Materials Research Series

Standard Practice for Determining the Components of Historic Cementitious Materials

2002-20

National Center for Preservation Technology and Training
Technology Serving the Future of America's Heritage
www.ncptt.nps.gov/products

Standard Practice for Determining the Components of Historic Cementitious Materials

Elizabeth S. Goins
Laboratory for the Analysis of Cultural Materials
University of Delaware

This Project was made possible by grants from NCPTT and the Samuel H. Kress Foundation. Special thanks to Bob Bennett at the Lime Centre, UK for supplying traditional mortar materials.

US Department of the Interior
National Park Service
National Center for
Preservation Technology and Training
Publication No. 2002-20

This is the working copy of the new protocol for the analysis of historic mortars. This will be sent out to reviewers in the field for comments. Also, the methods are to be refined from further laboratory studies of weathered samples.

Elizabeth Goins
Goinses@shore.intercom.net

INTRODUCTION:

The analysis of historic mortars has, in the past, been dominated by traditional wet chemical methods that determine the bulk oxide composition. An increasing number of analysts are turning to microscopical methods in order to study the interaction between aggregate, relict hydraulic grains, and matrix. Analyses of polished sections provide information on the mineral phases, interactions and microstructure that are responsible for imparting properties characteristic to cement'. The purpose of the standard practice is to combine the best methods currently employed and to adapt them to the analysis of historic cementitious materials.

There can not be too much emphasis placed on the importance of careful sample taking. "The quality of the conclusions reached in aninvestigation depend on the quality and relevance of the samples taken.. .[2] Prior to the removal of material for samples it is imperative that clear objectives must be formed in order to direct the investigation and to remove a minimum of material. A basic assumption of this procedure is that experienced persons, ideally involved in the pre-analysis of the structure to determine sampling strategy, will be carrying out the sample selection and removal.

The purpose of this method is to insure consistent analytical standards within the study of historic mortars for academic study and conservation purposes. Conservation and restoration may involve the identification of aggregate and binder, mineralogy, analysis of decay mechanisms and salt content. It is not within the scope of this work to determine original mortar constituent volume proportions.

Scope:

This test method is for the determination of aggregate, air voids, cement, pozzolana and hydraulic materials of historicmortar by petrographic analysis.

Referenced documents:

ASTM C-856-95 Standard Practice for Petrographic Examination of Hardened Concrete.

ASTM C 457-90 Practice for Microscopical Determination of Air-Void Content and Parameters of the Air-Void System in Hardened concrete

ASTM C294-92 Descriptive Nomenclature of Constituents of Natural Mineral Aggregates

ASTM C295-92 Guide for Petrographic Examination of Aggregates for Concrete.

ASTM C1084-92 Standard Test Method for Portland-Cement Content of Hardened Hydraulic-Cement Concrete

ASTM C114-85 Test Methods for Chemical Analysis of Concrete.

St. John, D., Poole, A.W. and Sims, I. Concrete Petrography. (John Wiley & Sons, New York, 1998).

Campbell, D.H. Microscopical Examination and Interpretation of Portland Cement and Clinker (Portland Cement Association, Skokie, Illinois, 1986).

Terminology:

Definitions

Air content-The proportion of the total volume of the concrete that is comprised of air voids.

Air voids - Entrapped and entrained air or space enclosed by the cement paste and filled with air or other gas before setting. This does not include porosity.

Hydraulic lime - Cement that will harden under water. Defined by the setting mechanism, different from carbonate cements, hydraulic lime sets by the formation of hydrated calcium silicate compounds present as impurities or deliberately added components.

Cement- A material for uniting other materials or articles. It is generally plastic at the time of application but hardens when in place. The matrix portion of any cementitious material or "neat" cement paste

Concrete - A mixture of cement, sand and gravel or stone chips with water in varying proportions according to use.

Mortar- A pasty substance formed normally by the mixing of cement, sand and water, or cement, lime. sand and water in varying proportions. Used normally for the binding of brickwork or masonry

Non-hydraulic lime- A cement that contains less than 5% of potentially hydraulic materials. Also known as fat lime (95%+ pure lime).

Semi-hydraulic lime- A cement that contains at least 5% of a potentially hydraulic material.

Lime- Limestone heated to at least 825°C to produce CaO (quicklime, caustic lime, unslaked lime)

Portland Cement- Ordinary Portland Cement (OPC) or Type I.

Cementitious material- Ambiguous term for all things "cementitious" - lime based cement, Portland cement, proto- and meso- cements, mortars, grouts etc

Lime putty- Hydrated (slaked) and aged lime.

Summary of Test Method:

Samples of mortar are impregnated with epoxy resin and sawn. The sections are prepared by careful grinding and polishing in a non-aqueous media. The polished surfaces are studied with at least 50x magnification and features of interest are measured by traditional point counting techniques or image analysis. More detailed studies use auxiliary methods like Scanning Electron Microscopy (SEM) coupled with Back Scattered Electron Imaging (BEI) to evaluate the hydraulic content. X-Ray Diffraction (XRD) is also used for determination of some crystalline components.

Significance and use:

This test may be used to characterize historic mortars. The petrographic analysis is based on the assumptions typically stated for modal analysis in order to satisfy the Delesse (4) relationship.

1. Samples are random
2. Sample sizes are large enough to include variations present within the material.

DISCUSSION OF PROCEDURES

Selection of Test Specimens

The first issue in deciding on a sampling strategy is to determine the objective of the analysis. Analytical procedures to be used should be chosen after the questions that the analysis hopes to address are dearly formulated. Typically, the analysis is either focused on the identification of the original components, decay mechanisms, or key parameters on which to base conservtition treatment.

1.) Characterization of the material to identify original components: Samples should be chosen from sheltered and protected areas. Samples should also be collected randomly from other areas for comparison.

2.) Characterization of local areas: The samples would be collected from the area(s) exhibiting the feature of interest. Samples should also be collected randomly from other areas for comparison.

3.) General characterization of the material: Samples should be chosen that most closely reflect the middle ground. Areas that should not be included in such a study would be those showing severe deterioration, loose or detached pieces. Likewise, pristine "like new" surfaces would also be avoided. This type of study might be conducted in order to help identify physical parameters, like porosity, for selection of repair materials.

In many cases, combinations of analytical and sampling strategies are necessary. For example, a general characterization of the cementitious material and a local study of a particular area may be called for. In this case, two sampling strategies should be conducted.

The method of sample determination must also be chosen and noted in the report. If random samples are to be taken from an area they must be truly random. This does not mean that a person may walk up to the area and choose in a seemingly random fashion.

Factors that may influence choice are numerous. One method of random sampling is to divide the area up into a grid. Numbers are then assigned to grid areas and these numbers are then randomly chosen, (methods may include use of a calculator or by tearing up bits of paper with the numbers on them and drawing them from a hat).

The samples must be gathered in accordance with the Standard Sample Sheet (Figure 1). The minimum area per sample to be collected must be 5x the nominal or maximum grain size for all dimensions. The minimum number of samples is three per area of interest. If pre-analysis shows great heterogeneity, the number of samples must be increased. The samples may be removed by coring, sawing or with hammer and chisel. All sample strategies and methodologies must be noted on the Standard Sample Sheet for each sample.

Sample sheet

Sample Name Location ID No.

Number of samples taken from location:

Reason for selection: (random, grid, deteriorated area etc)

Method of sample removal:

Sample relationship to the object (sketch object and mark sample area)

Sample's relationship to the surface (sketch)

Distance from the surface (mm)

Description

Environmental conditions

General description of material

Figure 1: Standard Sample Sheet

Analytical Procedures and Methods

Sample Preparation

The following lists include equipment and materials generally used.

Apparatus and Materials for Sample Preparation

Diamond saw

Cutting lubricant for the diamond saw

Horizontal Lap Wheel(!;) for grinding samples

Polishing Wheel

Hot plate or oven

Abrasives - Silicon carbide grits (No. 100, 220, 320, 600, 800); optical finishing and polishing powders (1000 alumina)

lubricant for polishing (glycerin)

Glass squares - for hand finishing

Impregnating media - low viscosity epoxy

Mounting Media - Canada balsam

Microscope slides

Cover glass

INITIAL EXAMINATION

The mortar sample must be given a preliminary examination. General observations as to the fabric, nominal grain size, friability etc. of the material are to be noted. From the initial examination, the procedures to be employed in the analysis are determined. All available information regarding the sample should be reviewed and noted. A freshly broken or sawed surface should be examined under low (6-10x) magnification.

The visual examination sheet (

Figure 2) which has been modified from ASTM C 856 should be followed.

From the initial examination, several key points should be clear:

1. Matrix strength and general composition - Non or weak hydraulic limes vs. strongly hydraulic lime and Portland cements.
2. Aggregate composition - are carbonate-based aggregates present?
3. Other materials - Organic materials like straw and hair may be visible as well as clay or remnant grains of pozzolanic materials.

Most historic cementitious materials will have to be consolidated before sections are to be prepared but this is determined by sample strength and aggregate - matrix bond strength.

Depending on the research objectives determined prior to sampling, the analytical procedures may now be outlined

Aggregate		Matrix	Voids and Pores	Embedded Items
Coarse	**Fine**			
Composition Maxiumum dimension (mm) Percentage of total (%)				
Type 1. Gravel 2. Crushed Stone 3. Mixed gravel and crushed stone 4. Other (Name) 5. Pozzolan (name) 6. Mixed	Type I. Natural Sand 2. Manufactured sand 3. Mixed 4. Other 5. Pozzolan (name) 6. Mixed	• Color National Research Council Rock Color Chart; Munsell system) Color distribution 1. Mottled 2. Even 3. Gradational changes	• Approximate percentage of total, mainly spherical voids • Approximate percentage of total, many nonspherical voids • Voids Empty, filled, lined, partly filled Color change from interior surface to matrix?	Type, size, location, kinds of metal. other items (like organic materials)
If type is 1, 2 or 4: homogeneous or heterogeneous? Range of grain sizes (mm):				
Fabric (of aggregate)				
• Shape • Distribution • Packing • Grading (even, uneven, excess or deficiency of size(s)) • Direction in relation to surface (flat sides or long axes - normal to direction of placement or parallel to formed and finished surfaces	Distribution • Particle shape • Grading Preferred orientation	• Distribution - homogeneous or heterogeneous? • Fractures around or through aggregate? • Describe contact of matrix and aggregate. • Describe cracks.	• Shape • Distribution • Grading • Parallelism of long axes of irregular voids or sheets of voids; with each other; with flat sides or long axes of coarse aggregate	• Are there any voids connected with the material? Note there location in relation to the material (below, horizontal) • Are metal objects clean or corroded? Are there cracks associated with embedded material?
Sample history - list historical information available. Note approximate age, if known. Also note the general sample environment (urban vs. rural etc.).				
Condition: Note the general degree of weathering. Also, the friability or density of the sample. Give general description of color. Material strength - can you break it with your hands? Are there cracks? How are they distributed? Do they run through coarse aggregate? Are the cracks filled with anythii? Did the aggregates tear from the matrix during sawing or coring? Surface: Deposits? Any dry or wet looking areas? Rims on aggregates?				

Figure 2: Visual/Low Magnification Examination of Concrete (modified from ASTM C 856)

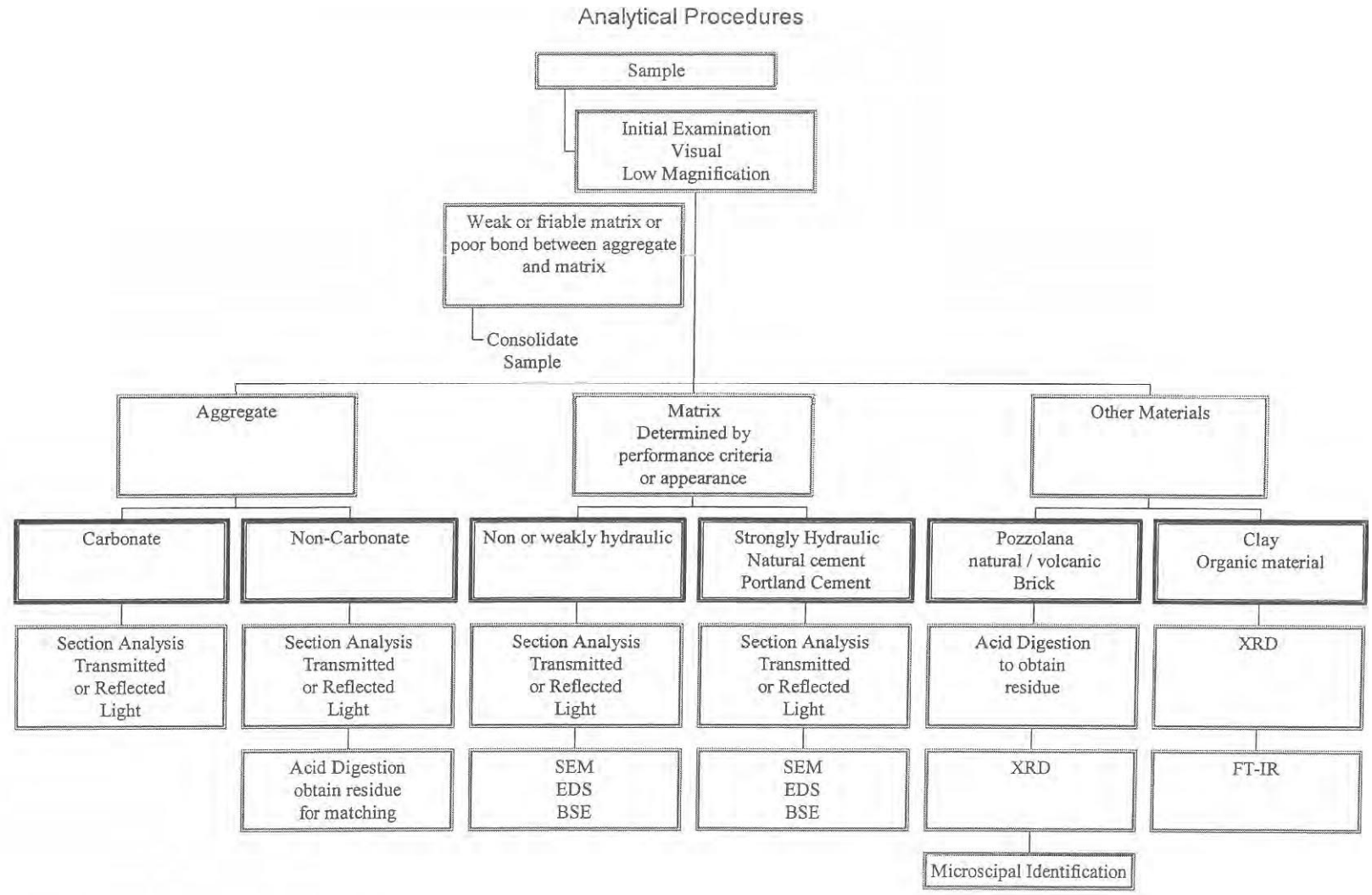


Figure 3: Chart of Analytical procedures for the study of historic cementitious materials.

