APPLICATION OF PETROGRAPHY IN RESTORATION OF HISTORIC MASONRY STRUCTURES

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Abstract

Restoration of historic masonry structures often require identification of the composition of masonry units and jointing mortars so that a suitable modern masonry unit or a re-pointing mortar can be chosen. Petrographic examination has significant applications in restoration projects in providing detailed information about: (a) the overall condition, composition, and quality of the original masonry unit; (b) the condition, composition, and quality of the original mortar; (c) the type, composition, lithology, size, distribution, soundness, alkali-aggregate reactivity, and durability of sand in the mortar, (d) the type of cementitious materials originally used (e.g., lime putty, lime-pozzolans, portland cement, masonry cement); (e) proportions of sand and cementitious materials used; (f) effects of atmospheric weathering and alterations on the overall condition and serviceability of the mortars and the extension of these effects inside the mortar; (g) composition and sources of efflorescence and staining on masonry walls; (h) evidence of physical attacks on masonry from fire attack, frost attack, reversible salt hydration, and salt weathering; and (i) evidence and extension of various internal and external chemical attacks in the masonry. Based on this information, an engineer or architect can propose a suitable and durable modern mortar or masonry unit that will not only have a close aesthetic match in color, texture, and composition to the ancient material, but also have a consanguineous coexistence to the adjacent ancient materials.

Sculptures and architectural buildings made using cast stones or various natural stones (limestone, marble, sandstone, granite, etc.) can also be examined by petrography. The type of sand and cementitious materials used in the cast stone, the quality and condition, the depth of deterioration of alteration (if any), the causes of cracking or spalling of the stone, and evidence of freeze-thaw deterioration, etc. can be assessed. Since petrography is the science of the description and classification of natural rocks, it is at the nucleus of the examination of natural stone structures.

Petrography has significant applications in condition assessment and failure investigation of all types of ancient masonry and architectural buildings constructed with clay, stone, concrete, lime, gypsum, portland cement, masonry cement, or other materials.

Keywords: Petrography, Microscopy, Restoration, Historic Structures, Masonry

Introduction

Ever since the dawn of civilization, prehistoric people discovered the cementitious properties of mud in holding the stones and cobbles for their shelters. Later, they discovered that certain mud holds stone better than others and resists erosion. Egyptian builders of the twenty-seventh century B.C. first invented masonry mortar, when a mixture of burned gypsum and sand was used in the construction of the Great Pyramid at Giza. Greeks and Romans mixed volcanic ash (a natural pozzolan) with lime to create a hydraulic lime for their masonry structures, many of which are still in service today.

Historic masonry structures stand as the symbol of fortune and glory – the sign of the architectural marvels of the past – the sign of the ancient masterpieces that are worthy of preservation with full respect and honor. Perhaps the ideal examples are the pyramids built 4000 years ago with large limestone blocks transported and placed by gypsum-based jointing and lubricating mortars following ingenious engineering designs. The Roman Empire fell, but it's historic structures endured and continued to show the majesty of Roman architecture.

Before the advent of portland cement, the cornerstone of modern construction, masonry units in the ancient structures were bonded together by using a gypsum or, more commonly, a lime-based mortar. Both products show acceptable strength, durability, and resistance to atmospheric weathering and erosion – the former in dry, arid environments and the latter in both dry and wet environments.

Portland cement was patented in Great Britain in 1824, first manufactured in the United States in 1872, and became a common choice of mortar mix for the masons in the early 20th century. By the 1930's, masons used a mix of equal parts of portland cement and lime putty. Mortars in historic structures built between 1873 and 1930 range from lime putty and sand mixes to a wide variety of lime, portland cement, and sand combinations. Although the cementitious materials used in the pre-portland cement era are still available today, and are in fact in use in some projects, the rapid strength gain property of portland cement supersedes its use over the other materials and makes it an ideal choice of material for modern masons. The introduction of masonry cement in the 1930's as a premixed bagged product, and machine-slaked "hydrated lime" (instead of hand-slaked "lime putty") gave new dimensions to the masonry industry. Since the mid-1950's, the use of masonry cement has increased significantly due to the presence of portland cement and many property-enhancing additives.

Restoration of historic masonry structures requires a thorough understanding of the composition, behavior, and properties of these materials,

as well as their microstructures, the role of the microstructure in controlling the properties and performance of these materials, and the properties that were particularly responsible for long-term durability and performance.

Architectural natural or cast stone sculptures and monuments often carry signs of century-long atmospheric weathering and physico-chemical alterations, which require careful restoration with compatible modern materials that will not only have a visual match but also a consanguineous relationship with the existing material. Stones that were used in many masonries and sculptures ranged from limestone, sandstone, marble, granite, and gneiss (as ashlar stones or rubble stones) to relatively uncommon types such as serpentinite, amphibolite, diabase, travertine, and other igneous and metamorphic rocks. Cast stones made using a specially formulated mix of portland cement and sand, resembling natural stones in the hardened state, were also used in many sculptures.

In any restoration project, one must determine what type of material was used. Petrography provides detailed and accurate information about the composition of the material as well as its texture, microstructure, and other properties that are helpful in selecting the most suitable modern match. This article explains the role of petrography and various petrographic techniques useful in the examination and restoration of the ancient masonry and architectural structures.

