# Laboratory Analyses Of Historic Mortars From Fort Washington, Maryland


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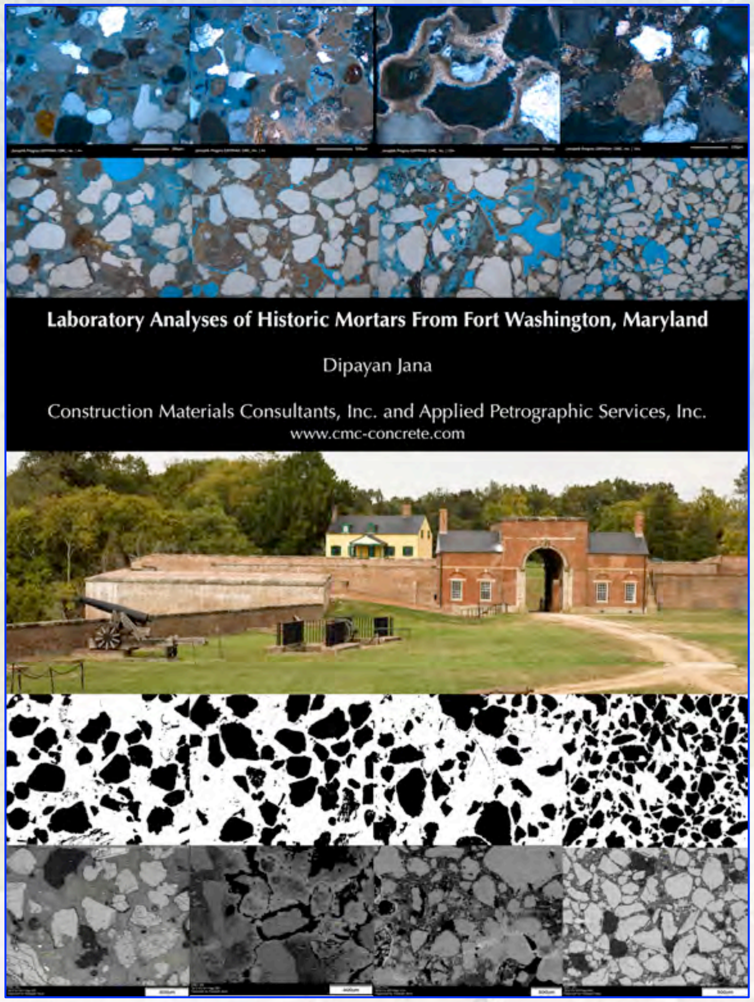
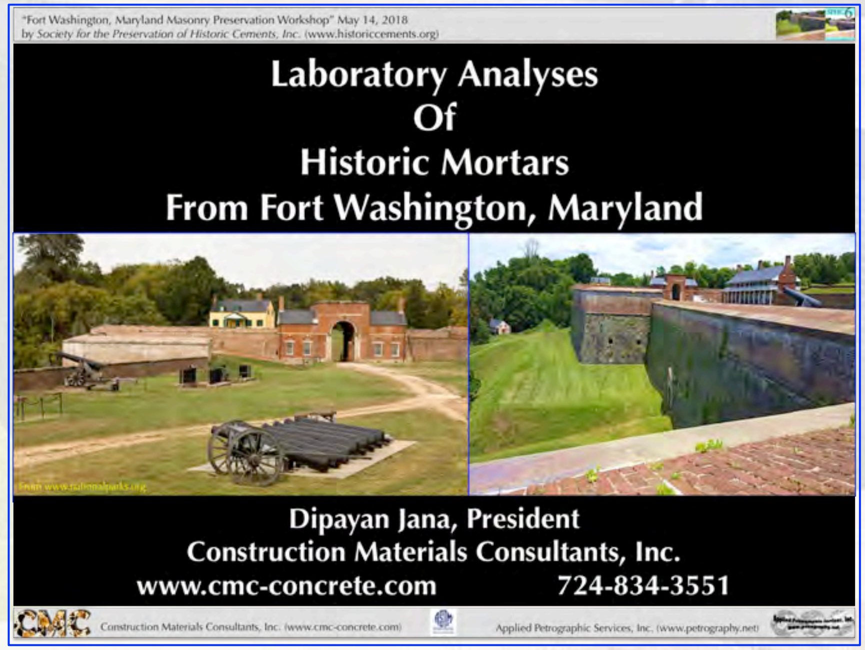
*Professional Report*




*Presentation*



# Acid Digestion – Mason's Favorite Test



**Sand color & grain-size distribution**

*Assumption*

*Binder entirely dissolves in acid*

Problem

- Gypsum, Clay, Pigments
- Hydraulic Component, Pozzolans
- Multiple Binders
- Leaching, Alterations

Residue = Sand Content (lb.)

*Mortar weight minus Sand weight*

Dissolved = Binder Content (lb.)

Binder (bulk density 40 lbs/ft$^3$)

Sand (bulk density 80 lbs/ft$^3$)

**Binder : Sand, by volume**

*Assumption*

*Sand does not dissolve in acid*

Problem

- Calcareous sand
- Marine shells
- Beach sands
- Mixed siliceous-calcareous sand
- Soluble constituents in silica sand

# Acid vs. Water Digestion – Mortar From The Fort Wall


Sand from Acid-Insoluble Residue = 68.6%
Binder = 31.4%

Sand Bulk Density = 80 lbs./ft$^3$
Binder Bulk Density = 40 lbs./ft$^3$

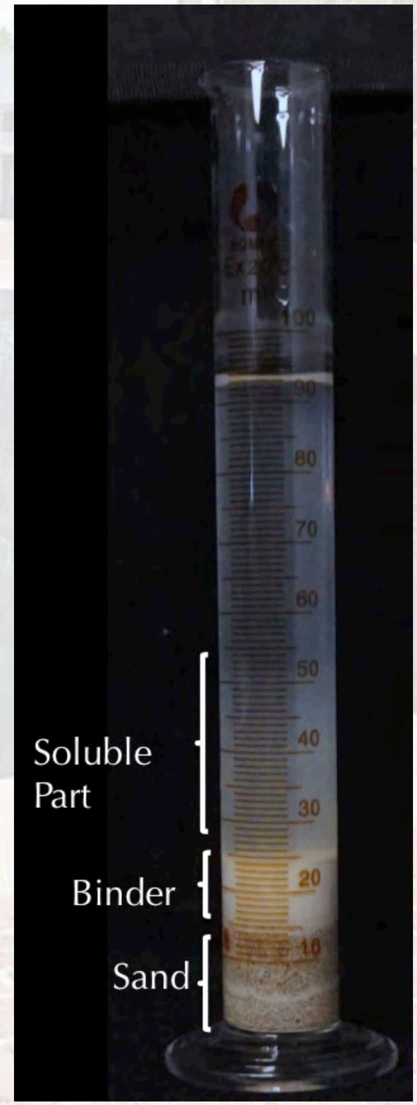
Sand Volume = 0.858
Binder Volume = 0.785

**Binder : Sand = 1:1.1**

Acid Digestion

Water Digestion

**Binder : Sand = 1:1.6**

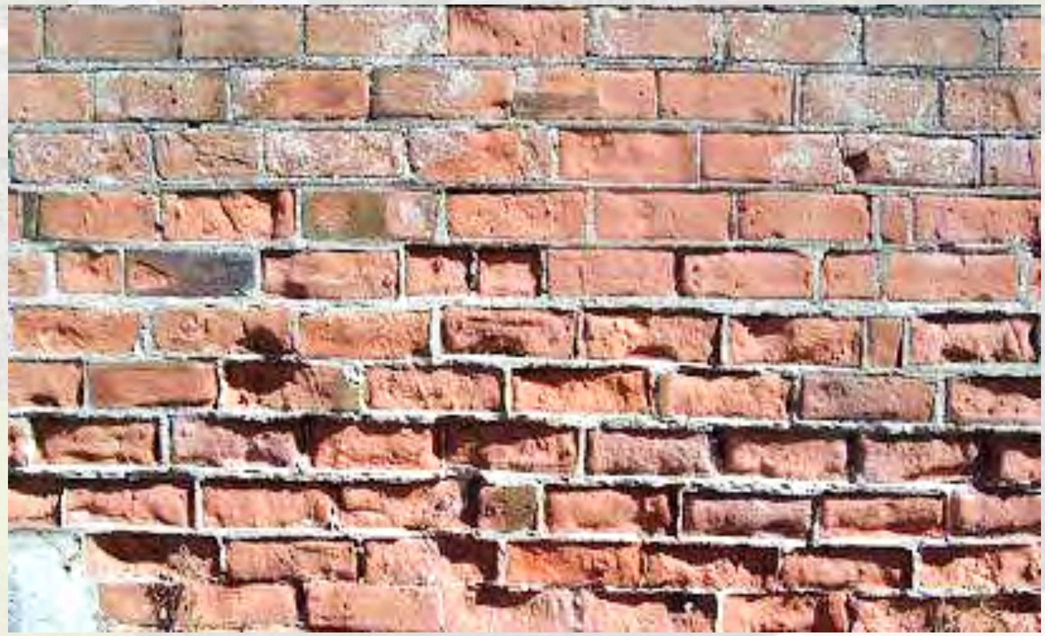



*Grossly underestimated sand*

*Underestimated sand*

# Wrong Mortar or Wrong Mix Brings New Problems

Repointing a lime mortar with a cement-based mortar in a brick masonry wall can lead to (1) de-bonding of pointing mortar at the joints and (2) chipping of bricks



Repointing brick with mortar harder than the brick. Moisture will escape through the softer brick damaging it while allowing only the mortar to remain (www.oldhouseguy.com)

# Wrong Mortar or Wrong Mix Brings New Problems

Repointing Failures

1. **Too much cement** – Shrinkage cracking in mortar, de-bonding, chipping of brick

2. **Too much lime** – Slow strength gain, high water retention, de-bonding from a brick of low initial rate of absorption (IRA)

3. **Less Lime** – Low water retention, de-bonding from a brick of high IRA

4. **Lime-cement ratio** – Workability, Masonry type, Stone type, IRA of brick, Mortar Strength, Bond Strength, Durability

5. **Too much sand** – Crumbling and softening of mortar, moisture penetration

Stone Masonry? – Type of Stone

Brick Masonry? – IRA of Brick

# ASTM C 270 Mix Recommendations are for Modern Cement-Lime Mortars

| Type of Masonry Unit | Mix Proportions (Cement – Lime – Sand) | | |
|---|---|---|---|
| | Sheltered | Moderate | Severe |
| Very hard and durable (e.g., granite, hard-cored brick, etc.) | O (1-2-9) | N (1-1-6) | S (1-0.5-4.5) |
| Moderately hard and durable (e.g., limestone, durable stone, molded brick) | K (1-3-11) | O (1-2-9) | N (1-1-6) |
| Minimally durable, soft (soft hand-made brick) | L (0-1-3) | K (1-3-11) | O (1-2-9) |

| Type of Exposure | Mortar Type | |
|---|---|---|
| | Recommended | Alternative |
| Interior | O | K or N |
| Exterior - Above Grade, Exposed on one side, unlikely to be frozen when saturated, not subject to high wind or other lateral load | O | N or K |
| Exterior – Other than above | N | O |

**M**-A-**S**-O-**N**-W-**O**-R-**K**

*Lime Increases, Cement Decreases*
*Workability, Water Retention Increases, Strength Decreases*

| | Binder : Sand |
|---|---|
| Modern Mortars | 1 : 2½ to 3 |
| Historic Mortars | 1 : 2 |

# Why Do We Need Laboratory Analysis Of Masonry Mortar?

## Mortar Sands
- ✦ Natural vs. Manufactured Sand
- ✦ Siliceous Sand
- ✦ Calcareous Sand
- ✦ Mixed Sand
- ✦ Sea Shells
- ✦ Ceramics

## Mortar Binders
- ✸ High-Calcium (Non-Hydraulic) Lime
- ✸ Magnesian or Dolomitic Lime
- ✸ Hydraulic Lime (Natural Hydraulic Limes)
- ✸ Natural cement
- ✸ Portland Cement
- ✸ Blended Cement
- ✸ Slag Cement
- ✸ Masonry Cement

## Mortar Types
- ✧ Lime Mortar
- ✧ High-Calcium vs. Dolomitic Lime Mortar
- ✧ Non-hydraulic vs. Hydraulic Lime Mortar
- ✧ Natural Cement – Lime Mortar
- ✧ Cement-Lime Mortar
- ✧ Masonry Cement Mortar

## Mix Proportions
- ★ Lime-Sand Ratio (Lime Content, Sand Content)
- ★ Cement-Lime-Sand Ratio (Lime-Cement-Sand Contents)
- ★ Improper Mix – Over-sanded, Under-sanded, Improper lime-to-cement ratio for a masonry unit

## Pigments, Fillers, Pozzolans
- ⊙ Pigments (Carbon, Mineral Oxides)
- ⊙ Fillers (Limestone Fines, Quartz Fines, Ceramic Dusts)
- ⊙ Pozzolans (Natural vs. Manufactured)

## Mortar Deteriorations
- ☑ Shrinkage
- ☑ Expansion
- ☑ Softening, Dusting
- ☑ Lime Leaching
- ☑ Secondary Calcite Precipitation
- ☑ Secondary Gypsum From Acid Rain
- ☑ Efflorescence
- ☑ Salt-related Distress

# Laboratory Analysis of Masonry Mortar

## 1. Optical Microscopy

- Sand Type
- Sand Size Distribution & Color Variations
- Binder Type(s), Raw Feed
- Mortar Types
- Texture & Microstructure
- Mix Proportions
- Calcareous Sand, Sea Shells
- Pozzolans, Slag, Filler, Pigment
- Mortar Deteriorations, Alterations

## 2. Scanning Electron Microscopy & X-ray Microanalysis

- Binder Types From Paste Chemistry
- (Lime, Hydraulic Lime, Natural Cement, Portland Cement Binders from $CaO$-$MgO$-$SiO_2$ contents of Paste
- Hydraulicity from CI of Paste
- Mortar Types
- Calcareous Sand, Sea Shells
- Pozzolans, Slag, Filler, Pigment
- Mortar Deteriorations

## 3. Acid Digestion (Wet Chemical)

- Binder to Sand Ratio from
- Acid-Insoluble Residue (Siliceous Sand) Content
- Sand Size Distribution & Color Variation (Siliceous Sand)
- Filtrates for Soluble Silica, XRF, AAS, ICP (Dissolved Binder)

**Problems with Acid Digestion**

- Calcareous Sand, Sea Shells
- Pigments, Pozzolans, Slag, Clay, Gypsum
- Leaching and Alterations

## 4. Gravimetry

- Loss on Ignition at
- 110°C (Free Moisture Content)
- 550°C (Combined Water Content)
- 950°C (Carbonates and Carbonation)

**Problems with Gravimetry**

- Calcareous Sand, Sea Shells
- Pigments, Pozzolans, Slag, Leaching

## 5. Instrumental Chemical Analysis

(XRF, AAS, ICP)

- Bulk Composition
- Binder Composition
- Soluble Silica From Binder

## 6. X-ray Diffraction

- Sand Mineralogy
- Binder Mineralogy
- Deleterious Constituents
- Efflorescence and Other Salts
- Pigments, Additives, Fillers

## 7.Thermal Analysis

(DTA, TGA, DTG, DSC)

- Binder and Mortar Type
- Hydrates, Sulfates, and Carbonates
- Dolomitic Lime Content from Brucite
- Deleterious Constituents, Salts
- Quantitative Analysis

## 8. Ion Chromatography

- Soluble Salts (e.g., $Cl^-$, $SO_4^{2-}$, $NO_3^-$)

## 9. Infrared Spectroscopy

- Organic compounds
- CSH, Sulfate, Carbonate, Hydrates

→

*Sequence of steps to be followed in laboratory analysis*

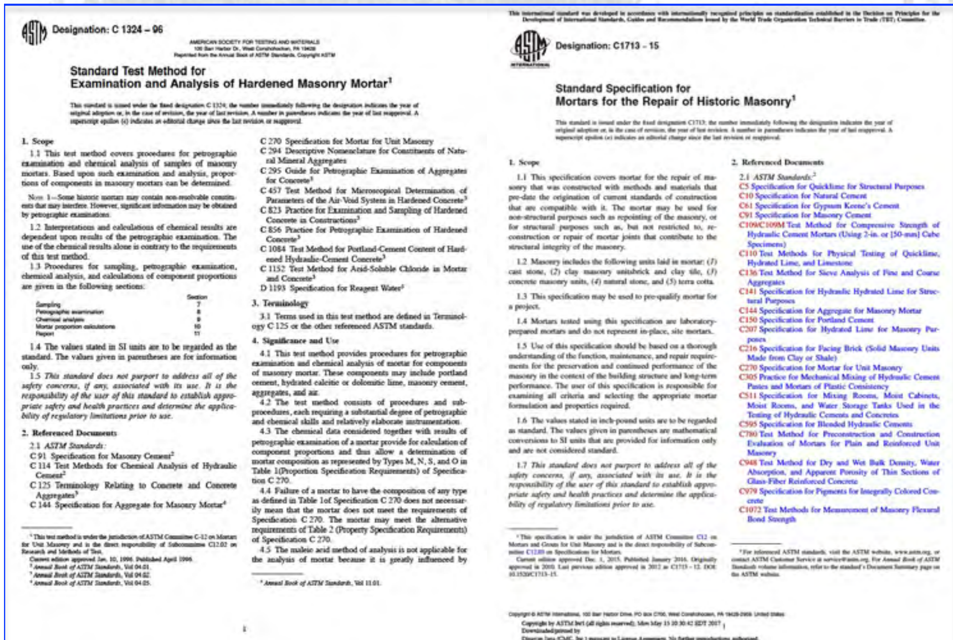
# Laboratory Analysis of Masonry Mortar

## Methods of Laboratory Analyses of Masonry Mortars

- Optical Microscopy
- Scanning Electron Microscopy & X-ray Microanalysis
- X-ray Diffraction (Bulk mortar, Binder)
- Chemical Analyses
  - Acid Digestion
    1. Insoluble Residue Content
    2. Sand extraction for grain-size distribution
  - Cold Acid and Hot Alkali Digestion (Soluble silica content)
  - Loss on Ignition at
    - 110°C (free water)
    - 110-550°C (combined water)
    - 550-950°C (carbonation)
  - Instrumental
    - XRF
    - AAS
    - ICP
- Thermal Analyses (Hydrates, Hydroxides, Sulfates, Carbonates, quantitative analysis)
  - DTA
  - TGA (DTG)
  - DSC
- Other Methods
  - FTIR (organics, clay, carbonates, sulfates, CSH, polymer, etc.)
  - Ion Chromatography (anions, e.g., chloride, nitrate, nitrite, sulfate, phosphate, bromide)
  - Pore size distribution

*Sequence of steps to be followed in laboratory analysis* →


# Test Methods on Analysis of Masonry Mortar – ASTM C 1324, RILEM (Middendorf et al. 2005)




ASTM C 1324: Laboratory analysis of hardened mortar

- Petrographic Examinations (Optical Microscopy, SEM)
- Chemical Analyses
  (Insoluble Residue, Soluble Silica, Loss on Ignition)
- XRD
- Thermal Analysis

ASTM C 1713: Mortars for the Repair of Historic Masonry

RILEM: Investigative methods for the characterization of historic mortars

- Part I: Mineralogical Characterization
- Part II: Chemical Characterization

# Publications on Historic Mortar Analysis

INVESTIGATIVE TECHNIQUES

## Evaluating Mortar Deterioration

**Bernard Erlin and William G. Hime**

Mortar has been around since the early days of man, shortly after he huddled on cold clods beneath clear, moonlit skies and found that certain muds, when mixed with sand, sealed cobbles placed adjacent to, and on top of, each other. He later found that not all muds were the same; some washed away, while others remained strong.

The Egyptians found that burnt gypsum, when gauged with water, hardened and could seal limestone blocks (hence used in some of the pyramids). The Romans found that light-burned-lime was better, and better yet when volcanic ash and sand were mixed with the lime.

Among early brick masonry structures that remain today is the Cathedral of Florence, built around the time of Columbus. A petrographic examination of that mortar, done for an "archeological engineer" who "borrowed" a thimble-full, revealed that the cementitious component was relatively pure hydrated lime (long since entirely carbonated by normal atmospheric carbon dioxide), plus, surprisingly, a small amount of sodium carbonate.

It is interesting that sodium carbonate is a potent accelerator of portland cement hydration. The mortar of the Cathedral was reported to have had "unusual" properties. From whence the sodium carbonate came may never be known. Whether a natural component of the lime or a purposeful addition, its presence is interesting.

The Great Wall of China is of brick masonry construction. A tiny sample, examined using petrographic methods, revealed it to be carbonated hydrated lime containing trace to minor amounts of residual ferruginous material.

Mortars have come a long way since the time of early man, the construction of the Great Wall, and the erection of the Cathedral...or have they? The lime mortars of the past are long gone. Today, "modern" ASTM C270 mortars are typically composed of either mixtures of portland cement, hydrated lime, and sand, or masonry cement and sand. Occasionally, an oddball creeps in and causes more problems than do the ASTM C270 mortars.

There is a need today to identify the composition of mortars, to closely match that in old structures during rehabilitation, or to investigate why failures occurred. Restoration dollars should not be spent on repairs without clearly understanding the existing materials so that the "repairability" of materials can be evaluated.

### Analyzing Mortar

The analysis of mortars is difficult, but a lot of data can be obtained using modern and not-so-modern methods. The "modern" includes petrographic microscopy, x-ray diffractometry, atomic absorption spectroscopy, and differential thermal analysis. The not-so-modern includes classical "wet" chemistry.

The old and the modern are of equal importance in identifying and quantifying the mineralogical and chemical make-up of mortars. In the deft hands of those who cannot only analyze, but also understand and decipher the analytical data, very meaningful information can be obtained. That information can be used to make sense out of apparent chaos, and provide necessary answers.

### Petrographic Microscopy

Using methods of petrographic microscopy, the mineralogy of the aggregate and, thus, the presence of minerals that interfere with certain chemical and physical analyses can be identified, and the mortar type can be indexed. For example, calcareous components, such as limestone and dolomite, are digested (or partially digested) during certain of the chemical analyses. The chemical and physical data thus obtained could cause overestimation of the amount of cementitious components and underestimation of the amount of sand. An advance warning of these chemical interferences by petrographic identification of interfering minerals can shorten the analysis time and avoid misinterpretation of the data.

### What the Analysis Reveals

Using suitable methods of analyses, as appropriate for the mortar under study, the following information can usually be obtained:

- Mineralogical composition and gradation of sands
- Components originally used to make the mortars
- Proportions by weight and by volume of original components used to make the mortars
- Air-void parameters
- Degree of portland cement hydration and paste carbonation
- Presence of contaminants
- Use of organic and/or inorganic substances such as calcium chloride or integral water-proofers, etc.
- Type and amount of destructive chemicals
- Manifestations of the effects of destructive agents such as cyclic freezing, free lime, periclase, or sulfate attack
- Retemperings

Methods for analyzing mortars are presented by Erlin and Hime in "Methods for Analyzing Mortar," *Proceedings of the Third North American Masonry Conference*, sponsored by the Masonry Society, 1985.

Once the petrographic, chemical, and physical data have been obtained, evaluations of the following can be made:



Erlin and Hime, 1987

10th Euroseminar on Microscopy Applied to Building Materials, Scotland, 2005

## 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.

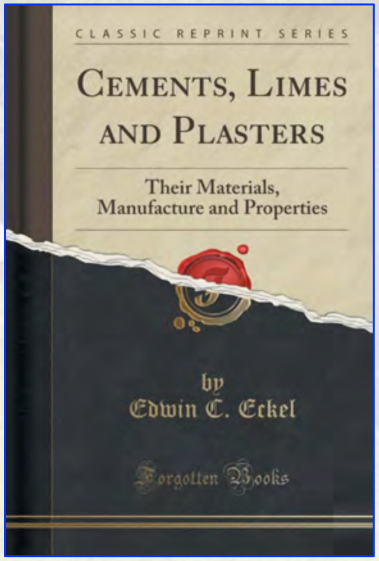
**Keywords: Petrography, Microscopy, Restoration, Historic Structures, Masonry**

Jana 2005

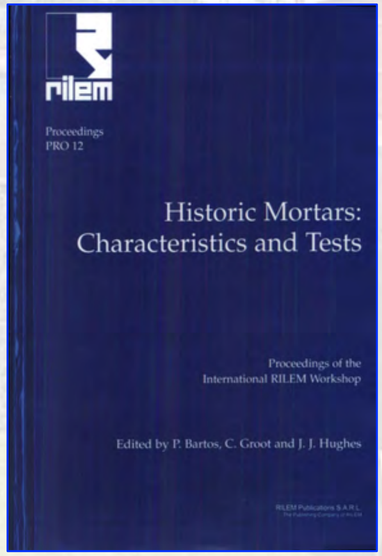
# Publications on Historic Mortar Analysis

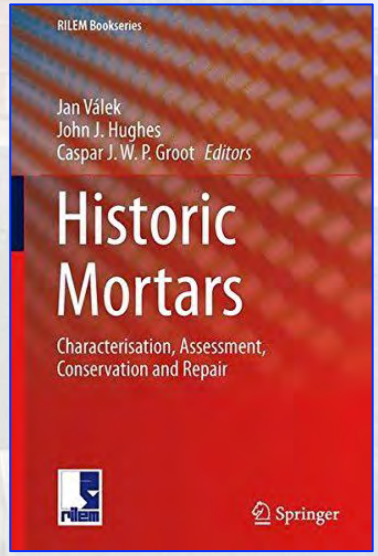
A Masterpiece!