SAMPLES

Samples should be taken from whole chunks or cores. The collection of broken fragments or pieces for analysis is to be avoided if at all possible as they may not be representative of the material. The ***minimum*** sample size, after processing, for analysis should be three times the nominal or maximum size of the aggregate. Ideally, the sample area should be five times the maximum aggregate size. The sample should usually be sawn or prepared perpendicular to the surface so that a cross section of the material may be studied. The location of the sample and its orientation to the core or original chunk must be noted.

CONSOLIDATION OF SAMPLES

If the specimen is weak, friable or exhibits low bond strength between the aggregate and matrix, it should be impregnated with a low viscosity epoxy resin. Place specimen in a mold or polypropylene cup coated with a realease material. Mark the orientation of the sample to the original surface. A slow curing, low viscosity epoxy resin (like Buehler's Epo Thin) should be used. Pour freshly mixed epoxy and hardener over the sample. If thin sections are to be made from the sample and the determination of its thickness is necessary, quartz grains (50-100 mesh) may be added. Thin section thickness can be calculated from the quartz of known birefringence of 0.009.

Allow the epoxy to cure. Vacuum impregnation is to be avoided as the matrix can be disrupted. The benefits of using a slow, long cure resin are that much more time is allowed for the resin to penetrate the material.

THE MAKING OF POLISHED SECTIONS, AN OVERVIEW

Sections for reflected and transmitted light and Scanning Electron Microscopy (SEM) studies are prepared in much the same way. All polishing and grinding must be carried

out with a non-aqueous lubricant. This is to prevent the washing away of water-soluble components and the etching of minerals associated with hydraulic materials.

Quantitative microscopy and photographs must include a reference to the nominal magnification or field size. The nominal magnification includes the objective, eyepiece and tube (Figure 4).

Objective	Nominal :Magnification	µm/ (micrometer) division	Field size (mm)
x2.5	x32	32.5	4.8
x6.3	x80	12.5	1.85
x16	x200	5.0	0.74
x25	x315	3.2	0.48
x40	x500	2.0	0.30
x50	x620	1.61	0.24
x100	x1250	0.80	0.12

Figure 4: Calibration of transmitted light objectives (x 10h eyepiece, x 1.25 tube factor) after St. John et al. 1998.

THE MAKING OF SECTIONS FOR REFLECTED LIGHT

Reflected light may be used to quickly determine aggregate, air void and cement proportions. Reflected light may also be used to determine particular areas for further study by x-ray diffraction (XRD) or SEM-BSE.

Saw the specimen, unless experimental objectives dictate otherwise, perpendicular to the bedding plane with a diamond saw. Lap and polish the surface to be studied by using progressively finer abrasives. The surface should be finished to a highly reflective, mirror-like surface by a fine polishing powder (5µm aluminum oxide). When changing from a coarse abrasive to finer grit the sample must be thoroughly cleaned of the coarse abrasive. Clean with a brush or stream of pressurized air. Do not wash in water or use an ultrasonic tank as these methods may harm or alter the surface. The surface is finished

when there are no scratches, no visible relief between the aggregate and the matrix and the surface shows excellent reflection of light when viewed from a low incident angle.

If the purpose of the reflected light sample is to help identify features of interest for further identification a slight modification of procedure should be followed. The sample should be sawed in hall: One side, a mirror image of the half to be polished, will be retained for further study. The second half will be polished as described above. The polished half is studied and features of interest may be marked or removed with a fine point for XRD. In the case of the second half of the specimen being reserved for SEM-BSE analysis, the surface must be very carefully polished to prevent smearing. If the sample does smear, as is the case for some weak plasters, the analysis may be conducted without polishing.

THE MAKING OF THIN SECTIONS

The study of cementitious materials by transmitted light allows for better identification of aggregate and for the study of residual hydraulic components in the matrix. Traditional petrographic methods state that the thin sections should be ground to a thickness of 30μm. The study of cementitious materials requires the preparation of a thinner section, nearer 20μm. At this thickness, however, other constituents begin to loose coherence and are difficult to see.

The preparation of thin sections is beyond the scope of this method. The thin sections should be prepared according to procedure as described in **(3)** or other standard methodologies.

There are two options for the analyst. If the nature of the experimental goals and the material itself are such that the visual and low magnification study gather enough information, then a thin section of 20μm is sufficient. An example of this scenario would be the case in which the aggregate was clearly composed of quartz (primarily) with no evidence of carbonate aggregate. The objective of the study is to 1.) Match the aggregate

and 2.) Determine the degree/nature of the hydraulic components. In this case, a simple acid digestion of the matrix to retrieve the aggregate for matching purposes would suffice. The thin section would then be for the purpose of studying residual hydraulic grains.

On the other hand, if the case were that the aggregate was comprised of carbonates, two thin sections would be made. One section at 30 μm to determine component proportions, the other, 20μm section to study the hydraulic constituents.

Sample Examination

EQUIPMENT AND MATERIALS

Microscopes (stereomicroscope, polarizing microscope, metallographic) with low, medium and high objectives
Eyepiece micrometer
Stage micrometer
Image Analysis Software
Camera (35mm or digital)
Point counting device (manual or computer driven)
Needle holders and Points
Immersion Media

Microscopic Examination

The samples should be arranged in a logical sequence and comparisons made between them. Any changes in color, deterioration, and apparent porosity are to be reported. Significant features should be noted and marked for further or more detailed study. The initial visual examination should be supplemented with an examination under low magnification. The results should be recorded in a chart such as shown in Table 1.

SECTION ANALYSIS WITH REFLECTED LIGHT

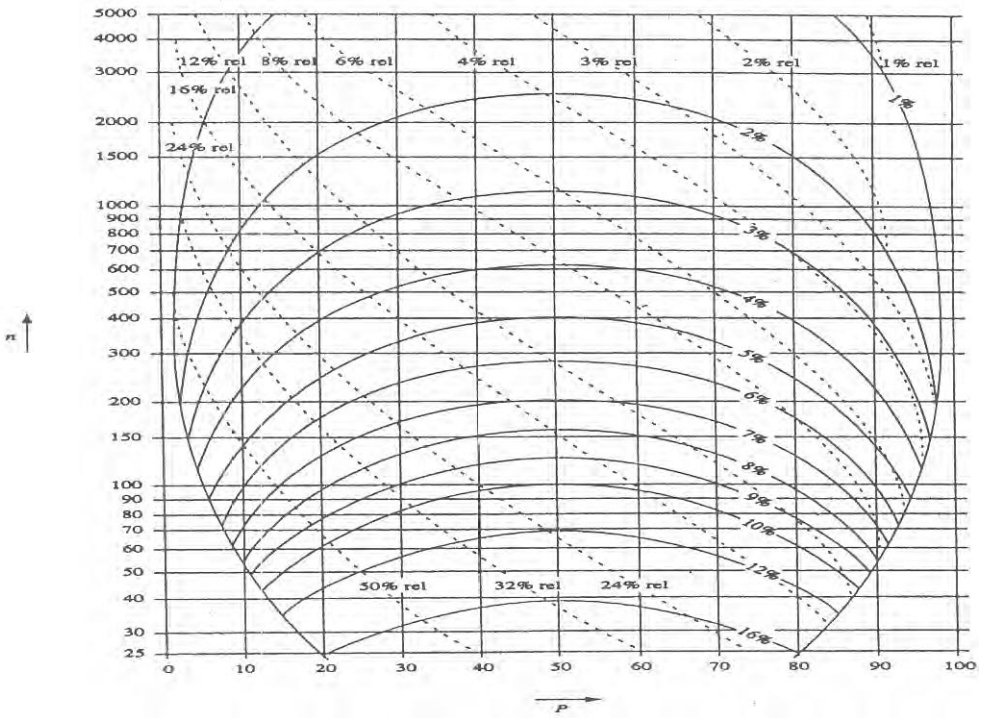
The analysis of a samp'e with reflected light is most often used for determination of the cementitious material's constituents. Point counting, linear traverse or modal analysis methods may determine the constituent proportions. The modified point counting method and linear traverse method are described in ASTM C457. The determination of the area ratios of the section by use of image analysis software is another method. The advantage of using modem image analysis software is that information on grain sizes, texture and photography is all carried out in one step. Also, the point count and linear traverse methods are more time consuming.

All three methods are those of modal analysis and have the same basic assumptions. The Delesse relationship assumes that the ratio of the area occupied by a single component in a randomly cut surface to the total measurement area is a consistent estimate of the volume percentage of the component in the whole sample. Note that the step size in point counting techniques should, if possible, be greater than the maximum grain size.
Common sources of error:

- Size of the sample
- Non-random sample selection
  Sample heterogeneity -preferential orientation, segregation and banding of components, grain size variation etc.
- Observer bias

The number of samples and points or area to be examined depends on the adequacy of the sampling and the accuracy required. Figure 5 shows the number of points necessary for the required degree of accuracy. ASTM C 457 specifies the minimum area of finished surface to be examined for the determination of air content (Table 1) - these areas may also be used for determination of other constituents as well. These values refer to reasonably homogeneous, well-compacted concrete.

Figure 5 : **Number of points necessary for the required degree of accuracy.**



, Chart for estimation of error in point counting. The total number of points *n* counted on the specimen are shown on the y axis and the percentage P of a component on the x axis. At the intersection point of *n* and P the relative error is read from the dotted lines and standard deviation at 95 per cent probability from the solid curved lines.

Table 1 : Minimum area of finished surface to be examined

Nominal maximum size of aggregate in the concrete (mm)	Minimum area of surface for measurement (cm^2)	Approximate Sample Size (cm)
150	1613	40x40
75	419	21x21
37.5	155	13x13
25	77	9x9
19	71	9x9
12.5	65	8x8
9.5	58	8x8
4.8	45	7x7
3	36	6x6
1	12	4x4
0.5	6	3x3
0.25	3	2x2

Generally, the standard *25* x 25mm size petrographic section is not large enough for constituent determination. Edge dimensions of at least 100mm are preferred. Alternatively, several smaller sections may be prepared of *75* x 50mm in size but, depending on the aggregate size, these may not be large enough for modal analysis. A good working rule is that it is best to count over as many samples and the largest surface area possible. If the size of the sample to be examined is limited due to material availability, this must be noted on the examination record.

THIN SECTION

The examination of thin sections is standard procedure for the petrographic analysis of rock texture and components. Petrographic samples are traditionally ground and polished to a thickness of 30μm. For the observation of cementitious materials a thickness of 25μm usually reveals better texture of the paste.

Thin section examination of cementitious materials encounters the same problems as described in the previous section of examination under reflected light. The main problem is again sample size. It is difficult to obtain and prepare samples large enough to account

for the heterogeneous nature of the material. Several sections may be taken over a sample area but the loss of edges during preparation must be taken into consideration.

Small sample size is a fact of life in the study of many historic materials. In such cases, multiple sections must be examined. Interpretation must be carefully considered with regard to samples from the whole structure.

Detailed examination of the paste matrix require thinner sections of 20-25μm. Thicker sections may be desirab'e when studying more fragile components like void deposits or matrix aggregate contact. It is sometimes necessary to prepare multiple thin sections of different thickness. ASTM C 856 gives a nice discussion of the characteristics of Portland type concrete. In general, thin section analysis should discuss the features listed in the Table 2 outline, adapted from ASTM C 856.

Outline for Thin Section Examination - see tables for lists of common minerals

Aggregate	Relict cement grains and hydration products	Characteristics of Matrix
• Mineralogy, texture, fabric, degree of homogeneity Grading, grain size, nature of internal boundaries • Bond with matrix, cracks regarding aggregate-matrix bond, interior cracks	• Hydraulic components • Large grains of hydraulic material are resistant to hydrolysis Pozzolanic additives • Trapped pockets of lime	Mineralogy, texture, fabric, degree of homogeneity, density • Depth of carbonation • Secondary deposits • Calcium hydroxide crystals, indicative of acid leaching, water-cement ratio etc.

Table 2 : Thin section features to note - historic mortars, cements and conretes.

CALCULATIONS FOR MODAL ANALYSIS OF AGGREGATE, AIR VOIDS AND PASTE

The relative proportions of the cementitious material's constituents may be estimated by point count, linear traverse or area estimation (image analysis). The proportions are calculated as follows (4, 5, ASTM C 457-90).

1. Point Counting Method

Percentage Air Content:

$$V = \frac{\text{Number of points in air}}{\text{Total Number of Points}} \text{ X } 100$$

Percentage Paste Content

$$P = \frac{\text{Number of points in paste}}{\text{Total Number of Points}} \text{ X } 100$$

Percentage Aggregate

$$Ag = \frac{\text{Number of points in aggregate}}{\text{Total Number of Points}} \text{ X } 100$$

2. Linear Traverse

Percentage Air Content:

$$V = \frac{\text{Length of the traverse in air void}}{\text{Total Length of the Traverse}} \text{ X } 100$$

Percentage Paste Content

$$p = \frac{\text{Length of the traverse in paste}}{\text{Total Length of the Traverse}} \text{ X } 100$$

Percentage Aggregate

$$Ag = \frac{\text{Length of the traverse in aggregate}}{\text{Total Length of the Traverse}} \text{ X } 100$$

3. Area Analysis

$$V = \frac{\text{Air void area}}{\text{Total area}} \text{ X } 100$$

$$P = \frac{\text{Paste area}}{\text{Total area}} \times 100$$

$$Ag = \frac{\text{Aggregate area}}{\text{Total area}} \times 100$$

XRD

XRD may be used to determine both matrix and aggregate minerals. The crystalline components of the material are to be analyzed in accordance with individual XRD equipment techniques. There are three sub-sampling techniques that may be helpful in determining the presence of minor components.

1. Acid Digestion

   The acid insoluble residue may be studied under the microscope. Grains of interest may be separated out, manually, and ground for analysis. Alternatively, the residue may be sieved.

2. Manual grinding or crushing

   A mortar and pestle may be used to crush the material. The resulting powder is then fed through a number of sieves and the component of interest may be studied.

3. A sample is cut into two pieces. One half is polished and studied under reflected or transmitted light, depending on procedure followed. If an area of interest is located on the polished sample, the reserved sample half may be mined for the component of interest with a fine probe.

SEMIEDSIBSE

SEM may be used in conjunction with EDS and BSE to study hydraulic components. By using BSE, hydraulic phases clearly stand out. Reportedly ([6]), the outlines of the original hydraulic grain is visible even after aging.