Petrography

Petrography is the 150-year old discipline of geology that deals with the description and classification of natural (igneous, sedimentary, and metamorphic) and extraterrestrial (lunar, meteoritic) rocks, including the man-made rock we called concrete. Petrographic examinations involve detailed microscopical examinations of material at various magnifications by using stereomicroscopes, petrographic microscopes and scanning electron microscopes, x-ray diffraction, and associated chemical and physical tests.

During the investigation of a historic structure, petrography provides detailed information on:

(a) The composition and condition of the ancient masonry units consisting of manufactured clay products (e.g., brick, terra cotta, structural clay tile), natural stones, and cementitious masonry units (e.g., concrete brick, cast stone, calcium silicate brick, and concrete masonry unit);
(b) The type, composition, overall condition, and quality of the original mortar used in the masonry;
(c) The type, composition, lithology, mineralogy, color, size, shape, distribution, soundness, gradation, alkali-aggregate reactivity, and durability of the sand used in the mortar;

(d) The type of the cementitious material(s) originally used (e.g. lime putty, hydrated or hydraulic calcitic or dolomitic lime, lime-pozzolans, gypsum, or portland cement); the degree of portland cement hydration and paste carbonation; the presence of contaminants;
(e) Mass and volume proportions of sand and cementitious materials used to make the mortars;
(f) Effects of atmospheric weathering and chemical alterations (e.g., carbonation) on the overall composition, condition, and serviceability of the mortars; and the extension of these effects inside the mortar;
(g) Composition and sources of various efflorescence deposits on the masonry walls and their potential influence in masonry deterioration;
(h) Evidence and extension of various physical attacks on the structure in the past such as fire attack, or volume changes due to heating and cooling, wetting and drying (salt hydration and/or crystallization), freezing and thawing, freezing of mortar at plastic state, and delayed hydration of free lime and/or magnesia in the paste;
(i) Evidence and extension of various internal and external chemical attacks (e.g., attack of acid rain, sulfates, corrosion of embedded metals), etc.
(j) Evidences of improper materials or poor workmanship;
(k) Effects of long-term temperature and moisture fluctuations on the masonry panels;
(l) Identification of any foreign deposits precipitated on the surfaces of the masonry from the atmosphere over the life of the structure; and
(m) Degree of intimately of bond between mortar and masonry units.

Based on the information obtained during the restoration project, a petrographer can assist a restoration engineer in:

(a) Determining a suitable match for the ancient material; and evaluating the proportion of different ingredients in the repair material (e.g., sand and cement in re-pointed mortar);
(b) Deciding the depth of the original material to be replaced by the repair material;
(c) Providing suggestions for appropriate surface preparations needed prior to the installation of the repair material;
(d) Evaluating freeze-thaw durability of the repair material; and
(e) Evaluating the effectiveness of the repair and restoration; and the nature of interfaces between the repair material and the existing elements in the structure.

Petrographic and chemical methods of analysis of hardened mortar

ASTM C 1324 describes the "Standard Test Method for Examination and Analysis of Hardened Mortar". This standard provides methods of petrographic examinations and chemical analysis of hardened mortar. The analysis reports the overall composition of the mortar, estimated mix proportions, type and composition of aggregates, nature of the paste, air content, secondary deposits, efflorescence deposits, the original cementitious ingredients used in the mortar, and evidence of deterioration. Chemical analysis includes the determination of: (a) soluble silica and (b) calcium/magnesium oxide in the mortar by wet chemical analysis or by other instrumental methods (e.g., x-ray fluorescence or atomic absorption spectroscopy), (c) dilute hydrochloride acid insoluble residue, (d) loss on ignition to 950ºC, and (e) magnesium hydroxide content in mortar (having dolomitic lime) from thermal analysis. The results provide the volumetric proportions of cementitious materials and sand used in the hardened mortar. Petrographic examination determines the type of sand present (siliceous or calcareous) based on which the appropriate chemical method (soluble silica or calcium/magnesium oxide) is followed. Petrographic examinations of the masonry units (clay, stone, and cementitious units) are done in accordance with the methods described in ASTM C 856 "Standard Practice for Petrographic Examination of Hardened Concrete". Other references that provide detailed descriptions of various methods of petrographic examinations include: ASTM C 856, St. John et al. (1998), Mielenz (1962), and Walker 1992.

Common methods of petrographic examination include:

(a) Visual examinations of masonry units and mortars in the field and/or in the samples received in the laboratory;
(b) Careful preparation of the sample for microscopical examinations such as sectioning, grinding, polishing, thin-sectioning, pulverizing, etc.;
(c) Examinations of sawed, lapped, freshly fractured sections and "as received" samples in a low-power stereomicroscope;
(d) Examinations of oil immersion mounts and thin sections in a petrographic microscope;
(e) Examinations of powder mounts, saw-cut sections, lapped sections, thin sections, or "as received" samples in a scanning electron microscope with ancillary energy-dispersive x-ray spectroscopy (SEM-EDS);
(f) Examinations of lapped section or a finely pulverized section of mortar in a x-ray powder diffractometer (XRD); and
(g) Various ancillary chemical (XRF, FTIR), thermal (DTA, TGA), and physical (strength) analyses to determine the composition and additional properties that may not be possible to obtain from microscopical methods.

