating V-shaped carbonation fronts along the paths of the microcracks), and (b) small zones of leached and porous paste at the surface, immediately beneath the spots, within the carbonated paste, which are highlighted by the fluorescent dye-mixed epoxy (marked with arrows).

The middle and bottom row photos are reflected-light photomicrographs of sections (by using an Olympus SZX12 stereo zoom microscope), where porous areas of paste around the microcracks and situated beneath the spots are readily highlighted by the yellow fluorescent dye-mixed epoxy.







Figure 27 – Photomicrographs of fluorescent dye-mixed epoxy-impregnated thin sections (~ 30 microns thick) of plaster and concrete in the core, cross-sectioned through the spots (of the same samples shown in Figure 25 but after further grinding the sample thickness from ~ 100 to ~ 30 microns), showing: (a) carbonation of plaster at the surface region, down to a depth of  $^{1}$ /s to  $^{3}$ /16 in., greater depth of carbonation along shrinkage microcracks (creating V-shaped carbonation front along the paths of the microcracks, and (b) small zones of leached paste immediately beneath the surface spots, where carbonated paste has been leached out relative to aggregates.

Sequence of events depicted by these photomicrographs in Figures 26 and 27 is – microcracking in plaster, followed by deep carbonation along the microcracks, which was followed by local leaching of carbonated paste beneath the spots in areas significantly smaller than the carbonated zone of paste.

The top and middle row photos are of the same thin sections, scanned on a flatbed scanner, by using a black and a white background, respectively. The lower row photos were taken by using a Nikon Labophot 2 POL petrographic microscope in plane polarized-light mode.





Figure 28 – Backscatter electron images of polished cross section of plaster (taken by using a CamScan Series II SEM) showing preferential leaching of paste relative to aggregates (areas within the dashed lines) beneath the surface spots causing proud exposure of aggregate against the paste, and, more or less non-differentiated aggregate and paste (carbonated) in areas away from the leached zones. Arrows mark shrinkage microcracks.



Figure 29 – X-ray elemental analyses of polished cross section of plaster showing P, Cu, and Cl enrichment in an area beneath the surface spot (marked as '1') and their depletion in an area away from the spot (marked as '2').



#### Substrate

Figure 30 – A model of spot alteration based on the present case study, and recent researches of Rothstein et al. [11] and Arch Chemicals [12]. Preexisting microcracks on the plaster provided pathways for entry of pool water and chemicals. Certain chemicals (probably of high chloride and/or low pH chemistry) precipitated on the plaster surface, entered through the microcracks, and created a local high chloride and/or low pH environment at the surface have caused preferential leaching of cement hydration products, increased porosity of paste beneath the point of entry and, as a result, spot like discoloration of plaster at the sites of precipitation. The presence of microcracks helps entry of chemicals but is not necessary for spot alteration from excess chemicals in water.

Based on the present case study of occurrence of spot alteration at the locations of preexisting microcracks, as local leaching of paste beneath the spots, with no evidence of excess calcium chloride or improper finishing, and slightly elevated chloride levels in paste at the spots than elsewhere (Figure 29, similar to the findings of Rothstein et al. [11]), the author proposed a model (see Figure 30) where entry of water and chemicals having a high chloride/low pH chemistry (e.g., stabilizers) caused spot alteration at the loci of precipitation of chemicals on plaster surface at and around the microcracks. The presence of a preexisting microcrack, however, is not essential, since a local high chloride/low pH environment at the point of precipitation of such chemicals on the plaster surface can cause spot-like leaching of paste.

Author's own studies of spot alteration are consistent with previous findings of the absence of overall etching of plaster on or away from the spots and smoothness (on touch) of spots, evidence of localized paste leaching and porous paste at the spots, heavy metal enrichment from preferential staining at the spots, etc. The interpretation of findings by previous researchers, i.e., related to excess calcium chloride and improper plastering, however, is open to question, especially in lieu of the facts that:

- (a) Author's own observation of spot alteration in many cases, such as the one presented here, show normal calcium chloride dosage, and no evidence of finishing improprieties in the plaster, and,
- (b) Recent researches on the importance of excessive dosage of trichlor/CYA water treatment chemicals on spot alteration indicate influences of local high chloride/low pH environment causing spot-like leaching of surface paste, even in a balanced water pool, without necessarily causing an advanced etching.



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The author did not detect any evidence of the occurrence of spot alteration around weakened aggregate-paste bond, or, it's nucleation around other areas of pre-existing weak areas on the plaster surface, but rather formation of spot-like leaching and associated localized porous paste (many around a preexisting microcracks acting as the entry path for the water and chemicals) on plasters that have been proportioned and finished properly. Spot alteration became common in the pool and spa industry more or less from the same time as the use of such high chlorine/low pH stabilizers<sup>10</sup>. In author's opinion, localized influences of such water-treatment chemicals (sanitizers, acidic stabilizers) in pool water (not necessarily aggressive) on selective leaching/pitting/staining of paste at the points of precipitation of chemicals on the plaster surface deserve a thorough and systematic research.

#### PLASTER SURFACE PITTING BY UNSOUND OR REACTIVE SAND

Apart from the above example of small surface pitting of plaster by spot-like leaching of paste, pitting on plaster surface can also occur by other ways. Sand used in plaster should be free of any impurities, non-reactive and in conformance to the guidelines of ASTM C 926 and ACI 524. Some unsound or reactive sand in plaster can react with plaster cement, in the presence of moisture to cause alkaliaggregate reaction and associated popout of plaster surface. Such reactions, however, seldom occur due to the neutral pH environment and low to moderate alkalinity of pool water in contact with the plaster. Small size of sand also reduces expansive stresses from such reactions, if it occurs, and limits the resultant popout size to less than 3 mm to a maximum 12 mm in the worst case. Other impurities in sand can cause small spots of staining or deterioration of plaster surface, e.g., certain clays, chert, zeolite, shale, opaline material, iron or copper metal contaminants in sand, etc.