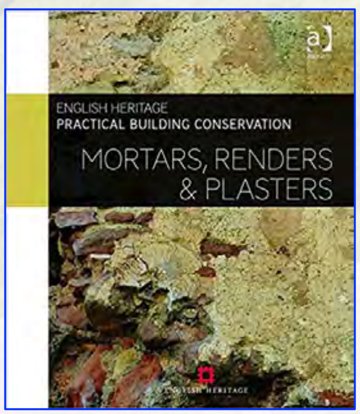
Eckel 1922



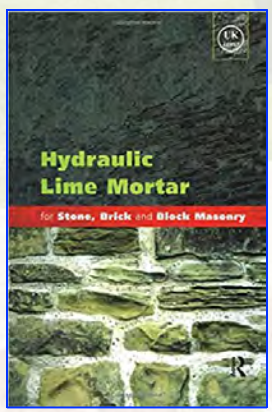

Three Excellent Resources on Laboratory Testing of Historic Mortars

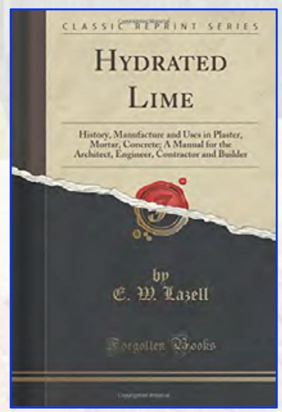


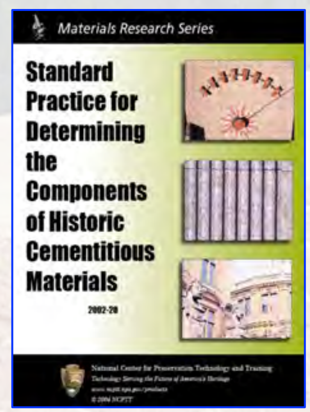



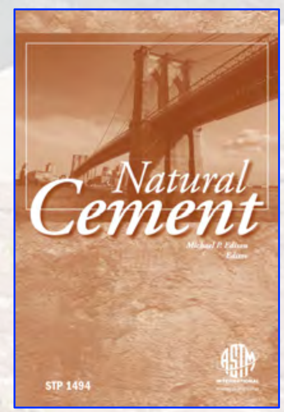







# Laboratory Analysis – Proper Sampling is the Key

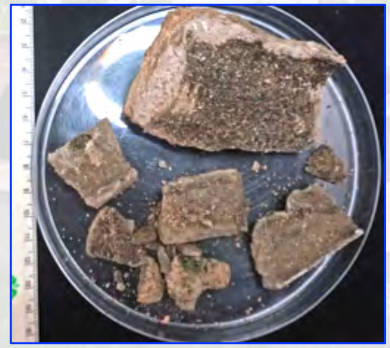
1. Take a photo of the location from where mortar sample will be taken

2. Take a photo of the joint from where mortar sample will be taken

3. Use a flat head chisel and hammer to carefully remove the jointing mortar as intact as possible

4. Mark the Sample ID and exposed side on the sample

Please be liberal in sampling



- Provide at least 50 grams to 100 grams of sample in a sealed Ziploc bag
- Preferably multiple intact pieces, not powders
- Of uniform appearance
- Representative of the purpose of examination


- Avoid providing multiple sample types, e.g., brick chips mixed with mortar, or original mortar mixed with later repointing mortar

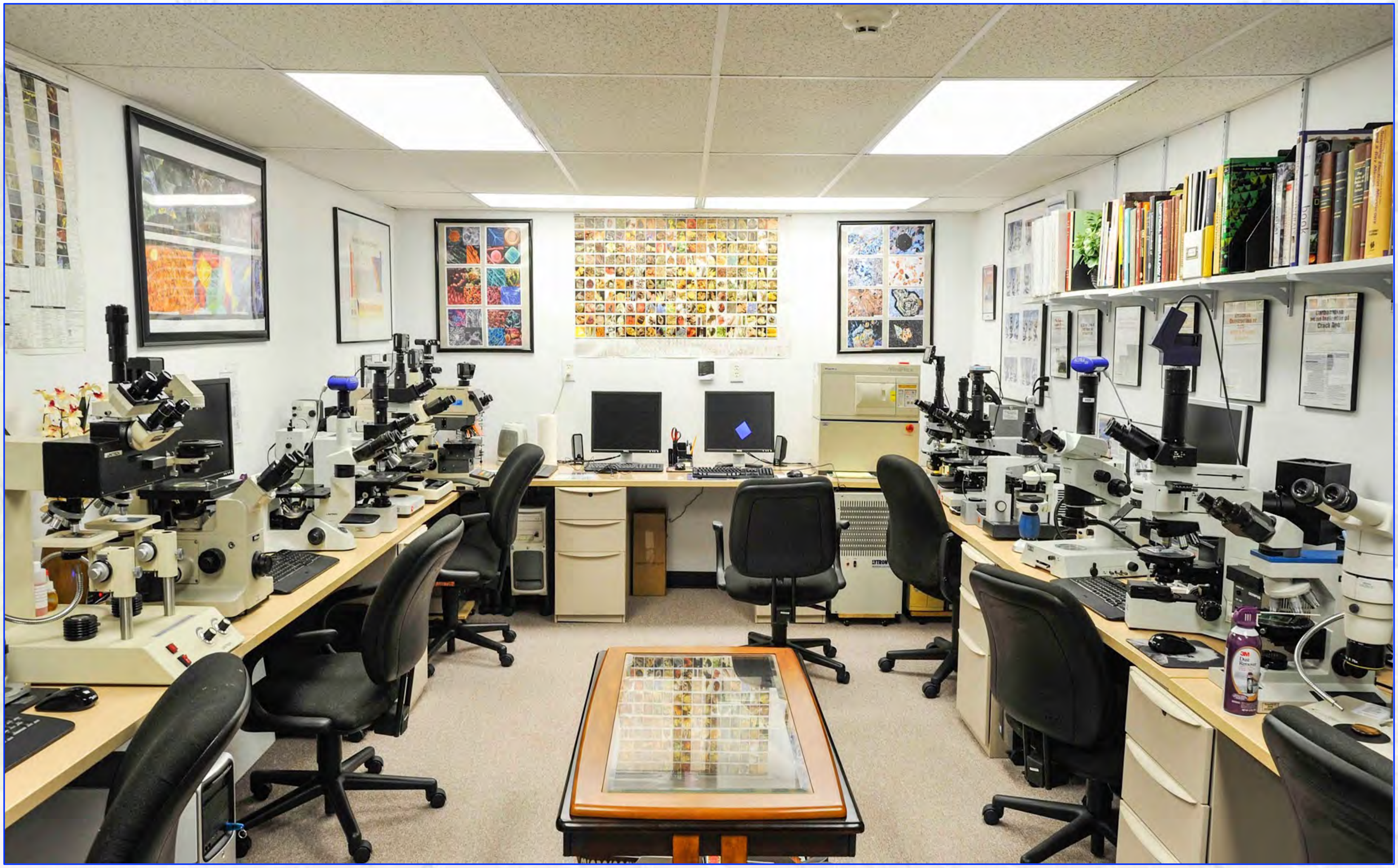
- From multiple intact pieces adequate representative samples can be selected for microscopy, chemical, XRD-XRF, sand size distribution, and other laboratory tests

# Mortar Samples From Fort Washington



25g 15g 26g 260g 58g 208g 1151g

# Optical Microscopy



# Three Essential Optical Microscopes for Mortar Analysis

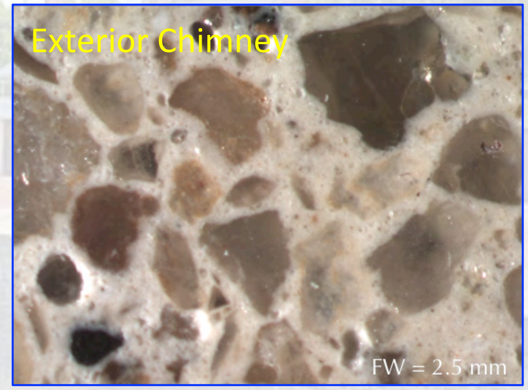

Nikon Eclipse E600 POL
Polarizing(Petrographic) Microscope

Olympus SZH Reflected/Transmitted/Polarized
Stereozoom Microscope

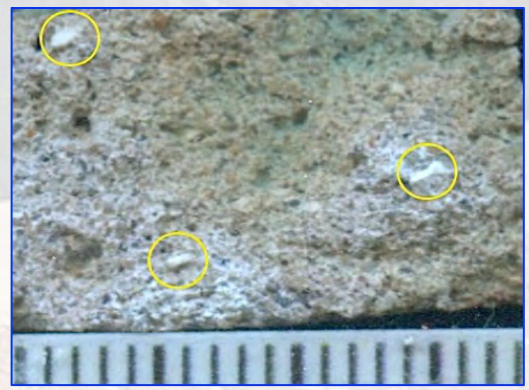
Nikon SMZ-10A
Stereozoom Microscope

# Low-power Stereo Microscope for Mortar Analysis





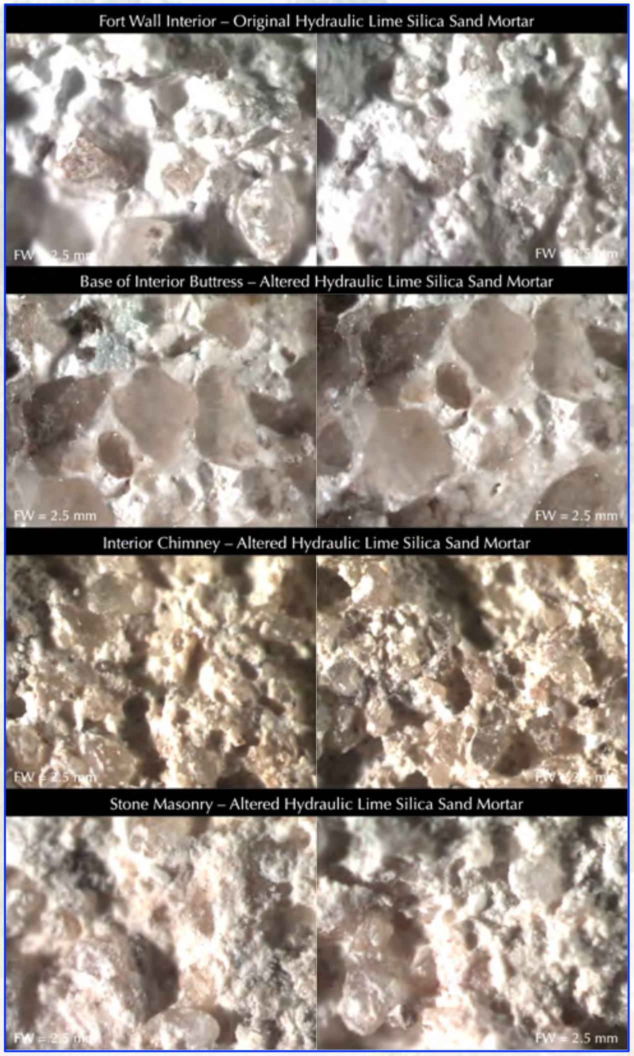


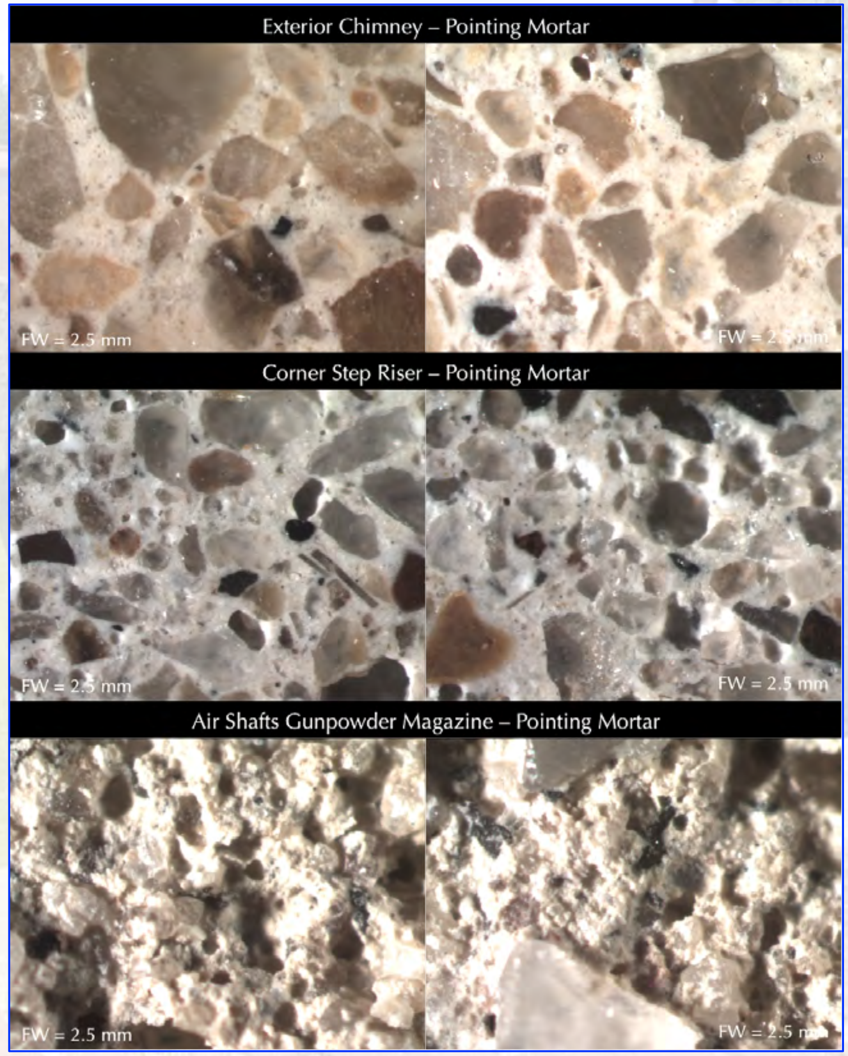


*Sand types, color, size, shape, angularity, gradation, paste color and hardness, lime lumps, air entrainment*

# Low-power Stereo Microscope for Mortar Analysis

Original Lime Mortars



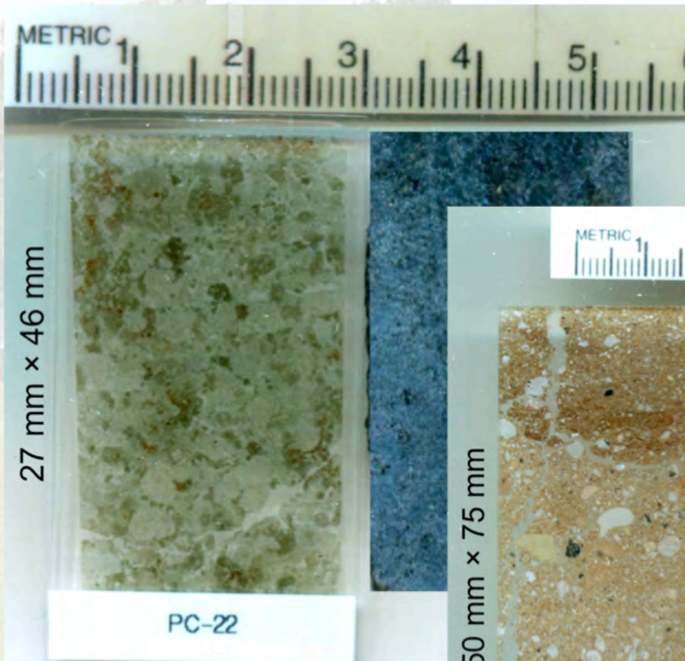




Later Cement - Lime Mortars

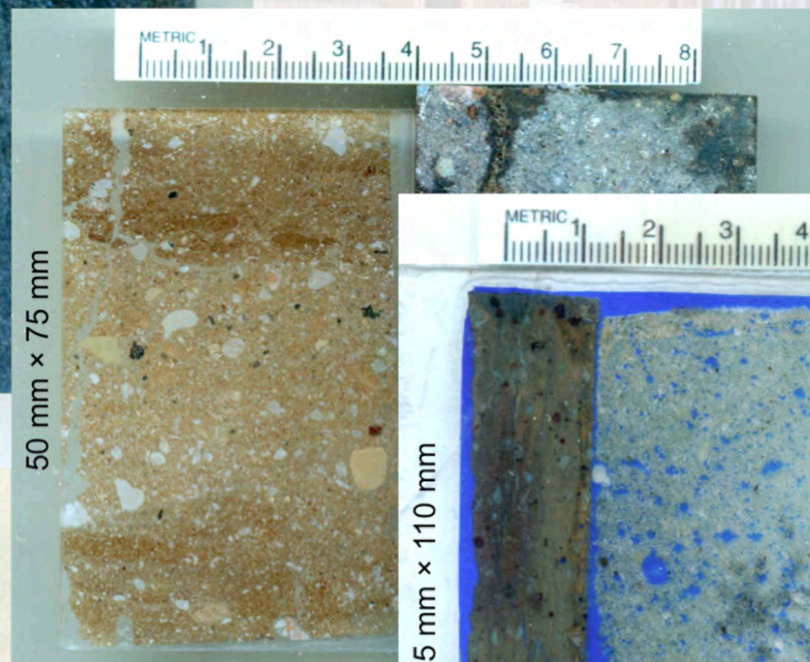
*Sand types, color, size, shape, angularity, gradation, paste color and hardness, air entrainment*

# Thin Section Microscopy – At the Heart of Mortar Analysis

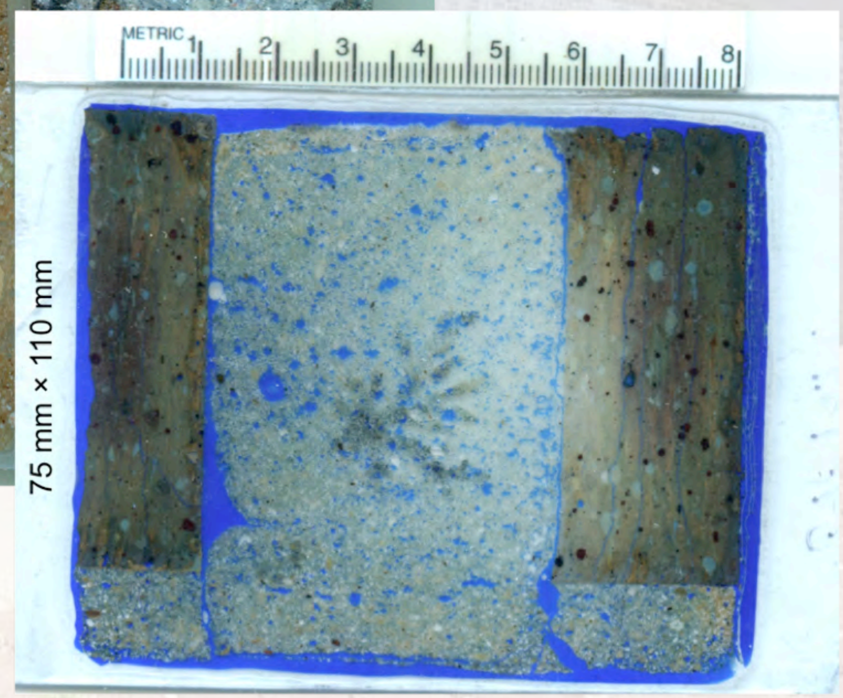
Impregnation
- No Epoxy
- Clear Epoxy
- Colored Epoxy
- Fluorescent Epoxy




Rocks

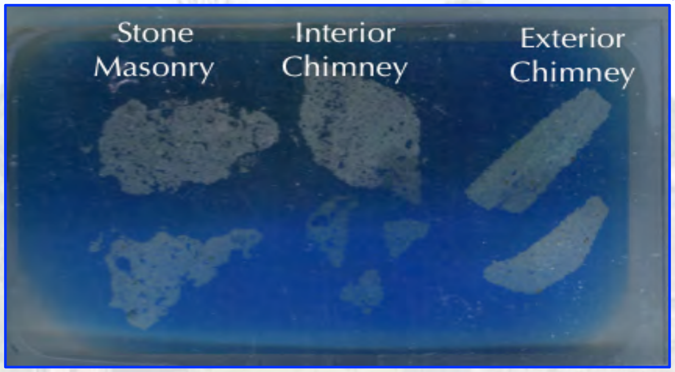


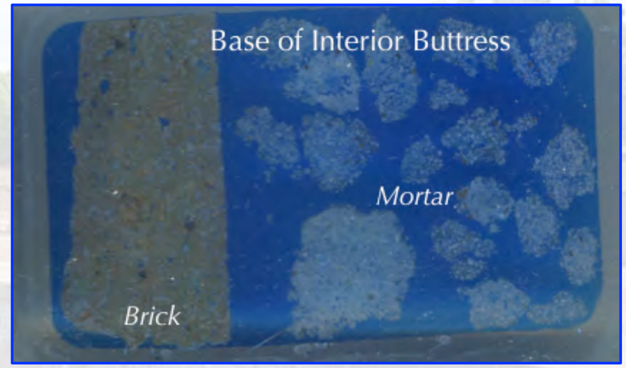

Concrete



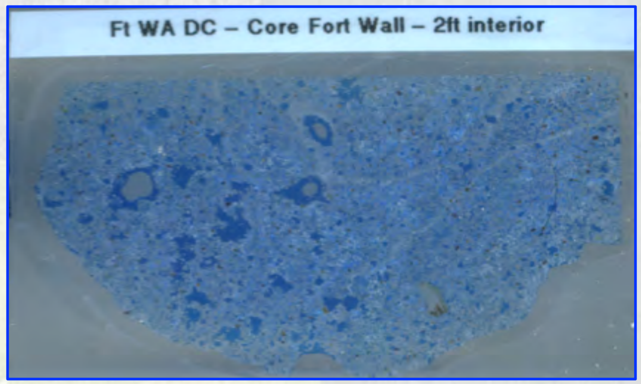

Masonry

# Thin Section Microscopy – At the Heart of Mortar Analysis

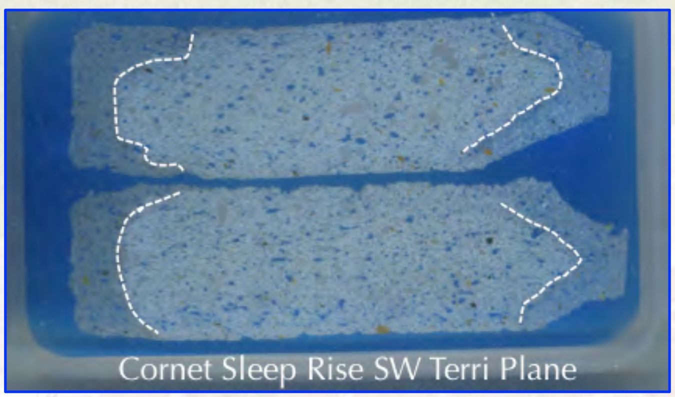


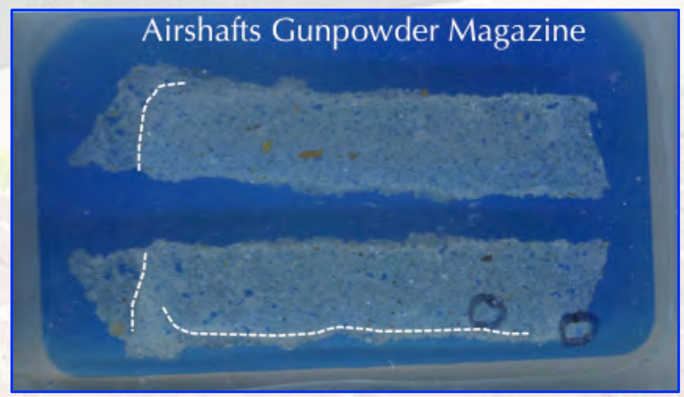




50 mm × 75 mm size blue dye-mixed epoxy-impregnated thin sections

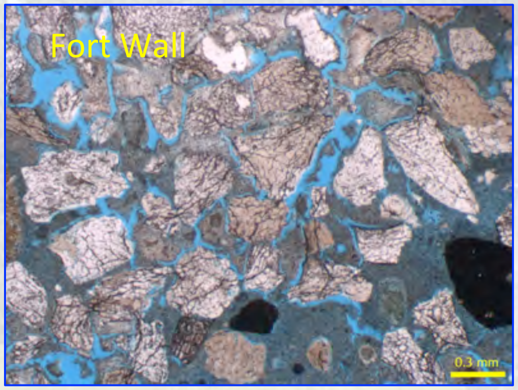



Blue dye highlights pore and void spaces, cracks, and porous areas of paste

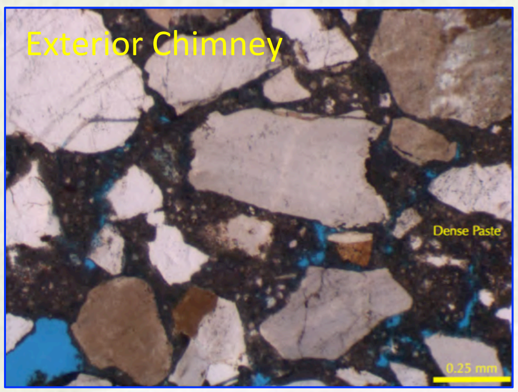


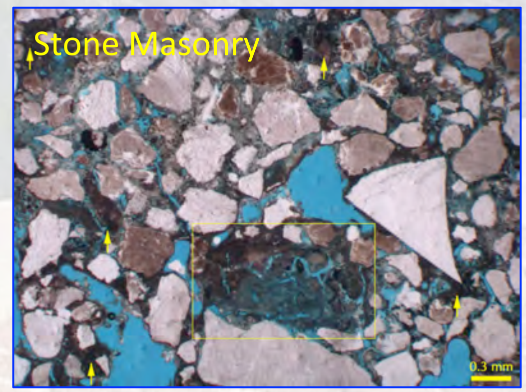



# Transmitted and Polarized-Light Stereo Zoom Microscope for Mortar Analysis



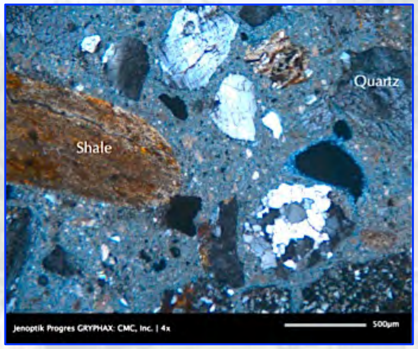


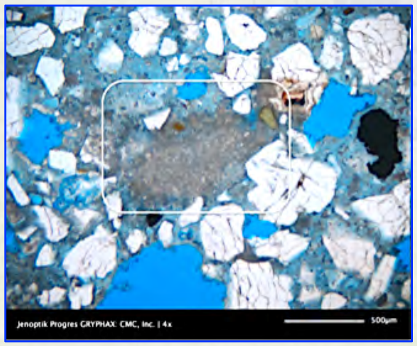




*Dense vs. porous paste, carbonated paste, shrinkage microcracks, sand type, lime lumps, air entrainment*

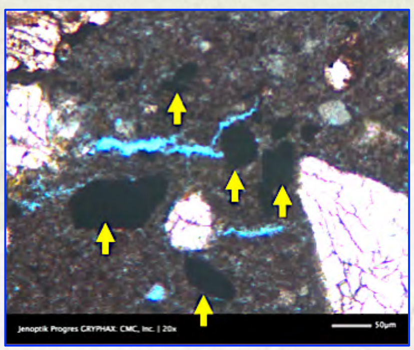
# Petrographic Microscope for Mortar Analysis