Thin-section microscopy provides a wealth of information about the overall mineralogy, texture, and microstructure of the mortar. Since the ancient

materials may be soft, fragile, cracked, and highly altered due to long periods of chemical and/or physical weathering processes, and a limited amount of material may be available, extreme care and caution are needed during the sample preparation. Samples should be representative of the field conditions. The number of samples should adequately provide the whole range of variations of the conditions or degrees of deteriorations in the structure. In a typical restoration project, only a handful of broken chips of masonry units or the jointing mortars may be available. Preferably, the mortars should be collected not only from the exposed side of the masonry walls but also from the interior of the head or bed joints where the mortar may or may not have the atmospheric alteration effects. Mortar pieces should either be collected by hand or by a using a hammer and small chisel without damaging the masonry units. Only a few small pieces may be available for restoration of stone masonry or sculpture. Conditions of the samples may range from small fragments to powders.

Visual Examinations and Photographic Documentation

As mentioned before, samples should first be examined visually in as much detail as possible. Properties that can be documented from visual examination include but are not limited to: original color and any color variation, dimensions, weight, surface texture, hardness, softness, integrity, density, porosity, water droplet absorption, variations of these properties between the surface and the interior, visual effects of atmospheric alterations, cracking, spalling, evidence of any other distress or alterations, and any other relevant or even irrelevant features that are worth recording. Prior to any sample preparation, all samples should be adequately photographed to preserve the pristine condition of the sample by using a 35 mm camera, digital camera, or a high-resolution scanner with a scale bar. Photographs should document any particular feature in the original material that might have some relevance to the performance of the material (cracks, efflorescence, color variation, alterations, etc.).

Sample Selection and Initial Preparation

Following the detailed visual examination and photographic documentation, depending on the sample size or volume, a single or multiple small representative portion of the original sample is selected for preparing appropriate sub-samples for various modes of examinations, such as: (a) thin section for observation in a petrographic microscope, (b) lapped or polished section for observation in a stereomicroscope, (c) freshly fractured section for examination of oil immersion mounts in a petrographic microscope, (d) thin section, polished section, freshly fractured or saw-cut section, or powder mount for examination in a scanning electron microscope, and (e) pulverized sample for chemical analysis or x-ray diffraction. If an adequate sample is present, it is

a good practice to retain at least some of the original sample intact for any future study, if necessary.

Low-power stereomicroscopical examination

Information obtained from examinations in a stereomicroscope include: color, density, scratch hardness, porosity and water droplet absorption; size, grading, composition, and type of sand used in mortar and in cementitious masonry unit; degree of consolidation; whether or not the mortar is over-sanded; nodules of hydrated lime, which is common in many ancient lime-sand mortars; depth of carbonation in portland cement based materials; depth of alterations, the presence and condition of any embedded items such as wire mesh or metal reinforcement; and many other properties depending on the nature of the sample.

Examinations of oil immersion mounts in a petrographic microscope

Examination of oil immersion mounts in a petrographic microscope is very helpful for quick and easy determination of the composition of the mortar, the composition of efflorescence deposits, limestone fines in masonry mortars, the presence of portland cement and other cementitious materials in the mortar, and the secondary deposits in the mortar. Immersion mounts are carefully prepared by: (a) removing a small representative sample from an area of interest (while viewing the area under a stereomicroscope) with a sharp-pointed needle, (b) transferring that powder to a glass slide, (c) immersing it in an oil of a known refractive index, (d) covering it with a small, thin glass cover slip, (e) evenly distributing the powder by gentle pressure with the help of the rubber in a rubber-headed pencil, and (f) examining the oil-immersed powder in a petrographic microscope. Many minerals can be positively identified using their characteristic optical properties such as refractive index, shape, crystal habit, relief, extinction angles, pleochroism, birefringence, interference color, and dispersion staining.

Thin-sectioning

Thin sections (a thickness less than 30 microns) provide the most detailed information about the overall composition and microstructure of masonry materials. Steps for thin-sectioning of mortar involve: (a) oven drying a small piece at 40-50ºC to a constant mass to remove the free moisture (drying at high temperature may induce thermal or shrinkage cracks); (b) vacuum impregnation of the oven-dried piece with a very low-viscosity epoxy resin and hardener that can deeply and thoroughly impregnate the sample to improve its integrity (a pigmented or fluorescent dye mixed epoxy can be used to highlight the voids, cracks and porous areas in the sample); (c) trimming of the hardened epoxy-impregnated mortar with a thin, diamond-bonded tile saw or a precision

saw to obtain a flat surface; (d) an optional step of a second epoxy impregnation on the saw-cut surface if it is not dense and hard enough by the epoxy; (e) a first, fine grinding of the saw-cut surface on a lapping wheel (e.g., solid iron) with a suitable abrasive (silicon carbide powder or a diamond-bonded magnetic grinding disc) of successively finer grain size and appropriate lubricant (water); (f) ultrasonic cleaning and oven-drying of the lapped surface to obtain a smooth, flat, clean, dry surface; (g) impregnation of the finely ground surface to a clean, dry, and preferably frosted glass slide with a thin, liquid adhesive having a very high tensile bond strength; (h) a second thin-sectioning of the bonded slice with a thin diamond precision saw to obtain a very thin (less than 1 mm) slice of the glass-bonded sample; (i) successive fine grinding of the thin slice on a grinding wheel with a fine abrasive or on a diamond-bonded fine grinding wheel until the final thickness of the sample on the slide is about 50 microns; (j) a final, ultra-fine grinding on a polishing cloth or on a glass slide with fine abrasive (e.g., 10 micron alumina) until the desired thickness (20 to 25 microns) is achieved; and (k) an optional polishing of the thin section if examination in a scanning electron microscope is intended. The above steps are the general procedures that the author's laboratory follows for masonry mortars; the details of thin sectioning procedures can be found in St. John et al. (1998) and Walker (1992). Automatic thin-sectioning machines (e.g., manufactured by Buehler, Logitech, Struers, Wards Natural Science, Microtec, or German Instruments) are very helpful for bulk production of good thin sections. The author's laboratory uses Logitech PS2000 and Lapmaster Model 15 precision grinding and lapping machine, and Buehler's PETRO-THIN and Isomet 1000 precision thin sectioning machines for bulk production of high quality, blue dye or fluorescent dye-mixed epoxy-impregnated, 27 mm × 46 mm and 50 mm × 75 mm thin sections.

