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RILEM TECHNICAL COMMITTEES

RILEM TC 167-COM: CHARACTERIZATION OF OLD MORTARS

Quantitative analysis of historical mortars using optical microscopy

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ABSTRACT

As a part of the activities of the RILEM TC 167-COM committee two methods of quantitative microscopy have been developed for analysing historical mortars. This paper gives background information for the application of these methods. The methods concern the determination of mix proportions and aggregate size distribution using microscopical methods. A method is also described for correcting determinations of mix proportions based on chemical analysis of acid-soluble calcium oxide for the presence of carbonate in the aggregate.

RÉSUMÉ

Dans le cadre des activités de la Commission RILEM TC 167-COM, deux méthodes de microscopie quantitative ont été développées pour l'analyse des mortiers historiques. Ce document donne des informations sur les antécédents de l'application de ces méthodes. Celles-ci concernent la détermination des proportions de mélanges et la répartition des tailles des appareils en utilisant la méthode microscopique. Une méthode est également décrite pour la correction des déterminations des proportions de mélanges, à partir de l'analyse chimique de l'oxyde de calcium soluble dans l'acide pour déterminer la présence de carbonate dans l'appareil.

1. INTRODUCTION

This paper is a contribution from the RILEM TC 167-COM committee, Characterisation of Old Mortars. The aim of the committee is to provide tools for characterisation, damage diagnosis and formulation of requirements in connection with the restoration of masonry and renderings in historical monuments. Establishing new analysis techniques is a part of the work focused on characterisation. This paper discusses the application of quantitative optical microscopy to historical mortars. The emphasis of this paper is on quantification of binders and aggregate. The methods for determination of mixing proportions and aggregate size distribution outlined in this paper will be published separately [1, 2].

Microscopical analysis of mortars is widely used but the method is less frequently used for quantitative analysis. Quantitative microscopical methods are much used in other fields such as biology and metallography but less so in geology. As most of the experience in the field of microscopic analysis of mortars and concrete comes from geology this is reflected in the use of quantitative methods. The introduction of PC-based image analysis systems is now changing this situation.

One characteristic of historic mortars is the wide variation in their properties. This makes it advantageous to use flexible test methods, such as quantitative microscopy that give broad information about the studied mortars.

For most of the analyses discussed in the present paper other methods are available. When different methods are used in order to analyse a property they will sometimes provide significantly different results. These differences can give important information about the analysed material.

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2. BASIC QUANTITATIVE METHODS

2.1 Preparation

Sample preparation is a crucial step in the microscopic analysis of mortars. The analysed surface can be a plane polished sample, but the most important technique is the thin section. The latter is produced in several stages. In short these are diamond-sawing of a chip that is glued onto a glass slide. This chip is vacuum-impregnated with epoxy glue containing pigment or fluorescent dye. The samples are then prepared by grinding and lapping to a thickness of 25 microns (0.025 mm) and protected by a cover glass. This specimen can be used for several types of analysis such as quantification of aggregate type, hydraulic phases, admixtures such as bricks or slag. It is possible to carry out analysis of very thin layers, such as lime wash layers.

Air void analysis can be carried out on the thin section but is more often done on the face-ground samples.

2.2 Manual methods

The most common method is point counting. In this method an eyepiece with a cross-hair or a test grid is attached to the microscope. The points are distributed uniformly over the sample. The microscope table is equipped with a counter which makes it possible to manually register what is marked by the cross-hair, whether it be aggregate, lime paste, air voids or different types of lumps in the lime paste. When a point is registered the table is automatically moved a predefined distance. The points are distributed evenly over the surface of the prepared specimen. The number of points depends on what is being analysed and the required precision. The method is very flexible and it is easy to adapt the analysis to the studied problem.

Another manual method is the analysis of intersections along test lines of unit length. These can be in the form of linear or circular grids, or a cross-hair that is moved over the specimen. The lines are distributed evenly over the sample, either systematically or randomly. Lineal analysis, or lineal traverse analysis, is a method in which the length of the intersecting lines are measured. This can be done using a motorised stage. The different methods are described by Underwood [3].

Manual methods can be applied when it is difficult to write an algorithm for an image analysis system that would make it possible for a computer programme to identify the objects.