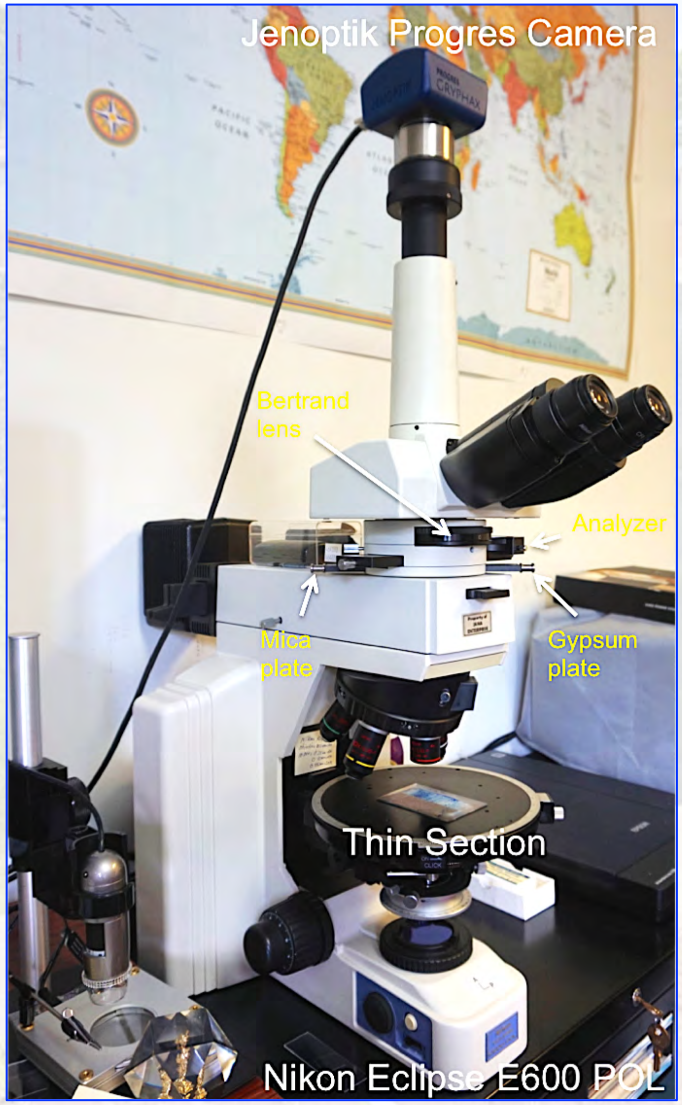

*Sand Mineralogy, Texture, Type, Soundness*



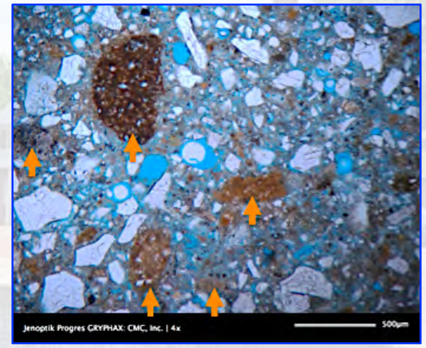
*Dolomitic Hydraulic Lime Mortar*



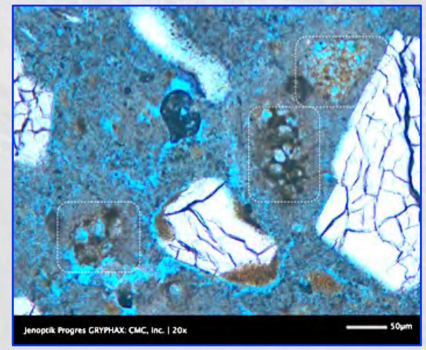
*Pigmented Lime Mortar*



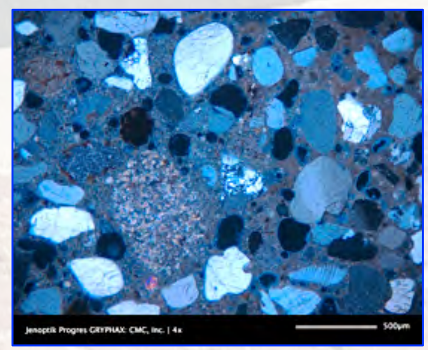

*Petrographic Microscope – Powerhouse of Mortar Analysis*



*Natural cement - Lime Mortar*

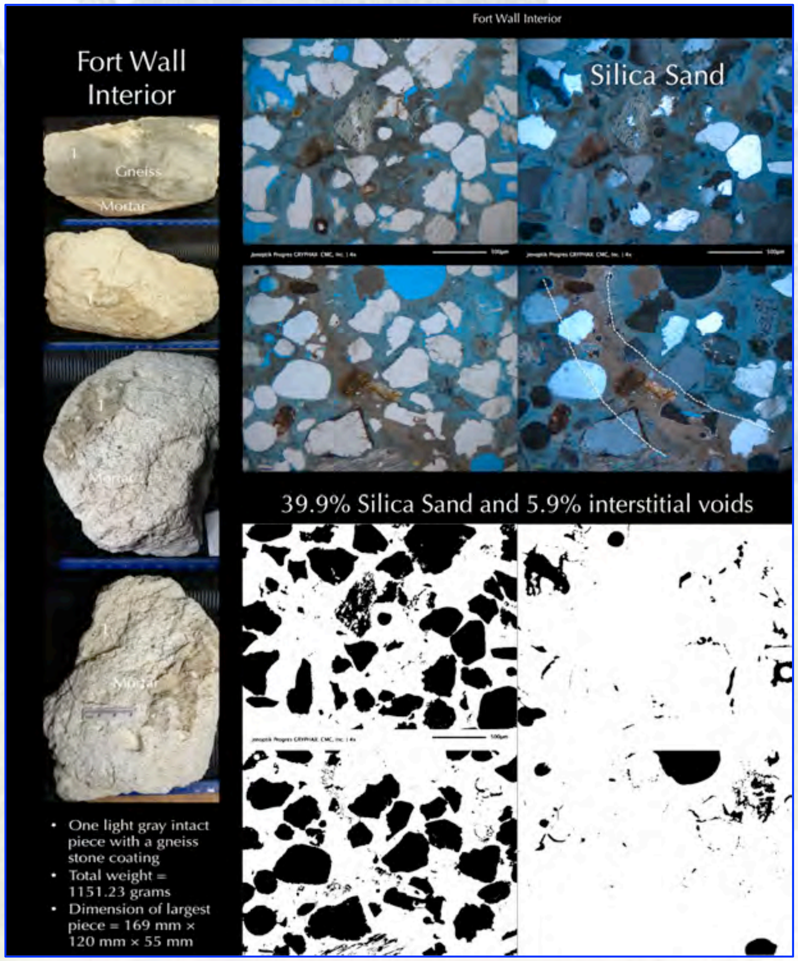


*Portland cement - Lime Mortar*

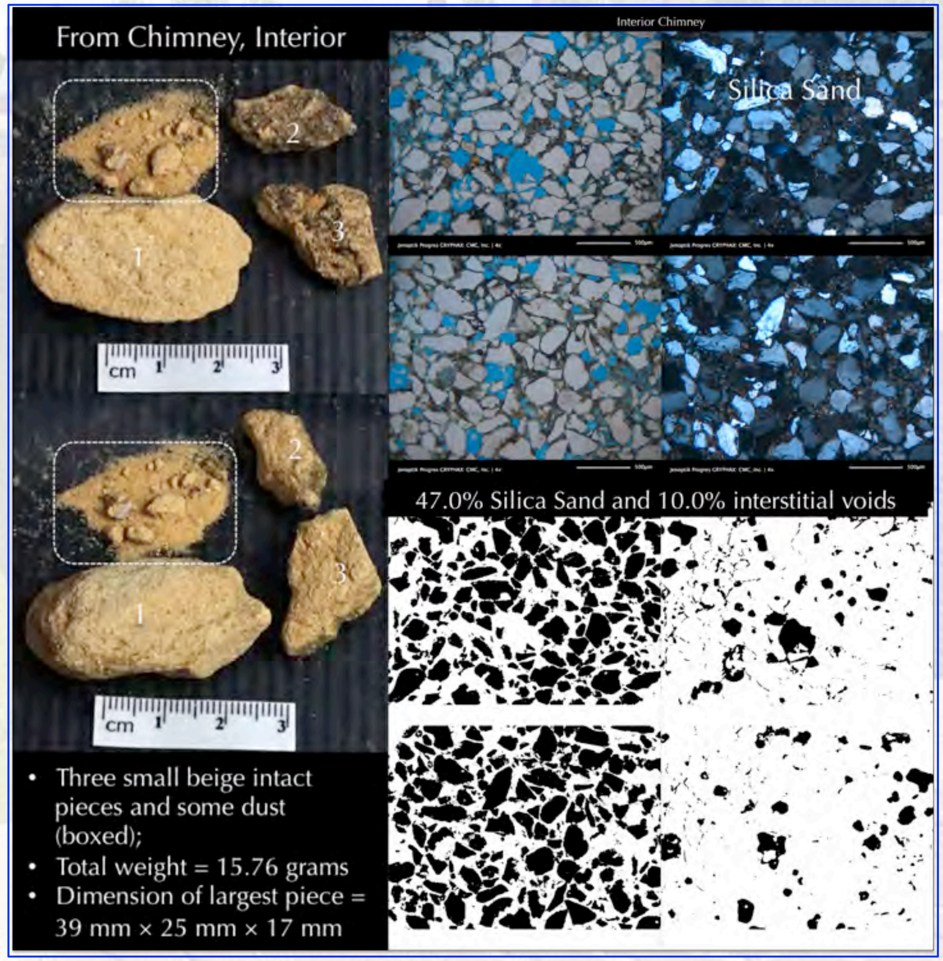


*Masonry cement Mortar*

# Optical Microscopy & Image Analysis

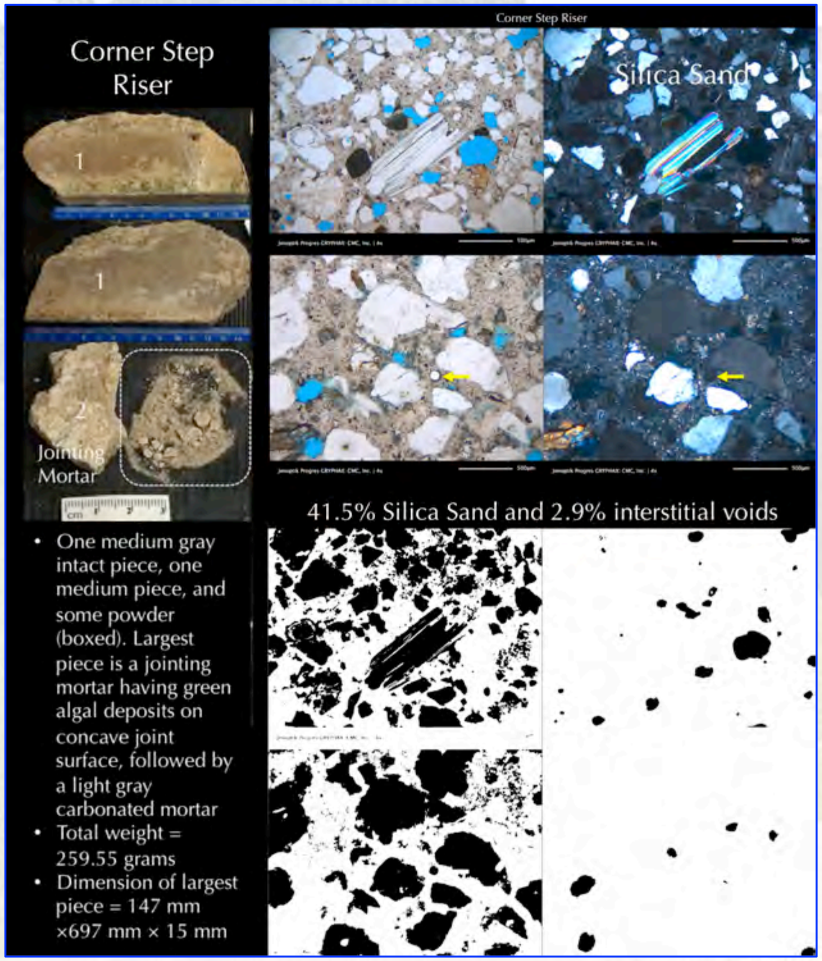



Sand in most samples from the Fort as in mortar from interior of Fort Wall

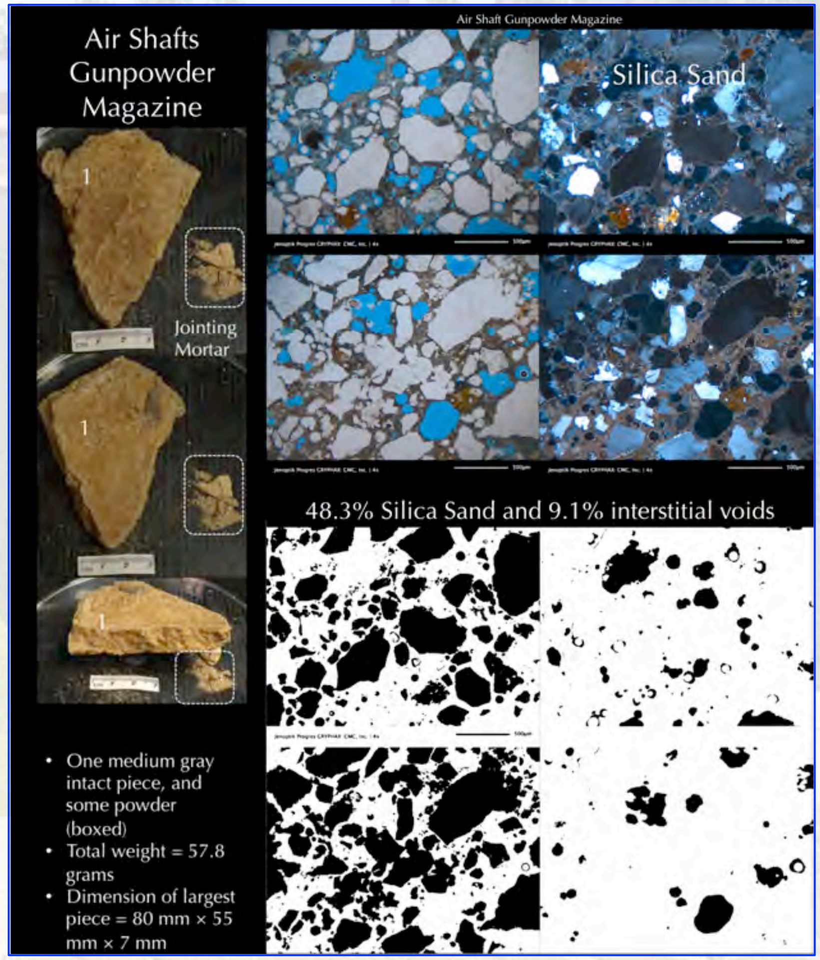



Finer, crushed sand in mortar from Interior Chimney

# Optical Microscopy & Image Analysis



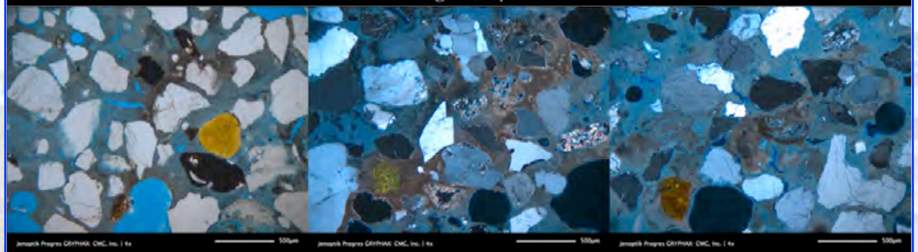

Dense, non-air-entrained Corner Step Riser Terri Plane mortar



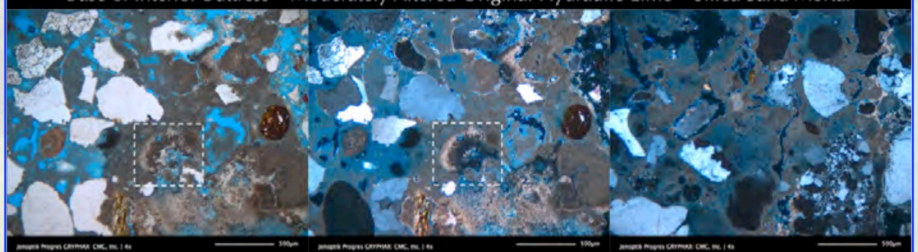

Air entrainment from masonry cement in Air Shafts Gunpowder Magazine

# Optical Microscopy

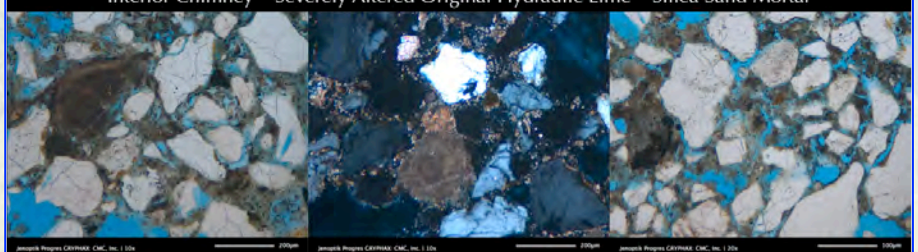
Fort Wall Interior – Least Altered Original Hydraulic Lime – Silica Sand Mortar



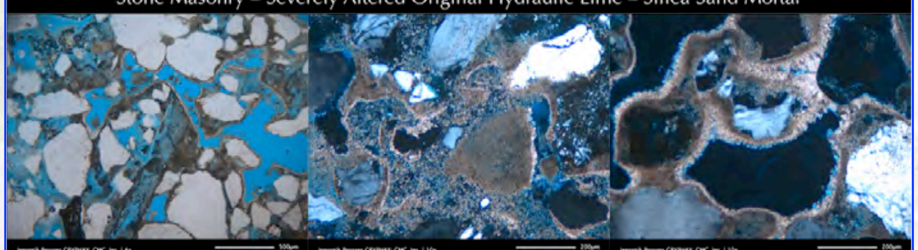
Base of Interior Buttress – Moderately Altered Original Hydraulic Lime – Silica Sand Mortar



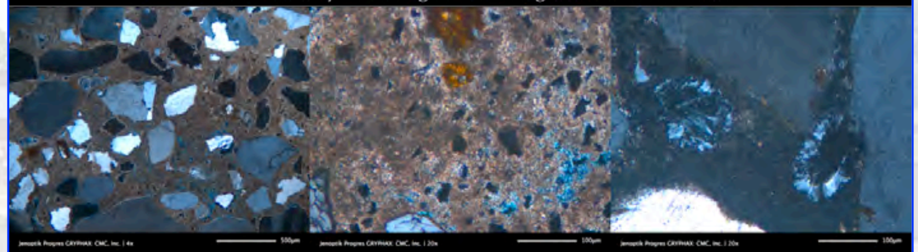
Interior Chimney – Severely Altered Original Hydraulic Lime – Silica Sand Mortar



Stone Masonry – Severely Altered Original Hydraulic Lime – Silica Sand Mortar

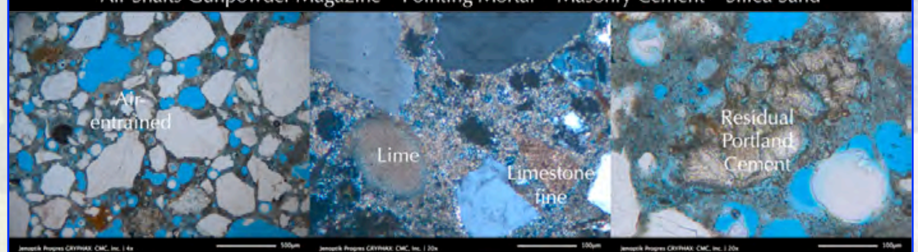


Exterior Chimney – Pointing Mortar - Slag Cement – Silica Sand

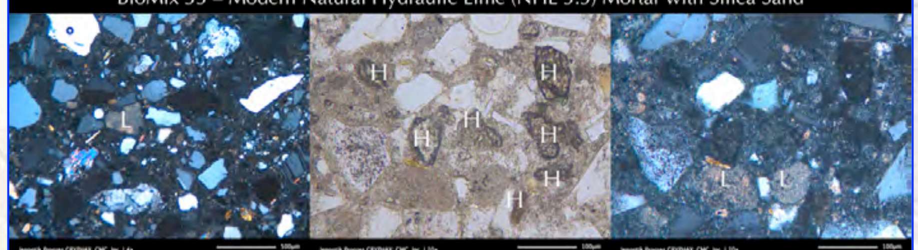


Corner Step Riser – Pointing Mortar - Blended Cement – Silica Sand

Air Shafts Gunpowder Magazine – Pointing Mortar – Masonry Cement – Silica Sand

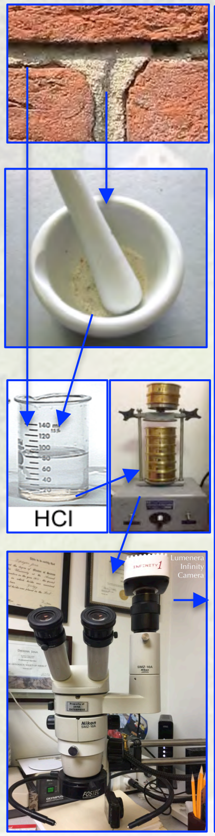



BioMix 35 – Modern Natural Hydraulic Lime (NHL 3.5) Mortar with Silica Sand

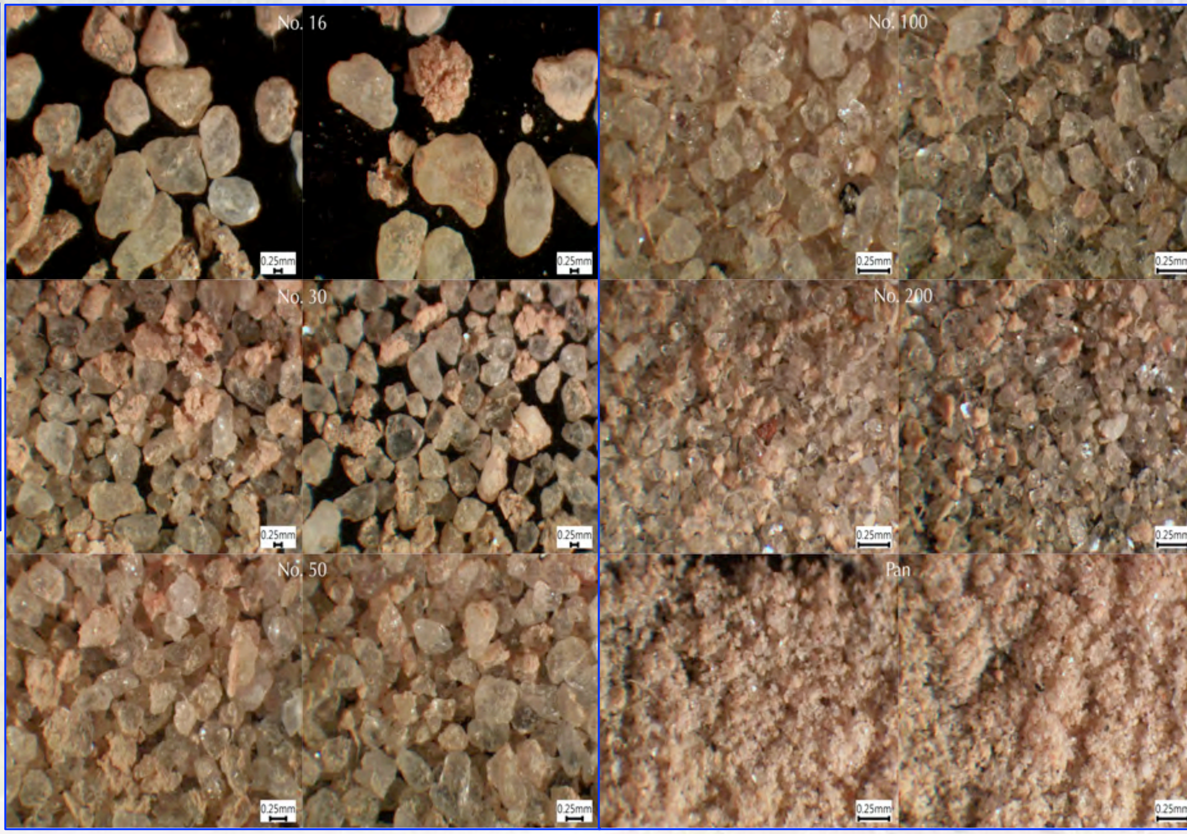


# Sand Extraction, Size Distribution & Color Variation

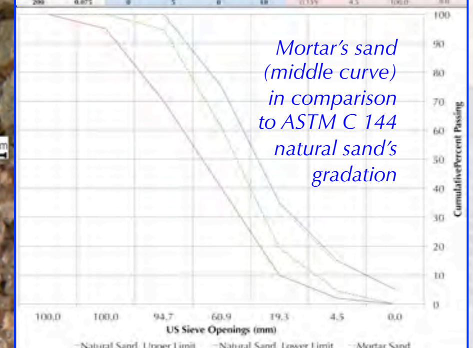
Sand extraction by acid digestion with minimal or without crushing followed by Sieve Analysis in Gilson Mini Sieve Shaker and examination in a stereo microscope

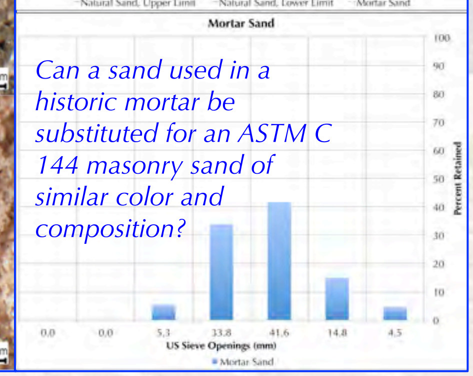



*Photomicrographs of sand retained on various sieves*



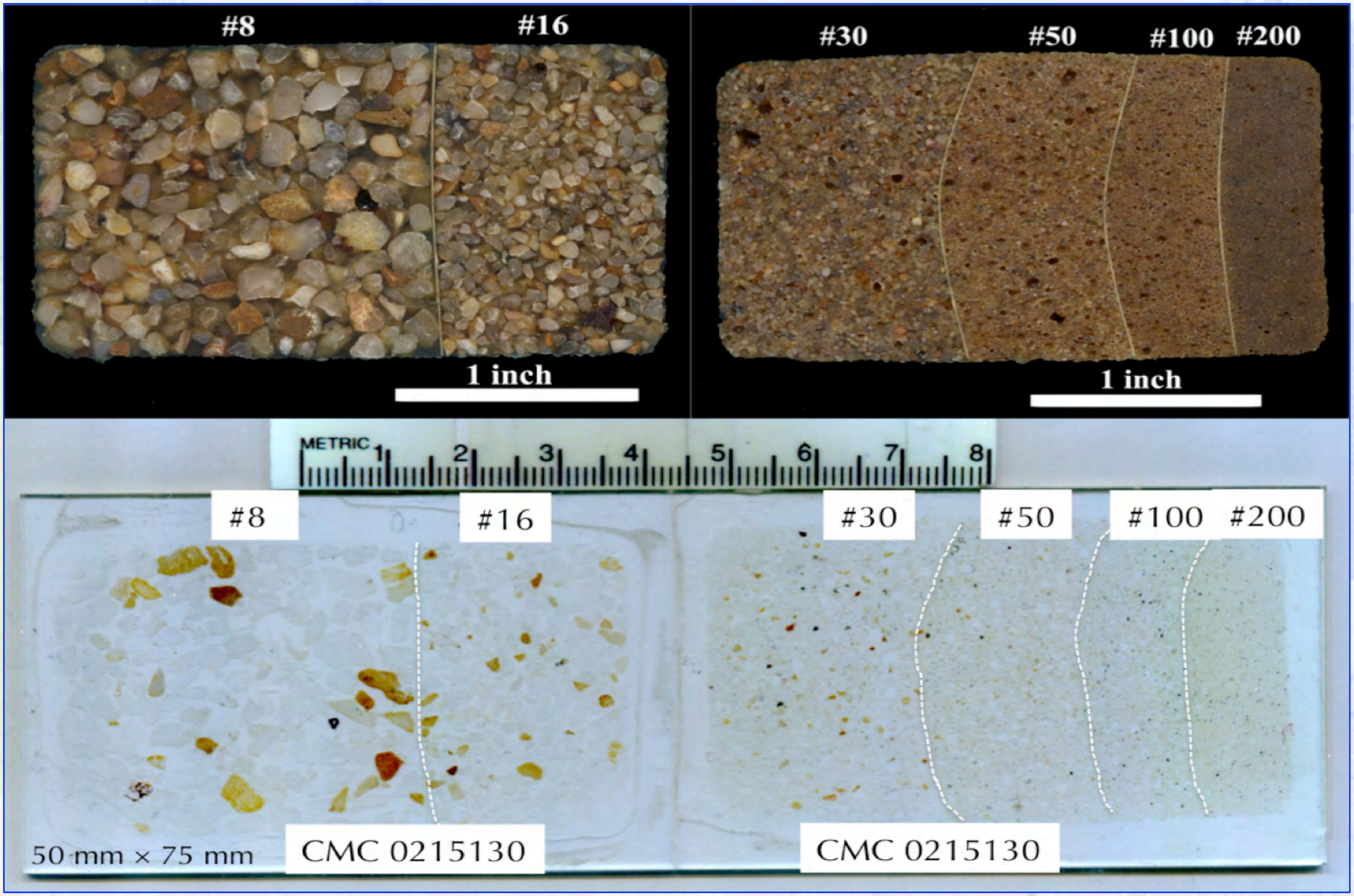

| Sand Sieve Sizes | | Percent Passing for Natural & Manufactured Sand | | | | Weight Retained, g | Percent Retained | Cumulative Percent Retained | Percent Passing |
|---|---|---|---|---|---|---|---|---|---|
| US Sieve No. | mm | Natural Sand Lower Limit | Natural Sand Upper Limit | Manufactured Sand Lower Limit | Manufactured Sand Upper Limit | Mortar | Mortar | Mortar | Mortar |
| 4 | 4.75 | 100 | 100 | 100 | 100 | 0.000 | 0.0 | 0.0 | 100.0 |
| 8 | 2.36 | 95 | 100 | 95 | 100 | 0.000 | 0.0 | 0.0 | 100.0 |
| 16 | 1.18 | 70 | 100 | 70 | 100 | 0.186 | 5.3 | 5.3 | 94.7 |
| 30 | 0.6 | 40 | 75 | 40 | 75 | 1.190 | 33.8 | 39.1 | 60.9 |
| 50 | 0.3 | 10 | 35 | 20 | 40 | 1.463 | 41.6 | 80.7 | 19.3 |
| 100 | 0.15 | 2 | 15 | 10 | 25 | 0.522 | 14.8 | 95.5 | 4.5 |
| 200 | 0.075 | 0 | 5 | 0 | 10 | 0.159 | 4.5 | 100.0 | 0.0 |



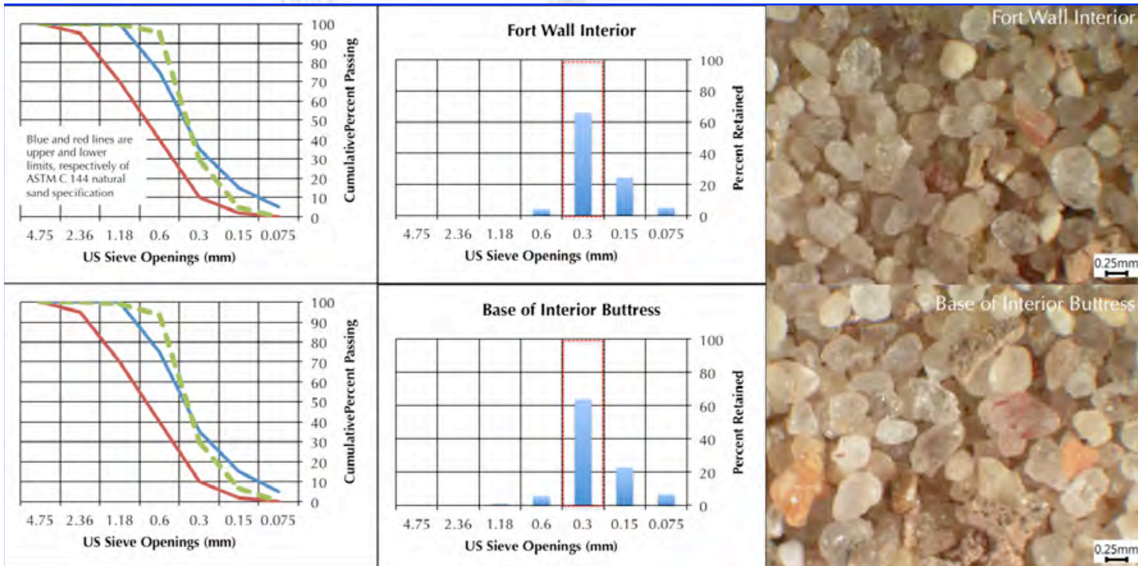




*Sand gradation has a strong influence on workability, water retention, binder content, appearance, and performance of a pointing mortar.*

# Sand Types In Individual Sieves



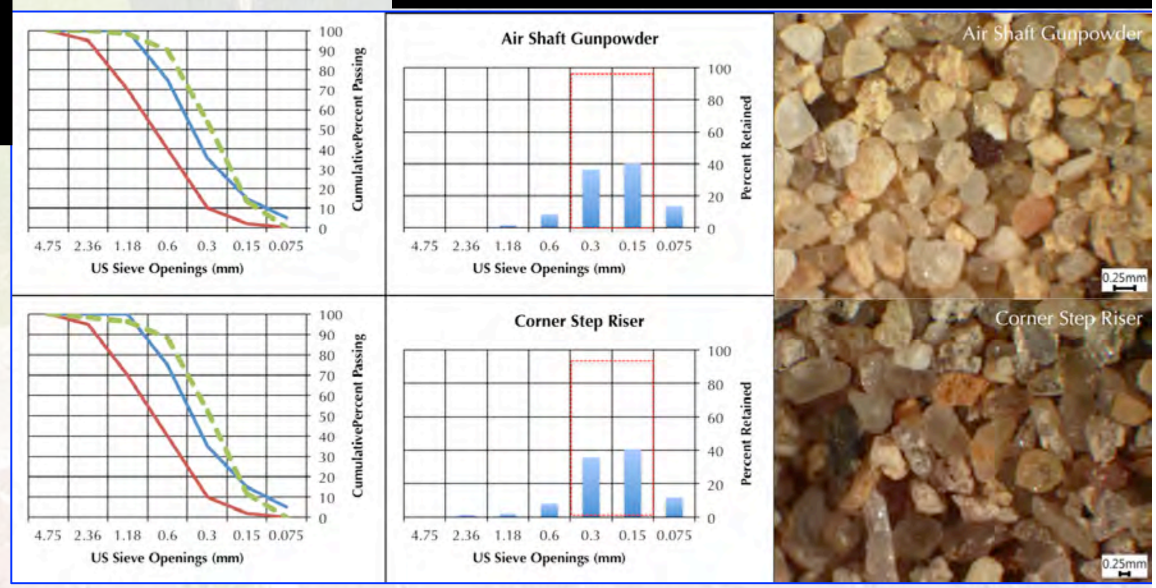
# Sand Size Distribution & Color Variation




Sands used in original mortars and later pointing ones have different grain-size distribution.