Examinations of thin section in a petrographic microscope

Thin-sections thus prepared are examined in a petrographic microscope at magnifications up to 1000X. Samples are examined in plane-polarized light, crossed-polarized light, and fluorescent-light modes. The author's laboratory uses Nikon Labophot2-Pol, Nikon Optiphot-Pol, Olympus BX40, and Olympus BHSP trinocular petrographic microscopes that are equipped with digital cameras, 35-mm cameras, fluorescent attachments, and image analysis softwares for examinations and photomicrographic documentations at various modes. Information obtained from thin-section petrography is numerous and includes: detailed texture, microstructure, and mineralogy of the material; type, composition, and condition of the original masonry unit; type, lithology, grading, deleterious constituents, soundness, reactivity, and many other properties of sand used in mortar or architectural cast stone; the volumetric proportions of sand and cementitious materials used; evidence of chemical and

physical deteriorations in the sample; and the exact type of stone used in the stone masonry or sculpture.

X-ray diffraction analysis

X-ray diffraction analysis is a very powerful method in mortar analysis. The author's laboratory uses a Siemens D5000 powder diffractometer having a Θ-2Θ geometry that is connected to a PC loaded with the data acquisition, search/match, and quantitative analysis software (MDI's Datascan, JADE 7+, Search/March, Easy Quant, and ICPD's PDF2). A sample can be examined in three modes – (a) a small piece of sample can be finely pulverized in a mill to a talc-like consistency and analyzed in the diffractometer; (b) a lapped slice or thin-section of sample can be directly analyzed; or (c) a very small sample (e.g., efflorescence deposit) can be directly analyzed. The analysis detects the presence and the amount of many fine crystalline materials from their characteristic sets of diffraction peaks in the powder diffraction pattern. Chatterjee (2001) summarizes the techniques and applications of XRD in cement and concrete sciences.

Scanning electron microscopical examinations

Scanning electron microscopical examination not only provides the detailed microstructure and 3D morphology of a mortar or masonry unit at a very high magnification but also provides the elemental composition of an area of interest. Samples can be examined in various modes: (a) as a small piece of the original sample, (b) a polished, uncovered thin section coated with gold, gold-palladium, or carbon, (c) a polished and coated thick slice, (d) a powder mount from the original sample (which can be coated or uncoated depending on the vacuum system of SEM), or (e) an aliquot of powder prepared for x-ray diffraction or chemical analysis. Secondary electron image from the near-surface region provides the detailed morphology a mineral; and backscatter electron image provides the detailed microstructure of the mortar. Energy-dispersive x-ray spectroscopy determines the elemental or oxide composition of sand, cement hydration products, stain-producing material, efflorescence deposits, or secondary deposits in mortar. The author's laboratory uses a Cambridge Scanning Electron Microscope (Camscan Series II SEM) that is equipped with a Robinson backscatter electron detector and a Kevex energy-dispersive x-ray spectrometer with 4Pi Revolution software. Sarkar et al. (2001) summarizes the techniques and applications of SEM in cement and concrete sciences.

Chemical Analysis

Chemical analysis of mortar determines: (a) the bulk composition, (b) quantitative proportions of sand and cementitious materials, (c) composition of

pigmenting materials, if any, (d) detection of any contaminants, (e) the presence of any additives or admixtures (usually in modern masonry), etc. Common techniques used include: (a) wet chemical analysis (gravimetric) or other instrumental analysis (x-ray fluorescence or atomic absorption spectroscopy) to determine the soluble silica and calcium/magnesium oxide in the mortar; the dilute hydrochloride acid insoluble residue (which in case of a mortar with siliceous aggregates represents the proportions of aggregate); and loss on ignition to 950ºC; (b) infrared and UV-Visible spectroscopy to determine the presence of organic admixtures and water repellants; or (c) any other methods as deemed necessary. Hime (2001) and ASTM C 1324 summarize various chemical methods for hardened mortar analysis.

Thermal Analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) are helpful for rapid identification of various hydrous, sulfate, and carbonate phases in the mortar. ASTM C 1324 recommends thermal analysis for quantitative determination of magnesium hydroxide in the dolomitic lime mortar. Ramachandran (2001) summarizes the techniques and applications of various thermal analyses in cement and concrete sciences.

Physical Testing

Various methods of physical testing such as cold and boil water absorption, saturation coefficient, density, volume of permeable voids, compressive strength, freeze-thaw durability, and accelerated weathering tests according to various standard (e.g., ASTM C 67, C 109) and non-standard tests are done for determining the durability, resistance of masonry units and mortar in severe weather, and conformance to project specifications. ASTM Volume 4.08 on "dimension stones" has a list of standard tests for compressive and tensile strength, absorption, density, and modulus of rupture for various dimension stones that are useful to evaluate these physical properties in natural stones of historic structures.