In order to estimate the degree of hydraulic material, and so classify the material as weakly, moderately or strongly hydraulic, traditional point counting may be applied. The sample is to be carefully polished, as for reflected light. Roughly divide the sample surface into quarters, by paint or tape so that the sections may be identified when viewed with the SEM. Each quarter is to contain three randomly chosen sites. At each site, 50 points are to be counted or an equivalent area (if image analysis is to be used). EDS may be used to help identify components. After the 12 sites have been evaluated, the hydraulic content is to be estimated by the ratio of the hydraulic material to the total area of paste examined. The calculation is similar to that used to determine aggregate or air void percentages. The material may then be classified by the percentage of hydraulic material present (Table 3).

These estimations are useful for roughly characterizing the hydraulic component of a lime based paste. Portland cement types are readily distinguished by this method as they have hydraulic components present in the paste of greater than 80%.

weakly hydraulic	Moderately hydraulic	Strongly hydraulic
5-15%	16-25%	26-36%

Table 3 : Guidlelines for estimation of hydraulic components of lime paste.

CALCULATIONS FOR SEM-BEI ESTIMATION OF HYDRAULIC CONSTITUENTS

$$H = \frac{\text{amount of hydraulic material (number of points or area)}}{\text{Total number of points (or area) - amount of aggregate - air voids}} \times 100$$

Note that this calculation is to be used solely to ratio the amount of hydraulic material in the **paste.** Any aggregate or air voids are not to be included in the calculations. The magnification employed may vary with the nature of the study

Report

The following information is to be included in the final report.

1. Sample Information

   Taken from the original sample sheet, list: the nature of the investigation; sampling method; physical description, environmental description, samples position to surface, samples relation to surface, samples' location in the original structure.

2. Sample Preparation

   Briefly outline procedural steps followed. The size and number of samples analyzed must be stated.

3. Sample Examination

List the results of the initial examination.

4. Analytical results:

   Thin section / *reflected* light

   Volume percentages - state: the method used (point count, linear traverse, area); the total number of stops, length of traverse or area examined; the calculated values.

   Identification - List minerals and components identified; include descriptions of features of note (texture, grading, secondary deposits).

   The field size (mm) or nominal magnification (Table 5) must be listed with every photomicrograph. Additionally, a measurement bar may be included in the image.

   XRD

   Report will include: instrumental make and type, parameters; peak identification results along with peak table (plots must be accompanied by peak table); method of sample preparation (ground, acid digested and ground etc.)

SEM-EDS/BSE

Report will include instrumental make and type, parameters; element identification; photomigrographs must include micron measurement bar. Quantitative work must report total number of points analyzed.

Table 4: **Secondary Deposits**

Compounds/minerals	Occurence	Comments
Calcium carbonate ($CaCO_3$); calcite (7, 8)	Common in all paste types	White or gray, fine grained masses or coatings. Present in the paste, voids fractures, cracks and exposed surfaces. Very common.
Calcium carbonate ($CaCO_3$); vaterite (3,4)	Common	Spherulitic, form-birefringet
Calcium carbonate ($CaCO_3$); aragonite	Rare in Portland type cements.	Minute, white prisms or needles in voids and fractures
6-calcium aluminate trisulfate-32 hydrate $\{Ca_6[Al(OH_6)]_2 \bullet 24H_2O\}(SO_4)_3 \bullet H_2O$; ettringite (3,4)	Common in Portland type cements	
Calcium sulfate dihydrate ($CaSO_4 \bullet 2H_2O$); gypsum (3,4)	Unusual	White to colorless crystals in voids, the paste or along surface of aggregate particles. Commonly found in cementitious materials affected by sulfates or sea water.
Calcium hydroxide ($Ca(OH)_2$); portlandite (3,4)	Very common	White to colorless, hexagonal plates or tablets. Present in the paste, fractures and voids.
Magnesium hydroxide ($Mg(OH)_2$); brucite (3,4)	Unusual	White to yellow, fme grained encrustations and fillings. Found in cementitious materials exposed to seawater.

Table 5: List of Common Minerals and Compounds found in the Matrix or Paste

Compound/ Mineral	Test methods	Optical Properties	Comments
Tricalcium silicate, C_3S ($3CaO \bullet SiO_2$), alite *(4,9, 10)*	Thin section (20-25 μm), reflected light, XRD (may be present in amounts below instrument detection limits	Biaxial, α=1.716-1.720 γ=1.722-1.724	Colorless lath, table-like or equant. Crystals are usually six sided in thin section. Alite is rare in adequately cured Portland type cement except as crystals embedded in the matrix of large, unhydrated clinker particles
β-dicalcium silicate, larnite, C_2S ($2CaO \bullet SiO_2$), belite (4, 5, 6)	Thin section (20-25 μm), reflected light, XRD (may be present in amounts below instrument detection limits)	Uniaxial, α=1.717 β=1.722 γ=1.736	Rounded grains often in clusters or nests. Color may be colorless or pale yellow through amber depending on substitution and kiln conditions.
Tricalcium aluminate, alkali aluminate, C_3A ($3CaO \bullet Al_2O_3$) *(4,5,6)*	Thin section (20-25 μm), reflected light, XRD (may be present in amounts below instrument detection limits)	Isometric, n=1.710	Cubic form usually fills interstices between belite and femte crystals.
Ferrite phases, brownmillerite, C_4AF ($4CaO \bullet Al_2O_3 \bullet Fe_2O_3$) *(4,5,6)*	Thin section (20-25 pm), reflected light, XRD (may be present in amounts below instrument detection limits)	biaxial, α=1.98 β=2.05 γ=2.08	Brown to yellow color. Form dependent on cooling rate, varies from bladed, prismatic, dendritic, fibrous, massive or infilling. Common in paste where clinker grains have failed to hydrate due to large size or low water content.
Calcium silicate hydrate (C-S-H), tobermorite gel (4)	Thin section (20-25 μm), reflected light, SEM	Transparent, colored, isotropic amorphous gel	Indefinite mass infilling space and surrounding components like CH, remnant cement grains, pores and aggregates. May appear as hydration rims.

Compound1 Mineral	Test methods	Optical Properties	Comments
Calcium Hydroxide ($Ca(OH)_2$), portlandite (4)	Thin section (20-25 μm), reflected light, XRD	Uniaxial, ε=1,545-1.547 ω=1.573-1.575	White to colorless, hexagonal plates or tablets. Present in the paste, fractures and voids.
Dolomite ($Ca(Mg,Fe,Mn)(CO_3)_2$) (4)	Thin section (20-25 μm), reflected light, XRD	Uniaxial, ε=1.500-1.526 ω=1.680-1.716	Fine to coarse grained, colorless to gray crystals in thin section. Raw material used for dolomitic limes.
Calcium Carbonate ($CaCO_3$), calcite (4)	Thin section (20-25 μm), reflected light, XRD	Uniaxial, ε=1.486 ω=1.658	Raw component of Portland cement and lime based materiais. Found in carbonated areas due to the conversion of CH.
Pozzolana, natural	Thin section, XRD of acid insoluble residue	Various	Remnant grains may have reaction rims. Volcanic minerals see aggregate list)
Pozzolana, brick	Thin section	Various	Dark red-brown matrix with aggregate. Remnant grains may have reaction rims.

Table 6: Common Materials Found as Aggregates

Compound/Mineral	Test Methods	Comments
Limestone, marble ($CaCO_3$)	Thin section, XRD	Very common
Quartz	Thin section, XRD	Very common
Feldspar	Thin section, XRD	
dolomite	Thin section, XRD	
Clay	Thin section, XRD	
Shale	Thin section, XRD	
Mica	Thin section, XRD	
Magnetite	Thin section, XRD	
chert	Thin section, XRD	
Granite	Thin section, XRD	
Gabbro (11)	Thin section, XRD	
Diabase (11)	Thin section, XRD	
Diorite (11)	Thin section, XRD	
Mafic minerals (11)	Thin section, XRD	
Iron flakes (9)	Thin section	Found in early (meso) portland type cements as an impurity from the iron bars in the kiln (9)
Old mortar (12)	Thin section	
Lime lumps (8, 12)	Thin section	Underburned limestone (core) .Only the exterior of the lump is calcined.
Charcoal(8, 13)	Thin section	Present as an impurity from the calcination process. May be deliberately added as a colorant (12)
Wood (12)	Thin section	
Organic material (hair, straw)	Thin section	Easily distinguished by thin section.
Brick	Thin section	Relic Grains. Dark red brown matrix + aggregate, may have reaction rims. Imparts a red or pink color to the cementitious materials.
Natural pozzolana (14)	Thin section, XRD of the acid insoluble residue	Relic grains (leucite, analcite, pyroxenes (augite, diopside), olivine, iron oxides, plagioclase)

STANDARD PRACTICE SUMMARY

- An overview of the steps to be followed.

Clearly define research goals and the nature of the analysis.

- Pre-Analysis - Develop sampling strategy and determine sample size
- Remove Samples
- Visual Examination - Low magnification
- Prepare sample specimens

Saw, consolidate, and prepare polished sections

- Aggregate Determination

Acid Digestion - If the nature of the analysis is to simply match and grade the aggregate and, if that aggregate is acid insoluble, this technique may be used. The sample is to be crushed in a mortar and pestle. Diluted hydrochloric acid is then used to dissolve the carbonate paste. The contact between acidified solution and aggregate should be kept to a minimum. Filter with distilled water to neutralize the acid. The acid insoluble residue is then sieved through a series of geological sieves and reported as weight percent of the total (ASTM C295-92).

Section analysis - If the sample contains carbonate or otherwise soluble aggregate, or if a more detailed study of the aggregate is required, a polished section may be studied. Thin sections of 30 μm are useful for identifying minerals. Any of the approved modal analysis techniques - point counting, linear traverse or image analysis may be employed. These studies can give more detailed information on matrix and aggregate including grading, shape, texture. depth of carbonation etc.

XRD - useful in determining crystalline components. Minerals that are present in low amounts, less than 5% are often difficult to determine by this method. Acid digestion or mechanical crushing of a portion of the sample, followed by sieving or sorting to separate certain components may be used, if appropriate. Alternatively, microsampling techniques may be used. In this approach, two halves of a sample are used. One is polished and studied under a microscope to look for features of interest. The second have is then used to provide material for auxiliary techniques like XRD.

- Characterization of the Matrix

In order to study the paste itself, several techniques may be used. XRD may be used to determine the bulk components. Air voids, pozzolan and cement relic grain percentages are determined by modal analysis of polished section. Thin section analysis can be used to study the cement relic grains if the section is made thinner than the usual 30μm (20-25 μm).

The depth of carbonation should be evaluated

1. by the study of a cross section and marking the transition zone of calcium carbonate to portllandite or
2. spray a dilute sollution of phenolphthalein over a freshly sawn surface.

The estimation of relic cement and pozzolan will give some indication of the hydraulic nature of the material. BEI in combination with modal analysis is to be used for estimation of the hydraulic material. This technique clearly differentiates phases present and areas of C-S-H gel are distinct. Note: This method has not yet been tested on weathered materials.

Report

Prepare a detailed report including sample sheets, research goals, techniques used and results, calculations, conclusions and photographs. Sources of error that could effect the interpretation must be listed. Common sources of error: heavily weathered samples, small sample size or number etc.

CONCLUDING REMARKS

Theoretically, the classification of cementitious materials into their appropriate group types should be simple. There are some cases in which the sample very clearly belongs to a particular category, say Portland cement or a pure lime mortar. However, historic mortars and cements art: often complicated by the fact that different materials were used simultaneously or perhaps accidentally. A pure or "fat" lime mortar may have a sand aggregate that contains some hydraulic component. Portland cement may be mixed with lime that makes it appear similar to a hydraulic lime. Great care and experienced analysts must be used when interpreting the petrographic analyses of historic cementitious materials. Figure 6 lists some phases and textures that are useful in differentiating between the different cement pastes.

Thin and Polished Sections

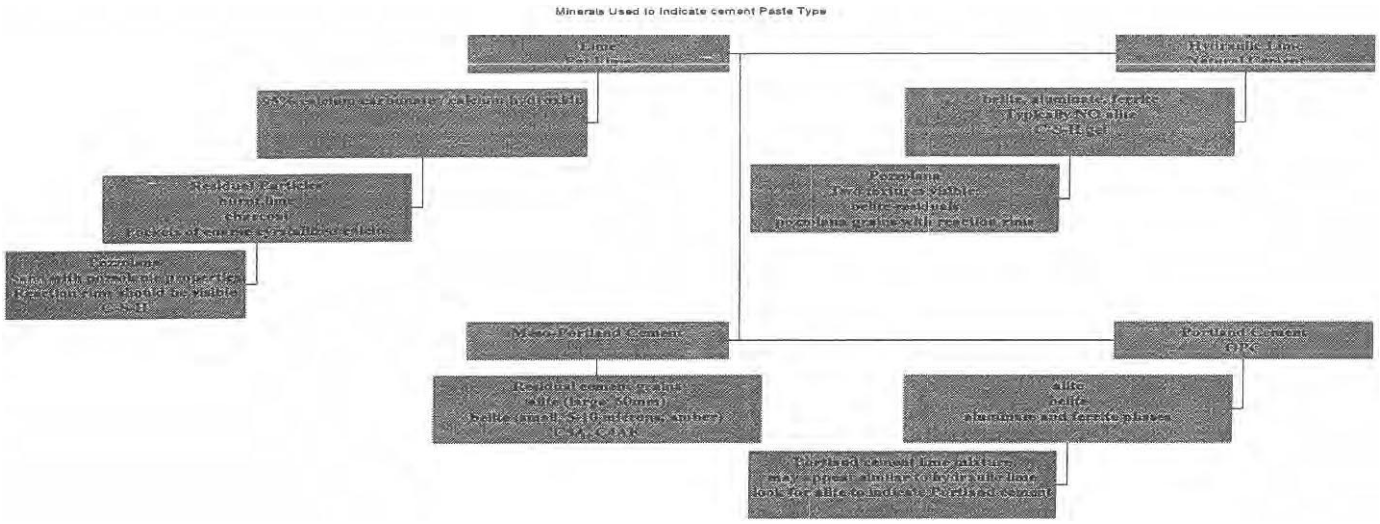


Figure 6 : Common phases used to indicate cement type

References

1 Goins,E.S. A New Protocol for the Analysis of Historic Cementitious Materials: Interim Report. In: Intemational Workshop Historic Mortars: Characteristics and Tests, Pre-Prints (RILEM, Paris, 1999).

2 Hughes, 3. Practical Sampling of Historic Mortars. In: Intemational Workshop Historic Mortars: Characteristics and Tests, Pre-Prints (RILEM, Paris, 1999).

3 Cambell, D. H. Microscopical Examination and Interpretation of Portland Cement and Clinker (Portland Cement Association, Skokie, Illinois, 1986).

4 Chayes, F. Petrographic Modal Analysis (John Wiley & Sons, New York, 1956).

5 Petruk, W. (ed.), A Short course on Image Analysis Applied to Mineral and Earth Sciences. (Mineralogical Association of Canada, Ottawa, 1989).