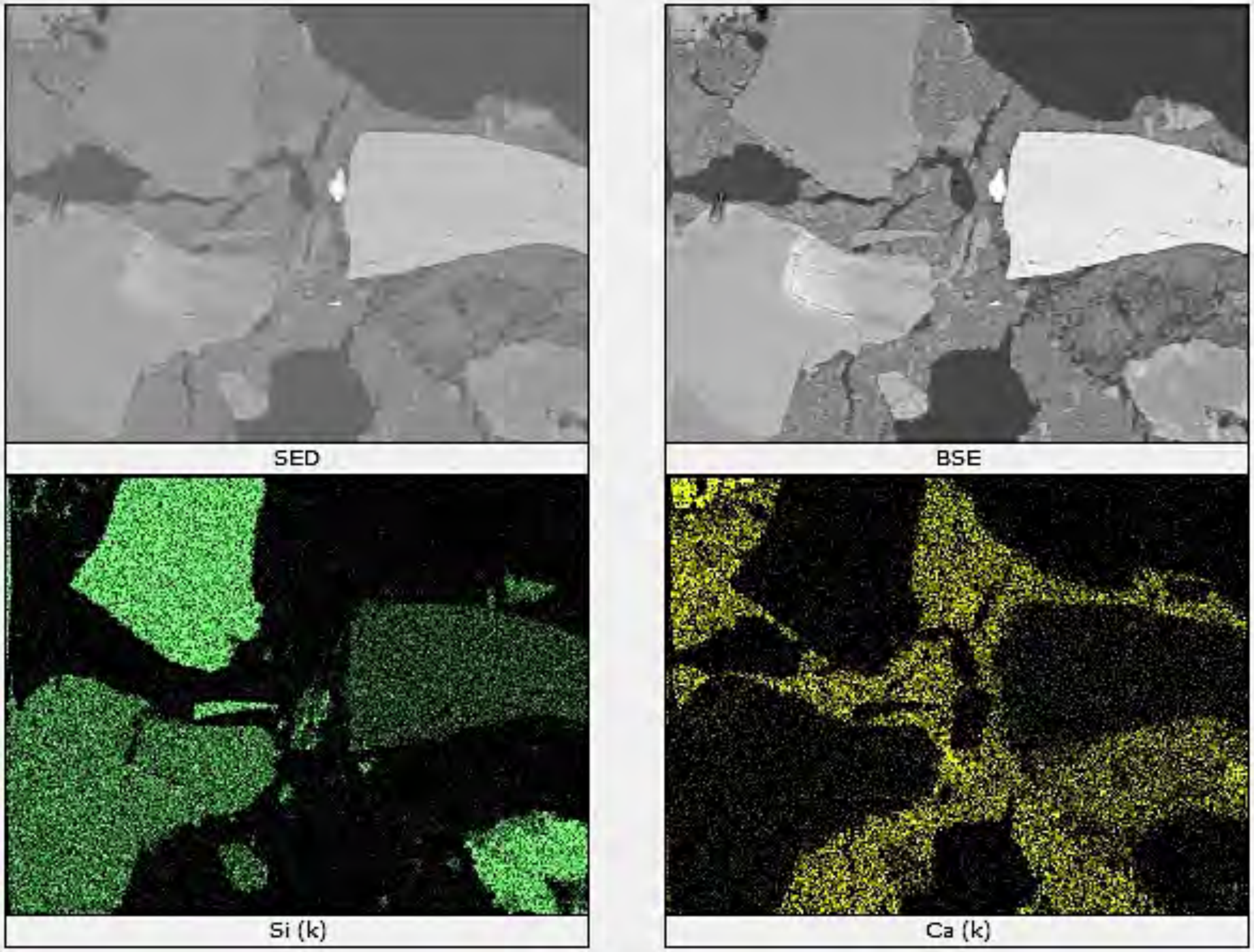
Sands used in Air Shafts Gunpowder and Corner Step Riser have very similar grain-size distribution

Sands used in Fort Wall Interior and Base of Buttress have very similar grain-size distribution



# Scanning Electron Microscopy & X-Ray Microanalysis

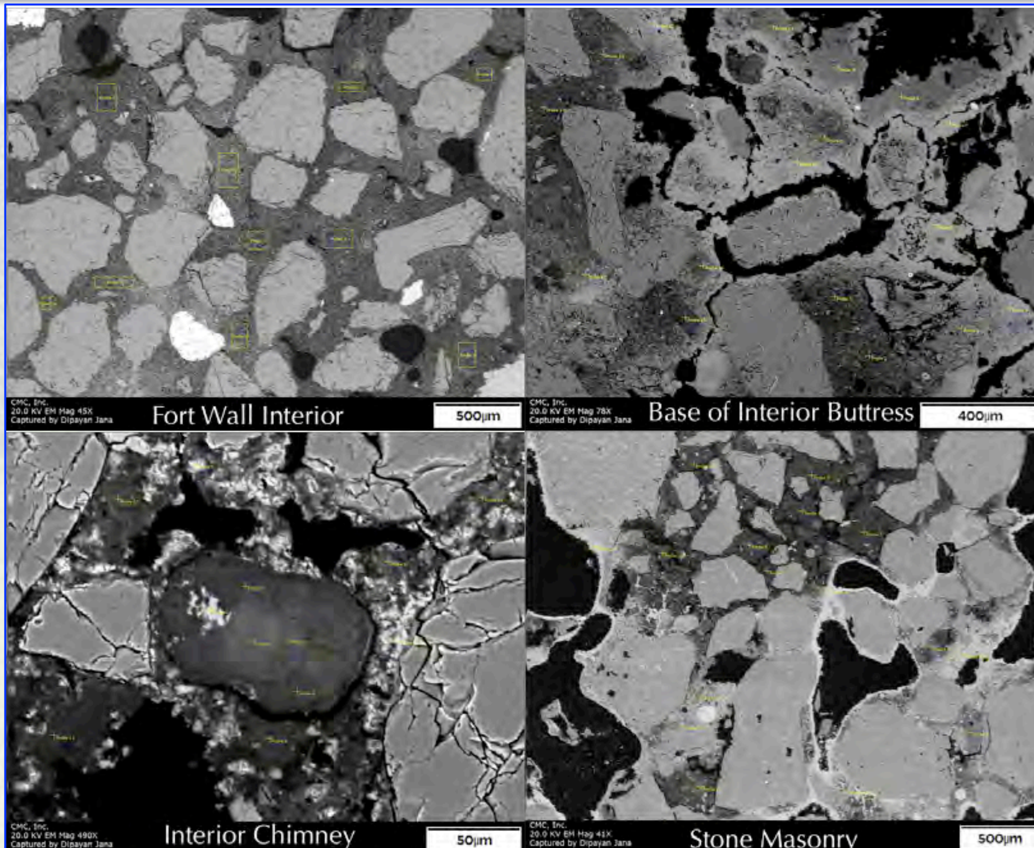
# Application of SEM-EDS: Chemical Variations in Sand and Binder



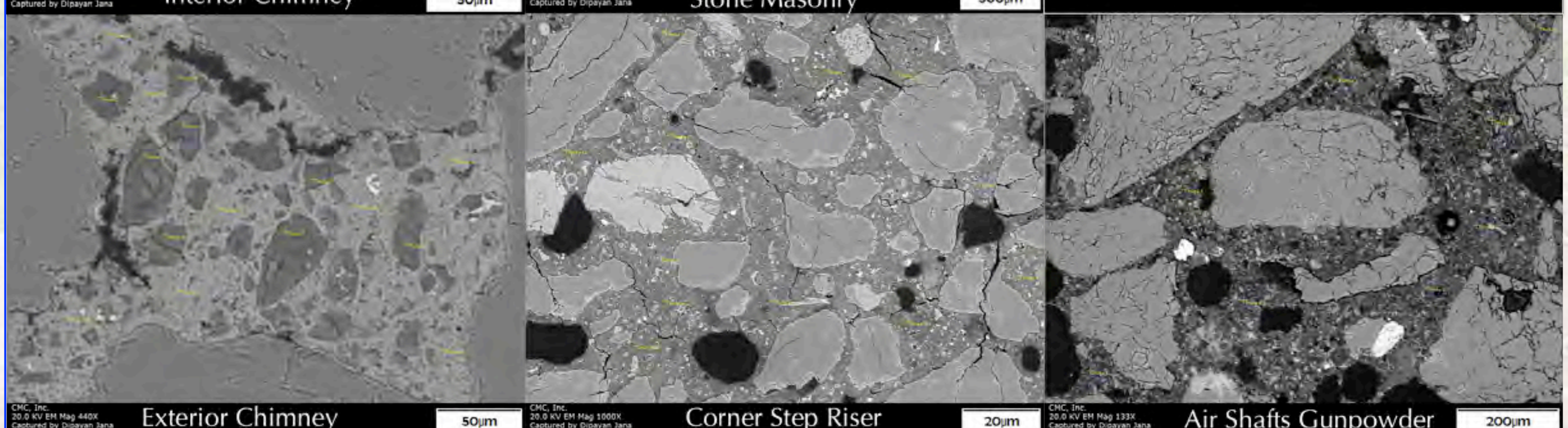
# Application of SEM-EDS: Microstructural Variations in Paste

Degree of alteration of paste from lime leaching to secondary calcite precipitation from darker to brighter paste patches, respectively in BSE images in Buttress, Interior Chimney, and Stone Masonry mortars.

Relatively homogeneous paste in mortars from Fort Wall, Exterior Chimney, Corner Step Riser, and Air Shafts.

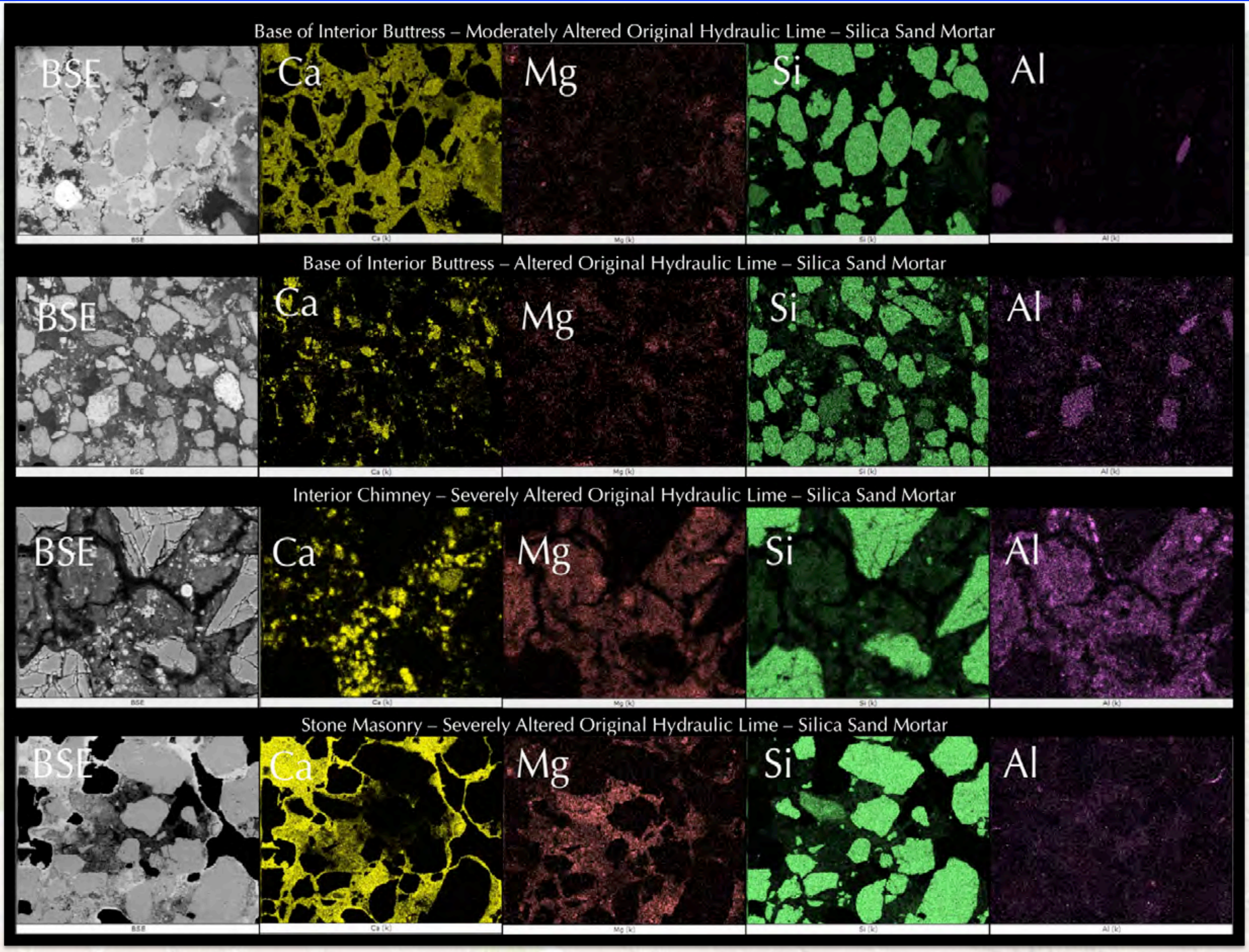



1. Least altered, most homogeneous mortar – Fort Wall Interior
2. Moderately altered mortar (patchy-texture paste) – Base of Interior Buttress
3. Most Altered mortar (lime leaching and granular secondary calcite precipitation) – Interior Chimney
4. Most Altered mortar (lime leaching and granular secondary calcite precipitation) – Stone Masonry
5. Dense less altered pointing mortar with slag – Exterior Chimney
6. Dense less altered pointing mortar– Corner Step Riser
7. Dense less altered pointing mortar with masonry cement – Air Shafts Gunpowder Magazine

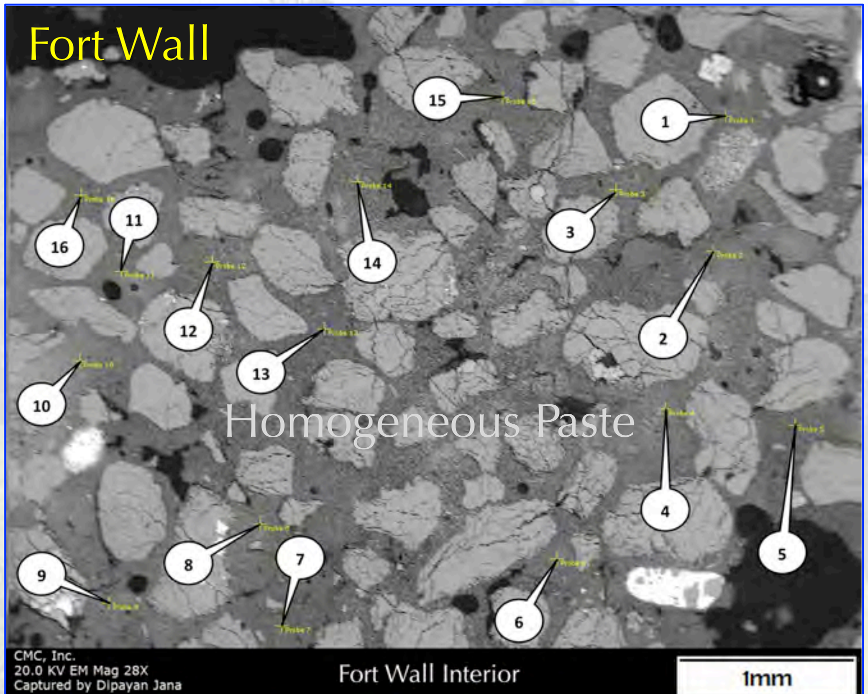


# Application of SEM-EDS: Compositional Variations in Paste From Elemental Mapping

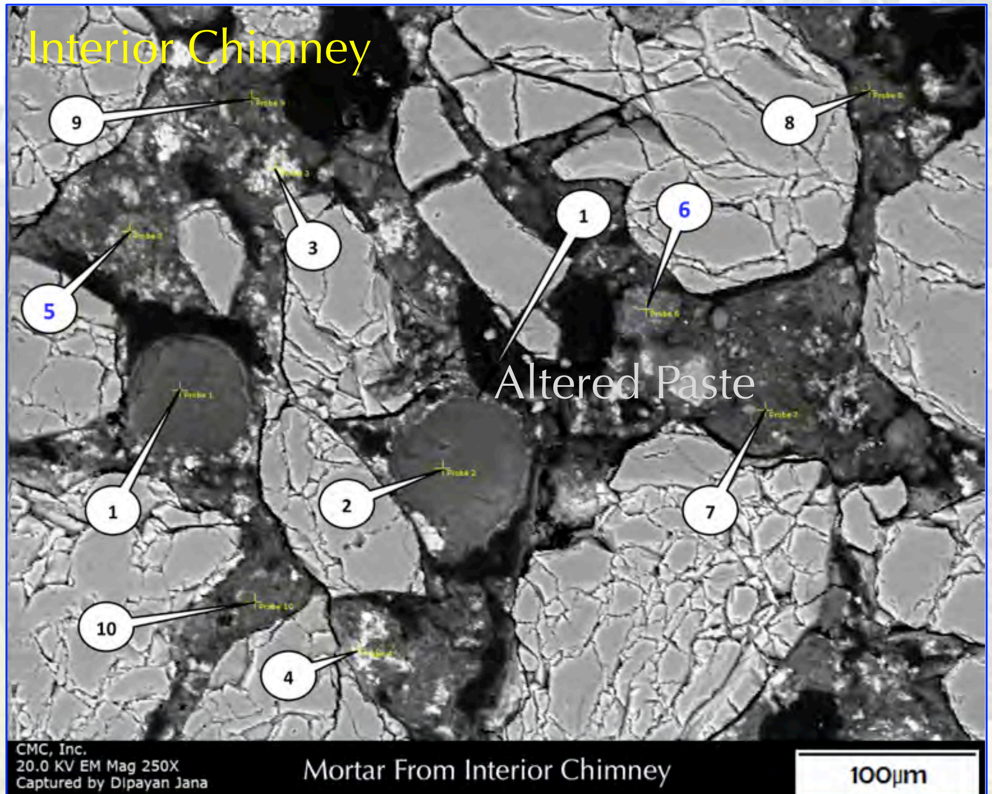
Degree of alteration of paste from lime leaching to secondary calcite precipitation from darker to brighter paste patches, respectively in dot maps of Ca in Buttress, Interior Chimney, and Stone Masonry mortars



# Application of SEM-EDS: Chemical Variations in Pastes




| Probe | CaO | SiO2 | Al2O3 | Na2O | MgO | SO3 | K2O | TiO2 | FeO | Total | Phase | Paste CI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 82.29 | 15.53 | 0.35 | 0.00 | 0.60 | 0.00 | 0.57 | 0.00 | 0.66 | 100.00 | Paste | 0.53 |
| 2 | 72.03 | 21.78 | 2.65 | 0.00 | 1.91 | 0.00 | 0.24 | 0.00 | 1.39 | 100.00 | Paste | 0.87 |
| 3 | 82.54 | 15.20 | 1.10 | 0.00 | 0.43 | 0.00 | 0.14 | 0.00 | 0.59 | 100.00 | Paste | 0.53 |
| 4 | 72.33 | 19.90 | 2.54 | 0.00 | 2.34 | 0.00 | 0.50 | 0.00 | 2.39 | 100.00 | Paste | 0.80 |
| 5 | 0.39 | 97.99 | 1.01 | 0.00 | 0.00 | 0.35 | 0.00 | 0.22 | 0.04 | 100.00 | Quartz | - |
| 6 | 74.11 | 20.51 | 1.99 | 0.00 | 2.47 | 0.22 | 0.35 | 0.00 | 0.34 | 99.99 | Paste | 0.77 |
| 7 | 0.00 | 97.26 | 1.84 | 0.00 | 0.16 | 0.00 | 0.00 | 0.49 | 0.24 | 99.99 | Quartz | - |
| 8 | 80.99 | 14.74 | 1.66 | 0.00 | 1.02 | 0.00 | 0.27 | 0.00 | 1.32 | 100.00 | Paste | 0.53 |
| 9 | 74.43 | 20.48 | 2.33 | 0.00 | 1.50 | 0.00 | 0.45 | 0.00 | 0.81 | 100.00 | Paste | 0.79 |
| 10 | 77.09 | 17.91 | 1.98 | 0.00 | 1.78 | 0.00 | 0.46 | 0.00 | 0.78 | 100.00 | Paste | 0.66 |
| 11 | 72.59 | 19.96 | 2.20 | 0.00 | 3.00 | 0.00 | 0.68 | 0.00 | 1.57 | 100.00 | Paste | 0.77 |
| 12 | 83.37 | 13.36 | 0.68 | 0.00 | 1.74 | 0.00 | 0.00 | 0.44 | 0.40 | 99.99 | Paste | 0.45 |
| 13 | 82.03 | 15.60 | 1.36 | 0.00 | 0.14 | 0.00 | 0.39 | 0.00 | 0.48 | 100.00 | Paste | 0.55 |
| 14 | 75.43 | 18.82 | 3.11 | 0.00 | 1.43 | 0.00 | 0.31 | 0.00 | 0.89 | 99.99 | Paste | 0.73 |
| 15 | 73.06 | 19.91 | 2.61 | 0.00 | 2.25 | 0.00 | 0.28 | 0.00 | 1.88 | 99.99 | Paste | 0.79 |
| 16 | 76.85 | 18.44 | 2.16 | 0.00 | 0.69 | 0.00 | 0.39 | 0.02 | 1.44 | 99.99 | Paste | 0.71 |




| Probe | CaO | SiO2 | Al2O3 | Na2O | MgO | SO3 | K2O | P2O5 | TiO2 | FeO | Total | Phase | Paste CI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.17 | 42.59 | 18.51 | 0.47 | 19.28 | 3.09 | 0.02 | 14.69 | 0.00 | 1.17 | 99.99 | Si-Al-Mg-P grain | 5.17 |
| 2 | 0.14 | 41.41 | 17.41 | 0.00 | 13.82 | 7.23 | 0.00 | 19.54 | 0.00 | 0.44 | 99.99 | | 6.95 |
| 3 | 85.74 | 4.96 | 2.55 | 0.00 | 1.06 | 1.24 | 0.66 | 1.78 | 0.45 | 1.57 | 100.01 | Secondary calcite | 0.20 |
| 4 | 74.94 | 7.09 | 5.76 | 0.00 | 4.15 | 1.66 | 0.31 | 2.35 | 0.42 | 3.32 | 100.00 | | 0.35 |
| 5 | 44.37 | 26.77 | 7.45 | 0.00 | 11.52 | 3.00 | 0.00 | 3.40 | 0.40 | 3.09 | 100.00 | Ca-Si-Mg Paste | 1.41 |
| 6 | 44.21 | 27.80 | 7.52 | 0.00 | 12.19 | 2.79 | 0.07 | 3.04 | 0.00 | 2.39 | 100.01 | | 1.43 |
| 7 | 2.51 | 41.65 | 16.27 | 0.00 | 13.34 | 6.87 | 0.00 | 15.02 | 0.05 | 4.29 | 100.00 | Altered (Si-Al-Mg-P) Paste | 6.49 |
| 8 | 0.49 | 48.52 | 15.83 | 0.00 | 13.33 | 5.16 | 0.34 | 10.43 | 0.11 | 5.79 | 100.00 | | 8.21 |
| 9 | 5.09 | 47.75 | 15.14 | 0.00 | 6.88 | 6.99 | 0.67 | 11.33 | 0.12 | 6.03 | 100.00 | | 10.5 |
| 10 | 0.48 | 44.44 | 18.70 | 0.00 | 12.09 | 5.37 | 0.11 | 14.69 | 0.04 | 4.09 | 100.01 | | 8.50 |

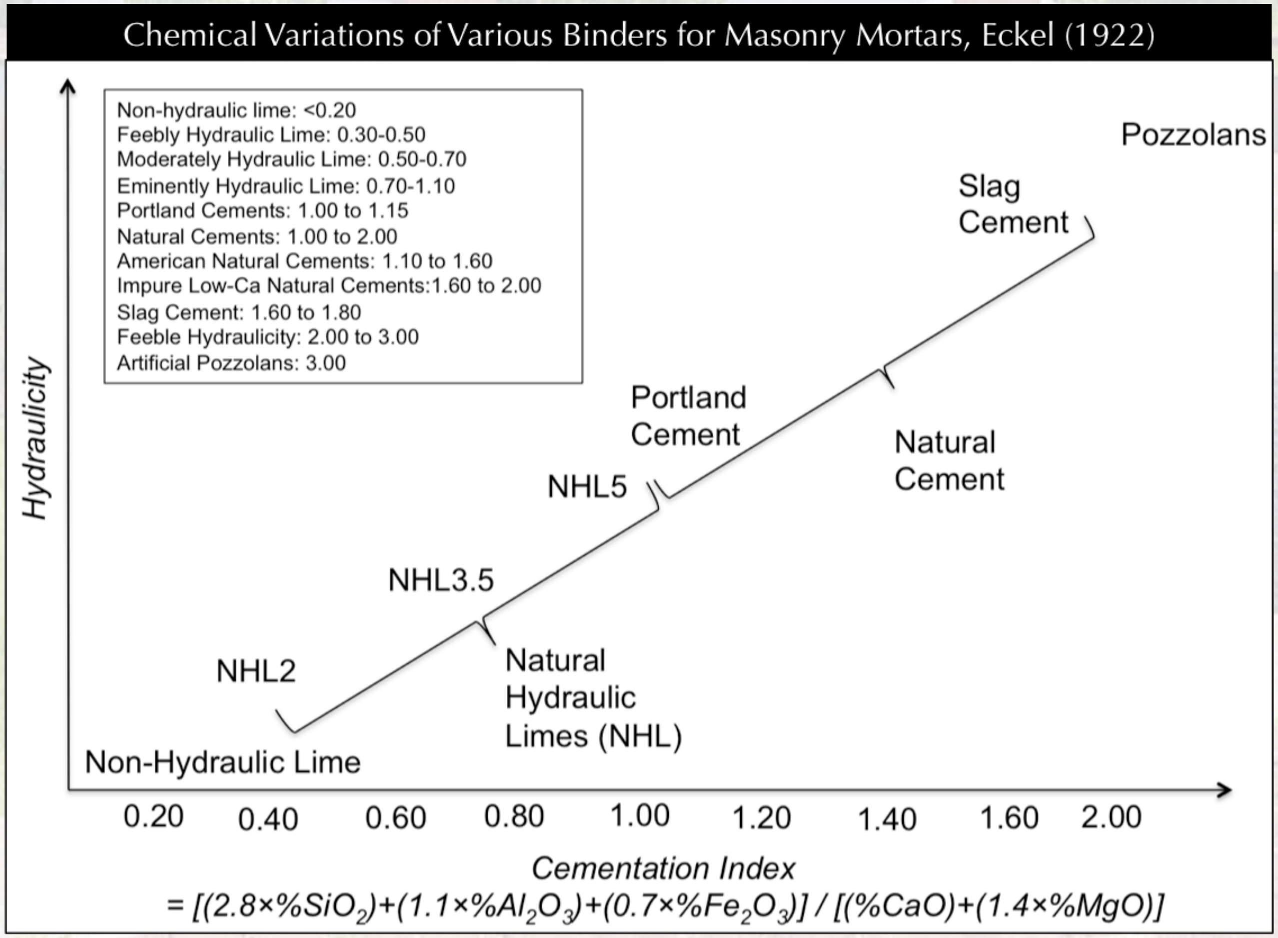
# Application of SEM-EDS: Chemical Variations in Paste from Cementation Index, CI (Eckel 1922)