Microstructure of various masonry materials

Petrographic Identification of Masonry minerals – Detailed characterization of the microstructure of a masonry product requires an initial mineralogical identification of various masonry minerals present in the product. Two common methods of rapid identification of various masonry minerals involve: (a) examination of oil immersion mounts of masonry material in a petrographic microscope, where various minerals are identified by their characteristic refractive indices, and (b) x-ray diffraction. Table 1 provides a list of various masonry minerals, their characteristic refractive indices, and their

Bragg diffraction angles at four major peak intensities – these two properties are very helpful for rapid positive identification of various crystalline phases in a masonry product.

Table 1: Rapid petrographic identification of various masonry minerals (from St. John et al. 1998, see that reference for detailed optical properties)

Mineral	*Refractive Indices*	*XRD Peaks Degrees 2Θ (Cu-Kα)*
Quartz	ω = 1.544, ε=1.553	26.65_x, 20.85_2, 50.14_1, and 59.95_1.
Residual Alite	α = 1.716-1.720, γ=1.722-1.724	32.07_x, 34.29_9, 41.15_8, and 32.33_7.
Residual Belite	α = 1.717, β=1.722, γ=1.736	32.14_x, 32.05_x, 32.59_8, and 41.21_5
Portlandite	ω = 1.573-1.575, ε=1.545-1.547	34.09_x, 18.09_7, 47.12_4, and 50.79_4
Calcium oxide	n = 1.838	37.35_x, 53.86_5, 32.20_4, and 64.15_2
Magnesium oxide	n = 1.732-1.738	42.91_x, 62.31_5, 78.61_1, and 109.73_2
Calcite	ε = 1.486, ω=1.658	29.41_x, 39.40_2, 43.15_2, and 47.49_2.
Aragonite	α = 1.530, β=1.682, γ=1.686	26.21_x, 33.13_6, 45.85_6, and 27.22_5
Vaterite	ω = 1.550, ε=1.640-1.650	27.05_x, 32.78_9, 50.08_7, and 24.90_7
Dolomite	ε=1.500-1.526, ω = 1.680-1.716	30.94_x, 41.43_2, 44.95_1, and 50.53_1
Thermonatrite	α = 1.420, β=1.506, γ=1.524	32.32_x, 32.56_6, 37.96_6, and 33.43_6
Natron	α = 1.405, β=1.425, γ=1.440	29.04_x, 29.23_7, 30.50_6, and 16.45_5
Trona	α = 1.412, β=1.492, γ=1.540	33.82_x, 29.08_8, 18.14_6, and 9.05_5
Gypsum	α = 1.520, β=1.523, γ=1.530	11.59_x, 20.72_x, 29.11_8, and 31.10_5
Hemihydrate	α = 1.558, β=1.559, γ=1.586 (α-form) α = 1.550, γ=1.556 (β-form)	29.69_x, 31.90_4, 14.72_8, and 25.67_5
Anhydrite	α = 1.570, β=1.576, γ=1.614	25.44_x, 31.37_3, 38.64_2, and 40.82_2
Thenardite	α = 1.464, β=1.473, γ=1.485	32.12_x, 19.04_7, 28.99_6, and 28.03_5
Mirabilite	α = 1.394, β=1.396, γ=1.398	16.13_x, 27.77_8, 27.34_6, and 28.68_6
Epsomite	α = 1.433, β=1.455, γ=1.461	20.72_x, 21.08_8, 16.53_3, and 14.76_3
Hexahydrate	α = 1.426, β=1.453, γ=1.456	25.60_x, 18.30_8, 26.30_7, and 26.65_7
Kieserite	α = 1.523, β=1.535, γ=1.586	20.09_x, 16.20_5, 17.31_4, and 21.85_4
Ettringite	ω = 1.466, ε=1.462	9.09_x, 15.74_8, 22.75_3, and 34.48_3
Thaumasite	ω = 1.504, ε=1.468	9.25_x, 16.08_4, 26.13_2, and 23.53_2.
Glauberite	α = 1.507, β=1.527, γ=1.536	28.20_x, 28.25_8, 27.76_8, and 31.40_7
Halite	n = 1.544	31.30_x, 44.30_6, 54.10_2, and 27.08_1
Sylvite	n = 1.490	28.00_x, 39.76_6, 48.49_2, and 62.80_2

Brick, Stone, and Cementitious Masonry Units – Brick, stone, and cementitious masonry units come in a wide range of color, shape, surface texture, and composition. Petrography is the best method to determine the microstructure of these units. In addition to the microstructure, petrography also determines: (a) the composition, density, and texture in the interior of these units; (b) any color variation and its significance; (c) degree of burning (for clay bricks), and degree of chemical reaction or hydration (for cementitious masonry units); (d) causes of high water absorption, low strength, and poor freeze-thaw durability of masonry units; (e) the type, composition, mineralogy, and

condition of various natural stone masonry units (e.g., limestone, granite, marble, slate, sandstone), causes of their sometime irreversible dimensional changes (hysteresis) due to moisture and/or temperature fluctuations, and effects of atmospheric weathering and erosion on stone panels; and (f) overall condition, composition, and type of aggregate used in various cementitious masonry units such as concrete brick, calcium silicate (or sand-lime) brick, cast stone, and the most common, concrete masonry unit.