2.3 Image analysis

In computerised image analysis as applied to optical light microscopy a video or digital camera is attached to the microscope. The video signal is taken to a frame grabber in a computer, where the analogue video signal is converted into a digital image. The image is then composed of pixels, typically about 1024*1024. This gives one million pixels in the image. Each pixel defines a point in the image where the position and grey scale value or colour is known. It is then possible for the computer to identify objects in the image according to criteria given by the operator. The image characteristics used can be grey scale, colour or patterns in the image. An area with light pixels can be identified as an air void in the mortar.

Image analysis is a method that gives much information about the measured objects. One single measurement can give information about shape, size, number, position, grey scale value, to mention just a few examples. This permits rapid measurement of properties that cannot practically be quantified using manual methods.

2.4 Stereology

Analysis on a thin section or a plane polished surface can be considered as analysis in a two-dimensional plane. The aim is, however, to describe the analysed objects in three dimensions. The tool for doing this is stereology, which deals with the investigation of a three-dimensional space when only two dimensions are available. This can be in the form of projected areas where the objects are seen as silhouettes, or in the form of a two-dimensional plane cut through the studied objects. The latter is the case in the analysis of a thin section, provided that the studied objects are sufficiently larger than the thickness of the sample, which is about 0.025 millimetres.

Stereology deals mainly with trigonometrical and statistical methods to describe properties such as orientation, size, shape and volume proportion. Stereological methods are described by Underwood [3] and Reed and Howard [4], among others.

The studied structures can be divided into points, lines, surfaces and volumes. A basic relationship is that the surface proportion in a two-dimensional plane cut through a space is equal to the volume proportion. This relationship was first demonstrated by Delesse in 1848 [5].

3. APPLIED QUANTITATIVE MICROSCOPIC METHODS

3.1 Analysis of mix proportions of aggregate and paste

The results from the determination of area percentage of aggregate and paste give the volume percentage directly. By making assumptions about the density of the lime paste and the aggregate it is possible to calculate the mixing proportions in mortars [6] and concrete [7]. The lime lumps can be calculated as aggregate or binder.

These methods makes it possible to calculate the lime/cement proportion in a LC mortar. But it is not possible to quantify the hydraulic component in a mortar made using an unknown binder. One reason for this is that some hydraulic binders are too fine-grained to be

resolved in the optical microscope. Mortars with a very low content of elements other than calcium and silica may have a very light colour. It may not even be possible to qualitatively identify such a mortar as hydraulic in the optical microscope. A modern example of this is Lafarge Chaux Blanche.

3.2 Calculation of the mix proportion in lime cement mortars using NT BUILD 370

For a lime cement mortar the weight proportion of aggregate / binder (F) is calculated using the equation:

$$F = \frac{\alpha * volume\ \ aggregate}{volume\ \ paste - volume\ \ unhydrated\ \ cement\ \ clinker} - \beta$$

The term β varies between 0.5 and 1.5 depending on the minute suction of the substrate. This is a correction for the water content in the mortar, which affects the hydration and the porosity of the mortar. The term α depends on the density of paste, aggregate and the water content. It is about 2.2 for a cement mortar and about 3 for a lime mortar. For a cement mortar it is given by:

$$\alpha = \frac{aggregate\ \ density}{density\ \ paste * \left(1 - water\ \ content\right)}$$

and is approximately:

$$\alpha = \frac{2.67}{1.75 * \left(1 - 0.3\right)}$$

3.3 Calculation of mix proportions in lime mortars according to TC-COM C2

In this calculation the β term and the water content correction are excluded. The calculation of α is done according to the following formula:

$$\alpha = \frac{density\ \ aggregate * mole\ \ weight\ \ CaCO_3}{density\ \ paste * mole\ \ weight\ \ Ca\left(OH\right)_2}$$

the density of the lime paste is 1.2-1.3 g/cm^3 which gives approximately:

$$\alpha = \frac{2.67 * 100}{1.2 * 74}$$

this is then used in the calculation of F according to the equation:

$$F = \frac{\alpha * volume\ \ aggregate}{volume\ \ paste}$$

Example of the calculation of the composition of a lime mortar. The result from point counting is given in Table 1.

This gives an aggregate/binder ratio (F) of:

$$F = \frac{3 * 190}{299}$$

$F = 1.9$

Which compares to a weight-based mix proportion lime-paste aggregate of 100/200.