Cementation Index (CI, Eckel 1922) =

$[(2.8 \times SiO_2) + (1.1 \times Al_2O_3) + (0.7 \times Fe_2O_3)]$

divided by

$[(CaO) + (1.4 \times MgO)]$

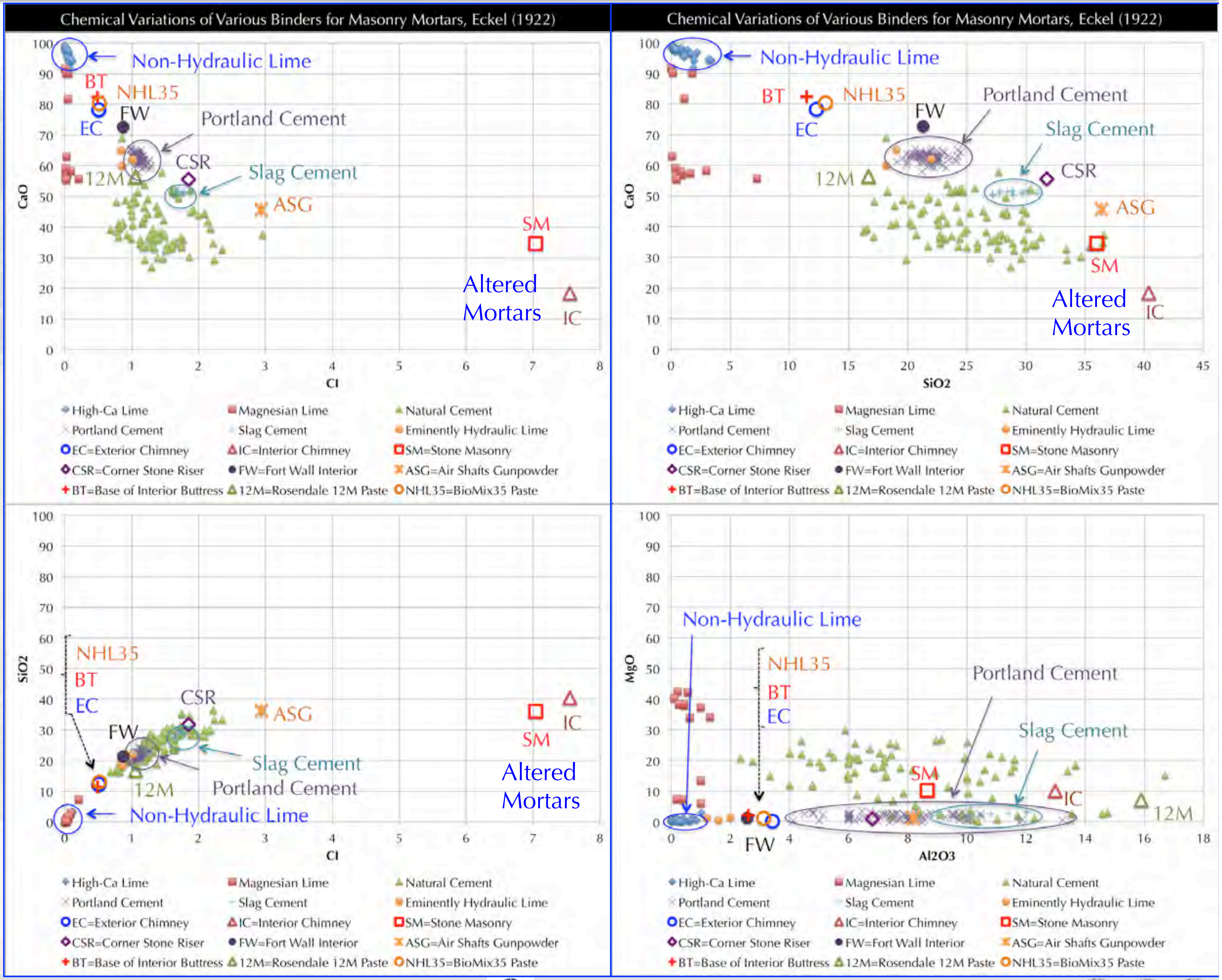


# Application of SEM-EDS:

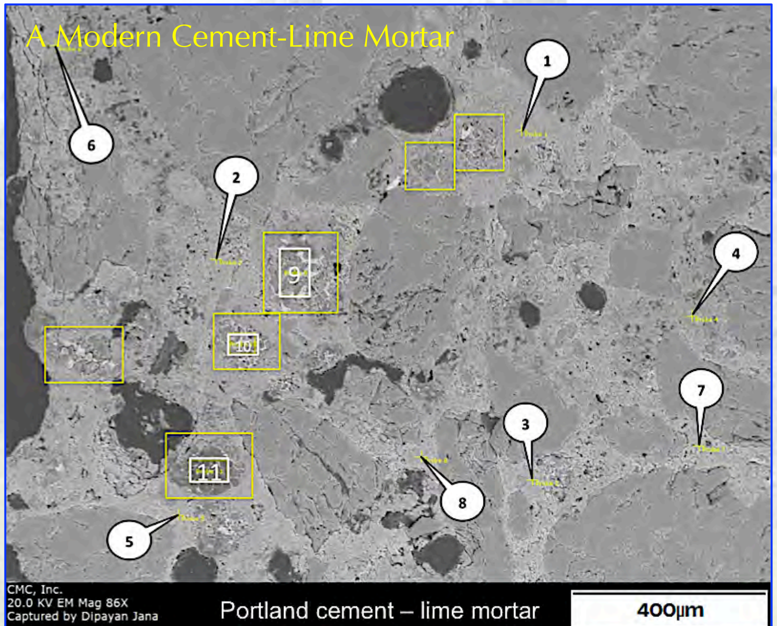
Chemical Variations In Paste Of The Present Mortars

Compared To -

Common Masonry Binders From Eckel (1922)



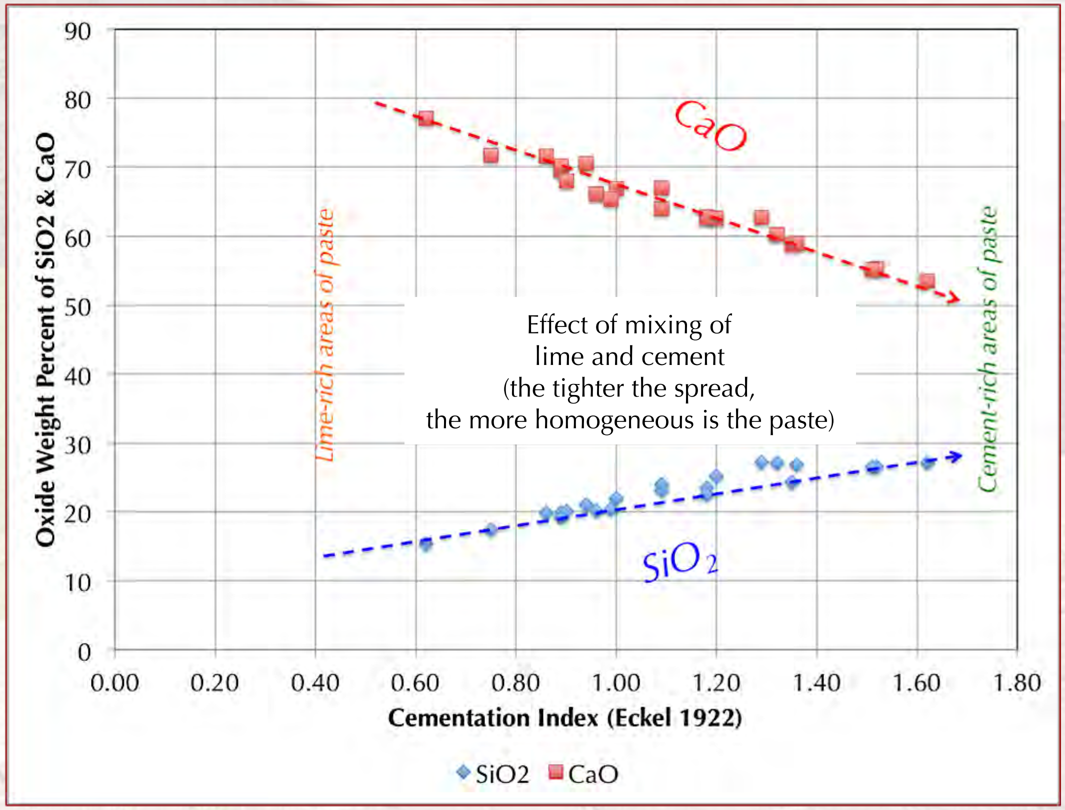
# Application of SEM-EDS: Chemical Variations in Portland Cement-Lime Mortar Paste




| Probe | CaO | SiO2 | Al2O3 | Na2O | MgO | SO3 | K2O | TiO2 | FeO | Total | Phase | Paste CI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 80.96 | 12.23 | 3.60 | 0.00 | 0.16 | 0.00 | 1.11 | 0.90 | 1.03 | 99.99 | Paste | 0.48 |
| 2 | 90.83 | 6.47 | 1.77 | 0.00 | 0.12 | 0.00 | 0.33 | 0.00 | 0.47 | 99.99 | Paste | 0.22 |
| 3 | 54.57 | 18.91 | 6.43 | 0.00 | 1.61 | 0.00 | 1.31 | 1.16 | 16.01 | 100.00 | RCP | - |
| 4 | 12.28 | 49.26 | 5.14 | 0.23 | 2.72 | 0.00 | 7.36 | 0.00 | 23.01 | 100.00 | RCP | - |
| 5 | 80.25 | 11.99 | 4.00 | 0.00 | 0.30 | 0.00 | 1.89 | 0.04 | 1.53 | 100.00 | Paste | 0.48 |
| 6 | 86.83 | 9.09 | 1.98 | 0.00 | 0.07 | 0.00 | 0.86 | 0.21 | 0.96 | 100.00 | Paste | 0.33 |
| 7 | 87.47 | 8.23 | 2.02 | 0.00 | 0.21 | 0.00 | 0.54 | 0.00 | 1.52 | 99.99 | Paste | 0.30 |
| 8 | 88.78 | 6.86 | 2.34 | 0.00 | 0.48 | 0.00 | 0.71 | 0.00 | 0.83 | 100.00 | Paste | 0.25 |
| 9 | 36.36 | 38.04 | 12.39 | 0.33 | 1.54 | 0.00 | 1.34 | 1.24 | 8.75 | 99.99 | RCP | - |
| 10 | 32.64 | 43.86 | 10.19 | 0.59 | 1.27 | 0.00 | 1.57 | 1.07 | 8.81 | 100.00 | RCP | - |
| 11 | 15.41 | 60.51 | 13.76 | 0.14 | 1.13 | 0.00 | 1.60 | 1.41 | 6.03 | 99.99 | RCP | - |

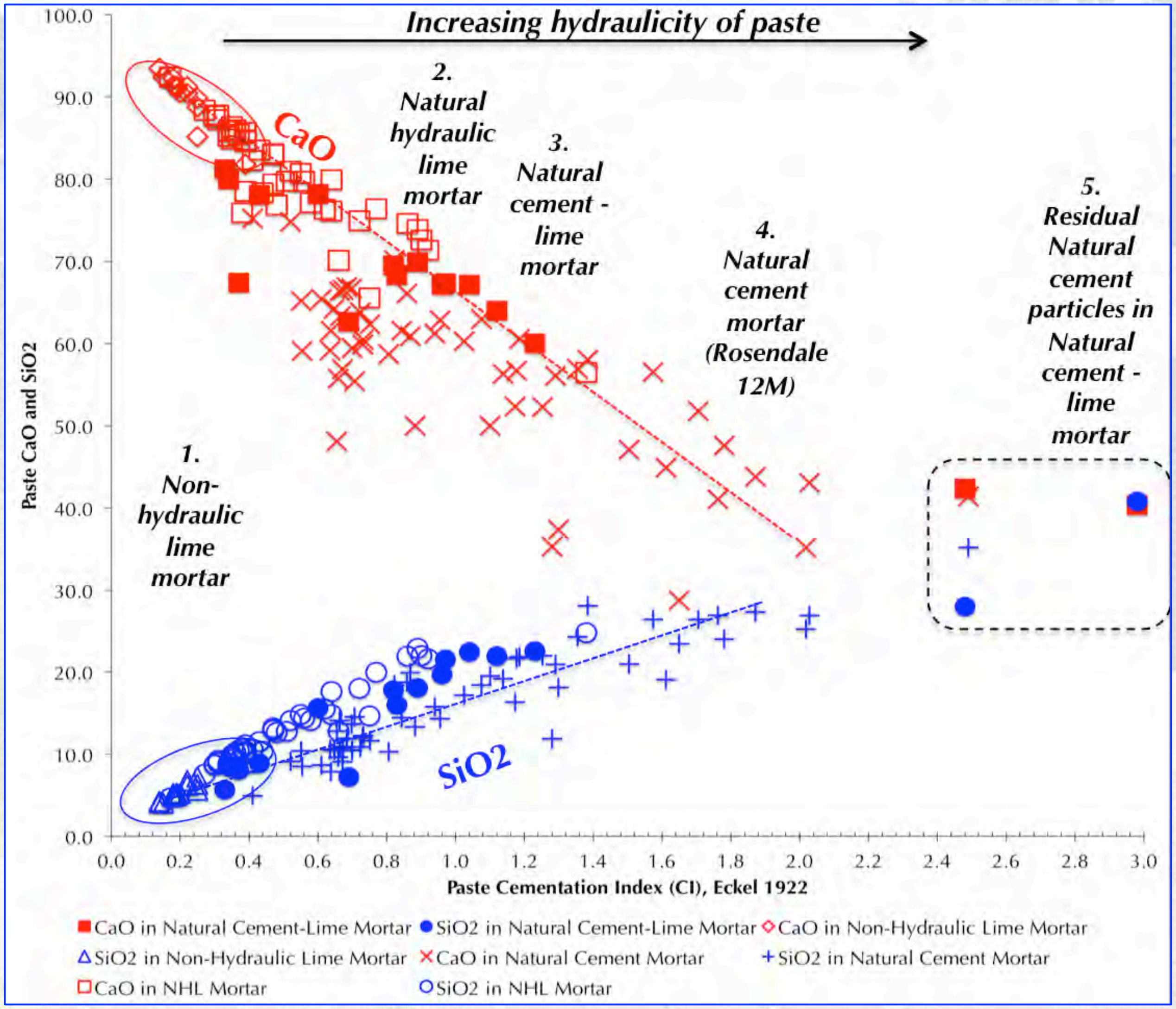
*SEM-EDS analysis of a paste fraction of a cement-lime mortar. Yellow boxes show residual cement particles, white boxes show area-mode analysis of residual cement particles and tips of callouts show locations of analysis of paste. The Table below shows results of analysis of paste and residual cement particles (RCPs).*

*CI, or Cementation Index, after Eckel 1922, which is $[(2.8*SiO_2+1.1*Al_2O_3+0.7*Fe_2O_3)/(CaO+1.4*MgO)]$ is a parameter of hydraulicity of a mortar, e.g., a lime mortar has a CI of < 1 whereas a cement-lime mortar has a CI of >1. Hence determination of CI of a mortar's paste from SEM-EDS analysis can provide the first-hand clue of its hydraulicity. CI of paste progressively increases from non-hydraulic lime mortar to hydraulic lime mortar, natural cement-lime mortar, natural cement mortar, and Portland cement – lime mortar.*

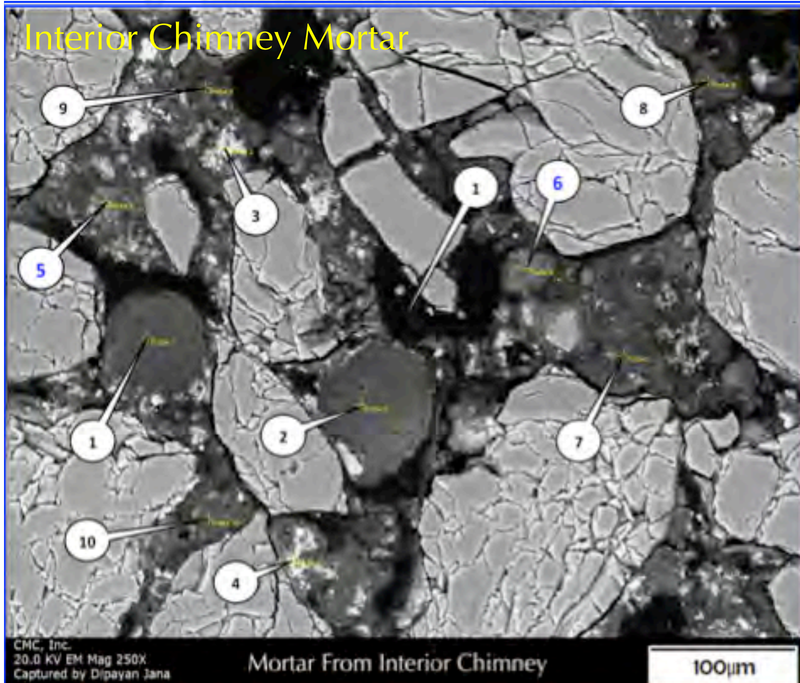


# Application of SEM-EDS: Chemical Variations of Pastes in:

1. A Historic Non-Hydraulic Lime Mortar;
2. A Modern Natural Hydraulic Lime Mortar (BioMix 35 having NHL 3.5);
3. A Historic Natural Cement – Lime Mortar
4. A Modern Natural Cement Mortar (Rosendale 12M)
5. Residual Natural Cement Particles

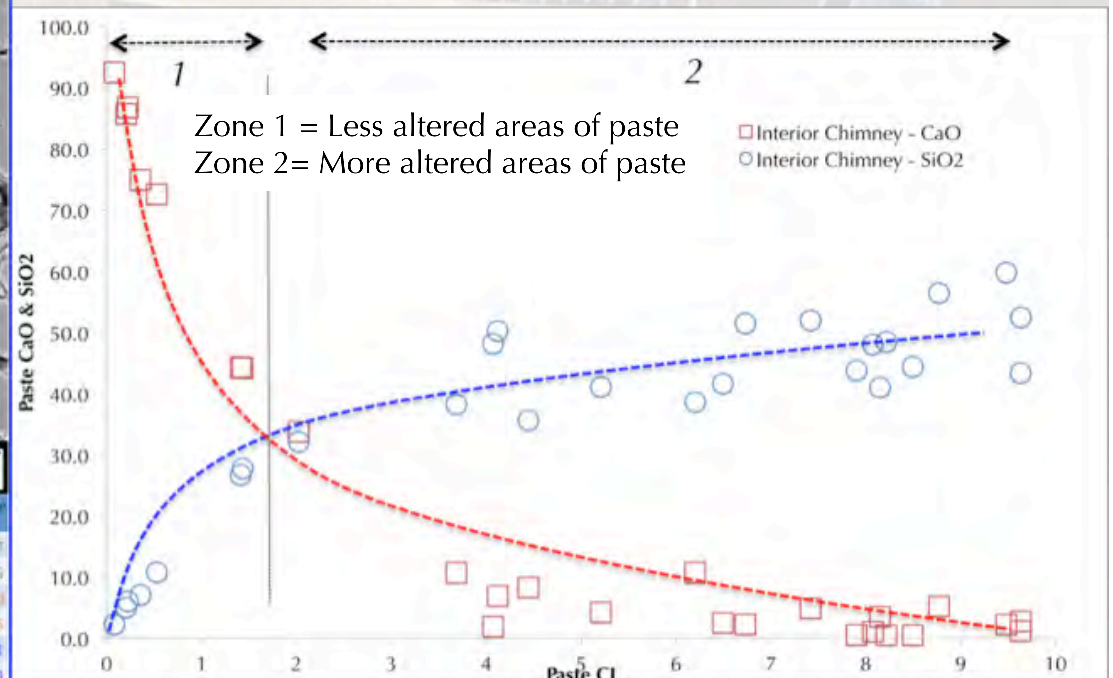


# Application of SEM-EDS: Effects of Alterations In Chemical Composition of Paste




| Probe | CaO | SiO2 | Al2O3 | Na2O | MgO | SO3 | K2O | P2O5 | TiO2 | FeO | Total | Phase | Paste CI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.17 | 42.59 | 18.51 | 0.47 | 19.28 | 3.09 | 0.02 | 14.69 | 0.00 | 1.17 | 99.99 | Si-Al-Mg-P grain | 5.17 |
| 2 | 0.14 | 41.41 | 17.41 | 0.00 | 13.82 | 7.23 | 0.00 | 19.54 | 0.00 | 0.44 | 99.99 | | 6.95 |
| 3 | 85.74 | 8.96 | 2.51 | 0.00 | 3.06 | 1.24 | [illegible] | 1.70 | 0.05 | 3.57 | 100.01 | Secondary calcite | 0.20 |
| 4 | 74.94 | 7.09 | 5.76 | 0.00 | 4.15 | 1.66 | 0.41 | 2.55 | 0.42 | 3.32 | 100.00 | | 0.35 |
| 5 | 44.37 | 26.77 | 7.45 | 0.00 | 11.52 | 3.00 | 0.00 | 3.40 | 0.40 | 3.09 | 100.00 | Ca-Si-Mg Paste | 1.41 |
| 6 | 44.21 | 27.80 | 7.52 | 0.00 | 12.19 | 2.79 | 0.07 | 3.04 | 0.00 | 2.39 | 100.01 | | 1.43 |
| 7 | 2.51 | 41.65 | 16.27 | 0.00 | 13.34 | 6.87 | 0.00 | 15.02 | 0.05 | 4.29 | 100.00 | Altered (Si-Al-Mg-P) Paste | 6.49 |
| 8 | 0.49 | 48.52 | 15.83 | 0.00 | 13.33 | 5.16 | 0.34 | 10.43 | 0.11 | 5.79 | 100.00 | | 8.21 |
| 9 | 5.09 | 47.75 | 15.14 | 0.00 | 6.88 | 6.99 | 0.67 | 11.33 | 0.12 | 6.03 | 100.00 | | 10.5 |
| 10 | 0.48 | 44.44 | 18.70 | 0.00 | 12.09 | 5.37 | 0.11 | 14.69 | 0.04 | 4.09 | 100.01 | | 8.50 |

*Unlike an unaltered modern cement-lime mortar, an altered historic mortar shows significant spread in paste-CI due to various alterations during service, e.g., lime leaching (causing very high CI) to secondary calcite precipitation (causing very low CI).*

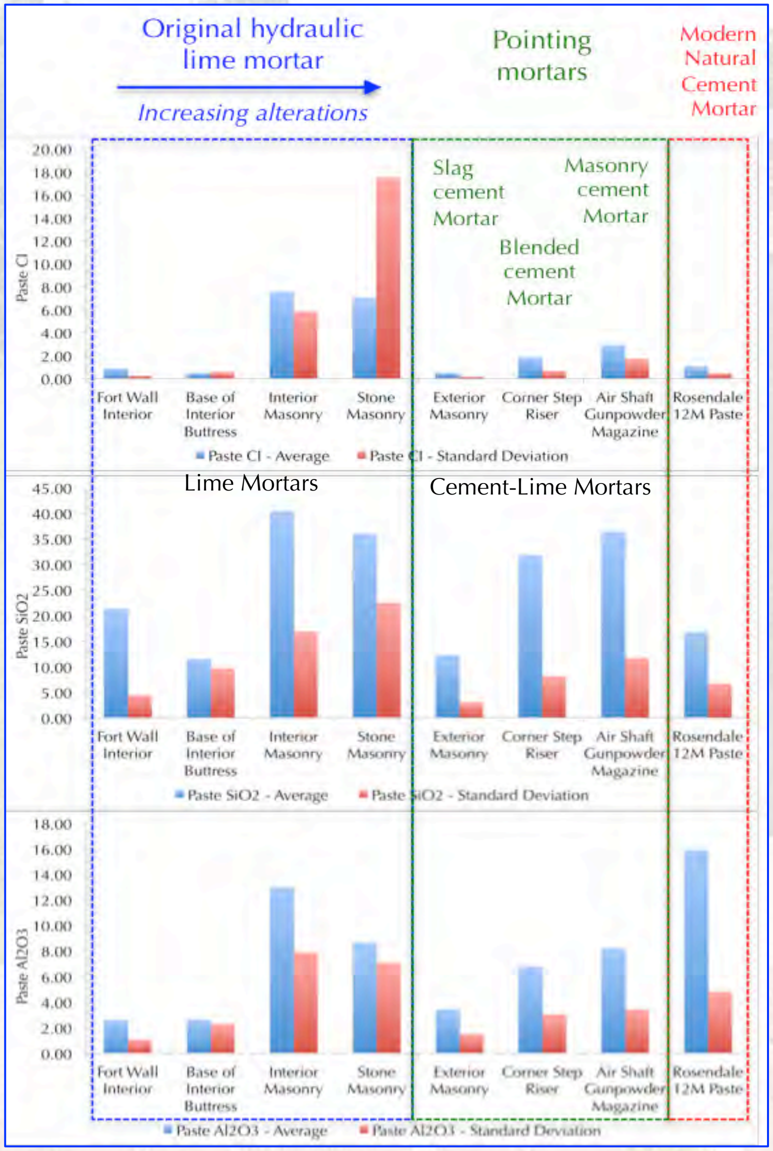


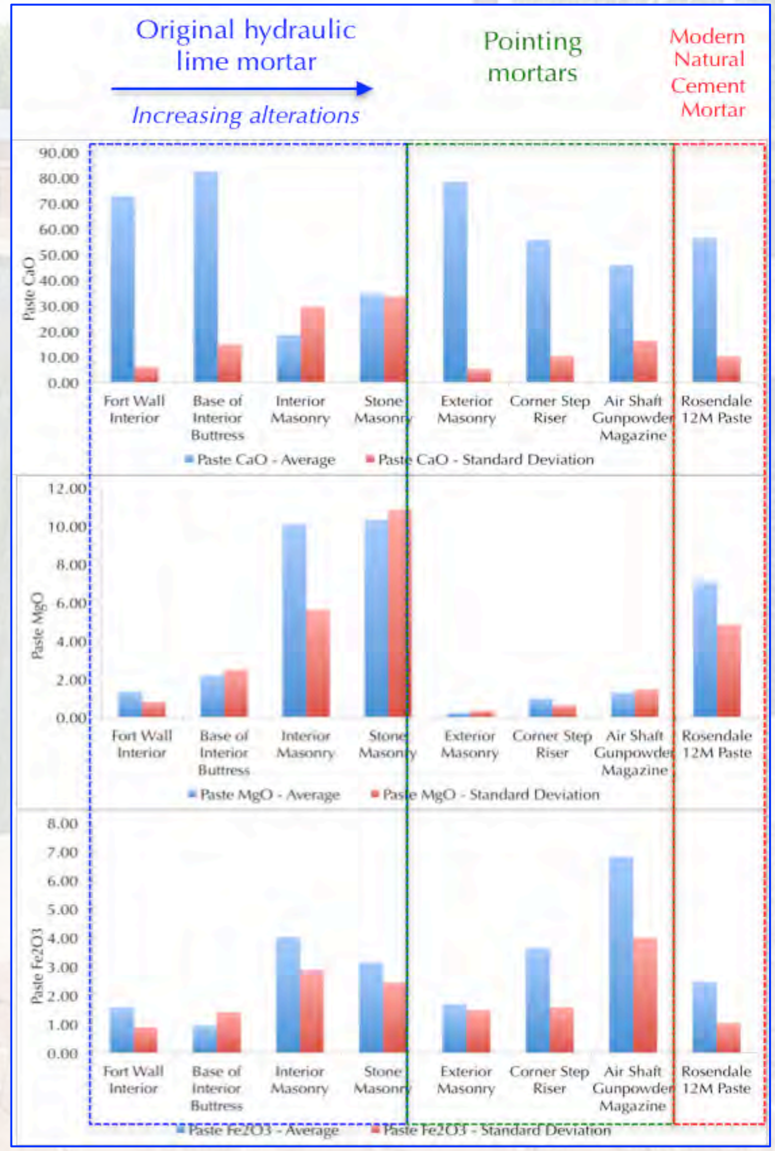

Region 1: Effect of mixing between lime (Ca)-rich and cement (Si, CI)-rich components;
Region 2: Effect of secondary alterations, e.g., lime leaching, secondary calcite precipitation, etc. that causes enrichment of silica, magnesia, alumina at the expense of calcium

# Application of SEM-EDS: Chemical Variations in Altered Paste

Measuring degree of alterations of paste from standard deviations of paste compositions from SEM-EDS.