Architectural Cast Stone – The microstructure resembles a portland cement - sand mortar, with or without hydrated lime, and sometime contains a pigmenting material. The matrix is usually carbonated at varying degrees (depending on the age) and is as dense as some stones (hence it is called cast stone). White portland cement (either alone or blended with grey cement and color pigments) is usually used to produce light colors in the modern cast stones. Aggregate can be natural gravel, washed and graded sand, and crushed and graded stone of granite, marble, quartz, or limestone. Because of the rich cement-sand ratio of 1:3 and warm, moist curing the matrix of cast stone is dense, near impermeable, and has a fine-grained texture. French builders made lintels and door trim out of cast stone as early as the twelfth century.

Clay Mortar – Clay is one of the oldest materials used in masonry mortar. It has been used historically with sun-dried brick, burned brick, and stone, mainly in arid climates (and also in humid climates for interior work such as in chimneys and in exterior, protected from rain). Ground fire clay is still used today in mortars requiring a mild refractory quality. Romans used ground clay from low-fired brick for pozzolanic additives to lime-sand mortars.

Lime-Sand Mortar – The lime-sand mortar was the most common type of masonry mortars used until the late 19th century. "Lime" is one of the most confusing terminologies in the masonry industry, which includes: *quicklime* (calcined limestone, mostly calcium oxide, capable of slaking with water), *refractory lime* (hard burnt dolomitic lime having little or no tendency for hydration), *lime putty* (slaking quicklime with water or mixing hydrated lime with water to a desired consistency), *mason's quicklime* (quicklime slaked to a lime putty for use in masonry), *milk of lime* (suspension of hydrated lime or slaked quicklime in water in proportions to resemble milk), *hydrated lime* (a dry power produced by machine treating quicklime with enough water to satisfy its water affinity, consists essentially of calcium hydroxide, or magnesium hydroxide or both), *hydraulic lime* (a hydrated, dry, cementitious product produced by calcining a limestone containing silica and alumina to a temperature of partial fusion to produce calcium oxide and calcium silicates having hydraulic characteristics), and *spray lime* (a hydrated lime where at least 95 percent of the particles are finer than 45 microns). "Lime" in the lime-sand mortar is commonly lime putty or hydrated lime. Despite low compressive strength and slow setting characteristics, lime-sand mortar offers good

workability, high water retention, high elasticity, excellent bond, and long-term durability even in severe climates. The microstructure of lime-sand mortar consists of a severely, uniformly, and thoroughly carbonated matrix of very fine-grained calcium carbonate (that has developed strength by long-term atmospheric carbonation of the original lime binder), and siliceous and/or calcareous aggregate particles. Ancient lime-sand mortars characteristically contain isolated, small, white spherical, near-spherical or irregular shaped nodules of carbonated or relatively less carbonated lime that has not been mixed with the sand-lime matrix. The Cathedral of Florence and the Great Wall of China are some oldest brick masonry structures built with sand-lime mortars and containing carbonated hydrated lime and sand (mortar in the former contains a small amount of sodium carbonate and in the latter a trace amount of residual ferruginous material, Erlin and Hime, 1987). Petrography determines the type, lithology, mineralogy, color, grading, distribution, and condition of the sand particles in the mortar and the estimated volumetric proportions of sand and the carbonated lime paste. If the sand is siliceous (i.e., quartz-based), a dilute hydrochloride acid insoluble residue content of the mortar shall provide the sand content of mortar and an opportunity to study the color and composition of the sand in detail. Hydraulic lime, made from limestone with clay impurities, and sand based mortars were used extensively for construction of canals, piers, and bridges during the nineteenth century. The paste of hydraulic lime mortar contains residual calcium silicate (e.g., residual belite) in the carbonated lime matrix. Natural cement (a hydraulic cement of ground and calcined argillaceous limestone) was sometime added to lime-sand mortar to increase its compressive strength.

Gypsum-based mortars and grouts – Gypsum-based mortars and grouts are made using major amounts of gypsum plaster (calcined gypsum containing alpha and/or beta forms of hemihydrate or bassanite or plaster of Paris, or, anhydrite plaster, or a mixture of hemihydrate and anhydrite), aggregates, and minor amounts of other constituents such as portland cement, hydrated lime, pozzolans, limestone fines, and various property-enhancing chemical additives. The microstructure of hard, rigid, set plaster shows a monotonous, homogeneous gypsum matrix consisting of ultra-fine, interlocking crystals of gypsum, often intermixed with minor amounts of hemihydrate, calcite grains, and anhydrite, etc.; and very fine siliceous and/or calcareous sand particles.

Portland cement – Lime Mortar – Since the latter part of the nineteenth century, portland cement has largely replaced hydraulic limes and natural cements in masonry mortars. Portland cement – lime mortar was common throughout the twentieth century and is still a common type. It contains a mixture of portland or blended cement, hydrated lime or lime putty, mason's sand and water and conforms to the specification of ASTM C 270. In straight cement-sand mortar, no lime was added (despite high strength and good freeze-