3.4 Quantification of lumps in the binder

The paste in old mortars is inhomogeneous. It contains lumps, lime lumps, with physical and chemical properties that differ from the matrix paste. These lumps were formed during different stages of binder production. It is necessary to analyse the proportion of lumps in the binder as a separate phase when analysing historical mortars. The reason for this is that when the mortars were mixed these lumps had the same function as the aggregate and there is a direct relation between the proportion of lumps, and the proportion of aggregate in the mortar (see Fig. 1). It is then possible to include the lime lumps in the aggregate or in the paste when calculating the mix proportion.

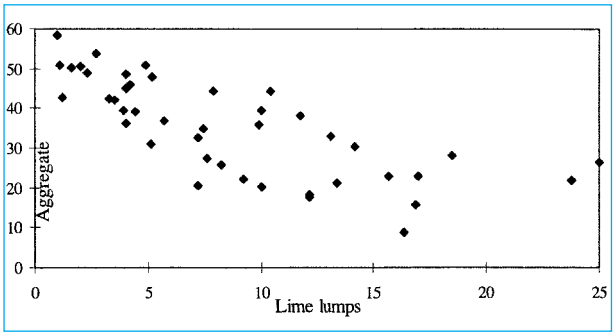

Fig. 1 – The relationship between the proportion of lumps in the binder and aggregate in Swedish lime mortar from the 12th to the 19th century. The determinations were carried out by point counting. It shows that mortars with a high content of lumps have a lower aggregate content [8].

3.5 Correction of chemical methods with regard to carbonate in the aggregate according to TC-COM C2; the Old Bridge in Mostar as an example

As the amount of limestone in the mortar can be quantified using microscopical methods this can be used in order to correct the chemical analysis of acid-soluble calcium oxide in mortars containing limestone. The analysis of a carbonate aggregate containing grouting mortar from the Old Bridge in Mostar can be used as an

Table 1 – Mortar from Forsby Industrial Museum, Sweden

	Points	Volume %	Precision +/-
Air	18	4	2
Aggregate	190	37	4
Paste	299	59	4
Total	507	100	

Table 2 – The content of acid-soluble calcium oxide (CaO) and silicon dioxide (SiO_2)	
	Weight-%
Acid-soluble CaO	53.0
Acid-soluble SiO_2	0.4
Loss on ignition	43.2

Table 3 – Composition of the mortar based on point counting using optical microscopy	
	Weight-%
Sample Mostar	Volume %
Air content	11
Carbonate aggregate	42
Siliceous aggregate	2
Paste	45
Total	100
Total number of points	1289

example (Berggren's ongoing project). The results from the analysis are given in Tables 2 and 3.

Point counting in the microscope demonstrated that the aggregate had a 95% limestone content. If the chemical analysis is not corrected for the limestone content the results from the chemical analysis will imply, on the basis of weight, a mixing binder/aggregate ratio of approximately 150/100. If the lime paste has a density of 1.3 g/cm^3 and the limestone 2.6 g/cm^3, the amount of lime from stone and paste calculated per cm^3 is then:

*$CaCO_3$ in the paste = density paste * volume part paste*

*$CaCO_3$ in the aggregate = density aggregate * volume part aggregate*

The corrected $CaCO_3$ content is given by the following equation:

$$CaCO_{3(cor)} = \frac{CaCO_{3(kem)} * CaCO_{3(paste)}}{CaCO_{3(aggregate)} + CaCO_{3(paste)}}$$

The terms $CaCO_3$ kem and cor can be replaced by CaO kem and cor. The amount of acid-soluble CaO in the paste can also be calculated by:

$$CaO = \frac{CaCO_3 * mole\ \ weight\ \ \mathrm{CaO}}{mole\ weight\ CaCO_3}$$

The amount calcium from the paste is then 0.6 g and from the aggregate 1.1 g. Thus about 35% of the calcium belongs to the paste. This gives about 19% acid-soluble CaO from the paste in the mortar. The calculated mixing proportion of lime binder/aggregate is thus about 100/300.