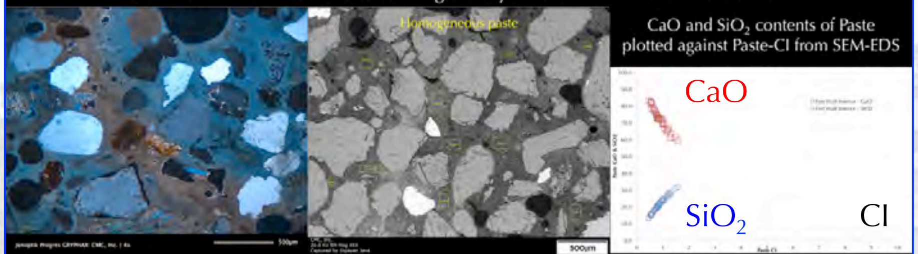
The higher the red bars, the more altered are the pastes.



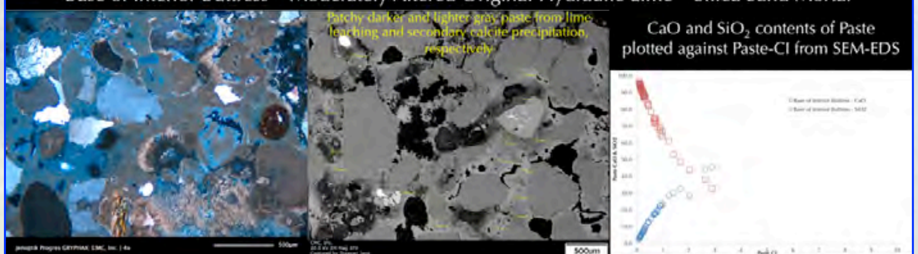



# Application of SEM-EDS: Microstructural & Chemical Variations in Pastes

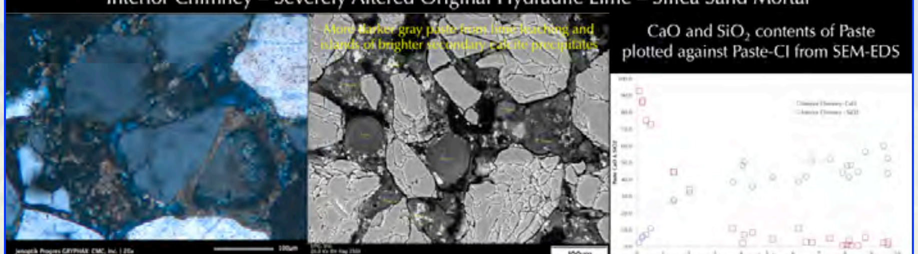
## Fort Wall Interior – Least Altered Original Hydraulic Lime – Silica Sand Mortar



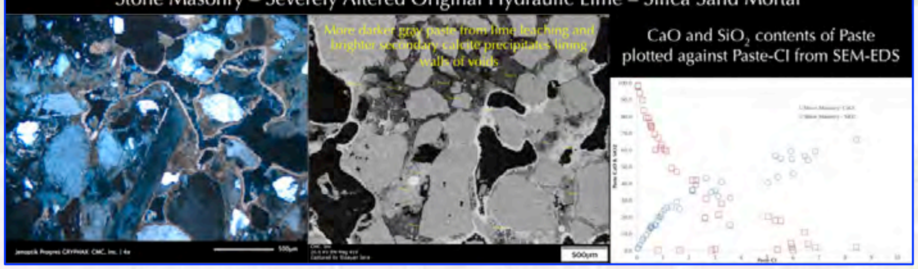

## Base of Interior Buttress – Moderately Altered Original Hydraulic Lime – Silica Sand Mortar



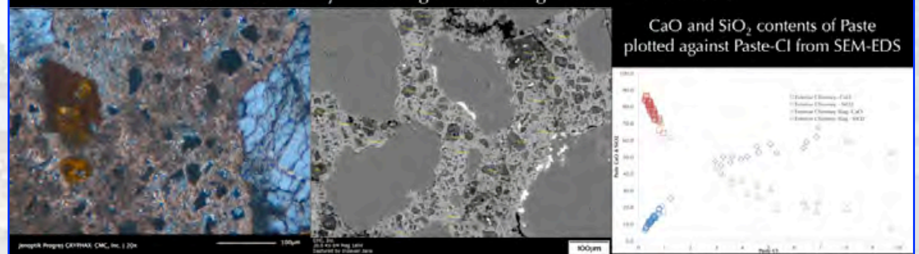

## Interior Chimney – Severely Altered Original Hydraulic Lime – Silica Sand Mortar



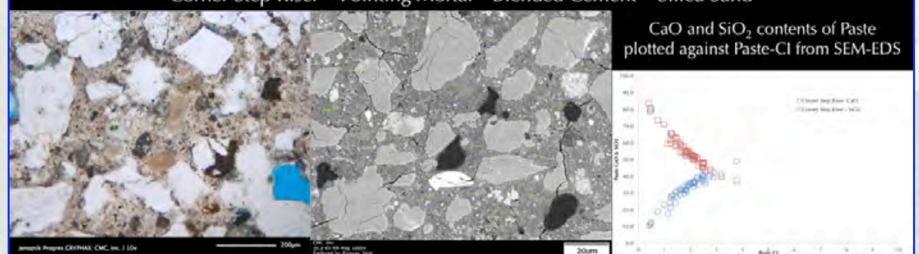

## Stone Masonry – Severely Altered Original Hydraulic Lime – Silica Sand Mortar



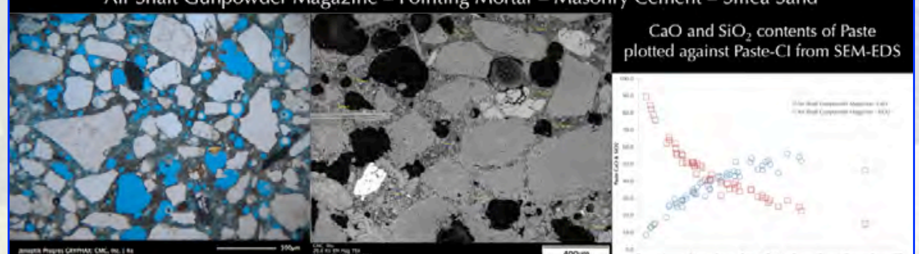

## Exterior Chimney – Pointing Mortar - Slag Cement – Silica Sand



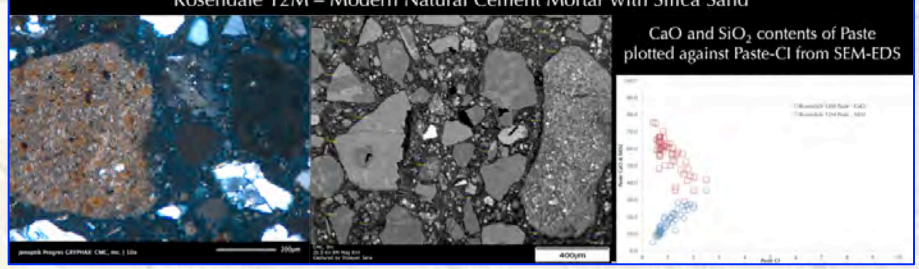

## Corner Step Riser – Pointing Mortar - Blended Cement – Silica Sand



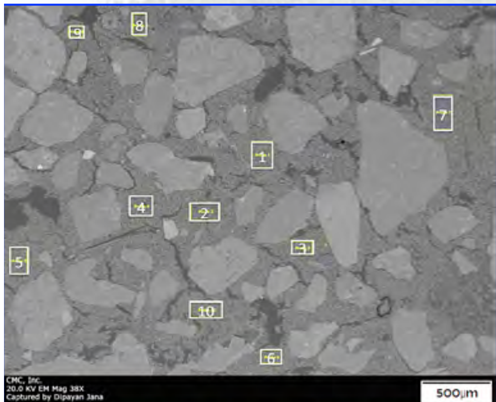

## Air Shaft Gunpowder Magazine – Pointing Mortar – Masonry Cement – Silica Sand




## Rosendale 12M – Modern Natural Cement Mortar with Silica Sand



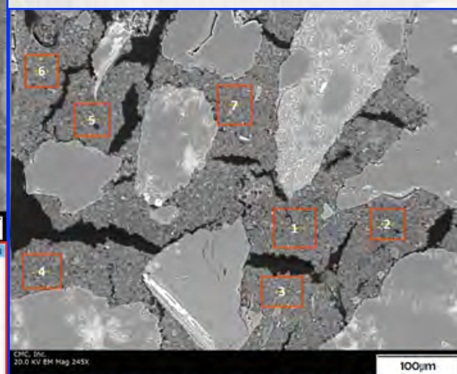
# Applications of SEM-EDS: Chemical Variations in Pastes of High-Ca Lime Mortar vs. Dolomitic Lime Mortar vs. Hydraulic Lime Mortar vs. Natural Cement – Lime Mortar




| Probe | CaO | SiO2 | Al2O3 | Na2O | MgO | SO3 | K2O | TiO2 | FeO | Total | Phase | Paste CI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 93.70 | 4.20 | 0.35 | 0.00 | 0.67 | 0.00 | 0.03 | 0.12 | 0.92 | 99.99 | Paste | 0.14 |
| 2 | 92.52 | 3.83 | 1.11 | 0.00 | 1.26 | 0.00 | 0.12 | 0.29 | 0.88 | 100.01 | Paste | 0.13 |
| 3 | 92.75 | 4.21 | 0.96 | 0.00 | 1.45 | 0.00 | 0.25 | 0.00 | 0.38 | 100.00 | Paste | 0.14 |
| 4 | 92.76 | 4.55 | 1.13 | 0.00 | 1.27 | 0.00 | 0.07 | 0.00 | 0.22 | 100.00 | Paste | 0.15 |
| 5 | 93.38 | 3.68 | 0.74 | 0.00 | 1.48 | 0.00 | 0.15 | 0.00 | 0.57 | 100.00 | Paste | 0.12 |
| 6 | 94.30 | 2.86 | 0.73 | 0.00 | 0.56 | 0.00 | 0.27 | 0.17 | 1.11 | 100.00 | Paste | 0.10 |
| 7 | 84.08 | 9.86 | 1.65 | 0.00 | 2.59 | 0.00 | 0.11 | 0.00 | 1.70 | 99.99 | Paste | 0.35 |
| 8 | 94.04 | 4.29 | 0.79 | 0.00 | 0.60 | 0.00 | 0.03 | 0.00 | 0.25 | 100.00 | Paste | 0.14 |
| 9 | 91.92 | 4.07 | 1.23 | 0.00 | 1.07 | 0.00 | 0.04 | 0.07 | 1.59 | 99.99 | Paste | 0.15 |
| 10 | 92.51 | 3.33 | 1.39 | 0.00 | 0.81 | 0.00 | 0.13 | 0.00 | 1.82 | 99.99 | Paste | 0.13 |

**1. Non-Hydraulic High-Ca Lime Mortar**

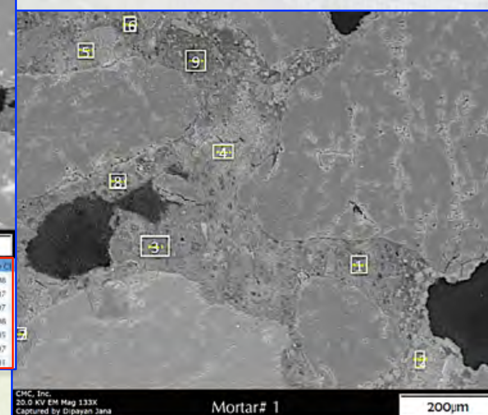
- Lowest CI
- Highest CaO
- Lowest $SiO_2$, MgO




| Probe | CaO | SiO2 | Al2O3 | Na2O | MgO | SO3 | K2O | TiO2 | FeO | Total | Phase | Paste CI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 78.03 | 2.58 | 0.71 | 0.62 | 17.70 | 0.01 | 0.35 | 0.00 | 0.65 | 99.99 | Paste | 0.08 |
| 2 | 78.54 | 2.05 | 0.79 | 0.41 | 18.18 | 0.02 | 0.02 | 0.07 | 0.34 | 100.00 | Paste | 0.07 |
| 3 | 81.18 | 2.54 | 0.03 | 0.81 | 14.70 | 0.02 | 0.72 | 0.00 | 0.04 | 99.99 | Paste | 0.07 |
| 4 | 84.03 | 1.97 | 1.41 | 0.50 | 11.97 | 0.01 | 0.11 | 1.66 | 1.66 | 99.99 | Paste | 0.08 |
| 5 | 80.97 | 1.37 | 0.85 | 0.85 | 15.78 | 0.01 | 0.17 | 0.00 | 1.10 | 99.99 | Paste | 0.05 |
| 6 | 78.72 | 2.11 | 0.99 | 1.06 | 17.07 | 0.01 | 0.03 | 0.37 | 0.68 | 100.00 | Paste | 0.07 |
| 7 | 88.19 | 0.02 | 0.44 | 1.37 | 9.55 | 0.01 | 0.41 | 1.03 | 0.56 | 99.99 | Paste | 0.01 |

**2. Non-Hydraulic Dolomitic Lime Mortar**

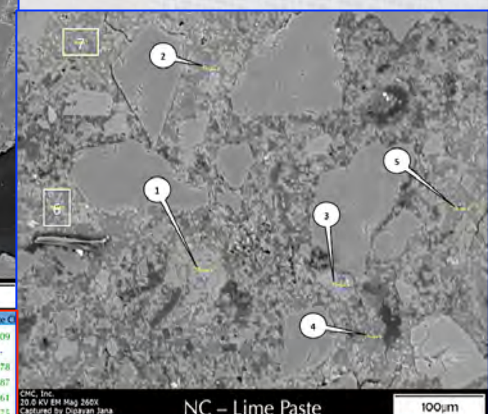
- Lowest CI
- Characteristically high MgO
- Lowest $SiO_2$




| Probe | CaO | SiO2 | Al2O3 | Na2O | MgO | SO3 | K2O | TiO2 | FeO | Total | Phase | Paste CI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 50.82 | 36.79 | 7.05 | 0.00 | 1.61 | 0.00 | 0.55 | 3.05 | 0.12 | 99.99 | Paste | 2.09 |
| 2 | 57.56 | 7.65 | 3.97 | 0.00 | 20.28 | 0.06 | 1.64 | 8.26 | 0.57 | 99.99 | Mg-rich | - |
| 3 | 51.50 | 32.50 | 9.99 | 0.00 | 4.33 | 0.00 | 0.40 | 0.62 | 0.65 | 99.99 | Paste | 1.78 |
| 4 | 59.28 | 19.45 | 2.88 | 0.70 | 6.06 | 0.00 | 0.27 | 9.89 | 1.47 | 100.00 | Paste | 0.87 |
| 5 | 44.11 | 36.01 | 14.47 | 0.00 | 0.53 | 0.00 | 3.04 | 1.11 | 0.73 | 100.00 | Paste | 2.61 |
| 6 | 46.95 | 28.42 | 12.45 | 0.11 | 4.96 | 3.41 | 0.62 | 1.21 | 1.85 | 100.00 | Paste | 1.75 |
| 7 | 36.22 | 43.77 | 11.65 | 1.21 | 0.21 | 0.00 | 0.47 | 4.57 | 1.88 | 100.00 | Paste | 3.74 |
| 8 | 50.37 | 36.81 | 8.68 | 0.00 | 1.68 | 0.00 | 0.75 | 0.67 | 1.03 | 99.99 | Paste | 2.15 |
| 9 | 51.46 | 35.37 | 7.68 | 0.00 | 1.37 | 0.00 | 0.11 | 0.17 | 1.85 | 100.01 | Paste | 1.96 |

**3. Hydraulic Lime Mortar**

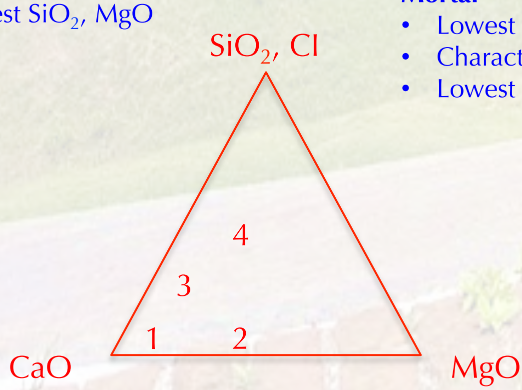
- Characteristically high $SiO_2$
- CI >1



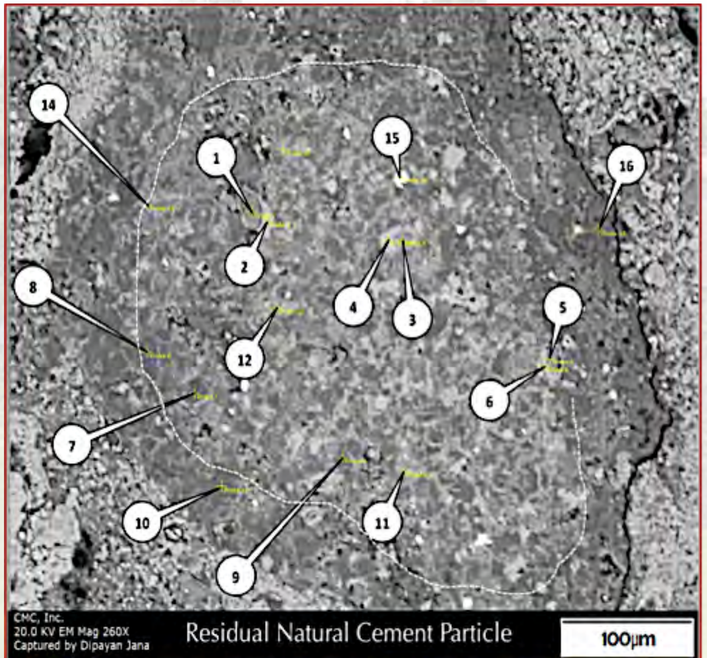

| Probe | CaO | SiO2 | Al2O3 | Na2O | MgO | SO3 | K2O | TiO2 | FeO | Total | Phase | Paste CI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 77.53 | 8.36 | 1.22 | 0.00 | 7.56 | 0.00 | 0.07 | 0.00 | 5.26 | 100.00 | Ca-rich Mg-Al-Fe-Silicate | 0.12 |
| 2 | 30.93 | 50.65 | 8.43 | 0.14 | 13.88 | 0.00 | 0.65 | 0.21 | 5.12 | 100.01 | Ca-poor Mg-Al-Fe-Silicate | 1.81 |
| 3 | 75.00 | 6.47 | 2.65 | 0.00 | 8.78 | 0.00 | 0.61 | 0.36 | 6.12 | 99.99 | Ca-rich Mg-Al-Fe-Silicate | 0.29 |
| 4 | 16.14 | 49.56 | 11.61 | 0.13 | 14.05 | 0.00 | 0.29 | 0.58 | 7.64 | 100.00 | Ca-poor Mg-Al-Fe-Silicate | 4.18 |
| 5 | 13.12 | 57.06 | 9.16 | 0.21 | 11.54 | 0.00 | 0.55 | 1.19 | 7.16 | 99.99 | Ca-poor Mg-Al-Fe-Silicate | 5.97 |
| 6 | 37.64 | 37.71 | 6.92 | 0.07 | 11.82 | 0.00 | 0.68 | 0.77 | 4.40 | 100.01 | Ca-Mg-Al-Silicate | 2.15 |
| 7 | 41.27 | 35.72 | 6.96 | 0.18 | 10.57 | 0.00 | 1.13 | 0.00 | 4.16 | 99.99 | Ca-Mg-Al-Silicate | 1.97 |

**4. Natural Cement - Lime Mortar**

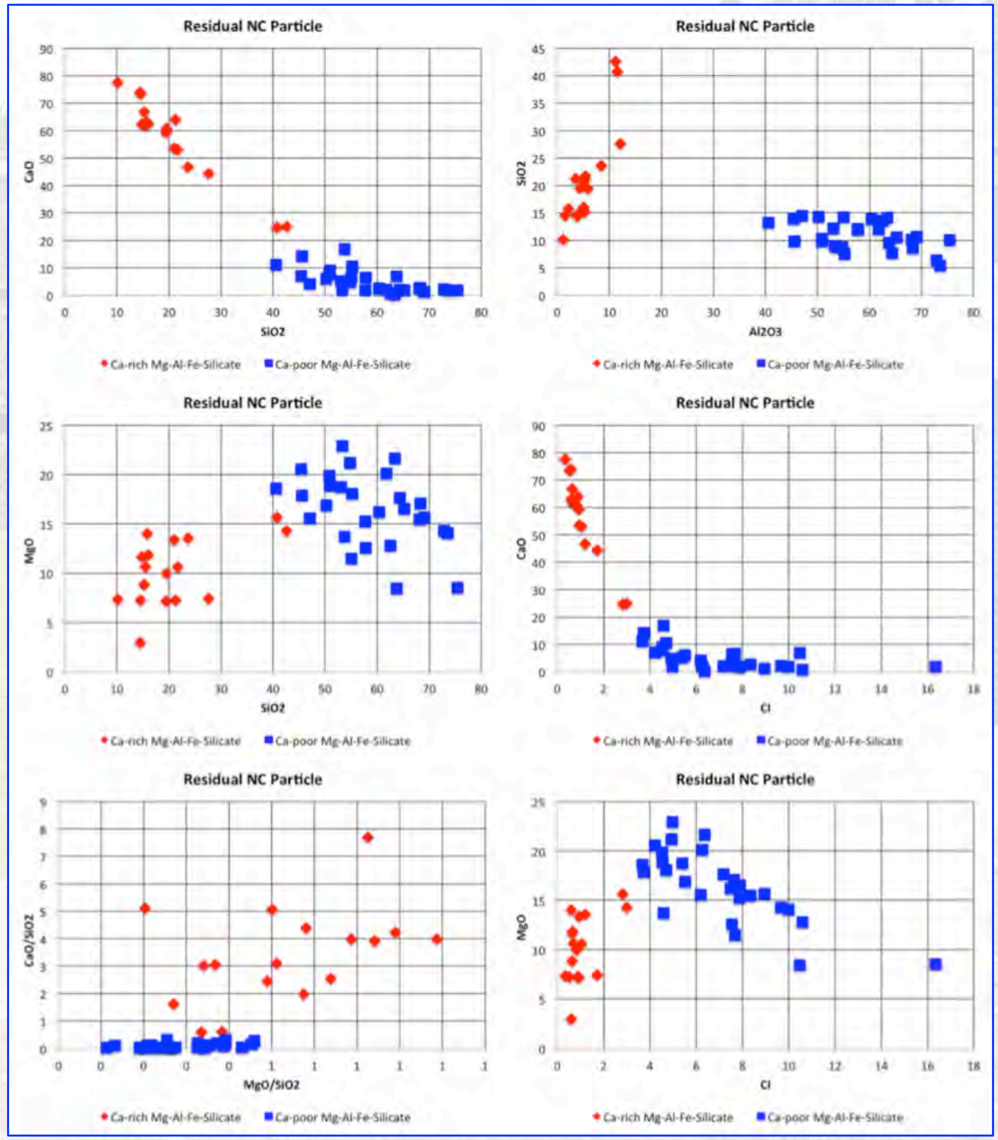
- High MgO and $SiO_2$
- CI <1 for Ca-rich areas and >1 for Ca-poor areas



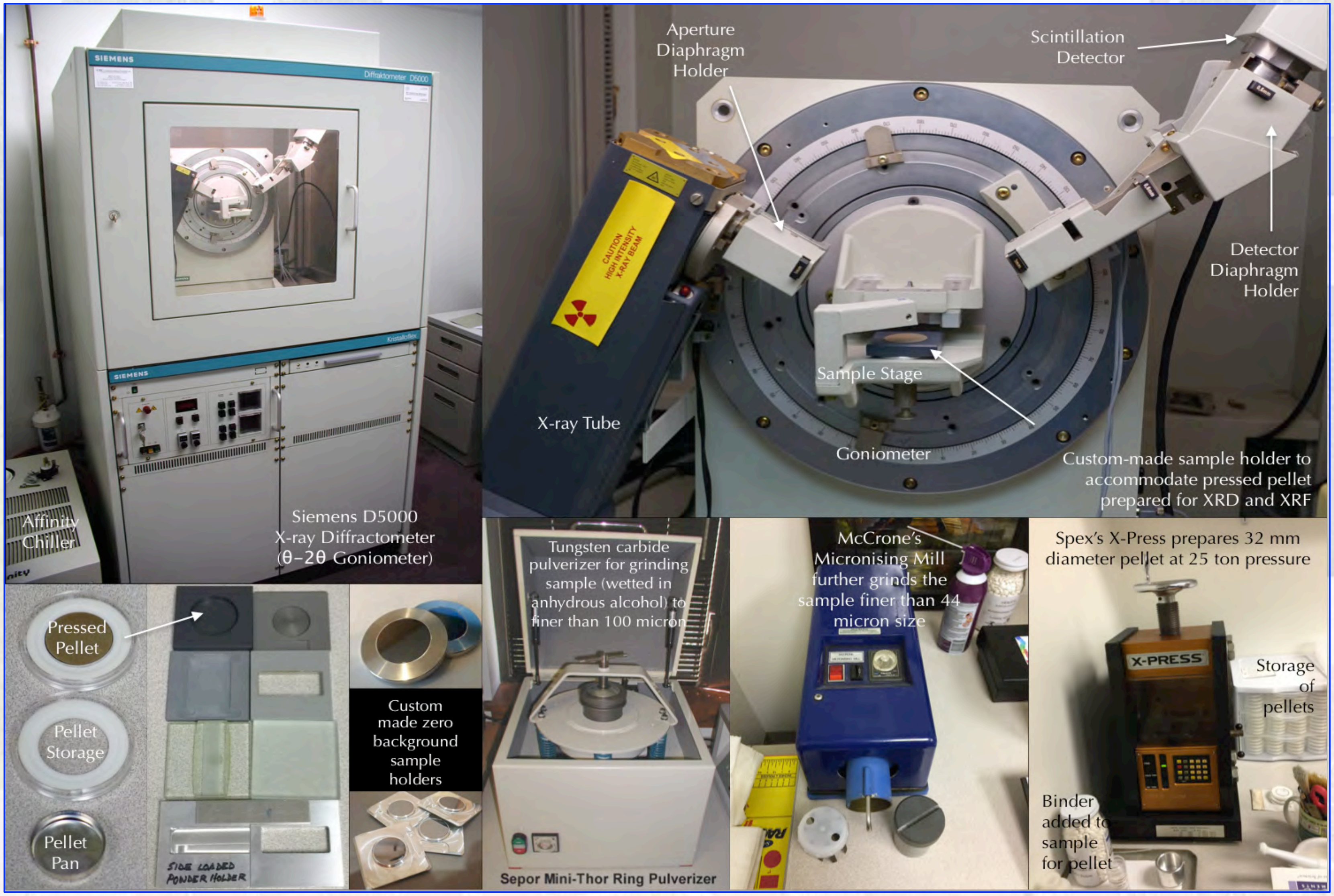
# Application of SEM-EDS: Detecting Raw Feed From Chemical Variation in Residual Natural Cement