thaw durability, due to the lack of lime, straight cement-sand mortars were stiff and unworkable, and had low water retention and poor bond). Portland cement-lime mortar was a good compromise between the extremes of lime mortar and straight cement-sand mortar, where the desired fresh and hardened mortar properties could be achieved by carefully proportioning the portland cement, lime, and sand contents. The microstructure portland cement-lime mortar shows portland cement hydration products (calcium silicate hydrate and very fine platy and patchy crystals of calcium hydroxide); residual and relict portland cement particles (alite with hydration rims, belite crystals often as clusters, and dark reddish brown residual ferrite phases); a very fine-grained carbonated matrix of hydrated lime; meager occurrences of areas in the paste with relatively less carbonated or non-carbonated ultra-fine matrix of hydrated lime; nodules of soft, white hydrated lime; and natural siliceous and/or calcareous sand. The hydrated mortar sometimes shows microcracks that are autogenously healed with calcium carbonate by the carbonation of the hydrated lime. Analysis of hardened mortar by petrography and chemical analysis can determine the volumetric proportions of portland cement, lime, and sand, and hence, the type of the mortar. The ASTM C 270 types are: M, S, N, O, or K arranged in the order of increasing proportions of hydrated limes and progressively decreasing compressive strengths of 2500 psi, 1800 psi, 750 psi, 350 psi, and 75 psi, respectively). The sand volume is 2¼ to 3 times the total volume of cement and lime.

Masonry Cement Mortar – Masonry cement mortars are the most widely used modern masonry mortars. They are characteristically air entrained and made using various types (M, S, N) of masonry cements (which usually contain portland or blended cement and limestone fine having the fineness close to that of portland cement, specified in ASTM C 91). Portland cement-lime mortar can also be air entrained, however, the presence of limestone fine particles usually separate masonry cement and its mortar from the portland cement-lime mixes. In addition to portland cement or blended cement, the other property-enhancing ingredients of masonry cement are the plasticizing materials (e.g., limestone fines, hydrated lime), air-entraining agents, and sometimes water-repelling agents and mineral oxide pigments. The characteristic microstructure of this mortar is therefore defined by the combined presence of air entrainment, limestone fines, residual portland cement, portland cement hydration products, residual pozzolans, possible hydrated lime, and a fine-grained matrix resembling a carbonated paste (due to the presence of limestone fines and rapid carbonation). Red, black, or brown pigments, if present, can also be detected by petrography. Masonry cement mortars, as specified in the ASTM C 270, contain four Types M, S, N, and O with progressively decreasing compressive strengths of 2500 psi, 1800 psi, 750 psi, and 350 psi. "Mortar cement mortars" (also specified in ASTM C 270) have similar microstructures

to the masonry cement mortars but differ in having tensile bond strength requirement and lower air contents (mortar cements M, S, and N are specified in ASTM C 1329). Depending on the proportion of portland cement in the masonry cement, a combined approach of petrography and chemical analysis can determine the type of the hardened masonry mortar (e.g., M, S, or N with progressively decreasing proportions of portland cement in the masonry cement).

Masonry efflorescence

Efflorescence deposits are soft, white films of salts on masonry walls that are the product of the dissolution of soluble salts and/or cement hydration products from within the masonry walls (from masonry units and/or jointing mortars) by the moisture and their precipitation on the surface during the evaporation of the solution. Oil immersion mounts, x-ray diffraction analysis, and energy-dispersive elemental analysis in a scanning electron microscope are the common methods of identifying efflorescence deposits on masonry walls. The deposits are commonly sulfates, chlorides, and carbonates of calcium and/or alkalis. Staining is discoloration of masonry wall due to oxidation of iron, manganese, or vanadium salts, which produce reddish or rusty brown, green-yellow, or brown stain on the wall. Petrography can detect the stain-producing minerals. Table 2 lists various efflorescence deposits and stain and common petrographic methods of identification.

Table 2: Common efflorescence and staining salts on brick or stone masonry structures, their possible sources, and various petrographic methods of identification.

Efflorescence Salts	*Composition*	*Probable Sources*	*Petrographic Methods of Identification*[*]
Calcium sulfate	$CaSO_4$. $2H_2O$	Brick	OM, XRD, SEM-EDS
Sodium sulfate (Thenardite and mirabilite)	Na_2SO_4. H_2O $Na_2SO_4.10H_2O$	Cement-brick reactions	XRD, OM, SEM-EDS
Potassium sulfate	K_2SO_4	Cement-brick reactions	SEM-EDS, OM, XRD
Calcium carbonate	$CaCO_3$	Mortar or concrete backing	OM, XRD, SEM-EDS
Sodium carbonate	Na_2CO_3	Mortar	XRD, SEM-EDS, OM
Potassium carbonate	K_2CO_3	Mortar	SEM-EDS, XRD
Trona	Na_2CO_3. $NaHCO_3.2H_2O$	Mortar	OM, SEM-EDS, XRD
Thermonatrite			OM, SEM-EDS, XRD
Potassium chloride	KCl	Acid cleaning	OM, SEM-EDS, XRD
Sodium chloride	NaCl	Seawater, set-	OM, SEM-EDS, XRD

		accelerator in mortar	
Vanadyl sulfate (green or yellow stain)	$VOSO_4$	Brick	SEM-EDS
Vanadyl chloride (green or yellow stain)	$VOCl_2$	Acid cleaning	SEM-EDS
Manganese oxide (brown stain)	Mn_3O_4	Brick	SEM-EDS
Iron oxide	Fe_2O_3 or $Fe(OH)_2$	Iron in contact or brick with black core	SEM-EDS, OM
Calcium hydroxide	$Ca(OH)_2$	Cement	OM, SEM-EDS, XRD

(*) OM = Optical Microscopy (including oil immersion mount and thin-section examinations); SEM-EDS (scanning electron microscopy with x-ray elemental analysis); XRD = X-ray diffraction. The most simple and easy method of identification is shown first and is followed by the other methods.