# FREEZING AND THAWING DAMAGE OF PLASTER

Damage due to cyclic freezing and thawing of plaster at critically saturated conditions is rare due to the underwater environment. Damage, however, can occur during plastering process by plastic freezing of plaster, or, prior to immersion in water. Portions of plaster not constantly underwater are susceptible to damage even during its service, due to the close proximity to a moist environment and intermittent drying and wetting phases [13] - those above-water portions of plaster in regions having anticipated sub-freezing temperatures in winter should have an added amount of air entrainment to increase resistance to freezing-related damage. Usually, a porous plaster is more resistant to freezing-related damage (due to its increased pore spaces to accommodate freezing-related stresses) than a dense, hard-troweled plaster.

# PLASTER CARBONATION

Carbonation of pool plaster occurs by reactions of cement hydration products with atmospheric carbon dioxide, or dissolved carbonate and bicarbonate ions in pool water. Carbonation proceeds from exposed plaster surface inwards, and can invade the entire plaster thickness. Usually, plaster carbonation is not deleterious. However, pool water having a low carbonate alkalinity can convert calcium carbonate of carbonated plaster into water-soluble calcium bicarbonate, which can cause plaster surface deterioration. Carbonation of a freshly-placed plaster prior to water immersion can aggravate mottled, blotchy discoloration of the hard trowel-finished surface. Carbonation of a newly plastered surface can also cause shrinkage cracks to remain open due to the loss of calcium hydroxide component of cement hydration, which usually seals the cracks (the higher solid volume of calcite, the carbonation product, relative to calcium hydroxide, the cement hydration product, however, could play a beneficial role in crack sealing).

<sup>&</sup>lt;sup>10</sup> Randy Dukes, NPC, Personal Communication, April, 2008.



## **REMEDIES OF PLASTER DETERIORATION**

The Technical Manual of National Plasterers Council provides various remedies of plaster deterioration as general guidelines [1]. A few remedial examples are:

- (a) Open plaster cracks are usually cleaned and filled (injected) with a cement paste, with or without sand and/or a polymer additive; extensive surface cracks may need to be resurfaced.
- (b) A soft or inferior plaster can gain strength by continued cement hydration underwater, otherwise, a surface hardener can be applied, which can reduce dusting, efflorescence, and strengthen the surface.
- (c) De-bonded plaster areas should be removed, exposed undercoat or substrate surface should be thoroughly cleaned of loose dirt or dust, and patched with a repair coat by a bonding agent, in a similar finishing/curing manner as the main plaster for intimate bond to the substrate and the remaining plaster.
- (d) Controlled acid washing, bleaching, sanding, grinding, and careful surface treatments with certain chemicals or stain removers are various methods of surface stain and scale removal. Acid washing, bleaching or chemical treatments can reduce large area discoloration.

Appropriate remedial actions are project-specific, which must be considered after consultation with the project personnel.

#### **CONCLUSIONS**

Various deteriorations of swimming pool plaster include cracking, softening, delamination, discoloration, staining, etching, scaling, surface pitting, carbonation, freezing-related damage, and spot alteration. Most of the pool plaster problems are associated with chemical or physical unsoundness in the substrate putting the plaster in tension, substrate settlement, improper plaster mix, disproportioning (e.g., excess CaCl<sub>2</sub> dosage), thickness, and finishing techniques, influences of pool water chemistry and water treatment chemicals on plaster, environments of plaster placement and service, and overall design. A systematic investigation of the plaster problem, including review of project background and thorough laboratory investigation of plaster samples can diagnose the cause(s) of problems, based on which appropriate repair strategies should be taken.

The paper presented fifteen different case studies of various such problems, summarized in Figure 31, diagnosed their causes, summarized as well in the Figure, and emphasized the importance of detailed laboratory investigation in determining reasons for these problems. Importance was given on the author's most frequently observed problems on plaster cracking, etching/scaling, delamination, discoloration, and spot alteration. Finally, a mechanism of spot alteration is proposed based on the observed chemical and microstructural properties of plaster in an interesting case study.

As seen in all cases, the basic issues of plaster problems are related to the quality and composition of plaster, the soundness and stability of substrate, the characteristics of pool water and its chemicals, pool maintenance, and the environment in which the plaster was placed and is in service (Figure 32). Improper plaster quality and/or mix proportions (e.g., excess sand, fines in sand, unsound or reactive sand, excess water, calcium chloride admixture, lime addition, etc.), and improper finishing practices (over-troweling, finishing with excess water, etc.) can lead to plaster cracking, softening, delamination, surface pitting, discoloration, and other problems. Imbalanced pool water can cause plaster scaling and etching. Heavy metals, minerals, contaminates in water can cause staining. An unstable substrate (e.g., expanding or settling) can induce plaster cracking. Plaster placement in a subfreezing temperature, or in a hot, dry, windy weather condition can cause cracking, softening, and delamination issues. Improper pool maintenance, e.g., excessive dosage of water treatment chemicals, or, inadequate brushing of leached lime from plaster and water at the early stage, etc. can cause plaster spotting or scaling. A good understating of all these systems, and their influences on plaster properties are, therefore, essential for prolonged durability and serviceability of swimming pool plaster.



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Figure 32 – Four major components responsible for most of the plaster problems (see the left photo). A basic understating of these four systems is, therefore, essential for prolonged durability and serviceability of plaster.



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# END OF REPORT<sup>1</sup>

 $<sup>^{\</sup>rm 1}$  The CMC logo is made using a lapped polished section of a 1930's concrete from an underground tunnel in the U.S. Capitol.