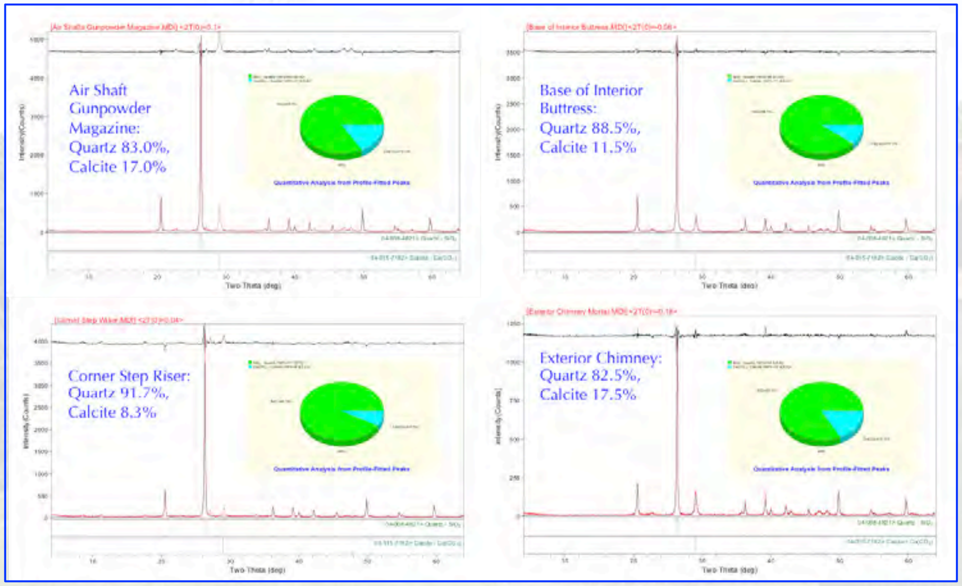

| Probe | CaO | SiO2 | Al2O3 | Na2O | MgO | SO3 | K2O | TiO2 | FeO | Total | Phase | Paste CI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.57 | 96.95 | 1.11 | 0.00 | 0.12 | 1.24 | 0.00 | 0.00 | 0.00 | 99.99 | Si-Core | - |
| 2 | 93.79 | 4.75 | 0.39 | 0.00 | 0.24 | 0.00 | 0.40 | 0.00 | 0.42 | 99.99 | Ca-rim | - |
| 3 | 1.40 | 95.51 | 1.40 | 0.00 | 0.04 | 0.35 | 0.00 | 0.66 | 0.63 | 99.99 | Si-Core | - |
| 4 | 94.31 | 4.01 | 0.58 | 0.00 | 0.21 | 0.00 | 0.53 | 0.36 | 0.00 | 100.00 | Ca-rim | - |
| 5 | 0.44 | 97.26 | 0.81 | 0.00 | 0.04 | 1.37 | 0.00 | 0.00 | 0.06 | 99.98 | Si-Core | - |
| 6 | 92.66 | 4.48 | 0.88 | 0.00 | 0.02 | 0.00 | 0.55 | 0.33 | 1.08 | 100.00 | Ca-rim | - |
| 7 | 1.22 | 51.42 | 20.90 | 0.24 | 24.96 | 0.00 | 0.03 | 0.12 | 1.10 | 99.99 | Mg-Al-Silicate | - |
| 8 | 0.42 | 57.38 | 16.04 | 0.00 | 24.03 | 0.00 | 0.08 | 0.07 | 1.99 | 100.01 | Mg-Al-Silicate | - |
| 9 | 5.84 | 44.00 | 21.79 | 0.00 | 27.97 | 0.00 | 0.09 | 0.00 | 0.29 | 99.98 | Mg-Al-Silicate | - |
| 10 | 1.00 | 52.16 | 17.34 | 0.00 | 26.58 | 0.00 | 0.00 | 0.10 | 2.81 | 99.99 | Mg-Al-Silicate | - |
| 11 | 71.86 | 10.97 | 0.57 | 0.20 | 8.78 | 0.36 | 0.32 | 0.54 | 6.40 | 100.00 | Ca-Mg-Si-Fe-Al Interstitial Phase | 0.43 |
| 12 | 66.24 | 10.00 | 5.47 | 0.00 | 11.23 | 0.00 | 0.31 | 0.36 | 6.36 | 99.99 | Ca-Mg-Si-Fe-Al Interstitial Phase | 0.47 |
| 13 | 69.16 | 10.15 | 5.04 | 0.02 | 10.64 | 0.00 | 0.43 | 0.33 | 4.22 | 99.99 | Ca-Mg-Si-Fe-Al Interstitial Phase | 0.44 |
| 14 | 59.71 | 16.06 | 6.81 | 0.11 | 11.73 | 0.26 | 0.45 | 0.92 | 3.95 | 100.00 | Ca-Mg-Si-Fe-Al Interstitial Phase | 0.73 |
| 15 | 9.35 | 16.40 | 0.98 | 0.00 | 0.85 | 0.00 | 0.46 | 0.27 | 71.68 | 99.99 | Fe-Oxide | - |
| 16 | 1.30 | 49.05 | 20.97 | 0.00 | 24.17 | 0.00 | 0.14 | 0.00 | 4.36 | 99.99 | Mg-Al-Silicate | - |



# X-ray Diffraction – Mineralogical Composition of Mortar

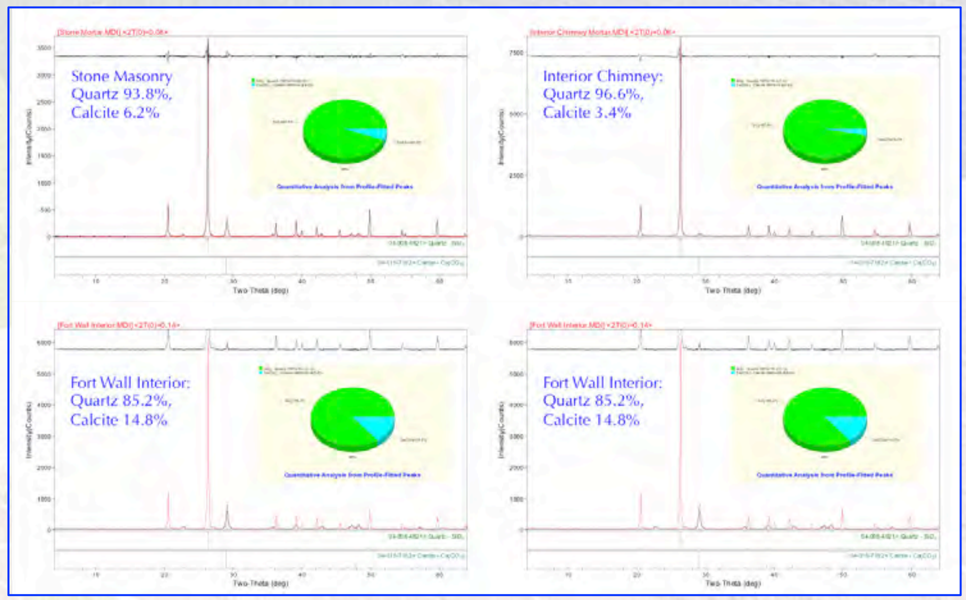


# X-ray Diffraction of Mortars From Fort Washington

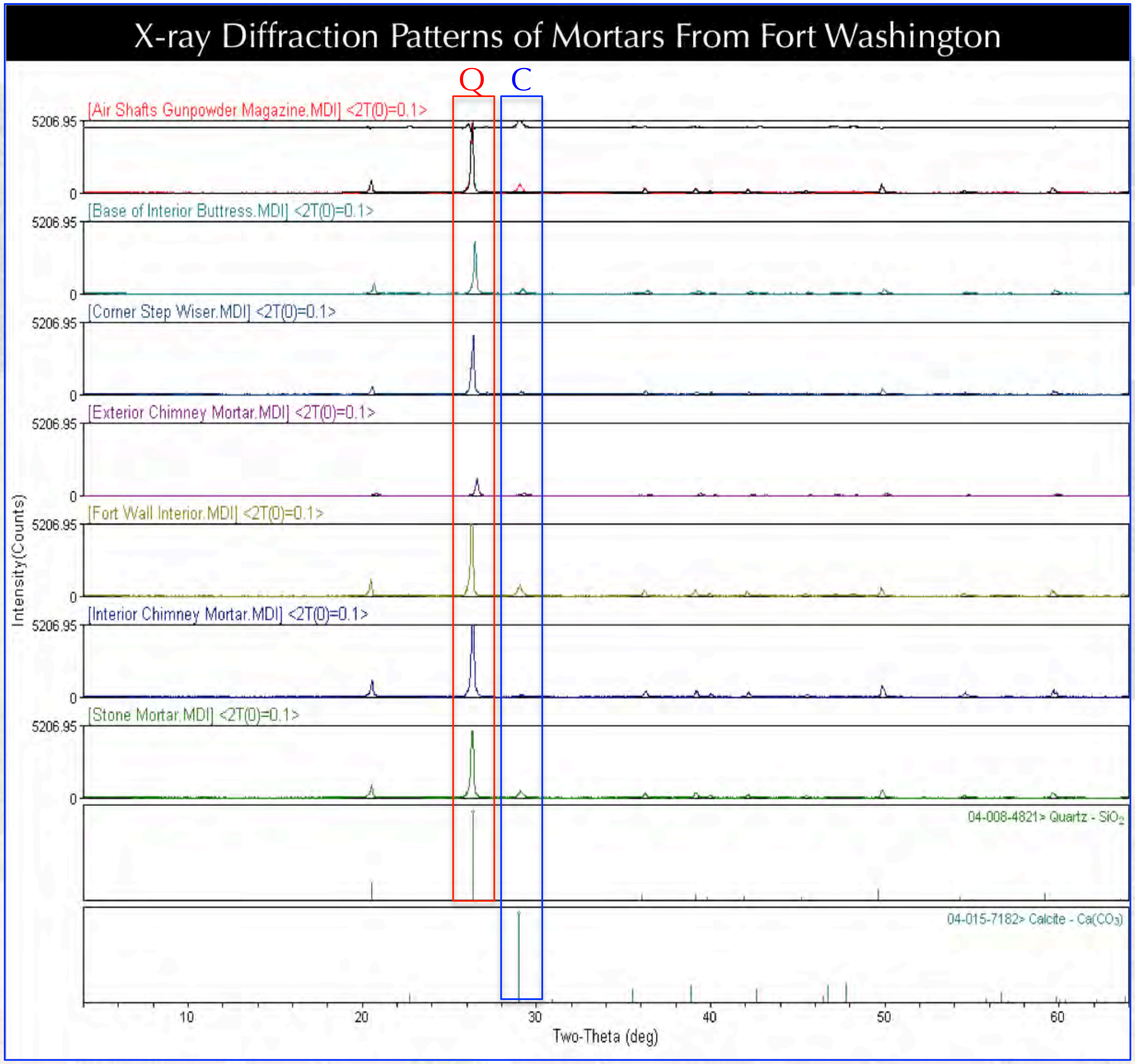



Qualitative and Semi-Quantitative Estimates of Minerals From

- Sand
- Binder
- Salts
- Pigments

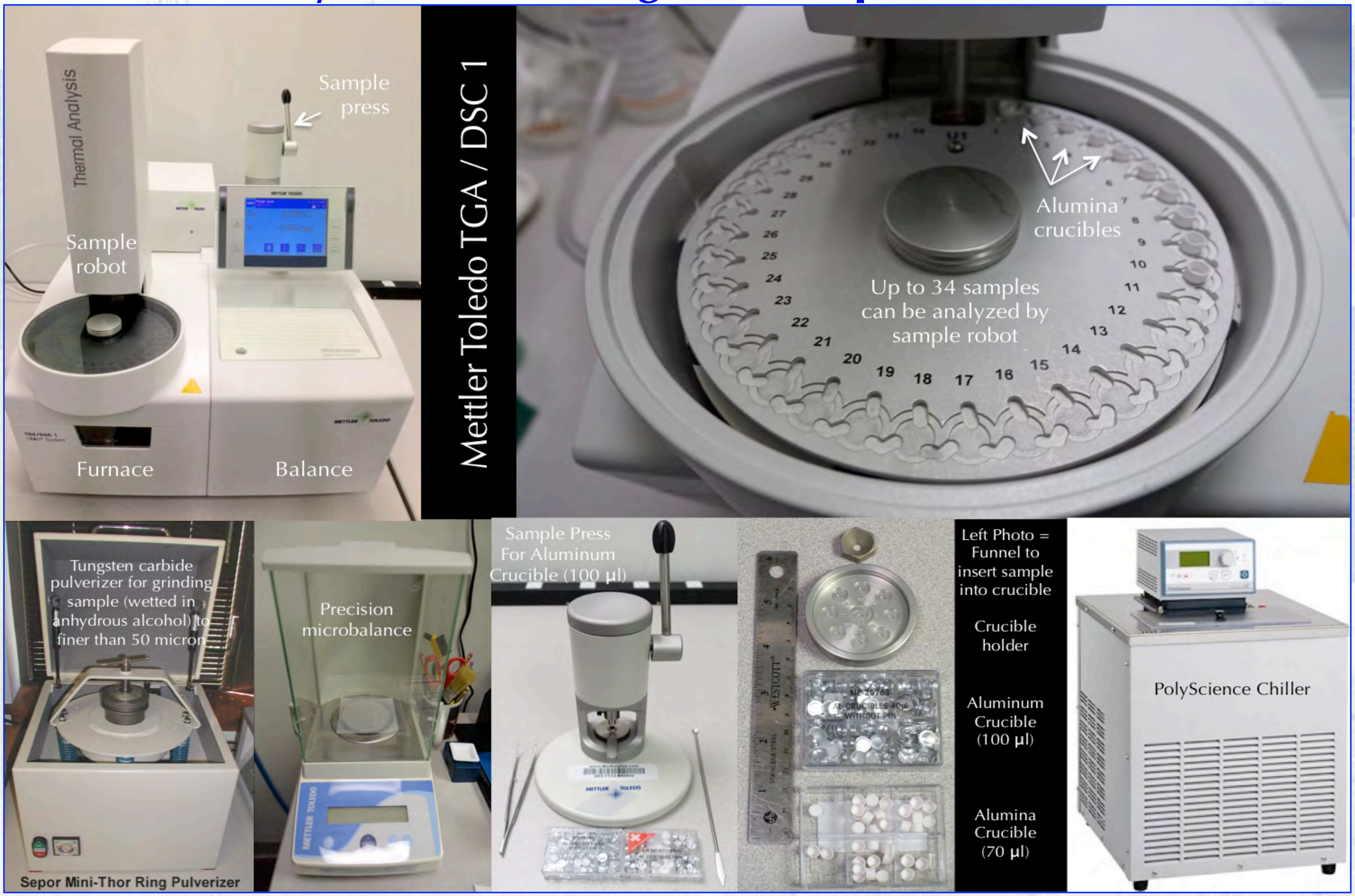


# Relative Proportions Of Quartz and Calcite In Different Mortars From Fort Washington



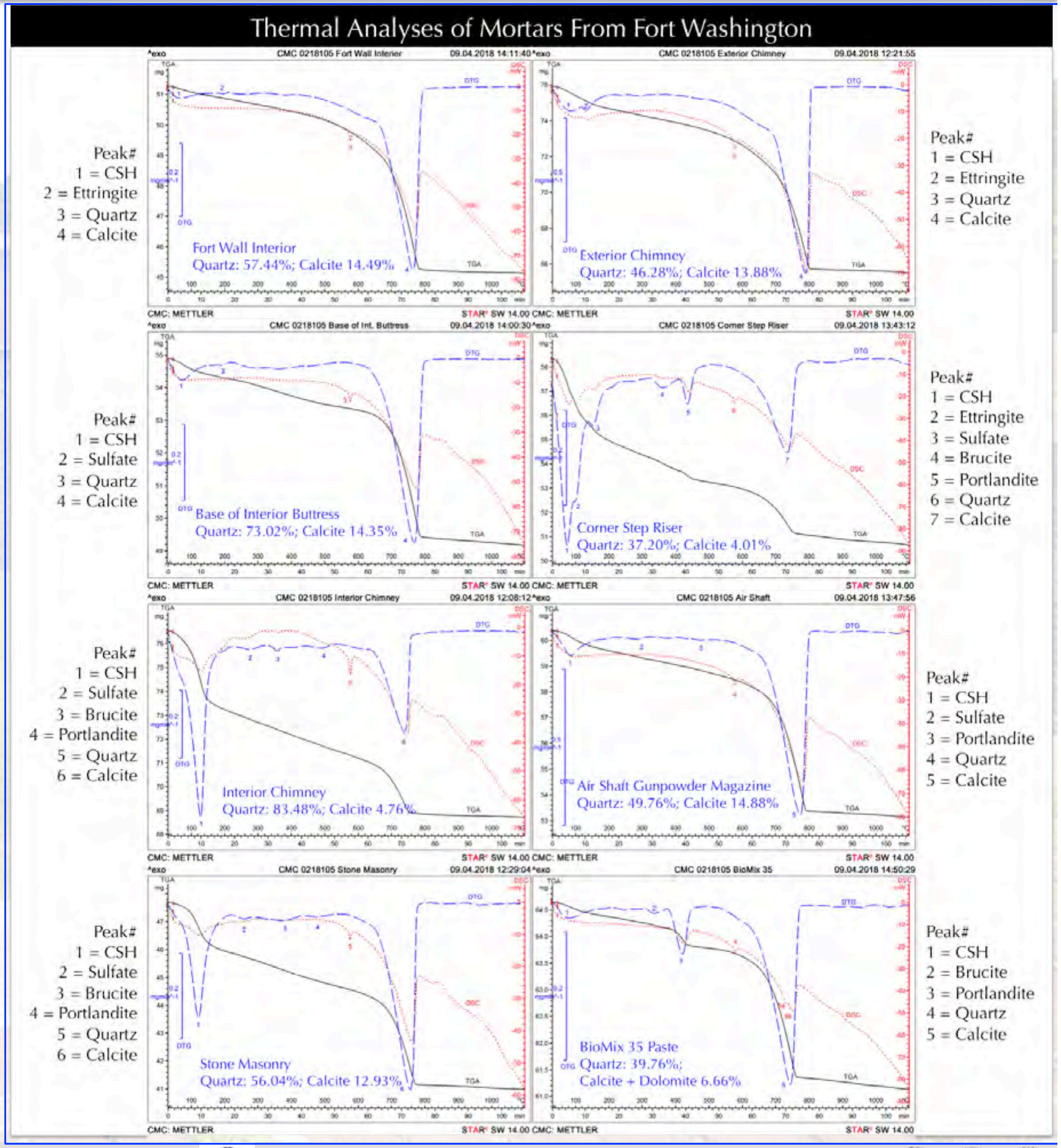
# X-ray Fluorescence – Chemical Composition of Mortar

# Thermal Analysis – Mineralogical Composition of Mortar

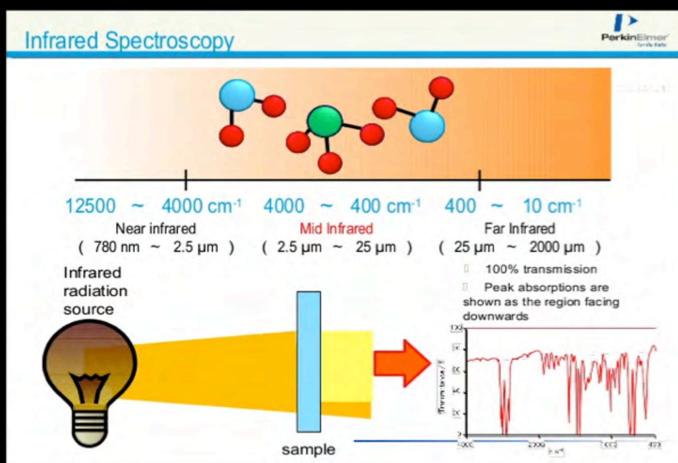


# Thermal Analyses Of Mortars From Fort Washington

- Lime mortars from Fort Wall, Interior Buttress have main peaks for Calcite and Quartz
- Altered Lime mortars from Interior Chimney, and Stone Masonry have main peaks for Hydrate water along with Calcite and Quartz
- Slag Cement – Lime mortar from Exterior Chimney has main peaks for Calcite and Quartz
- Blended Cement – Lime mortar from Corner Step Riser Terri Plane has most complex endotherms
- Masonry Cement mortar from Air Shafts Gunpowder has main peaks for Calcite and Quartz
- BioMix 35 has main peaks for Brucite, Portlandite, Calcite, Dolomite, and Quartz

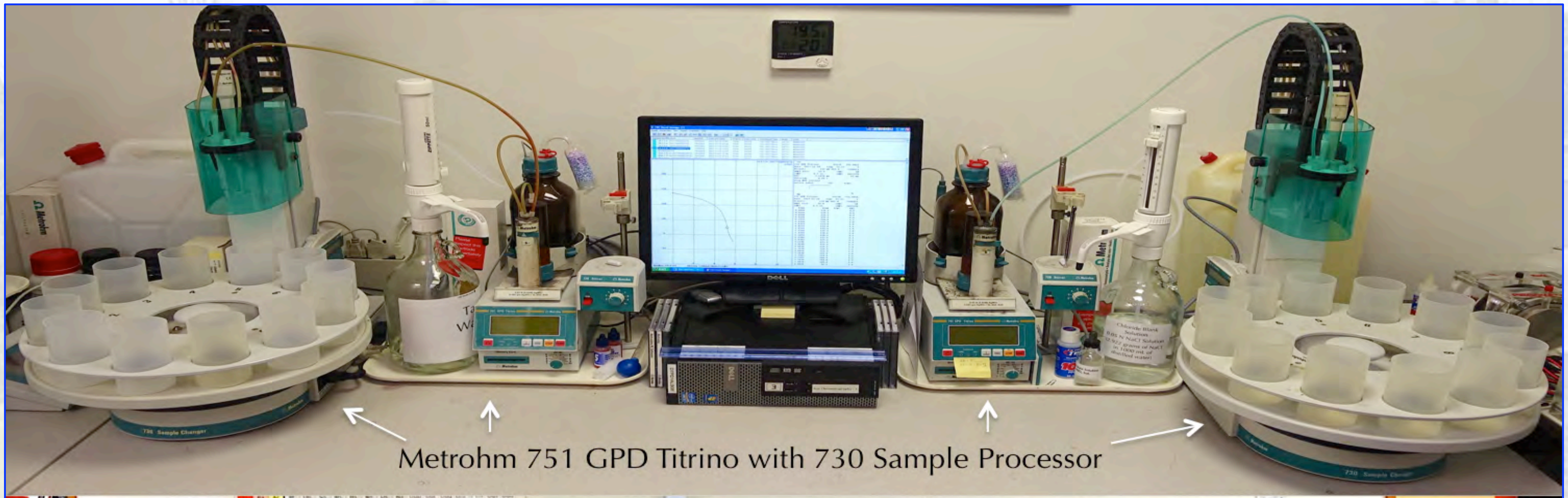


# Infrared Spectroscopy

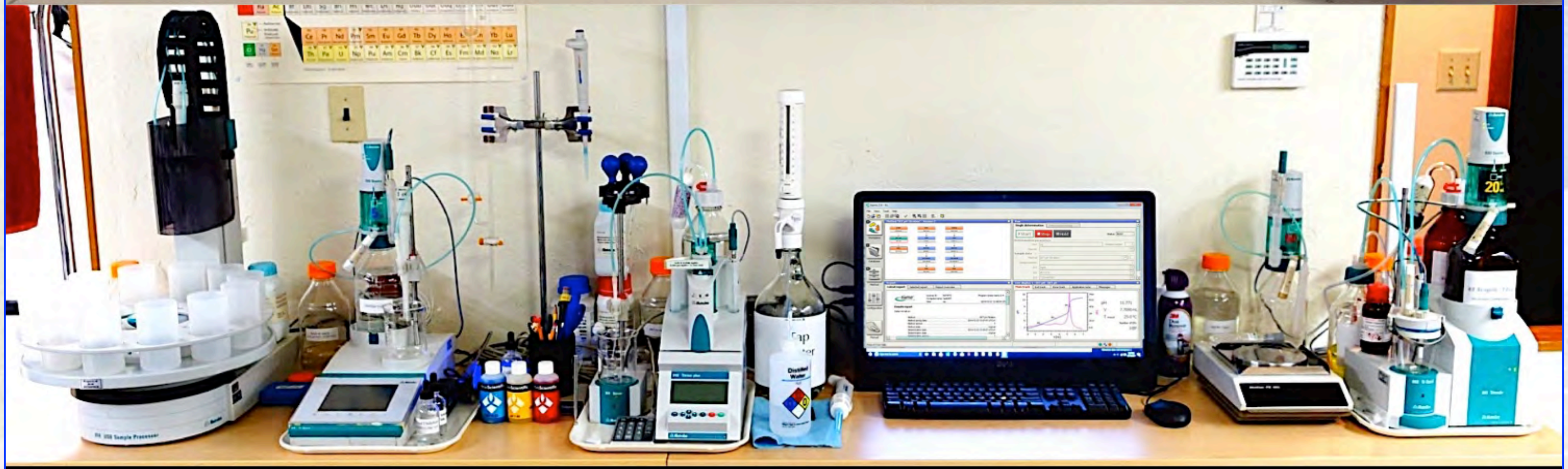




# Chloride Analysis



Metrohm 751 GPD Titrino with 730 Sample Processor



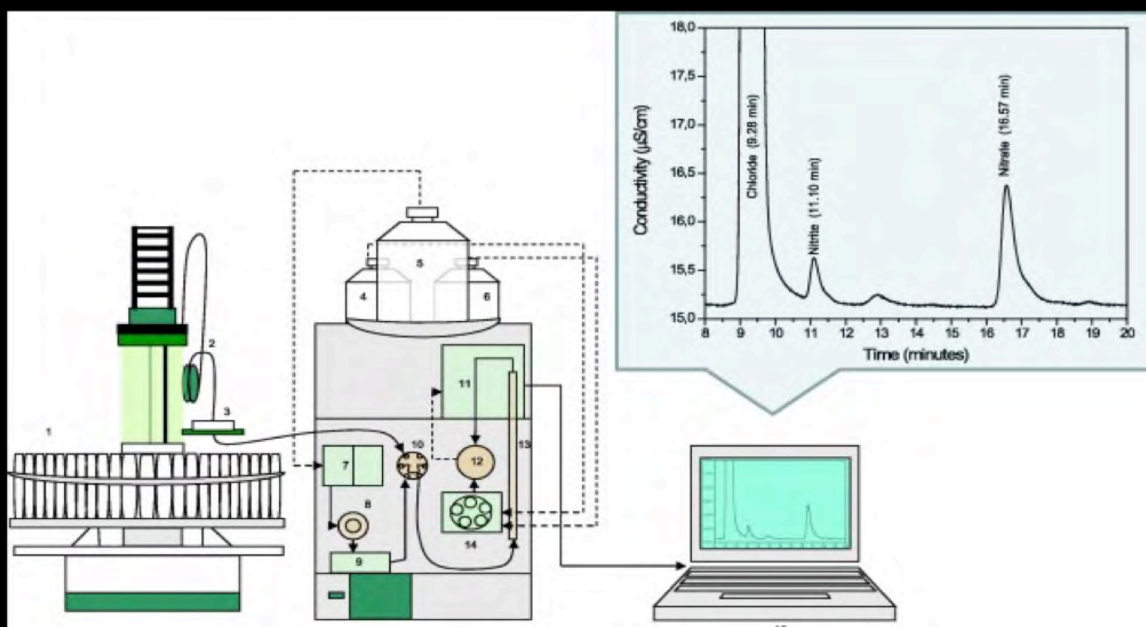
Metrohm 916 Ti-Touch with 814 USB Sample Processor for Chloride Titration

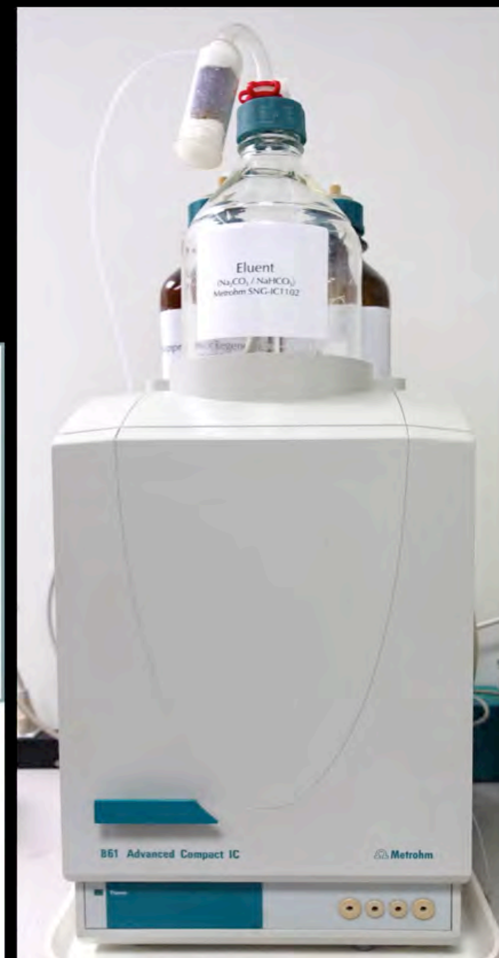
Metrohm 848 Titrino Plus for pH & Acid-Base Titration