Salt hydration and salt crystallization distress

Salt hydration distress and salt weathering are two common but separate physical distress mechanisms that occur in many masonry structures. Salt hydration distress occurs due to reversible phase transformations of calcium or sodium sulfate and/or carbonate salts of various hydration states due to cyclic variations in temperature and/or relative humidity causing solid-volume expansions (during transformations from the less hydrate to more hydrate forms) and subsequent cracking or spalling of the masonry unit, mortar, or both. Hime et al. (2001), Erlin and Jana (2003), and Jana (2004) provided various case studies of concrete and masonry deterioration by salt hydration distress (due to reversible phase transformation and associated solid volume expansion during thenardite to mirabilite transition). Salt crystallization or salt weathering is well known in natural stones and causes masonry deterioration due to crystallization pressures of salts (of alkali or calcium chloride or sulfate) in the pore spaces due to cyclic wetting and drying. Petrographic examination can identify the type of salts and provide an explanation of the causes of distress. Salt crystallization distress is more common in dense bricks or stones (causing spalling of bricks or stones) than in the relatively porous jointing mortars.

Repointing and tuckpointing masonry structures

Repointing is the process of removing deteriorated mortar from the joints of a masonry wall and replacing it with new mortar. Tuckpointing describes a primarily decorative application of a raised mortar joint or lime putty joint on top of flush mortar joints. In a restoration project, both terms, however, are used synonymously to indicate installation of a new mortar in an

existing masonry wall. Cracking and disintegration of mortar, loose bricks or stone, damp walls, or damaged plaster indicate the need for repointing. Repointing, if properly done (after proper determination of the cause of the problem), can restore the original visual and physical integrity of the building. Improper repointing can detracts the appearance of the building and even cause physical damage to the wall. An appropriate match in composition, strength, and moisture permeability between the new and historic mortar is essential. The new mortar should match the historic mortar in color, texture and tooling, and in the properties of sand; the new mortar should have greater moisture permeability and be softer (in strength) than the masonry units; and the new mortar should be as moisture permeable and as soft or softer than the historic mortar. A similar approach should be followed for masonry units if they are in the need of replacement.

If the original mortar were a lime-sand mortar, a close match for re-pointing purposes would be a hydraulic lime mortar, or an ASTM C 270 Type N portland cement-lime mortar or a masonry cement mortar. Other alternatives as suggested by ASTM C 270 are: (a) for interior applications – Type O (alternatives K or N); (b) for exterior above grade application unlikely to be frozen when saturated and not exposed to high wind or other lateral load –Type O (alternatives N or K); and (c) for exterior application other than the above – Type N (alternative O). The volumetric proportions of portland cement-to-hydrated lime-to-sand in these portland cement-lime mortars are: Type N – 1: (½ to 1¼): (4½ to 6¾); Type O – 1: (1¼ to 2½): (6¾ to 10½); Type K – 1: (2½ to 4): (10½ to 15). Due to good workability, water retention and freeze-thaw durability, a Type N masonry mortar (which is air entrained) can also be used.

The repointing mortar should be prepared properly, such as according to the following ASTM C 270 instructions: (a) Dry mix all dry, solid (sand and cementitious) materials; (b) Add sufficient water to produce a damp mix that will retain its shape when pressed into a ball by hand; (c) Mix for at least 3 and not more than 7 minutes, preferably with a mechanical mixer; (d) Let mixed mortar stand for not less than 1 hour nor more than $1^{1}/2$ hours for prehydration; (e) Add sufficient water to bring the mortar to the proper consistency for tuck pointing, somewhat drier than mortar used for laying masonry units; (f) Mix by hand for 3 to 5 minutes; (g) Use the repointing mortar within $2^{1}/2$ hours of its initial mixing; permit tempering of the mortar within this time interval.

Aggregates in the repointing mortar can be natural or manufactured sand, which can be siliceous, calcareous, or a mixture of the two. The lithologic type, size, color, texture, and gradation of the sand in the repointing mortar must match with that used in the original mix. Petrographic examinations provide this information. Sand may conform to the specification of ASTM C 144 "Specification for Aggregate for Masonry Mortar". The color of the particles should be as close as possible to the color of the original sand.

For removal of the original mortar, common industry recommendations for solid masonry units are to remove jointing mortar to a minimum 5/8-in. deep until solid and sound mortar is reached (up to a maximum depth of half the masonry unit depth or a minimum depth of 2 to 2½ times the width of the joint). Mortar should be removed cleanly from the head or bed joints without damaging the units. Repointing mortar should be placed in successive lifts, preferably without delay between the lifts.

Due to the long atmospheric weathering and chemical alteration of the existing mortar, an exact match between the freshly repointed hardened mortar and the adjacent original mortar (which has not been repointed), however, may not be possible. If the original mortar was pigmented, a close match to the color can be achieved by a trial and error with proper type and amount of modern pigment. A petrographer can help in detecting the type of the pigmenting material in the original mortar. A small test area should be repointed first for comparison to the existing mortar prior to a large-scale restoration.

Conclusion

This article describes various techniques and applications of petrographic examinations in masonry and architectural structures that can be used during restoration of historic buildings. Although the early use of masonry goes back long before the advent of petrography (4000 years of masonry use compared to the 150-year history of petrography), this relatively "new" science shows great potential in both materials evaluation of future masonry and failure investigation and restoration of ancient masonry structures.

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