Table 4 – The mineralogical composition of the aggregate from the church of Vestra Ingelstad given in volume percentage				
Sample	VI1	VI2	VI4	VI5
Quartz/feldspar	89	90	29	68
Calcite/limestone	3	6	44	12
Other	8	4	27	20

3.6 Characterisation of aggregates

In restoration work there is often an interest in using the same source of aggregate as in the original mortar. Properties of the aggregate such as its mineralogical composition or size distribution can be quantified. An example of the mineralogical composition of the aggregate in mortars from the church of Vestra Ingelstad in Sweden is given in Table 4. The results show that the aggregate was taken from more than one locality. The sample VI4 was taken from a minor repair of poor quality. In the same manner the amount of admixtures such as brick dust can be quantified.

3.7 Determination of aggregate size distribution according to TC-COM C1.

It is also possible to determine the size distribution of the aggregate using quantitative microscopy [1, 9]. The analysis is preferably performed using computerised image analysis. The original image is converted into a black and white binary image. The Feret diameters, which are the maximum lengths of the objects, are then measured in the 2D image. The objects are sorted into size classes. A 2D size distribution is calculated from these values. As an example, the number of objects with Feret diameter 32-63 microns is the first size class and those with a diameter of 63-125 microns fall in the second size class, etc. This size distribution is recalculated to give a 3D size distribution using stereological methods. This method gives a good reproduction of the sieve curve [10] which is a prerequisite for the analysis. The advantage of the microscopical method is that it does not require a separate sample for the analysis. The analysis is not biased by acid soluble minerals in the aggregate. It is also possible to carry out a more specific analysis. This could be an analysis of the size distribution of brick dust in a mortar or of the aggregate in a thin paint layer, which can be analysed separately. It is also possible to study size distribution gradients in the mortar. The disadvantage is the low number of analysed grains, a few thousand compared to a sieve analysis, which includes a few million grains. It is possible to measure the larger grains separately in order to improve the precision of the analysis.

4. PRECISION OF THE ANALYSIS

4.1 Sampling error

The sampling error depends on the size and number of the studied specimens. The size of the thin sections range from approximately 5 to 35 cm^2. Normally the thin section is made from one sample, but it is possible to include several small samples to obtain a more representative analysis of an inhomogeneous mortar. It is also possible to combine the thin sections with the analysis of plane polished samples. The latter are produced routinely in sizes up to 10*20 cm^2 for concrete analysis. They can then be used for analysis of larger structures.

Uncertainties in the assumed densities used in the calculations also contribute to the total error.

4.2 Counting statistics, point counting

The standard deviation in the point counting of a normal distributed population is obtained through the square root of the variance according to Equation [11]:

$$s = \sqrt{\frac{p(100-p)}{N}}$$

The 95% confidence level is obtained from 1.96*s. The precision improves rapidly and in most cases the number of points required is less than 1000. Due to the sampling error the improvement of the analytical precision will in most cases be insignificant even if a larger number of points are recorded in a single thin section. One requirement is that the points are distributed in such a way that the objects are not counted more than once. This restricts the number of points in each thin section. In historical mortars the mix proportion will vary between fairly small batches and the assumed normal distribution may not be correct. In this case the precision calculation of [12] can be applied.

4.3 Error in size distribution measurement

When calculating the error in the size frequency distribution determination the standard deviation for a given size class is calculated according to the formula above [13]. In this case p is the frequency in a given size class and N the total number of particles counted. The standard deviation for weight distribution $s(M_j)$ can be calculated according to the equation:

$$s(M_j) = \frac{M_j}{\sqrt{n_j}}$$

Where M_j is the percentage by weight in size class j, n_j is the number of particles in size class j.

5. COMPARISON WITH CHEMICAL ANALYSIS

When determining the mixing proportions by analysis of acid-soluble CaO, or the loss on ignition, the sources of errors are different from those in the microscopic methods. The main source of error is acid-soluble carbonate in the aggregate, which leads to an aggregate/ binder ratio that is too low. The analysis of mortars containing pozzolanic admixtures of clays also gives misleading results as their content of acid-soluble calcium oxide is lower than the assumed composition of the binder. This leads to a calculated aggregate/binder ratio that is too high. In Fig. 2 the aggregate/binder ratios calculated from microscopical and chemical results are compared. The lime mortars are from the 12th to the 19th century. The samples that fall above the line contain clay admixtures.