6 Scrivner, K.L. , A Study of the Microstructure of Two Old Cement Pastes" in 8th Intemational Congress on the Chemistry of Cement, Rio De Janeiro, **3** (1986) 389-393.

7 ASTM C-856 Standard Practice for Petrographic Examination of Hardened Concrete. (1992

8 St. John, D., Poole, A.W. and Sims, I.. Concrete Petrography (John Wiley & Sons: New York, 1998).

9 Blezard, R. G. Technical Aspects of Victorian Cement Chemistry and Industry **19** September (1981) 630-636.

10 Idorn, G. M. & Thaulow, N. Examination of 136 Years old Portland cement concrete, Cement and Concrete Research **13** (1983) 739-743.

11 Erlin, B., Hime, W.G. Methods for analyzing mortar. In: (eds.) Matthys, J.H., Borchelt, J.G. Proceedings of the Third North American Masonry Conference, Construction Research Center, University of Texas at Arlington, TX, Masonry Society (1985).

12 Middendorf, B. & Knofel, D. Investigations of mortars from medieval brick buildings in Germany. In: Proceedings of the Thirteenth International Conference on Cement Microscopy (International Cement Microscopy Association, Duncanville, TX, 1991).

13 Malinowski, R. & Garfinkel, Y. Prehistory of Concrete, ***Concrete International*** **March** (1991) 62-68.

14 Martinet, G. & Quenee, B. Proposal for an useful methodology for ancient mortars study. In: Intemational Workshop Historic Mortars: Characteristics and Tests, Pre-Prints (RILEM, Paris, 1999).

A NEW PROTOCOL FOR THE ANALYSIS OF HISTORIC CEMENTITIOUS MATERIALS: INTERIM REPORT

Elizabeth Goins
University of Delaware, U.S.A

Abstract

Several different standards and protocols are used to analyze historic mortars and cements: the ASTM standards, techniques based on Jedrzejewska and those of E.B. Cliver. Tests are typically based on the acid digestion of the sample to determine the ratios of original components. There are also a number of instrumental techniques that have been reportedly used: XRD, SEM, porosimetric measurements, FT-IR identification of granulometric fractions and thin section analysis. A thorough comparison of existing methods and a critical review of their use within the area of historic mortar analysis are the first step of this study. This report will review and discuss those methods currently used and the direction of further research.

1. Introduction

The identification and quantification of the materials present within historic concrete is a difficult and complex issue. While there has been a tremendous amount of research within the area of modem Portland cements, the hulk of the research has been focused on the improvement of engineering properties or quality control. Rapid chemical investigation methods, like ASTM C114 (1), enable quick and inexpensive determination of the bulk oxide components of a cement paste. Unfortunately, the cementitious materials encountered within the preservation and conservation studies do not fall neatly into the ASTM categories. The original materials, proportions and fabrication methods vary greatly. Also, the effect of weathering and aging on the materials is, for the most part, unknown. Techniques that are appropriate for materials made from a narrow set of parameters, like modem cements, may not be pertinent for a group as diverse as historic cement and concrete.

The goal of this project is to create a standard protocol for the analysis ofhistoric mortar, cement and concrete. The protocol will be developed from the existing techniques of

section analysis (both reflected and transmitted light), staining, macroscopic evaluation, X-Ray Diffraction (XRD), Scanning Electron Microscopy techniques (SEM-EDS and BSE). The samples used will be laboratory prepared from known constituents and proportions. The effect of specimen sampling on the statistical validity of the analysis will be studied. Additionally, sampling techniques and procedures will be evaluated. The current project is intended to be the first part of an ongoing study that will next tackle such supplementary techniques as FT-IR, thermal analysis and the effect of weathering.

The study of historic materials poses different problems than those of a modem industrial material. Therefore, one of the first goals of this project is to identify the motivating factors behind the analysis of historic cementitious materials. These factors may create specific research areas that require special techniques and sampling procedures. The four major areas of research identified are:

1. Original materials - The identification of starting materials (such as the aggregate, nature of the lime, pozzolana etc.) and the estimation of their original ratios.
2. Deterioration/weathering - The identification of deterioration and weathering mechanisms.
3. Technological studies - The indirect identification and study of historic technology.
4. Provenance - The identification of the source of the original materials and relative chronology.

The next step, in any study combining new and historic technology, is to clarify the terminology. Terms used for a number of years often develop a common definition that may be vague or even incorrect. The very term "mortar" is ambiguous. To many, mortar means a compound, that holds blocks of masonry or bricks together. To others, it has a broader meaning of any historic cement and tine aggregate. The following definitions, listed in Table 1, will be adhered to for the purposes of this project (2). Materials used in this project are checked for compliance to the standard definitions. Please refer to the following table for terms and definitions used in this study.

2. A Review of the Literature

2.1 Identifying the components

A number of different approaches and analytical techniques have been used to study cements. Some of these, such as the ASTM wet chemical tests, have been directly applied to the study of historic cements (that is, the cementitious matrix). Stewart and Moore (3) carried out a thorough study of three chemical techniques on laboratory prepared fine concrete samples. Their results describe the failings of all three methods: ASTM (1), Jdrewzjewska (4), Cliver (5). Both the ASTM and Jdrewzajewska method were unable to differentiate between soluble silicates. The Cliver technique was found to be unreliable due to a flawed assumption based on the categorization of cement type by color. In fact, X-Ray Fluorescence (XRF) is replacing the wet chemical techniques as a reliable method (6) for oxide analysis. Oxide analysis, while useful for complementary

Table 1 : Definitions of terms

Cement	A material for uniting other materials or articles. It is generally plastic at the time of application but hardens when in place (2). Includes all lime mortars and Portland cements. The matrix portion of any cementitious material or "neat" cement paste.
Concrete	A mixture of any cement type, sand and gravel or stone chips with water in varying proportions according to use (2). In this project, mortar and concrete are used interchangeably. That is, a concrete is a cement + aggregate. Types are differentiated by aggregate sizes (coarse vs. fme) and cement component.
Mortar	A pasty substance formed normally by the mixing of cement, sand and water, or cement, lime, sand and water in varying proportions. Used normally for the binding of brickwork or masonry (2).
Hydraulic cement	A cement which will harden under water *(2)*.
Semi-hydraulic cement	A cement that contains at least 10% of a potentially hydraulic material. It does not set under water.
Non-hydraulic cement	A cement that contains less than 10% of potentially hydraulic materials. Also known as fat lime (95%+ pure lime).
Natural Cement	Made by calcining natural mixtures of calcareous and argillaceous materials. Examples are Roman cement and eminently hydraulic lime.
Lime	Limestone heated to at least 825°C to produce CaO (quicklime, caustic lime, unslaked lime)
Portland cement	Ordinary Portland Cement (OPC) or Type 1.
cementitious material	Ambiguous term for all things "cementitious" - lime based cement, Portland cement, proto- and meso- cements, mortars, grouts etc.
Lime putty	Hydrated (slaked) and aged lime.

information, has been relegated to a secondary status for this study as it does not provide information on the mineral phases, interactions and microstructure that are responsible for imparting characteristic properties to cement.

The analysis of historic cementitious materials involves the study of three primary components: the aggregate, the binder or matrix and the hydraulic components. Other constituents, such as organic additives, have also been studied but will not be considered

for evaluation in this project. To date, chemical analyses and XRD have been the workhorses of historic concrete research. XRD is used to identify mineral phases within the concrete. The problem with XRD is that the phases of interest are usually swamped by the overwhelming presence of calcium carbonate. XRD carried out on the acid insoluble residue is often more useful but there is still the problem of dissolution of some components in the acid. Also, XRD is difficult to use for the study of phases present in amounts less than 5%.

2.1.1. The Aggregate

The aggregate can serve a number of different roles within the matrix. Different materials are used in order to modify the properties of the concrete. Perhaps the most common aggregate: is quartz, present as sand. A quartz-based aggregate does not interact chemically (to any great extent) with the cement paste. This type of aggregate is added to the mix to: counteract shrinkage, increase effective porosity, increase mechanical strength and act as filler (7). The separation and analysis of a pure quartz aggregate is relatively straightforward. There have been many studies **(8, 9,** 10, 11, 12,) that have used the acid digestion technique. This method consists of an initial mechanical crushing of the cementitious material followed by the dissolution of the carbonate matrix in a dilute acid. The binder to aggregate ratio may then be determined by subtraction of the remaining weight from the total weight. The problem with this method, as outlined by Stewart (3), is that samples may contain components soluble in the acid other than the hinder. Hydraulic constituents are also acted on by the acids, as are raw clays. The aggregate may also be partially or wholly calcium carbonate, which may have been originally introduced as powdered marble or crushed lime from various sources.

Researchers have recognized these factors and a variety of approaches have been adopted by some to avoid these problems. Perhaps the most promising is the analysis of the thin section. Ciach (10) used acid digestion and losses on ignition to calculate carbonate contents as preliminary tests but relied on the percentage volume of aggregate to binder to be indirectly determined from polarized microscopy of the thin sections. Lindqvisr (13) used polarized light microscopy in combination with image analysis and 500-700 point counts to determine particle size distribution, and hinder - aggregate - air void percentages.

Micrometric analysis is conducted using linear traverse or point counting methods (6). Volume proportions of cement paste, coarse aggregate, fine aggregate, air voids are determined. The original components are estimated from the volume proportions (6). One major problem is that aggregate particle size may be over or under estimated depending on particle shape and oblique or non-central sectioning. Another drawback to this type of technique is that it is slow and tedious. Image analysis, the digitizing and processing the image by a PC, is being employed to overcome laborious manual counting. This technique enables the analysis of large numbers of samples quickly and more easily than the traditional micrometric analysis. The problem in analyzing concrete

by the products available is that it is often difficult to obtain the amount of contrast necessary for the software to differentiate the phases present. However, it is theoretically feasible that an image analysis program could reliably identify cement phases, describe particleiaggregate rhape, particle size distribution etc.

2.1.2. The Binder and Hydraulic Materials

Perhaps the question most often asked of the hinder is to whether or not it is hydraulic. Pozzolana or unhydrated clinker relicts may be identified in thin section analysis during an aggregate study but these do not necessarily resolve the issue of the hydraulic components of the cement mahix. SEM-EDS and electron microprobe studies have been used to study the C-S-H gel (14, 15, 16) and carbonates (17). Typically, these methods are used to study small areas of interest but Steadman (18) employed EPMA measurements over 50-100 points over a polished surface to determine the calcium silicate ratios. Lewin (19) used SEM to identify mineral phases by crystal shape after finding that they were undetectable by XRD. The problem with SEM and EPMA studies is that they are subject to a number of both human and instrumental errors (20). The biggest human error is that micro-structural features are reported as characteristic when they are, in fact, minor. Using micromehic measuring techniques, such as point counting, over the surface may alleviate this.

Back Scattered Electron (BSE) analysis has been used to identify boundaries of the original cement grains in a 23 year old Portland cement paste and a meso-Portland cement paste (21). BSE was combined with image analysis software to determine the aggregate to binder ratio and other textural information (22). This method allowed for improved results in the analysis of compositional and textural features of cryptocrystalline binders. However, BSE suffers from the same human errors as SEM and the image analysis works well only for areas with high contrast.

Finally, a simple method for determining the depth of carbonation is to spray a freshly cut surface with phenolphthalein (23). This method is based on the solid acid or base characteristics that differentiate calcite from portlandite. The carbon dioxide reacts with Ca $(OH)_2$ to create $CaCO_3$ depending on the time, exposure conditions and concrete density. Calcium carbonate bas an effectively less base (more acid) nature and turns the indicator a dark violet red. The portlandite, with an effectively higher pH, is a light pink-red.

2.2 Dating, chronology, source identification and Technological Studies

Inductively Coupled Plasma (ICP) has been used to help identify the chronological sequence and relative dating of structures. ICP is used to determine the major and trace elements of a soluble sample. Carbonate structures retain certain elements (Co, Cs, Sr) and cement paste!: are reported to incorporate these elements into their structure during hydration (24). Therefore, carbonates coming from different sources should have different amounts of certain trace elements. Phillips (25) used ICP to determine the age

of a structure by comparing the elemental analysis to that of a quarry in operation from a known date. Vendrell-Saz (26) combined ICP and Atomic Absorption with clustered multivariate statistical analysis to determine relative structure dates. Historic documentation was used to compare unknowns with the result clusters for type grouping. The most obvious difficulty with this type of analysis lies with the application of appropriate sampling methodology. The number of samples, their state of preservation and past preservation interference are just some of the factors that may affect the results.

The study of historic technology perhaps began with Vicat (27) in 1837. He subjected a number of historic Roman mortars to strength testing and found that they varied considerably. Malinowski [28] studied Roman cements in aqueduct and tank linings with a combination approach that involved thin section, instrumental and chemical techniques. These studies found that the polishing techniques used by the Romans were primarily responsible for the success of the linings by inducing structural tightness.

Roy and Langton (29) used a variety of techniques to study ancient Greek and Roman plaster and concrete. Their primary interest was to study the technology that produced them and understand their resistance (response) to environmental exposure over the centuries. They concluded that both mineralogical and microstructural factors affected durability. An interesting area of their report concerned the study of the silicate structures by trimethylsilylation (TMS) (30). This method is based on the bonding of the trimethylsilanol to O^- groups of the cement silicates formed from an initial dissolution in acid. The degree of condensation of the poorly or non-crystalline silicates is then estimated by gas-liquid chromatographic analysis of the TMS derivatives. Sarkar and Roy (31) compared a laboratory prepared Portland cement paste to a 20 year old paste by this technique and found six anions present in both pastes that varied only in relative proportions: SiO_4^{4-}, $Si_2O_7^{6-}$, $Si_3O_9^{6-}$, $Si_3O_{10}^{8-}$, $Si_4O_{13}^{10-}$, $Si_5O_{15}^{10-}$. Interestingly, no crystalline silicates or organic siloxane compounds containing $Si_4O_{13}^{10-}$ or $Si_5O_{15}^{10-}$ anions are known.

2.3 Weathering and Deterioration Mechanisms

The study of deterioration mechanisms is not within the scope of this work. However, the effects of weathering on the interpretation of analytical results are important factors to consider. The degree of carbonation will influence the study of C-S-H gel. As carbonation proceeds, carbon dioxide converts the gel to calcium carbonate and silica. Also, leaching of the C-S-H gel removes the calcium preferentially until about half of the original amount remains. After this point, calcium and silicon are leached equally until the gel is gone (20). The composition of C-S-H in Portland cements were studied by Rayment and Majumdar (32). The study began by assuming the C-S-H phases in hydrated cement pastes show extensive solid solution. The distribution of calcium, silicon, aluminum, sulfur, iron and magnesium in Portland cement pastes prepared in the laboratory were compared by arranging the atomic ratios by a number of designs. The minimum amount of error was always found when the elements were arranged as:

$$\frac{Ca + Mg}{Si + Al + S + Fe} \quad (1)$$

This ratio is found to give more accurate results than simple calcium to silicon ratios as it takes into account the elements that may play substitution roles within the gel matrix.