Metrohm tiamo and tiBase software for titration

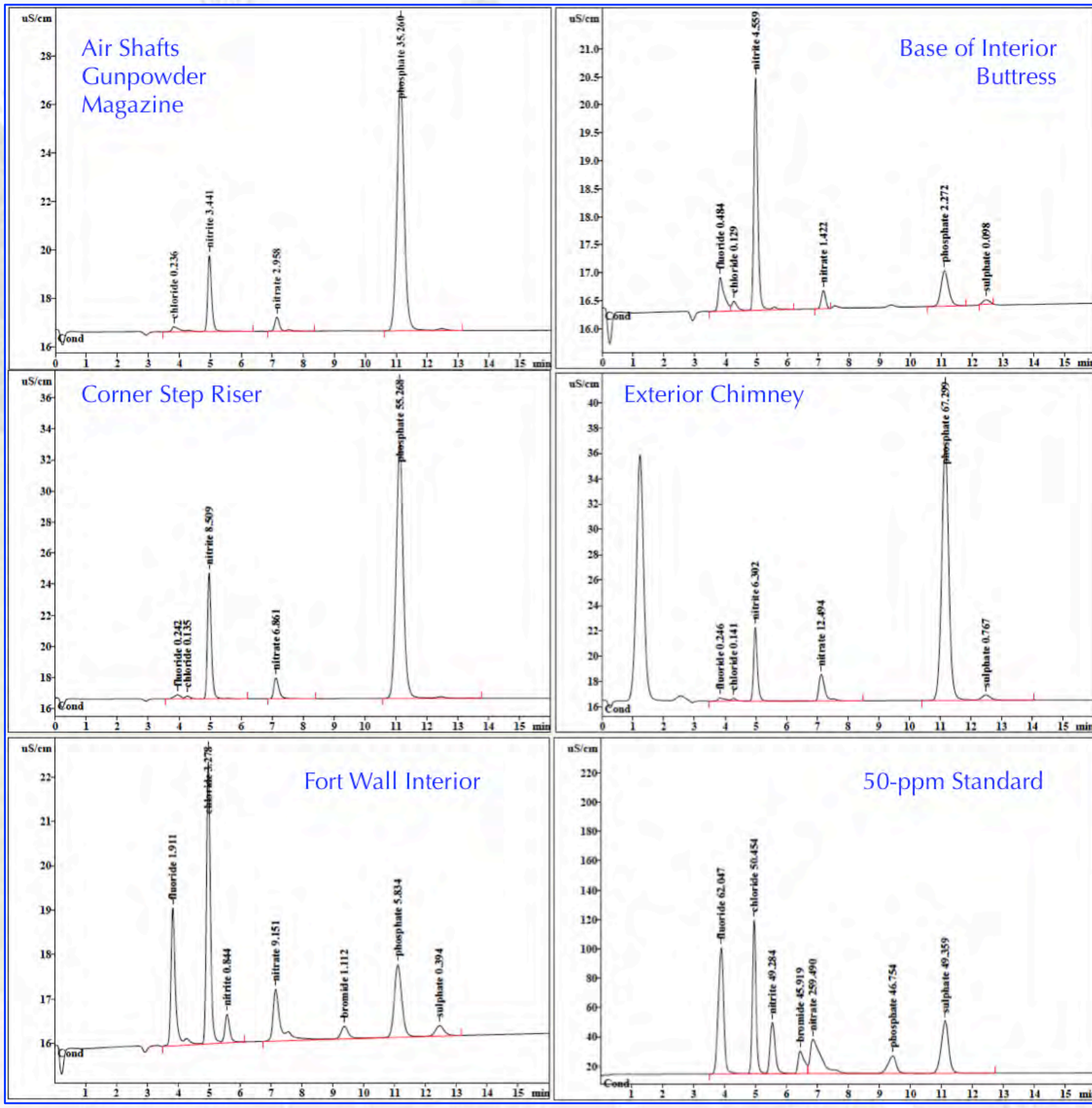
Metrohm 841 Titrando for KF, Chloride, & Sulfate Titration

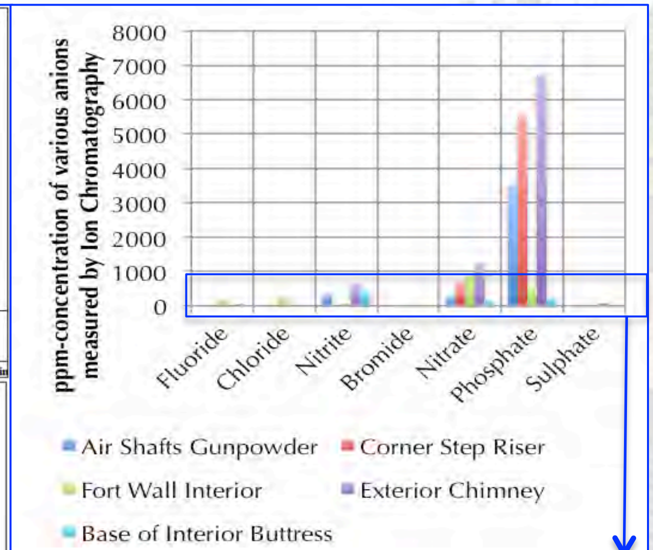
# Ion Chromatography
## (Chloride, Sulfate, Nitrate, Phosphate Salts)

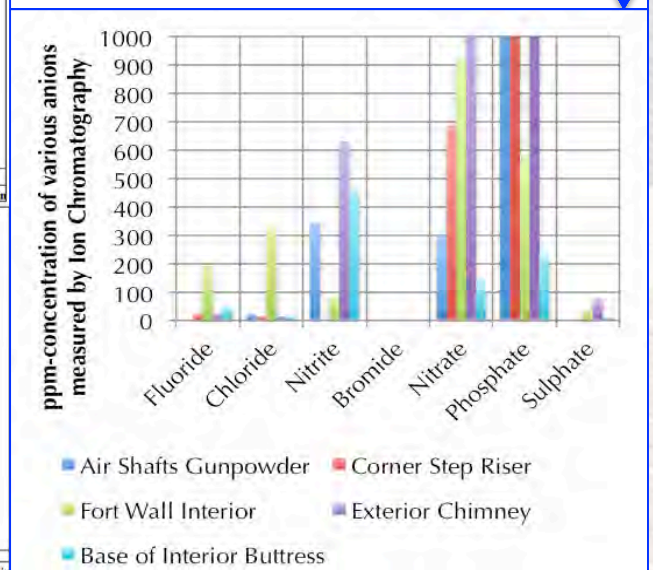


# Water-Soluble Salts in Fort Washington Mortars From Ion Chromatography



# Making Sense From XRF - Chemical - XRD – Thermal Data

| Data | Method | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | XRF | 69.1 | 75.5 | 74.8 | 65.2 | 68.6 | 57.3 | 65.1 | 62.2 | 67.7 | 63.8 | 51.2 | 69.5 | 78.4 | 1.24 |
| $Al_2O_3$ | XRF | 1.65 | 2.3 | 2.22 | 1.45 | 1.61 | 3.46 | 2.84 | 6.16 | 6.89 | 1.55 | 1.91 | 4.22 | 1.72 | 0.913 |
| $Fe_2O_3$ | XRF | 1.43 | 2.18 | 1.49 | 1.37 | 1.75 | 2.13 | 2.19 | 2.14 | 2.15 | 2.26 | 3.07 | 1.35 | 1.01 | 1.16 |
| CaO | XRF | 14.4 | 9.33 | 4.49 | 11.8 | 14.5 | 17.8 | 14.1 | 14.1 | 12.3 | 12.0 | 13.6 | 12.2 | 9.84 | 36.7 |
| MgO | XRF | 1.38 | 1.72 | 3.06 | 3.31 | 1.47 | 1.44 | 1.23 | 4.02 | 1.26 | 0.637 | 1.48 | 2.81 | 3.77 | ND |
| $Na_2O$ | XRF | ND | ND | ND | ND | ND | ND | ND | 1.25 | 1.4 | ND | ND | 2.85 | 0.093 | ND |
| $K_2O$ | XRF | 0.507 | 0.588 | 0.111 | 0.099 | 0.239 | 0.738 | 0.865 | 2.06 | 2.27 | 0.315 | 0.56 | 0.917 | 0.101 | 0.598 |
| $TiO_2$ | XRF | 0.188 | 0.239 | 0.114 | 0.127 | 0.37 | 0.604 | 0.578 | 0.2 | 0.155 | 0.435 | 0.955 | 0.112 | ND | 0.094 |
| $P_2O_5$ | XRF | 0.046 | 0.127 | 0.103 | 0.042 | 0.049 | 0.081 | 0.101 | 0.081 | 0.087 | 0.026 | 0.012 | 0.292 | 0.044 | 0.226 |
| $SO_3$ | XRF | ND | ND | ND | ND | 0.907 | 0.456 | 0.1 | 0.625 | ND | 4.55 | 6.63 | 0.298 | 0.038 | 0.489 |
| Balance | XRF | 11.6 | 8.34 | 14 | 16.9 | 10.5 | 16 | 12.8 | 7.16 | 6.06 | 14.4 | 20.5 | 5.42 | 4.95 | 57.8 |
| LOI @ 110°C 550°C 950°C | Wet | 4.0 | 1.8 | 2.7 | 4.6 | 2.7 | 8.9 | 4.5 | 0.6 | - | 0.39 | 1.90 | - | - | 4.8 |
| | | 3.4 | 2.8 | 4.9 | 5.4 | 2.4 | 3.7 | 2.2 | 2.8 | - | 2.00 | 4.10 | - | - | 8.6 |
| | | 8.6 | 6.1 | 3.8 | 8.0 | 10.1 | 3.9 | 8.0 | 5.2 | - | 7.20 | 7.40 | - | - | 28.9 |
| Acid-Insoluble Residue (%) | Wet | 68.6 | 74.7 | 76.3 | 64.3 | 63.9 | 57.8 | 66.8 | 65.5 | - | 74.4 | 62.5 | - | - | 0.67 |
| | | 52.4 | 53.9 | - | - | - | 53.7 | 61.8 | - | - | | | - | - | - |
| Soluble Silica, wt.% | Wet | 3.33 | 2.13 | 8.55 | 7.54 | 9.21 | 11.67 | 7.37 | - | - | | | - | - | - |
| Quartz | XRD | 85.2 | 88.5 | 96.6 | 93.8 | 82.5 | 91.7 | 83.0 | - | - | 66.9 | 63.2 | - | - | 2.8 |
| | TGA/DSC | 57.4 | 73.0 | 83.5 | 56.0 | 46.3 | 37.2 | 49.7 | - | - | - | - | - | - | - |
| Calcite | XRD | 14.8 | 11.5 | 3.4 | 6.2 | 17.5 | 8.3 | 17.0 | - | - | 15.7 | 29.5 | - | - | 26.2 |
| | TGA/DSC | 14.5 | 14.3 | 4.7 | 12.9 | 13.8 | 4.0 | 14.8 | - | - | - | - | - | - | 32.4 |

1–4: Original (lime) mortars of Fort Washington
5–7: Pointing (cement) mortars of Fort Washington
8: Rosendale 12M
9: BioMix 35
10: Historic Non-hydraulic Lime mortar
11: Historic NC-Lime mortar
12: Fort Sumter
13: Fort Moultrie
14: Fort Zachary Taylor

# Mix Calculations – From Petrography, Chemical, Thermal Data

## Steps Followed During Laboratory Testing of Hardened Mortar

### STEP 1

Visual Examinations
Photographs
Mortar Petrography
- Sand Type
- Sand Mineralogy, Microstructure
- Sand grain-size distribution
- Sand size, shape, color, gradation, distribution, soundness, reactivity
- Binder Mineralogy
- Binder Type(s)
- Mortar Type

*All from*
- Optical Microscopy
- SEM-EDS
- XRD

→

### STEP 2

Mortar Chemistry
- Acid-digestion for acid-insoluble residue content (siliceous component of sand; silt and clay residue in a mortar with calcareous sand)
- Wet chemistry (Cold-HCl and hot-NaOH digestion) followed by instrumental analysis (XRF, AAS, ICP) for soluble silica content of mortar
- Instrumental analysis (XRF, AAS, or ICP) for bulk oxide compositions of mortar
- Free and Combined Water, & Carbonation from Losses on Ignition

→

### STEP 3

Mortar Mineralogy from
- X-ray diffraction (for sand content, salts, clay, secondary deposits, binder mineralogy, etc.
- Thermal analysis (hydrous phases, CSH, sulfates, hydroxides, e.g., brucite, portlandite, carbonates, e.g., fine-grained carbonated paste, coarse calcite, dolomite, etc.)

→

### STEP 4

Methods of calculations of relative volumes of sand and binders

Assumed Compositions of the Binder Components
- Lime
- Historic Binder
- Portland Cement
- Masonry Cement
- Slag Cement
- Natural Cement

Assumed Densities of Mortar Ingredients

→

### STEP 5

Calculations of mix proportions of mortar from determined compositions of mortar and assumed compositions and densities of sand and binder

- Non-hydraulic Lime : Sand
- Hydraulic Lime : Sand
- Natural Cement : Sand
- Natural Cement : Lime : Sand
- Portland Cement : Lime : Sand
- Masonry Cement : Sand
- Final Mortar Type

Petrography → Chemistry → XRD, Thermal → Assumptions → Mix Calculations

SPHC6

# Mix Calculations Of Modern Masonry Mortars 1

# Problems in Mix Calculations of Historic Mortars 2

- Alterations 3
- Unknown Binder Composition
- Pozzolans 4

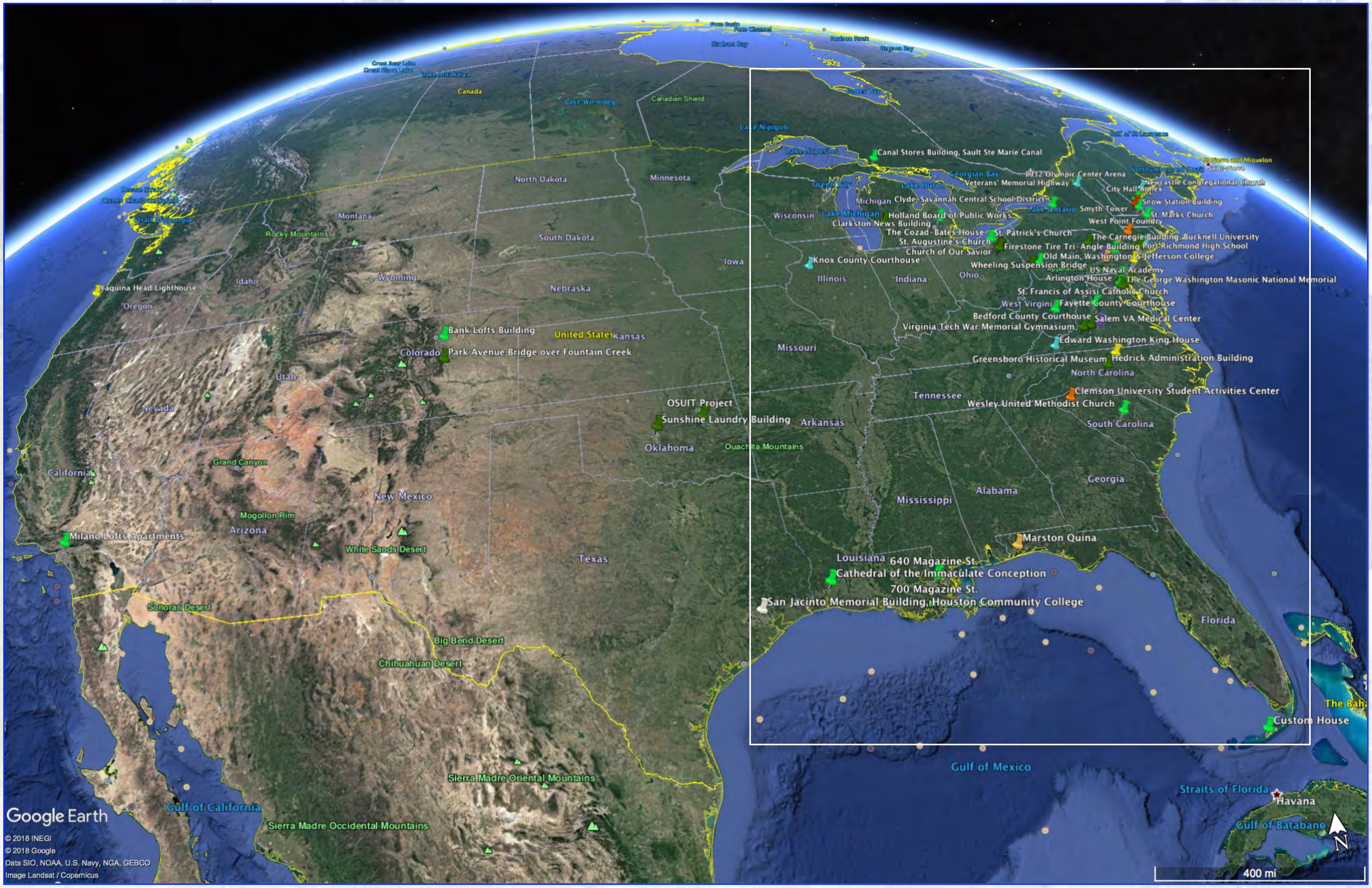
| Binders and Sand | Assumed Compositions and Methods of Calculation | Assumed Bulk Density (lbs./ft$^3$) |
|---|---|---|
| High-Calcium Non-hydraulic Lime | [$CO_2$ data from loss on ignition at 950°C divided by 0.594], where 0.594 is ratio of molecular weights of $CO_2$ to $Ca(OH)_2$ i.e. 44/74.09 | 40 |
| Magnesian Non-hydraulic Lime | [100 times (brucite content in mortar from TGA/DSC/5.8)], assuming magnesian lime has 71% CaO and 4% MgO, or 5.8% brucite, since ratio of molecular weights of brucite to MgO (58.32 / 40.32) is 1.447 | 40 |
| Dolomitic Non-hydraulic Lime | [100 times (brucite content in mortar from TGA or DSC divided by 42)], assuming dolomitic lime has 41% CaO and 29% MgO, or 42% brucite, since ratio of molecular weights of brucite to MgO (58.32 / 40.32) is 1.447 | 40 |
| Calcitic or Magnesian Hydraulic Lime | [100 times (soluble silica in mortar/0.07] assuming hydraulic lime has 7% $SiO_2$, or average $SiO_2$ content calculated from SEM-EDS data of paste | 40 |
| Dolomitic Hydraulic Lime | [100 times (soluble silica in mortar/0.07] assuming hydraulic lime has 7% $SiO_2$, or average $SiO_2$ content calculated from SEM-EDS data of paste<br>Or<br>[100 times (brucite content in mortar from TGA/DSC/38)], assuming lime has 38% CaO and 26% MgO, or 38% brucite, since ratio of molecular weights of brucite to MgO (58.32 / 40.32) is 1.447 | 40 |
| Portland Cement in Cement-Lime Mortar | 100 × [Soluble silica in mortar / 21.0], assuming 21% silica in Portland cement | 94 |
| Calcitic Lime in Portland Cement-Lime Mortar | Lime content = 1.322 × CaO assignable to Lime, which is [CaO content of Mortar – (CaO assignable to portland cement, which is portland cement content × 0.635, assuming 63.5% CaO in portland cement)], where the factor 1.322 comes from ratio of molecular weights of $Ca(OH)_2$ to CaO i.e. 74.09/56.03 | 40 |
| Dolomitic Lime in Portland Cement-Lime Mortar | 100 times (brucite content in mortar from TGA/DSC/42)], assuming dolomitic lime has 41% CaO and 29% MgO, or 42% brucite, since ratio of molecular weights of brucite to MgO (58.32 / 40.32) is 1.447 | 40 |
| Slag Cement | 100 × [Soluble silica in mortar / 27.0], assuming 27% silica in slag cement, or average $SiO_2$ content determined from SEM-EDS data | 90 |
| Natural Cement | 100 × [Soluble silica in mortar / 20.0], assuming 20% silica in natural cement, or average $SiO_2$ content determined from SEM-EDS data | 75 |
| Masonry Cement | (i) 100 – [Sand + Total Water], if sand is all siliceous and hence sand content is obtained directly from the acid-insoluble residue content;<br>(ii) PC content (from the soluble silica data) divided by factor 0.50, 0.66, or 0.75 with an assumed masonry cement type of N, S, or M, respectively. MC Type (M, S, N) is determined from PC/MC = 0.75 (for M), 0.66 (for S), or 0.50(for N) – if sand has calcareous component | 70 (Type N)<br>75 (Type S)<br>80 (Type M) |
| Gypsum Plaster | Gypsum content from XRD or thermal analysis times 0.843 (ratio of molecular weight of plaster to gypsum) | 70 |
| Sand | If sand contains acid-soluble component (carbonates),<br>Sand content = 100 – [Total Binder + Total Water from LOI to 550°C i.e. free plus hydrated water];<br><br>If sand has no acid-soluble component (i.e. all siliceous sand)<br>Sand content is directly obtained from the acid-insoluble residue content | 80 |

# Mix Calculations

| Locations | Fort Wall Interior | Base of Interior Buttress | Interior Chimney | Stone Masonry |
|---|---|---|---|---|
| Mortar Type | Least Altered *Hydraulic Lime – Silica Sand Mortar* | Moderately Altered *Hydraulic Lime – Silica Sand Mortar* | Highly altered *Hydraulic Lime – Silica Sand Mortar* | Highly altered *Hydraulic Lime – Silica Sand Mortar* |
| Calculated Hydraulic Lime: Sand, by volume | 1-part lime to 2.2-part sand | 1-part lime to 2.0-part sand | 1-part lime to 1.8-part sand | 1-part lime to 1.5-part sand |
| Proposed Lime-to-Sand Proportions, by Volume | ***1-part hydraulic lime to 2-part sand, by volume*** | | | |
| Suggested Pointing Mortars | BioMix 35 or 50 (Std. White to Std. Buff variety to try and match), or, 1-part BioLime NHL 3.5 (Buff to White variety to mix and match) to 2 to 2.5-part silica sand | | | |

| Locations | Exterior Chimney | Corner Step Riser Terri Plane | Air Shafts Gunpowder Magazine |
|---|---|---|---|
| Mortar Type | Slag Cement – Lime – Silica Sand Mortar | Blended Cement (Portland cement, Fly Ash) – Lime – Limestone fines – Silica Sand Mortar | Masonry Cement (Portland cement, lime, limestone fines) – Silica Sand Mortar |
| Calculated Binder: Sand, by volume | 1 : 2.3 | 1 : 2.2 | 1 : 2.2 |
| Proposed Binder-to-Sand Proportions, by Volume | ***1-part binder to 2½-part sand, by volume*** | | |
| Suggested Repointing Mortars | Slag cement – Lime Mortar; ASTM C 270 Type N or S Cement-Lime Mortar; Natural Cement-Lime Mortar | ASTM C 270 Type S Cement-Lime Mortar | ASTM C 270 Type N Masonry Cement Mortar |

# CMC's Historic Mortar Testing from East to West Coasts



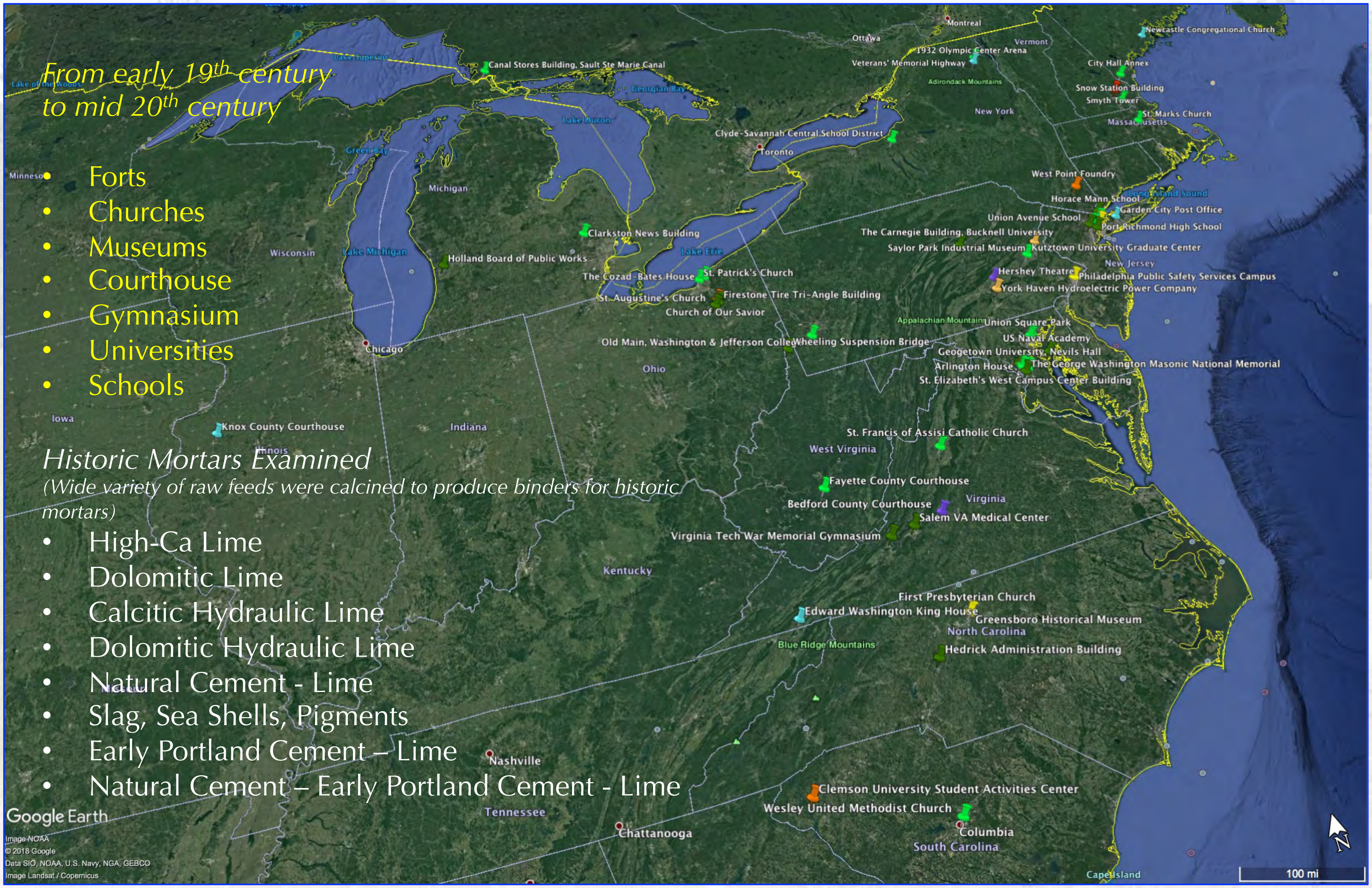
# CMC's Historic Mortar Testing From the East Coast

*From early 19th century to mid 20th century*

- Forts
- Churches
- Museums
- Courthouse
- Gymnasium
- Universities
- Schools

*Historic Mortars Examined*
*(Wide variety of raw feeds were calcined to produce binders for historic mortars)*

- High-Ca Lime
- Dolomitic Lime
- Calcitic Hydraulic Lime
- Dolomitic Hydraulic Lime
- Natural Cement - Lime
- Slag, Sea Shells, Pigments
- Early Portland Cement – Lime
- Natural Cement – Early Portland Cement - Lime



# CMC's Historic Mortar Testing From Various Forts

Fort Sumter (Charleston, SC)
*Natural cement concrete*
*Natural cement – lime mortar, circa 1850*

Fort Mott (Pennsville, NJ)
*Natural cement – lime mortar, circa 1872*


Fort Jackson (Columbia, SC)
*Masonry cement pointing mortar, circa 2009*

Fort Moultrie (Sullivan's Island, SC)
*Dolomitic lime mortar, circa 1812*

Fort Zachary Taylor East (Key West, FL)
*Natural cement – lime - beach sand mortar, circa 1845*

Fort Washington (Maryland)
*Hydraulic lime mortar, circa early 1800s*

# CMC's Historic Masonry Testing From Various Buildings

Great Pyramid of Giza
2560 BC.
Limestone casing stones

U.S. Capitol
Underground tunnels

St. Elizabeth's West Campus,
Washington D.C.
1850s Natural cement-lime mortars

Fayette County Courthouse,
Fayetteville, WV
Lime-pozzolan, hydraulic lime mortar


Virginia Tech War Memorial,
Blacksburg, VA
1920s cement-lime mortar

Saylor Park Cement Kilns,
Coplay, PA
1890s early Portland cement-lime mortar

Clemson University,
Clemson, SC
1900s natural cement-lime

Canal Stores Building, Sault
Ste. Marie Canal, Canada
1895s lime mortar

City Hall, Rochester, NY
1905 lime mortar

Kutztown University, PA
1880s hydraulic lime mortar

Church of Our Savior, Akron, OH
1895 natural cement-lime

Hershey Theatre, Hershey, PA
1930s slag cement-lime mortar

# Think CMC For your next Laboratory Testing Of Historic Mortars

"CMC employs an impressive array of technological tools to provide comprehensive analyses for historic masonry mortars. They also deliver results on a reliable schedule to meet the time pressure of our clients' projects."

**Mike Edison**
Edison Coatings, Inc.

"CMC, Inc. is an excellent resource for petrographic analysis of historic mortars. Mortar analysis for historic buildings must go beyond just understanding the components of the mortar to understanding how those components are contributing to the success or failure of that mortar over time. This is where CMC, Inc. succeeds in guiding architects towards the right restoration mortar mix. The reports are thorough yet concise with reliable turn-around times. Dr. Jana is always willing to discuss the findings and his clients can count on his expertise."

**Amanda Edwards**
Sr. Architectural Conservator

Acid Digestion ($350-500)

$2000

Comprehensive Analysis ($1500-$2750)