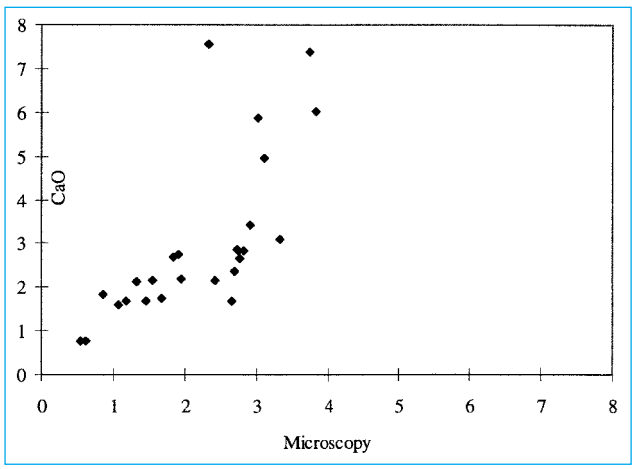

Fig. 2 – Aggregate/binder mix proportions calculated from acid-soluble CaO and microscopic analyses for 25 mortars. The results from the chemical analysis are corrected for the presence of carbonate in the aggregate.

The two main advantages of the microscopic methods are the ability to identify the carbonate minerals and the greater flexibility. This makes it possible to analyse mortars with limestone in the aggregate. It is also possible to modify the analysis to the present problem. The analysis of the amount of brick dust in the mortar is one example.

The limitations are mainly the limited analysis area, since the usual size of thin sections for concrete analyses is 15 cm^2. The resolution of the microscope is also a limitation. It is not possible to identify the hydraulic components of the most finely grained hydraulic mortars.

6. CONCLUSION

Experience from quantitative microscopical analysis applied to historical mortars shows that it is a very useful method. This is especially true for mortars containing carbonate aggregate and for more specialised analyses. Quantitative analysis can be based on the results from the qualitative analysis of the sample. In addition, combination with chemical methods can provide valuable

information concerning the properties of the sample.

One limitation is the difficulty in identifying very small objects such as hydraulic minerals in fine-grained hydraulic mortars. It is easier to obtain a representative sample of an inhomogeneous mortar by analysis of acid-soluble components rather than by thin section analysis.

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REFERENCES

[1] COM-C1 Assessment of aggregate size distribution in historical mortars using quantitative optical microscopy.
[2] COM-C2 Determination of mix proportions in historical mortar using quantitative optical microscopy.
[3] Underwood, E. E., 'Stereology', Addison-Wesley Publishing Company 1970.
[4] Reed, M. and Howard, V., 'Unbiased stereology: Three-dimensional measurements in microscopy', Microscopy handbooks Volume, 1998.
[5] Delesse, A., 'Pour déterminer la composition des roches', *Annales des Mines* **13:4** (1848) 379-388.
[6] NT BUILD 370: Mortar, hardened: Cement content and aggregate binder ratio. NORDTEST, 1991.
[7] Larbi, J. A. and Heinen, W .M. M., 'Determination of the cement content of five samples of hardened concrete by means of optical microscopy', *Heron* **42** (1997) 125-137.
[8] Lindqvist, J. E., Sandin, K, Sandström, H., Sandström, M., Schouenborg, Sidmar, E. and Sundnér, B. 'Analysis and evaluation of old lime mortar', Riksantikvarieämbetet, 1999 (in Swedish).
[9] NT BUILD 486: Aggregates: Size distribution. NORDTEST, 1998.
[10] Lindqvist, J. E. and Sandström, M., 'Determination of the size distribution, sieve curve for aggregates using optical microscopy', Proceedings of the 7th Euroseminar on Microscopy Applied to Building Materials, Eds: H. S. Pietersen, J. A. Larbi and H. H. A. Janssen (1999) 297-305.
[11] van der Plas, L. and Tobi, A. C., 'A chart for judging the reliability of point counting results', *Am J Sci* **263** (1965) 87-90.
[12] Howarth, R. J., 'Improved estimators of uncertainty in proportions, point-counting and pass-fail test results', *American Journal of Science* **298** (1998), 564-607.
[13] Allen, T., 'Particle size measurement', Powder Technology Series, Chapman and Hall, London, 1990.