3. *Towards a Standard Protocol*

After reviewing the literature, it has become clear that greater emphasis must be placed on the sampling and statistical techniques. First of all, the condition of the cementitious material to he studied will have a tremendous influence on the results. Secondly, the rationale behind sample selection must be evaluated. Finally, the amount of the specimen analyzed and its sampling procedure must be considered. For example, are the point counting and image analysis techniques being applied over large enough areas to give any kind of statistical validity?

The current work of this project involves

1. Development of a sampling strategy along with standardized forms for each sample.
2. Investigate the ability of some techniques (transmitted and reflected light microscopy, SEM-EDS, XRD) to accurately describe the original components.
3. Create image analysis software tailored to the specific needs of the analysis of historic cementitious materials.
4. Develop a protocol specific to the analysis of historic cementitious materials.
5. Begin a database of analyses to be accessed by the World Wide Web.

4. References

1 ASTM C 114-85, "A Standard Method for Chemical Analysis of Hydraulic Cement" (Philadelphia: American Society for Testing and Materials, 1985).

2 Walker, M.B. (ed.), "Cambridge Dictionary of Science and Technology" (New York: Cambridge University Press, 1988).

3 Stewart, John; Moore, James, "Chemical Techniques of Historic Mortar Analysis", in "Mortars, Cements and Grouts used in the Conservation of Historic Buildings", Nov 3-1981 Nov 6; (ICCROM, Rome, 1981) 297-310.

4 Jedrzejewska, Hanna, "Old mortars in Poland: a new method of investigation", Studies in Conservation, 5 (No. 4)(1960) 132-138.

5 Cliver, E. B. "Tests for the Analysis of Mortar Samples", Bulletin of the Association for Preservation Technology, 6 (No.1)(1974) 68-73.

6 St John, D.A.; Poole, A.W.; Sims, I., "Concrete Petrography" (John Wiley & Sons, New York, 1998).

7 Carrington, D. and Swallow, P. "Limes and Lime Mortars - Part Two" Journal of Architectural Conservation, No.1, March 1996.

8 Middendorf, B. and Knofel, D., "Investigations of mortars from medieval brick buildings in Germany", Gouda, George R.; Nisperos, Arturo, and Bayles, James (eds.), in "Proceedings of the Thirteenth International Conference on Cement Microscopy", April 8- 11 1991, Wyndham Harbour Island Hotel, Tampa, FL (International Cement Microscopy Association, Duncanville, TX 1991).

9 Dupas, Michel, "L'analyse des mortiers et enduits des peintures murales et des batiments anciens", in "Mortars, cements and grouts used in the conservation of historic buildings" (ICCROM, Rome, 1982).

10 Ciach, T. D.; Penkale, B., "Methods of Investigation for Mortars from the Ancient and Early - Medieval Buildings", in "7th triennial meeting", ICOM committee for conservation, Copenhagen (ICOM ,Rome, 1984) 84.10.5-84.10.7

11 Gulec, Ahmet and Ersen, Ahmet, "Characterization of Ancient Mortars: Evaluation of Simple and Sophisticated Methods"' Journal of Architectural Conservation (No.1)(1998) 56-67.

12 ASTM C1084-92, Standard Test Method for Portland-Cement Content of Hardened Hydraulic-Cement Concrete (American Society for Testing Materials, Philadelphia, 1992).

13 Lindquist, Jan Erik; Schouenborg, B.; Sandstrom, M.; Sandstrom, H.; Sandin, K., and Sidmar, E., "Comprehensive Studies of Old Mortars from Three Medieval Churches in Southern Sweden", International ***Conference on Cement Microscopy*** (1994) 306-322.

14 Rayment, D. L. and Petitifer, K., "Examination of durable mortar from Hadrian's Wall", ***Materials Science and Technology 3*** (1987) 997-1007.

15 Rassineux. F.; Petit, J. C., and Meunier, A., "Ancient Analogues of Modem Cement: Calcium Hydrosilicates in Mortars and Concretes from Gallo-Roman Thermal Baths of Western France, ***Communications of the American Ceramic Society***. 72 (6) (1989) 1026-1032

16 Rayment, D. L., "The Electron Microprohe Analysis of the C-S-H Phases in a 136 Year Old Cement Paste", ***Cement and Concrete Research 16*** (1986) 341-344.

17 Mazzullo. S.J. and Teal, C.S, "Mineralogic and Crystallographic Evidence of Lime Processing, Santa Cruz Maya Site (Classic to Postclassic), Ambergris Caye, Belize", ***Journal of Archaeological Science*** 21(1994) 785-795.

18 Steadman, J. A., "Archaeological Concretes as Analogues", CEC Natural Working Group, second meeting (Interlaken, Switzerland, 1986) pp.165-1771.

19 Lewin, S. Z., "X-Ray Diffraction and Scanning Electron Microscope Analysis of Conventional Mortars", in " Mortars, Cements and Grouts used in the Conservation of Historic Buildings, Nov 3-1981 Nov 6" (ICCROM, Rome, 1981) 101-131.

Annotated Bibliography

1. Abascal-M., R., Harbottle, G. & Sayre, V. Correlation between Terra Cotta Figurines and Pottery from the Valley of Mexico and Source Clays by Activation Analysis. In: *Archaeological Chemistry* (American Chemical Society, Washington, D.C., 1974), pp.81-99.
Use neutron activation and statistical analysis to group sherds by compositional patterns.

2. Adams, J., Dollimore, D. & Griffiths, D. L. Thermal Analytical Investigations of Ancient Mortars from Gothic Churches, *Journal of Thermal Analysis 40*, 275-284 (1993).
Developed mortar formulas for testing from the analysis of medieval mortars. Proportions of hydrated lime and gypsum in the mortars was determined by DTA and TG. The mortars were subjected to mechanical testing and the deformations and failures caused by the compressive forces were recorded.

3. Alastuey, A., Chinchon, J. S. & Lopez-Soler, A. *Study of Lime Renderings Used in Barcelona by Microscopic Methods*, SP Reoprt 1993:15 (Swedish National Testing and Research Institute, 1993).
Report on lime based renderings used in Barcelona between 1860 and 1936. XRD was used to identify binder mineral phases. Ca, Mg, Al and Si distributions were studied on polished sections with SEM-EDXA. Small spherical structures were found, by microscopic examination, to be heterogeneously distributed in some samples. These were found to be related to the distribution of Mg.

4. Allen, G. C.. Hallam, K. R., Radonjic, M., Elton, N. J., Farey, M. & Ashurst, J. X-Ray Diffraction and Environmental Electron Microscopy of Hydrated Limes. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
XRD and environmental scanning electron microscopy are used to study the mineral composition and curing mechanisms of several limes and lime mortars.

5. Andersen, H. D., Zimmermann, H. D., Friis, H. & Schnell, U. Examination of hydraulic lime mortars of Medieval churches in Denmark. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Case study of the examination of several mortars in order to study the deterioration mechanisms and specify a replacement mortar.

6. Anon. *Standard Operating Procedure* Standard Operating Procedure,(National Park Service, unknown).
NPS document developed from the method used at Columbia University, based on the acid digestion of components for quick oxide analysis.

7. Anonymous. Lime Mortars and Repointing, Hampshire County Council Web Site www.hants.gov.uk/plazhn/c1417.html, 1-5 (n.d.).
Practical information on materials and techniques.

8. Ashurst, J. Mortars, Plasters and Renders in Conservation. (Ecclesiastical Architects' and Surveyors' Association, London, 1983).
Review of materials and techniques for the conservation of mortars and plasters. Brief mention of mortar analysis limitations and recording, no details are mentioned. Gives practical advice on pointing, plastering and rendering.

9. ASTM *C294-92* Descriptive Nomenclature of Constituents of Natural Mineral Aggregates C294-92 Descriptive Nomenclature of Constituents of Natural Mineral Aggregates,(American Society for Testing Materials, Philadelphia, 1992).
Method for the determination of the Portland cement portion of a Portland cement based concrete.

10. ASTM *C295-92* Guidefor Petrographic Examination *of Aggregates*for Concrete C295-92 Guide for Petrographic Examination of Aggregates for Concrete,(American Society for Testing Materials, Philadelphia, 1992).
Method for the determination of the Portland cement portion of a Portland cement based concrete.

11. ASTM *C457-92* Practicefor Microscopical Determination of Air-Void Content and Parameters of the Air-VoidSystem in Hardened Concrete C457-92 Practice for Microscopical Determination of Air-Void Content and Parameters of the Air-Void System in Hardened Concrete,(American Society for Testing Materials, Philadelphia, 1992).
Method for the determination of the Portland cement portion of a Portland cement based concrete.

12. ASTM *C 1084-92* Standard Test Method for Portland-Cement Content of Hardened Hydraulic-Cement Concrete (American Society for Testing Materials, Philadelphia, 1992).
Method for the determination of the Portland cement portion of a Portland cement based concrete.

10. ASTM C *114-85* Test Methods for Chemical Analysis of Concrete (American Society for Testing and Materials, Philadelphia, 1985).
Standard for wet chemical analysis of the oxide components of hydraulic (Portland cement) cement.

11. ASTM C *856-95* Standard Practice for Petrographic Examination of Hardened Concrete. (American Society for Testing and Materials, Philadelphia, PA, 1996).

12. Bakos, F., Cimitan, L., Rossi, P. P. & Zaninetti, A.Caratterizzazione petrologica e

chimica di malte pozzolaniche antiche (II), *Materiali e Strutture IV*, 1-19 (1994).
This study uses trace elements to characterize pozzolanic additives.

13. Banfill, P. F. G. & Forster, A. M. A Relationship between Hydraulicity and Permeability of Hydraulic Lime. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Literature review of the relationship between hydraulic properties and permeability of Portland cement and lime based mortars.

14. Baradan, B. Pozzolanic plasters for adobe preservation. In: *Conservation of Stone and Other Materials. Proceedings of the International RILEM/UNESCO Congress* (E&F Spon, New York, 1993), pp. 652-656.
Brick powder, lime and fly ash were added to plain earth plasters used to cover and protect adobe buildings. Different plaster mixtures were tested in situ. It was found that the pozzolanic additives greatly improved the weathering properties of the plasters.

15. Barger, S. M. Materials Characterization of Natural Adobe Plasters: New Approaches for Preservation Strategies Based on Traditional Practice. In: *Materials Issues in Art and Archaeology IV* (Materials Research Society, Pittsburgh, 1995), pp. 389-394.
The durability of aged plaster used to protect adobe is characterized. The anlayses are based on XRD of separated fractions, Chittick analysis for carbonate percentage, optical microscopy. Two types of plasters were found: those with a high lime content and those with a high organic content. It was found that the mechanical stability of the plasters (ie. how hard it is) was not an indicator of the preservative ability of the plasters.

16. Baronio, G., Binda, L. & Saisi, A. Mechanical and Physical Behavior of Lime Mortars Reproduced After the Characterization of Historic Mortar. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Examined mortars prepared in a similar manner to historic mortars and evaluated compressive and flexural strength.

17. Bentz, D. P., Snyder, A. & Stutzman, P. E. Hydration of Portland Cement: The Effects of Curing Conditions. In: *International Congress on the Chemistry of Cement, 10th Proceedings* (National Institute of Standards and Technology, http://flame.cfr.nist.gov/bfrlpubslbuildY7/artOO2.html1997).
This paper discusses the effect of relative humidity on the hydration of cement pastes. Both experimental values, determined by measurement of non-evaporable water content, and computer simulated values were performed. The study found that even relatively minor changes in relative humidity, particularly for the low W/C ratio systems studied, were sufficient to slow or halt the hydrolysis.

18. Binda, L., Baroruo, G. & Tedeschi, C. Experimental Study of Mechanical Role of Thick Mortar Joints in Reproduced Byzantine Masonry. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Reproduced hydraulic/hydrated lime and brick/pozzolana stack bond masonry prisms and tested them mechanically. Conclude that the thick joints increased the durability of the structures.

19. Biscontin, *G.*, Bakolas, A., Zendri, E. & Maravelaki, P. Microstructural and compositional characteristics of historic mortars in Venice. In: *Conservation of Stone and Other Materials. Proceedings of the International RILEM/UNESCO Congress 'Conservation of Stone and Other Materials: Research-Industry-Media'* (E&F Spon, New York, 1993), pp.178-185.
Attempts to study, systematically, a number of different mortars from Venice. Porosimetric measurements determined by mercury porosimeter; DIN sieve series used to determine granulometric distributions, carbon dioxide was determined by the Dietrich-Fruhling method. FT-IR was used to identify granulometric fractions. Conclude that two types of mortar were used in Venice: one made with mostly 125 um particles; the second has a higher percentage of finer particles. Relationships between granulornetric distribution, chemical composition and porosity could be considered indicator elements in the study of mortars.

20. Blades, K. & Stewart, J. The Repair and remedial treatment of the East Block Parliament Buildings, Ottawa, Canada, *Conservation of Building and Decorative Stone* Vol. 2 Ashurst, J. & Dimes, F. *G.)* 114-124 (Butterworth-Heinemann, Boston, 1990).
Treatment of a masonry structure in which the use of a sacrificial lime rendering considered as possible alternative.

21. Blanco-Varela, M. T. *et al.* Environmental Effects of SO2 on Hydraulic Mortars. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Discussion of a study of the interaction between hydraulic mortars S02. Determined that the composition and total porosity determined the sulphation process. All the mortars tested were found to be effected by the SO2.

22. Blauer Bohm, C. Analysis of mortars containing pozzolanas. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Examined historic pozzolana-lime mortars. Found reaction between some of the pozzolana grains only.

23. Blen, K. *et al.* Procedure for a Mortar Type Identification: A Proposal. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-*

Prints (RILEM, Paris, 1999).
Discussion of a procedure to identify pozzolana in lime mortars based on the identification of certain minerals "pozzolana tracers".

24. Blezard, R. G.A Discussion of the paper "Examination of 136 Years old Portland cement concrete" by **G . M** Idorn and N. Thaulow, *Cement and Concrete Research* **14,** 154-156 (1984).
Disputes the suggestion from the Idorn and Thaulow paper that air entrainers were added deliberately. He states that air entrainment bubbles would have occurred accidentally, from the use of mould release agents.

25. Blezard, R. **G** Technical Aspects of Victorian Cement, *Chemistry and Industry 19* September (1981) 630-636..
Excellent review of proto, meso and Portland cements. Much of the discussion is based on analytical evidence. However, the analyses themselves are not covered. Interesting quote, "Oxide analysis data do not give a guide to hydraulic activity - the real criteria being the physical state of the hydraulic compounds formed in the firing.".

26. Boenkendorf, U & Knofel, D. Les mortiers d'enduit dans la construction en pan de bois. In: *Conservation of Stone and Other Materials Proceedings of the International RILEM/UNESCO Congress* (E&F Spon, New York, 1993), pp. 665-672.
Plasters used lo coat timber buildings were analyzed by XRD, Thermal methods (DSC, **DTA,** TG), thin section, an acid digestion chemical method was followed to determine the amounts of calcium carbonate and silica, chromatography, atomic adsorption. Mg^{2+} contents indicated dolomitic source materials. Conservation mortars were developed according to DIN 18555, part 2. The mortars were evaluated by physical and mechanical properties, in the lab as well as in situ.

27. Budelmann, H. The bond between joint mortar and stone in natural stone masonry. In: *Conservation of Stone and Other Materials. Proceedings of the International RILEM/UNESCO Congress* (E&F Spon, New York, 1993), pp. 613-620.
Use meclhanical testing to determine adhesive strength between natural stone and joint mortar is determined by the hygral properties of the stone.

28. Bugini, R. & Salvatori, A. Investigation of the characteristics and properties of 'cocciopesto' from the ancient Roman period. In: *Conservation of Stone and Other Materials. Proceedings of the International RILEM/UNESCO Congress* (E&F Spon, New York, 1993), pp. 386-393.
Examined mortar types based on lime, volcanic sand, brick powder and other fragments known as cocciopesto. The mortar is reported as medium hydraulio, suitable for lining aqueducts and tanks. **A** number of different archaeological sites were sampled. Samples were studies by: thin section; neutron activation analysis was used for elemental analysis. Concluded

that variations in composition linked to the purpose for which the mortar was intended. One of the few studies to emphasize the importance of sampling.

30. Callebaut, K., Elsen, J., Van Balen, K. & Viaene, W. Historical and scientific study of hydraulic mortars from the 19th century. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Use petrographic and SEM-BEI to identify a natural hydraulic mortar

31. Callebaut, K., Viaene, W., Van Balen, K. & Ottenburgs, R. Petrographical, mineralogical and chemical characterization of lime mortars in the Saint Michael's Church. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints (RILEM,* Paris, 1999).
Discussion of a case study and the use of petrographical, mineralogical and chemical analyses to characterize the complicated structure.

32. Cambell, D. H. Microscopical Examination and Interpretation of Portland Cement and Clinker (Portland Cement Association, Skokie, Illinois, 1986).
Comprehensive text on the use of thin and polished sections for the analysis of, primarily, clinker phases for the cement industry. One chapter reviews Ono's methods of kiln control through the microscopical analysis of clinker. Other chapters review the sampling and preparation of sections and particle mounts as well as stains and etches. Photos and detailed explanations of the microscopic characteristics of clinker phases (alite, belite, tricalcium aluminate free lime etc) as well as their interpretations are explained.

33. Campbell, D. H. &Folk, R. L. The Ancient Egyptian Pyramids - Concrete or Rock?, *Concrete International* **August,** 28, 30-38 (1991).
Discusses the controversy over the possibility of the pyramid blocks and their possible construction of man made materials. Primarily based on petrographic analysis.

34. Capannesi, G., Seccaroni, C. & Sedda, A. F. Classification of Fifteenth- to Nineteenth- Century Mortars from Gabii Using Instrumental Neutron Activation Analysis, *Archaeomety* 33,255-266 (1991).
Study uses neutron activation results with statistical analysis to determine provenance classifications.

35. Cardoso, A. A mortar's study for the Cantaber's house of Conimbnga, Portugal. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Case study focusing on the replacement of an old restoration comprised of Portland cement with traditional materials.

36. Carrington, D. & Swallow, P. Limes and Lime Mortars - Part Two, *Journal* of

Architectural Conservation 7-22 (1996).
This is the second half of a paper reported in a previous issue (Nov. 1995). Part Two addresses the specific use of limes in mortar production and compares them to modem Portland cement. Hydraulic limes are introduced, as are other basic mortar components like sand. Binder ratios are discussed and formulations for restoration mortars are given.

37. Charola, A. E. & Henriques, M. A. Hydraulicty in Lime Mortars Revisited. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Reviews the literature and discusses the need for more research in the area of identifying the nature of the hydraulic components of lime mortars.

38. Chayes, F. Petrographic Modal Analysis (John Wiley & Sons, New York, 1956).
Text on the modal analysis of rocks, an introduction to the statistics and applications to petrography.

39. Ciach, T. D., Gillot, J. E., Swenson, E. G. & Sereda, P. J. Microstructure of Calcium Silicate Hydrates, *Cement and Concrete Research 1, 13-25* (1971).
Study the changes in a cement (C3S) paste with XRD and electron microprobe over time. Identify product morphology.

40. Ciach, T. D. & Penkale, B. Methods of Investigation for Mortars from the Ancient and Early - Medieval Buildings. In: *7th Triennial Meeting, ICOM Committee for Conservation* (ICOM, Rome, 1984), pp. 84.10.5-84.10.7.
Describe a test method based on a multi-method approach. This approach combines macroscopic, chemical and quantitative microscopy with polarized light microscopy and SEM.

41. Cliver, E. B. Tests for the Analysis of Mortar Samples, *Bulletin of the Association for Presrrvation Technology* 6, 68-73 (1974).
A method of analyzing and classifying mortars based on wet chemical analysis.

42. Petrography of Cementious Materials. In: *Petrography of Cementious Materials* (editor Committees C-1 on Cement and C-9 on Concrete and Concrete Aggregates) (American Society for Testing and Materials, Philadelphia, PA, 1994).
Nine papers presented at the conference on the analysis of clinker and concrete sections by a number of petrographic methods. The articles cover point counting standards, SEM analysis and computer modeling, petrographic methods and Ono's methods.

43. Deloye, F.-X. Le Calcul mineralogique Application aux monuments anciens, *Bulletin De Liaison Des Laboratoires Des Ponts Et Chaussees 175,* 59-65 (1991).

Describes several methods for characterizing historic mortars (wet chemical, thermogravimettry, SEM). Uses a ratio of (Si+Al+Fe)/(Ca + Mg) to define "pouzzolanicite".

44. Deng, M., Han, S. F., Lu, Y. N., Lan, X. H., Hu, Y. L. & Tang, M. S. Deterioration of Concrete Structures Due to Alkali-Dolomite Reaction in China, *Cement and Concrete Research* **23,** 1040-1046 (1993).
Studied alkali-aggregate reactions of concrete by use of XRD, petrographic and chemical analyses. Structures were sampled and the cores were polished. The cracks running through the mortar were caused by the expansion of the coarse aggregate. The article describes petrographic elements that are illustrative of alkali-silicate reactions.

45. Depraetere, W., Carmeliet, J. & Hens, H. Moisture Transfer at Interfaces of Porous Materials: Measurements and Simulations. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Discussion of the nature of different interfacial zones between mortar and bricks.

46. Drdacky, M., Valek, M. J. & Prochazka, P. P. Spalling of Historic Mortars. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
A model developed to determine the mechanical behavior of mortars re-enforced with goat hair.

47. Dupas, M. L'analyse des mortiers et enduits des peintures murales et des batiments anciens. In: *Mortars, Cements and Grouts Used in the Conservation of Historic Buildings* (ICCROM, Rome, 1982).
Describes a chemical procedure for analyzing historic mortars and plasters from wall paintings. Calcium carbonate is determined by calcination and dilute hydrochloric acid solutions are used to digest samples. Procedure based on those of Jedrzejewska.

48. Ellis, P. R. Analysis of Mortars (to include historic mortars) by Differential Thermal Analysis. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Review of thermal analysis and its application to mortar analysis, uses case studies as examples combining DTA, chemical analysis and microscopic examination.

49. Erlin, B., Hime & W.G. Evaluating Mortar Deterioration, *Association for Preservation Technology* **XIX**, 8-10, 54 (1987).
General review of mortar analysis with emphasis on failed structures.

50. Facaoaru, I. & Lugnani, C. Contributions to the diagnosis of stone and concrete historical structure using non-destructive techniques. In: *Conservation of*

Stone and Other Materials. Proceedings of the International RILEM/UNESCO Congress (E&F Spon, New York, 1993), pp. 238-251.
Reviews several "non-destructive" techniques for determining the extent of damaged layers, voids, and metallic inclusions. Some of the methods recommended are: ultra-sonic pulse methods, radiometric methods, surface hardness methods and strain measurements.

51. Fischer, K. Traditional Craftsmanship in Modem Mortars - Does it Work in Practice? In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Discusses the need for skilled, experienced craftsman used in conjunction with analysis for successful mortar repair.

52. Furlan, V. & Pancella, R.Examen microscopique en lumiere reflechie de ciments, betons et mortiers, *Chantiers/Suisse* **13,** 25-30 (1982).

53. Garboczi, E. J., Bentz, D. P. & Snyder, K. A. Modeling the Structure and Properties of Cement Based Materials *An Electronic Monograph* (National Institute of Standards and Technology, http://cik s.cbt.nist.gov/garbocz/monograph, n.d.).
An extensive monograph of over 10 chapters on different aspects of computer modeling used to study the properties of cementious materials. Review: percolation theory; microstructural development; transport and elastic properties; degradation of mortar and concrete.

54. Gebhardt, R. F. Rapid Methods for Chemical Analysis of Hydraulic Cement 158 (American Society for Testing and Materials, Ann Arbor, MI, 1988).
Ten articles on rapid and instrumental methods used for the analysis of hydraulic cements. Appendix I is a direct determination method for alumina. Appendix II is ASTM methods for Chemical Analysis of hydraulic cements.

55. Goins, E. A New Protocol for the Analysis of Historic Cementitious Materials: Interim Report. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
A literature survey and review of the analysis of historic mortars.

56. Goldschmidt, A. & Marttens, H. Scanning Electron Microscopy and Microprobe analysis of an Aztec Mortar, *The Microscope* **39,** 187-194 (1991).
This study compares an "Aztec" mortar to modem Portland type cement by using SEM-EDS and microprobe analysis. The Aztec mortar was found to have been derived from a lime and clay mixture without the addition of any pozzolana type additives. These conclusions were based on alumina, silicon and calcium ratios determined for the Aztec mortar. The ratios were found to correspond to clay.

57. Grattan-Bellew, P. E., Quinn, E. G. & Sereda, P. J. Reliability of Scanning

Electron Microscopy Information, *Cement and Concrete Research* **8**, 333-34.2 (1978).
Reviews errors encountered with SEM analysis. One very important error was listed as the tendency to describe minor phases or structures as descriptive of the material.

58. Gulec, A. Characterization of mortars and plasters from historic monuments in Turkey, *Conservation of Historic Brick Structures* (eds. Baer, *N*. S., Fitz, S. & Livingston, R. A.) 209-221 (Donhead, Shaftsbury, 1998).
Case study to determine properties of restoration mortars.

59. Gulec, A. & Ersen, A Characterization of Ancient Mortars: Evaluation of Simple and Sophisticated Methods, *Journal of Architectural Conservation* 56-67 (1998).
This article reviews some of the more commonly used chemical techniques. Experimental procedures include: loss on ignition; sieve analysis; analysis of water soluble salts; petrographic analysis; XRD; SEM-EDXA; physical properties determined were specific gravity, total porosity and water absorption; mercury porosimmetry was used to determine pore size distribution.

60. Hansen, E. F., Tagle, A., Erder, E., Baron, S., Rodriquez-Navarro, C. & Van Balen, K. Effects of Aging on Lime Putty. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Discussion of the changing size and shape of portlandite crystals and their effect on the viscosity, plasticity and workability of mortar made from lime putty. Modify ASTM tests to study the physical properties of lime putty.

61. Analyses for Cement and Other Materials in Hardened Concrete *Standard Technical Publication* (American Society for Testing Materials, West Conshohocken, 1997).
An extended discussion of the chemical analysis of concrete ASTM STP 169.

62. Hoffmann, D. *EuorLime Colloquium* **Newsletter No. 1**, 32-35 (1991).
Places the importance of studying historic mortars on the evaluation of physical parameters as opposed to chemical which change over time.

63. Hoffmann, D. & Niesel, K. Change in Physico-technical Characteristics in Brick Masonry Effected by Modified Composition, *Conservation of Historic Brick Structures* (editors Baer, *N*. S., Fitz, S. & Livingston, R. A.) 361-380 (Donhead, Shaftesbury, Dorset, 1998).
Studies the effect of the aggregate particle size and distribution on moisture transport.

64. Hoffmann, D. & Niesel, K. Effects of Air Pollutants on Renderings - Exposure Tests, *Conservation of Historic Brick Structures* (editors Baer, N. S., Fitz, S. & Livingston, R. A.) 251-280 (Donhead, Shaftesbury, Dorset, 1998).

65. Hoffmann, D. & Niesel, K. Effects of Air Pollutants on Renderings - Reaction Zones on Buildings vs. Orientation, *Conservation of Historic Brick Structures* (editors Baer, N. S., Fitz, S. & Livingston, R. A.) 265-280 (Donhead, Shaftesbury, Dorset, 1998).

66. Hoffmann, D., Niesel, K. & Rooss, H. Effects of Air Pollutants on Renderings, *Conservation of Historic Brick Structures* (editors Baer, N. S., Fitz, S. & Livingston, R. A.) 235-249 (Donhead, Shaftesbury, Dorset, 1998).

67. Hughes, D. C. & Sugden, D. B. The use of brick dust as a pozzolanic addition to hydraulic lime mortars. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Discussion of experiments that suggest that the relative strength increase brought about by brick is a combination of particle size, curing conditions and age.

68. Hughes, D. & Swann, S. Hydraulic limes - a preliminary investigation, *Lime News* **6**, 41-52 (1998).

69. Hughes, J. J. & Callebaut, K. Practical Sampling of Historic Mortars. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
The development of sampling strategies based specific targets and variability of the materials.

70. Idorn, G. M. & Thaulow, N. Examination of 136 Years old Portland cement concrete, *Cement and Concrete Research* 13,739-743 (1983).
A piece of Portland cement, cast in 1847, was examined by petrographic methods. Clinker phases were studied by microscopical examination of the polished section. Conclude that the cement was made from coarsely ground particles with a low w/c ratio. This article is interesting in that it is not simply a description. Rather, petrographic methods are employed to try and re-create production methods and technological advancements used in the making of the cement.

71. Idorn, G. M. & Thaulow, N.A reply to a discussion by R.G. Blezard of the Paper: "Examination of 136 Years old Portland cement concrete", *Cement and Concrete Research* 14,157-158 (1984).
Further refine their conclusions in reply to Blezard's criticism of the original paper.

72. Jablczynska-Jedrzejewska, H.Dawne zaprawy budowlane, *Kwartalnik Architetury i Urbanistyki* **3,** 85-94 (1958).
Discussion of the principles for a new method, based on chemical

techniques, to classify historic mortars. The mortars are classified into groups by determining three basic constituents of the mortar: sand, carbonized lime and the hydraulic index. Abstract in English.

73. Jedrzejewska, H. Ancient Mortars as criterion in analyses of old architecture. In: *Mortars, Cements and Grouts Used in the Conservation of Historic Buildings* (ICCROM, Rome, 1982).
Attempts to define different procedures based on the needs of the research being carried out. Two kinds are listed: technological based studies versus chronological studies where mortars are used to establish relative dating of archaeological sites. Explains a procedure of "comparative analysis" for the archaeologist that is based on classifying mortars according to their original recipes. This can help identify groups of masons by acting as a signature or "calling card". Stresses the urgent need for standardization so that results may be compared across laboratories.

74. Jedrzejewska, H. Old mortars in Poland: a new method of investigation, *Studies in Conservation 5*, 132-138 (1960).
This method was developed to quickly screen for hydraulic lime mortars made in Poland. It is based on the acid digestion of the mortar. The amount of carbon dioxide is measured and subtracted from the initial sample weight. The difference is attributed to a "solubles" component, that is, substances soluble in acid without the evolution of carbon dioxide. The most common components found in the Polish mortars were established both by macroscopic observation and by analysis are: lime or gypsum binders; clay, crushed brick, powdered stone material, crushed iron ore hydraulic additives; sand, crushed limestone, crushed fragments of a gypsum mortar filler.

75. Karaveziroglou, M. & Papayianni, I. Compressive Strength of Masonry with Thick Mortar Joints. In: *Conservation of Stone and Other Materials. Proceedings of the International RILEM/UNESCO Congress* (E&F Spon, New York, 1993), pp.212-219.
The compressive strengths of masonry with thick mortar joints was determined. The formula for the mortar was based on an unspecified analysis of ancient mortars: lime, pozzolana from Santorin, natural sand, crushed brick.

76. Koschik, H. & Snethlage, R.Die romischen Thermen von WeiBenburg (Bayern) Kulturhistorischer Uberblick - Untersuchung an Morteln und Putzen, *Arbeitsblatter Fur Restauratoren* 6,134-148 (1980).

77. Lameille, J. M., Goutiere, G., Petit, J. C. & Regourd, M. Retention of Cobalt, Cesium and Strontium in the Hydrates of C3S, C3A, and Gypsum, *Journal of the American Ceramic Society* **70,** 604-614 (1987).

78, Larsen, P. K. Salt damage to the medieval plaster on a vault in Fanefjord Church.

In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Recommend climate control to slow down salt induced deterioration processes.

79. Leslie, A. B.; Gibbons, P. Mortar analysis and repair specification in the conservation of Scottish Historic Buildings. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
practical approach to mortar characterization used to determine compatible repair mortars. Acid digestion and thin section analysis are described.

80. Lewin, S. Z. X-Ray Diffraction and Scanning Electron Microscope Analysis of Conventional Mortars. In: *Mortars, Cements and Grouts Used in the Conservation of Historic Buildings* (ICCROM, Rome, 1981), pp. 101-131.
Methodical study of a number of different mortar samples prepared for the anlaysis. XRD and SEM were used to identify the different mineral phases occuring as mortar components changed.

81. Lindquist, J. E., Schouenborg, B., Sandstrom, M., Sandstrom, H., Sandin, K. & Sidmar, E. Comprehensive Studies of Old Mortars from Thtee Medieval Churches in Southern Sweden. In: *International Conference on Cement Microscopy* 1994), pp. 306-322.
Mechanical and mineralogical testing were carried out on 30 samples from three Swedish churches. The physical properties studied were: compressive strength, frost resistance and capillary coefficient. The binder content and the proportion of aggregate to binder was calculated from three different values: insoluble residue, calcium oxide content; and loss on ignition. Thin sections were evaluated by polarized light microscopy and computer assisted image analysis for determining particle size distribution etc. based on point counts of 500-700. Microscopy was used extensively to study the binder.

82. Lynch, G. Lime Mortars for Brickwork: Traditional Practice and Modern Misconceptions - Part One, *Journal of Architectural Conservation* 7-20 (1988).
Reviews historical sources to dispel the widely held belief that all historic mortars (for brickwork) are non-hydraulic. Also describes production methods.

83. Lynch, G. Lime Mortars for Brickwork: Traditional Practice and Modem Misconceptions - Part Two, *Journal of Architectural Conservation* 7-19 (1988).
This is the second part of a paper begun in the preceding issue (No. 1 1988). This section discusses eminently hydraulic limes and their associated problems or inconsistencies. Suggestions and a summary for

using traditional lime mortars for conservation are given.

84. Malinowski, R. Concretes and Mortar in Ancient Aqueducts, *Concrete International* **January,** 66-76 (1979).
Studied mortar and concrete from ancient Roman water conduits. Determined by a variety of methods that tank and aqueduct linings were comprised of several layers of different cement types. The linings did not depend on the incorporation of hydraulic materials for water resistance but on the impaction of the microstructure by physical methods like polishing. Also conducted experiments to imitate expanding sealant as described by Vitruvius.

85. Malinowski, R. & Garfinkel, Y. Prehistory of Concrete, *Concrete International* **March,** 62-68 (1991).
Reviews the very early history of ancient concrete floors and their structure.

86. Mallinson, L. G. & Davies, I. LI. A Historical Examination of Concrete, Nuclear Science and Technology (Commission of the European Communities, Luxembourg, 1987).
Report contains a review of the literature on the analysis of historic concrete. Describes results and conclusions of the analysis of a number of samples from Hadrian's Wall, an ancient Greek water tank and Woolston Quay, to name a few. The analyses focus on the study of the durability of these concretes for research in storing radioactive waste.

87. Martinet, G. & Quenee, B. Proposal for an useful methodology for ancient mortars study. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Description of an approach that combines petrographic analysis, chemical analysis and XRD.

88. Maurenbrecher, A. H. P., Suter, G. T., Trischuk, K. & Fontaine, L. Contribution to pointing mortar to Durability. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Study the failure of mortars by evaluating mechanical properties of stack bonded samples.

89. Mazzullo. S.J. & C.S. Teal. Mineralogic and Crystallographic Evidence of Lime Processing, Santa Cruz Maya Site (Classic to Postclassic), Ambergris Caye, Belize, *Journal of Archaeological Science* 21,785-795 (1994).
Use SEM and XRD to study calcium carbonate layers at Mayan archaeological sites. These layers were found to be the remnants of the lime pits used for lime processing. The basis for the experimental work is that if the calcium carbonate layers are altered limes, then mineralogic and crystallographic relics of the CaO and calcium hydroxide precursors should be present.

90. McCrone, W. C., Draftz, R. G. & Delly, J. G. The Particle Analyst 224 (Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1969).
Microscopy reference.

91. Meucci, C. & Rossi-Doria, P. Analyse et caracterisation de quelque type d'anciens mortiers orientals. In: *Mortars, Cements and Grouts Used in the Conservation of Historic Buildings* (ICCROM, Rome, 1982).
Mortars are analyzed by XRD, classic volumetric methods were used for carbonate and sulfate determination, mercury porosimetry was used to determine pore structure. Results indicate a direct correlation between the pore distribution and the chemical-mineralogical compositions.

92. Michoinova, D. Lime based Mortars for restoration of historical mortars especially under wall paintings. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Discusses the modification of mechanical properties of lime based mortars.

93. Middendorf, B., Baronio, g., Callebaut, K. & Hughes, J. Chemical-Mineralogical and Physical- Mechanical Investigations of Old Mortars. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints (RILEM,* Paris, 1999).
Description of method that combines thin section analysis, XRD and oxide analysis for characterization of historic mortars.

94. Middendorf, B. & Knofel, D. Characterization of Historic mortars from buildings in Germany and the Netherlands, *Conservation of Historic Brick Structures* (eds. Baer, *N*. S., Fitz, S. & Livingston, R. A.) 177-196 (Donhead, Shaftsbury, 1998).
Results of the chemical and mineralogical studies of a number of mortars from case studies. Contains appendices of investigative techniques and photographs of thin sections.

95. Middendorf, B. & Knofel, D. Gypsum and lime mortars of historic German brick buildings, *Conservation of Historic Brick Structures* (eds. Baer, *N*. S., Fitz, S. & Livingston, R. A.) 197-208 (Donhead, Shaftsbury, 1998).
Results of chemical and mineralogical investigations of gypsum containing mortars. Discuss the mechanical properties of restoration mortars.

96. Middendorf, B. & Knofel, D. Investigations of mortars from medieval brick buildings in Germany. In: *Proceedings of the Thirteenth International Conference on Cement Microscopy* (International Cement Microscopy Association, Duncanville, TX, 1991).
Historic mortars from Northern Germany were studied to identify the type of binder and aggregate used. Includes very detailed description of sampling procedures. Samples are digested and studied by Atomic

Adsorption Spectroscopy, SEM-EDX, XRD, and thin section analysis. A thorough description of experimental methodology and procedures are given. The main point of this paper is the microscopy work carried out to study aggregates and reactions between the binder and aggregate.

97. Mikhail, R. Sh. & Malek, R. I. A Microstructure of Hardened Gypsum Pastes, *Journal of Applied Chemistry and Biotechnology* 21,277-282 (1971).
Use SEM to study gypsum microstructure.

98. Montana, G. Mineralogical-petrographic characterization of plasters by BSE images and their digital processing, *Science and Technology for Cultural Heritage* 4, 23-31 (1995).
Describes the advantages of using BSE imaging (in conjunction with SEM). Discusses its use in resolving mineralogic and petrographic features like binder to aggregate ratio and pore area percentage.

99. Moriconi, G., Castellano, M. G. & Collepardi, M. Mortar deterioration of the masonry walls in historic buildings. A case history: Vanvitelli's Mole in Ancona, *Materials and Structures* 27,408-414 (1994).
Report uses XRD pattern enhancing and fitting combined with data from historical and environmental sources. Conclude that the original lime-pozzolana mortar deteriorated from different mechanisms than those that attacked areas of Portland cement.

100. Morin, A. *APT Bulletin, The Journal of Preservation Technology* **XXVII**, 16-17 (1996).
Excerpts from a report on experiments conducted by Morin in 1834, "Nouvelles experiences sur l'adherence des pierres et des briques posees en bain de mortier ou scellees en platre...faites a Metz en 1834 par Arthur Morin." Morin tested the cohesive strength of cured mortar in shear. The mortar was a hydraulic lime and sand mixture prior to the widespread use of Portland cement. The mortar was made from 3 parts of fine sand from the Moselle River, without pebbles, and one part of hydraulic lime from Vallieres, near Metz.

101. Moropoulou, A., Theodoraki, A., Bisbikou, K. & Michailidis, M. Restoration Synthesis of Crushed Brick Mortars Simulating Byzantine Lime and Material Technologies in Crete. In: *Materials Issues in Art and Archaeology IV* (Materials Research Society, Pittsburgh, 1995), pp. 759-768.
Characterize ancient mortars with the primary goal of creating an effective conservation mortar. Methods used are: optical microscopy, XRD, thermogravimetric, mercury porosimetry, IR Spectroscopy. concludes that a number of factors must be consistent to the traditional mortars: mixture ratio, lime technology, raw materials, crushed brick granulometry, texture and application techniques.

102. Moropoulou, A., Theoulakis, P., Bisbikou, K., Theodoraki, A. & Chondros, N. Study of mortars in the medieval city of Rhodes. In: *Conservation of Stone and Other Materials. Proceedings of the International RILEM/UNESCO Congress* (E&F Spon, New York, 1993), pp. 394-401.
A number of mortar samples were studied by XRD, DTA, thin section, SEM, mercury porosimetry, and chemical analyses. The mortars appeared to have the same binder to aggregate ratio and granulometric distribution. Therefore, it was concluded that the same production methods and materials were used throughout the different building periods of the city.

103. Morris, M. The Cast-in-Place Theory of Pyramid Construction, *Concrete International* **August,** 29, 39-44 (1991).

104. Nagele, E. Untersuchung historischer Baustoffe mit modernen physkikalischen Methoden, *Bautenschutz Bausaneirung* **10,** 118-123 (1987).

105. Niesel, K. Zum problem des Nachstellens von Kalkmorteln, *Bautenschutz+Bausanierung* **17,** 65-68 (1994).
Discusses the problems associated with reproducing mortars that have changed considerably over time.

106. Hydration and Setting of Cements. In: *Proceedings of the International RILEM Workshop on Hydration and Setting Organized by the Laborafoire De Recherche Sur La Reactivite Des Solides, Universite De Bourgogne, France* (E&F Spon, New York, 1992).
Book is comprised of 33 papers presented at the proceedings. Different sections of the proceedings deal with subjects such as microstructural evolution, strength development, particle interactions during hydration and setting. The research deals with Portland type hydraulic cements used for building and civil engineering.

107. Papayianni, I, & Karaveziroglou, M. Aggregate gradation of ancient mortars. Relationships to strength and porosity. In: *Conservation of Stone and Other Materials. Proceedings of the International RILEM/UNESCO Congress* (E&F Spon, New York, 1993), pp.493-500.
The samples in this study were crushed by hand in order to separate the aggregate from binder. The mortars studied were based on lime and pozzolana. It was concluded that strength was linked to porosity, which is obtained by use of even gradations of aggregate in the mix.

108. Papayianni, I. & Theocharidou, K. Efflorescence tendency of mortars used in interventions on old masonry. In: *Conservation of Stone and Other Materials. Proceedings of the International RILEM/UNESCO Congress* (E&F Spon, New York, 1993), pp. 621-928.
A number of laboratory mortars were prepared from pozzolanic materials, lime, brick powder, small amounts of cement. Soluble salts were included in the mortar mix. Mortars were evaluated by strength, water absorption,

capillarity and efflorescence tendency. They conclude that the porosity or pore size distribution is the significant factor in the tendency to form efflorescences between mortars of approximately equal alkali contents. They found that a lime to pozzolana ratio of 1:1 was the best at limiting the formation of soluble salts.

109. Petruk, W. ed. Short Course on Image Analysis Applied to Mineral and Earth Sciences (Mineralogical Association of Canada, Ottawa, 1989).
18 papers on image analysis applied to mineralogy, software packages, innovative techniques.

110. Phillips, M.A Source of Confusion about Mortar Formulas, *APT Bulletin* **XXV**, 50-53 (1994).
Discussion of errors that occur when following recipes or guidelines for proportioning and mixing mortars. Sizable errors can occur due to volume changes that occur when the ingredients are wetted.

111. Phillips, M. An Actual Mortar Analysis, *APT Bulletin (Association Preservation Technology)* **XXV**, 54-55 (1994).
Inductively Coupled Plasma (ICP) analysis carried out on a New England Mortar. In order to attempt to date the mortar, it was compared to samples taken from a local quarry known to be discovered ca. 1697. Profiles of trace elements were different between the two sets of samples indicating that the mortar used lime that did not come from the local source. It was concluded that the mortar predates the discovery of the local source.

112. Ragai, J., Sing, K. S. W. & Yates, M. Porosity of Ancient Egyptian Mortars, *Characterization of Porous Solids II* Studies in surface science and catalysis (editors Rodriquez-Reinoso, F. e. al.) 693-699 (Elsevier Science Publishers B.V., Amsterdam, 1991).
Mercury porosimetry studies indicate that Ancient Egyptian mortars are characterized by two sets of pore size distributions within the gypsum binder matrix.

113. Rassineux, F., Petit, J. C. & Meunier, A. Ancient Analogues of Modem Cement: Calcium Hydrosilicates in Mortars and Concretes from Gallo-Roman Thermal Baths of Western France, *Communications of the American Ceramic Society* **72,** 1026-1032 (1989).
Characterizes the materials using thin section analysis, SEM, XRD and electron microprobe. Were able to locate calcium aluminum silicate areas and compared compositions to OPC.

114. Rayment, D. L. The Electron Microprobe Analysis of the C-S-H Phases in a 136 Year Old Cement Paste, *Cement and Concrete Research* 16,341-344 (1986).
Use electron microprobe analysis to study C-S-H paste around alite grains of a meso-Portland cement.

115. Rayment, D. L. & Majumdar, A. J. The Compostion of the C-S-H Phases in Portland Cement Pastes, *Cement and Concrete Research* 12,753-764 (1982).
Use SEM-EDS to determine best way to characterize C-S-H gel ratios.

116. Rayment, D. L. & Petitifer, K. Examination of durable mortar from Hadrian's Wall, *Materials Science and Technology* 3,997-1007 (1987).
Studied cores from Hadrian's wall by SEM, EPMA, DSC, XRD and wet chemistry. They were able to locate substantial quantities of C-S-H gel.

117. Rodriguez-Navarro, C. & Hansen, E. G. W. S. Calcium Hydroxide Crystal Evolution upon Aging of Lime Putty, *Journal of the American Ceramic Society* 81, 3032-3034 (1998).
A model for portlandite evolution in slaked and aged putty is proposed. the crystals undergo a significant reduction in size as well as morpholgical changes that increase overall surface area.

118. Rossi-Doria, P. Mortars for restoration: basic requirements and quality control, *Materiaux Et Constructions* 19,445-448 (1986).
Reviews fundamental requirements for mortars used in restoration. Emphasizes the need for research to define standard parameters so that the restoration mortar may be as similar in nature as possible to the original mortar. Notes that the characterization of ancient mortars is often incomplete due to sampling difficulties. States that research to date studied different materials and characteristics so that it is impossible to extract a general methodology (of mortar analysis) from them. Reviews some testing methods for physical characteristics such as pore size distribution, surface hardness, water vapor permeability, color etc.

119. Roy, D. M. & Langton, C. A. Characterization of Cement-Based Ancient Building Materials in Support of Repository Seal Materials Studies, Technical Report BMI/ONWI-523 (Office of Nuclear Waste Isolation Battelle Memorial Institute, Columbus, OH, 1983).
Detailed report on analysis conducted on ancient Greek and Cypriot mortars The work is focused on understanding these materials and their long term stability. A number of different techniques were used: microscopy; SEM; XRD; chemical analysis; DTA; TGA; and more. They conclude that the long-term durability exhibited by the materials was a complex function of both chemical and microstructural factors.

120. Roy, D. M. & Langton, C. A. Longevity of Borehole and Shaft Sealing Materials: 2. Characterization of Cement-Based Ancient Building Materials,(prepared by the Pennsylvania State University for the Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, OH, 1982).

121. Sarkar, A. K. & Roy, D. M. A New Characterization Technique for Trimethylated

Products of Old Cement Pastes, *Cement and Concrete Research* **9**, 343-352 (1979).
Describes a technique for identifying poorly or non-crystalline silicate anions by use of trimetholsilanol. The TMS attaches to the surface of the oxygen anions on the silicate. The anions are identified by Gas Chromotography.

122. Sarkar, S. L. Microsturucture of a very low water/cement silica fume concrete, *The Microscope* **38,** 141-152 (1990).
The effect of low water ratios on concrete microstructure and paste strength are studied. By using silica fume, much lower W/C ratios can be used leading to great increases in compressive strengths. The paste microstructure was studied by TEM/SEM/EDXRA.

123. Sass, S. A case Study: Mortar analysis at Pigeon Island National Landmark and Morne Fortune, St. Lucia, West Indies, Interim report. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Analysis of mortars to direct future research.

124. Schafer, J. & Hilsdorf, H. K. Ancient and new lime mortars - The correlation between their composition, structure and properties. In: *Conservation of Stone and Other Materials. Proceedings of the International RILEM/UNESCO Congress* (E&F Spon, New York, 1993), pp. 605-612.
Mortars were analyzed in order to define parameters for the creation of mortars for preservation. The mortars were characterized by XRD, thermal analysis, chemical and thin section analyses, granulometric distribution of the aggregate. Laser granulometry and B.E.T. (specific surface area) were carried out on mortars made in the laboratory. The modem lime mortars were found to have a lower porosity.

125. Scrivener, K. L.A Study of the Microstructure of Two Old Cement Pastes, *8th International Congress on the Chemistry of Cement, Rio De Janeiro* **3,** 389-393 (1986).
Compare the microstructures of a 23 year old OPC paste and a meso-cement paste made by William Aspdin in 1848. BSE-SEM were used to study polished surfaces. Found evidence of original cement grain boundaries to determine the original particle size distribution.

126. St. John, D. A., Poole, **A.** W. & Sims, I. Concrete Petrography (John Wiley & Sons, New York, 1998).
Extensive text on the petrography of concrete, historic mortars and cements. Also includes reviews of other techniques used in the analysis of concrete.

127. Steadman, J. A. Archaeological Concretes as Analogues. In: *CEC Natural Working Group, Second Meeting* 1986), pp.165-1771.

Review of the work carried out at BRE on the study of ancient CSH gel. Gives some detail on the Hadrian's wall study.

128. Stewart, J. Chemical Techniques of historic mortar analyses, *Bulletin-Association for Preservation Technology 14*, 11-16 (1982).
Description of oxide analysis techniques for the study of historic mortars.

129. Stewart, J. & Moore, J. Chemical Techniques of Historic Mortar Analysis. In: *Mortars, Cements and Grouts Used in the Conservation of Historic Buildings* (ICCROM, Rome, 1981), pp.297-310.
The authors review three commonly used chemical methods of mortar analysis: the Jedrzejewska technique; the E.B. Cliver technique; and ASTM C85-66. They subjected prepared mortar samples to the three techniques and found that the Jedrzejewska technique was the one found to be the most applicable to the analysis of historic mortars. The technique is meant to be a rapid, semi-quantitative screening for hydraulic components. The ASTM method is only suitable for modem, Portland type cements. The E.B. Cliver technique did not successfully analyze the prepared samples.

130. Suter, G. T., Vandenberg, J. & Fontaine, L. Bond capacity of mortars for historic structures, *APT Bulletin, The Journal of Preservation Technology* XXVII, 27-35 (1996).
Different mortars, with a constant ratio of binder to aggregate of 1:3, were tested by evaluating compressive strength and bond capacity. Additives such as latex, pozzolana and porous particles were tested, as partial aggregate replacement, as to their ability to improve the bond. They conclude that each mortar mix should be adjusted as to its workability to the substrate (eg. sandstone masonry units had higher bond capacities when a dlrier mortar was applied). Also, that mortar compressive strengths can be substantially reduced while still maintaining adequate bond capacity

131. Swallow, P. & Carrington, D. Limes and Lime Mortars - Part One, *Journal of Architectural Conservation* 1, 7-25 (1995).
This paper reviews the history of the technology of lime and lime mortars. Sources and types of limes used in England and Wales are described. All process from slaking to developments in kiln design are covered.

132. Taylor, H. F. W. Cement Chemistry (Academic Press, New York, 1990).
Test book on the chemistry of the principal silicate and aluminate based hydraulic cements commonly used in building and civil engineering. This is a completely re-written successor to the earlier 'The Chemistry of Cements' written in 1964. The text deals with the chemistry rather than practical applications. Chapters include: Portland cement and its major constituent phases; High-temperature chemistry; The chemistry of Portland cement manufacture; Properties of Portland clinker and cement;

Hydration of the calcium silicate phases and of Portland cement; Structural properties; composite cements.

133. Taylor, H. F. W. & Newbury, D. E. An Electron Microprobe Study of a Mature Cement Paste, *Cement Concrete and Research* 14, 565-573 (1984).
EPMA analysis of a 23 year old paste showed that the shapes of the cement grains are preserved by the hydrated material.

134. Taylor, H. *Chemistry and Industry* 19,620-625 (1981).
Brief review of Portland cement phases, hydration products and C-S-H gel.

135. Teutonico, J. M., McCaig, I., Bums, C. & Ashurst, J. The Smeaton Project: Factors Affecting the properties of lime-based mortar, *Lime News* 2, 7-13 (1994).

136. Teutonico, J. M., McCaig, I., Burns, C. & Ashurst, J. The Smeaton Project: Factors .Affecting the properties of lime-based mortar, *Bulletin of the Association for Preservation Technology* **25**, 32-49 (1994).

137. Teutonico, J. M., McCaig, I., Burns, C. & Ashurst, J. The Smeaton Project: Factors Affecting the properties of lime-based mortar, *Eurolime Newsletter* **2**, 71-77 (1994).

138. Teutonico, J. M. A Comparative study of hydraulic lime mortars. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints (RILEM,* Paris, 1999).
Describes the results of the Smeaton project (English Heritage) and a new projected conducted with BRE.

139. Conservation of Stone and Other Materials. In: *Proceedings of the International RILEM/UNESCO Congress 'Conservation of Stone and Other Materials: Research-Industry-Media'* (E&F Spon, New York, 1993).
106 papers presented at this conference, mostly on the conservation of natural stone. However, there are a handful of articles on mortars and plasters.

140. Thomassin, J. H. & Rassineux, F. Ancient Analogues of cement-based materials: stability of calcium silicate hydrates, *Applied Geochemistry* 137-142 (1992).
Reviews two recent studies that have addressed the durability of ancient mortars. The methods used in these studies allow for precise mineralogical identification, the validity of which depends on rigorous sampling procedures. The study of the mineral phases present in the ancient mortars allows the authors to model cementious matrices of long term stability.

141. Thornson, M. L. Plasticity, water retention, soundness and sand carrying capacity: what a mortar needs. In: *International Workshop Historic Mortars:*

Characteristics and Tests, Pre-Prints (RILEM, Paris, 1999).
Discussion of various properties of dolomite and high calcium lime putties.

142. Toumbakari, E. E. & Van Gemert, D. Methodology for the design of injection grouts for consolidation of ancient masonry. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Discuss blends of Portland cement, lime and natural pozzolana to restore historic structures.

143. Toumbakari, E. E. & Van Gemert, D. Methodology for the design of injection grouts for consolidation of ancient masonry. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Compares new ready made restoration mortars to traditional materials.

144. Tuncoku, S. S., Caner-Saltik, E. N. & Boke, H. Definition of the materials and related problems of a XIIIth century Anatolian seljuk 'mescid': a case study in Konya City. In: *Conservation of Stone and Other Materials. Proceedings of the International RILEM/UNESCO Congress* (E&F Spon, New York, 1993), pp. 368-375.
Analyzed the mortars used for both bricks and stone masonry within the mescid. The mortars were found to have similar water absorption capacities, porosities, and densities. The mortar used for the stone, however, was slightly denser. The mortars and gypsum plasters were dissolved in dilute hydrochloric acid. They are reported as percentages of aggregate and acid-soluble material. The binder is assumed equal to the acid soluble material. Both mortars have a larger percentage of binder to aggregate (a little larger than 1:1 ratio). The plaster had very little aggregate. The aggregates were sieved and size distributions reported.

145. Valek, J., Hughes, J. & Bartos, J. M. Portable Probe Gas Permeametry in the Testing of Historic Masonry and Mortars. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Discussion of the application of permeatry to historic masonry and the measurement of a structure's permeability.

146. van Hees, R. P. J. Damage Diagnosis and Compatible Repair Mortars. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
The development of a guideline for understanding and correctly diagnosing deterioration mechanisms in order to choose compatible repair mortars.

147. Vendrell-Saz, M., Alarcon, S., Molera, J. & Garcia-Valles, M. Dating Ancient

Lime Mortars by Geochemical and Mineralogical Analysis, *Archaeometry* 38,143-149 (1996).
Investigate a technique of relatively dating mortar samples. The procedure is based on the analyses of trace minerals and element. The samples are crushed and then passed through a 50 micron sieve so that only the finest fraction was analyzed. The mineralogical components were analyzed by XRD. Samples were digested in HCl and the soluble components were analyzed by ICP. Multivariate statistical analysis techniques were used to cluster the groups. The chronology of unknown areas was then determined by comparing the analytical results to those of known/dated areas.

148. Vermeltfoort, A. T., Groot, C. J. W. P. & Wijen, E. Thermal strains in repointed masonry: preliminary investigations using ESPI. In: *International Workshop Historic Mortars: Characteristics and Tests, Pre-Prints* (RILEM, Paris, 1999).
Studied the mechanical behavior of bedding mortars and bricks with Electronic Speckle Pattern Interferometry. Concluded that hard repointing mortar applied to a softer bedding mortar show a high degree of incompatibility.

149. translated by Captain J.T. Smith. A Practical and Scientific Treatise on Calcareous Mortars and Cements, Artificial and Natural (John Weale, London, 1837).
Report on experiments conducted by the author on the study of hydraulic mortars.

150. Waldum, A. M. & Anda, O. Durability of lime-based mortars in a severe climate. Results from field and artificial aging tests. In: *International Workshop Historic Mortars: Characteristics and Tests. Pre-Prints* (RILEM, Paris, 1999).
Study of artificial and in situ aging of lime mortars. Noted an increase in calcium in the run-off water prior to the onset of deterioration.

151. Weaver, M. E. Cementious materials, *Conserving Buildings* 133-160 (John Wiley & Sons, New York, 1993).
Chapter on mortar, concrete and plasters for historic preservation. Lists some old mortar mixtures common to Canada and New York. Instructions on matching appearance by use of aggregate particle size, configurations and colors. Recommends types of mortar for use and some modem "recipes" suitable for preservation usage.

152. Znaczko-Jaworski, I. L.Badania Doswiadczalne Nad Starozytnymi Zaprawami Budowlanymi I Materialami Wiazacymi, *Kwartalnik Historii Nauki i Techniki* 3,377-407 (1958).Discusses the use of chemical analysis to analyze mortars. Find early use of carbonate filler/aggregate used in the production of a Greek site. Discusses the on-going processes that harden the mortar, reactions and new product formation.