The Analysis of Mortar
The Past 20 Years

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Where historic buildings are concerned, repairs should be carried out using materials and techniques which match those used originally as closely as possible. There are three main reasons for doing this: firstly, repair materials which match the originals will provide some continuity with the past, keeping intervention to the minimum; secondly, by matching the original materials and techniques closely, the repair materials will age in a similar way as the original; and finally, modern materials and techniques introduced in past repair work have often proved to be incompatible with the original, causing accelerated deterioration of building fabric. Changes are usually made only where the existing materials have been shown to be inappropriate.

In recent decades, specialists involved in the conservation and repair of historic buildings have become increasingly concerned by the damage caused by the use of certain types of mortar on historic brick and stonework, and by the use of ordinary Portland cement in particular. This has sparked renewed interest in traditional lime mortars, which are more compatible with old buildings. Some analysis of the existing mortar is now standard practice, if only to match aggregates. However, a better understanding of historic mortars is clearly required, not least because there have been some cases where modern lime renders have failed and, at the opposite extreme, there is now concern as some types of modern hydraulic lime mortars continue to gain strength as they age.

RECENT DEVELOPMENTS

In parallel with the conservation industry, mortar analysis has progressed dramatically over the last 20 years. The procedures pioneered by Ian Constantinides and others, based as so much was (and still is), on John and Nicola Ashurst’s excellent English Heritage Technical Handbooks have been replaced by various more sophisticated techniques.

Many individuals, companies, laboratories, and universities are now offering the service, and much research is being undertaken. Analysis is carried out with differing goals, from a simple colour match to ensure a sympathetic ‘matching’ repair mix, investigative assessments and performance evaluations, to academic studies that attempt to determine the precise reasons for the remarkable durability of ancient mortars.

Many analytical techniques are being employed, each with particular strengths and limitations. The established techniques are summarised in the following table.
ESTABLISHED TECHNIQUES OF ANALYSIS

Non-invasive techniques - Photography; visual inspection; and touch and feel. This group requires no samples, and allows consideration in context, especially with reference to performance and decay. Photography is useful for documentation of condition.

Light microscopy - Binocular microscopy; polarised light microscopy; thin sections. The binocular microscope equipped with incident and transmitted tungsten light, with the potential for observation of samples in cross-polars, allows determination of the mineralogy and distribution of components and their interrelationship.

Wet chemical analysis - The constituents of a mortar can be determined using various chemical tests after dissolution in both acid and alkali. Measurement of soluble silica provides data on the hydraulic property of the mortar, and this considered with the calcium result enables the proportion of hydraulic components to be estimated. A calcium result, reported as calcium oxide, does not mean that calcium oxide is present. Calcium can be present as calcium carbonate, calcium sulphate, calcium hydroxide, calcium silicate hydrates for example, or in combinations of these compounds.

Instrumental techniques for the analysis of component materials - Scanning electron microscopy (SEM); electron microscopy with x-ray analysis (SEM/EDX); and x-ray diffraction (XRD) SEM high resolution images of the surface of samples with magnification of up to 100,000x show the structure of the mortar. SEM/EDX allows elemental analysis of samples and is used for characterisation of morphologies and textural and compositional interrelationships of mortar components. XRD allows analysis of crystalline materials including binder phases; belite and alite; and crystallised alteration products. Data from the testing of complex materials is difficult to interpret, and a highly skilled analyst is crucial.

Instrumental techniques for the analysis of organic materials - Gas chromatography with mass spectrometry; ion, liquid and thin layer chromatography. These techniques are used (although rarely in mortars) for the identification of oils, resins, and proteins.

Instrumental methods for characterisation of organic and inorganic materials - Thermal analysis (DTA, TGA, DSC) and infra-red spectroscopy (FTIR). Thermal analysis can be carried out on very small samples and can positively identify the composition of certain components, including calcium carbonate, calcium hydroxide, calcium sulphate, calcium silicate hydrates, and depending upon the constituents remaining after ageing, complex calcium silicate and aluminate hydrates.

Physical testing (for durability assessment) Tests that determine pore structure such as water or gas permeability, freeze thaw resistance, porosity and pore size distribution provide data on durability.

Mechanical testing (for performance assessment) Testing for compressive, tensile or flexural strength on prepared samples will determine suitability for different applications.

Dating technology - Radiocarbon dating. This technique has recently been used to date mortars to an accuracy of about 30 years.
The important, but often underestimated first step is to ensure that any sample taken for examination is representative of the mortar to be analysed. Far too often the method of sampling influences the result, and taking small or insufficient samples can lead to poor assessments or diagnosis. The original ‘kitchen sink’ tests are no longer considered to be of any use for much more than insoluble aggregate type matching. Generally these tests consisted of dissolving a sample in dilute acid to separate the acid-soluble from the insoluble. The soluble proportion is (often incorrectly) assumed to be the binder, (as it so often includes soluble limestone aggregate and calcareous clays), and the binder is assumed to be carbonated lime (which of course it often isn't). In some cases the hydraulic component is being assessed on the insoluble ‘fines’ proportion. This is meaningless, as in the vast majority of cases where the proportion of ‘fines’ is high, the mortar includes unwashed clayey aggregates.

The more chemical tests undertaken, the better the overall understanding of the mortar, and the higher the confidence in interpreting the data on the sample.

The minimum requirement is to carry out recognised standard tests for sulphate (to determine whether the binder is, or contains, gypsum), calcium, soluble silica, and insoluble content. The soluble silica test is critical for assessing the hydraulic proportion as it determines the combined percentage of calcium silicates, calcium silicate hydrates and hydrated silica gel present. It is the amount of this material which determines the hydraulicity of binder, whether it be Portland cement, Roman cement, hydraulic lime (of any grade) or an added pozzolan. In fact, as this result is so critical, the soluble silica test should be carried out to a high degree of confidence and calibrated using two distinct methods, the BS technique listed in BS4551, and the colorimetric method. In common with much in the analysis of mortars, great caution must be exercised, as some granite aggregates will release soluble silica and this could be taken as part of the hydraulic component.

Other chemical tests can also help; a magnesium test for example determines whether the lime was dolomitic.

Physical properties, such as porosity, should be determined. All reliable data indicates a complex interrelationship between porosity, permeability, pore size distribution and durability.

More meaningful mortar analysis should consist not only of chemical tests properly conducted, but these tests should be augmented by one or more collaborative instrumental techniques such as DTA, microscopy, XRD, or SEM.

One of the most effective collaborative techniques is DTA (differential thermal analysis). This technique is particularly useful in determining the calcium compounds present. It positively determines calcium sulphate, calcium hydroxide (lime), calcium carbonate, often distinguishing between carbonated lime and calcareous aggregate, and calcium silicate hydrates. In older mortars, DTA cannot distinguish between hydrated alite (C3S) and hydrated belite (C2S) as these are essentially the same, and so on its own cannot be used to determine
whether the binder is cement or hydraulic lime. However, positive DTA identification of calcium silicate hydrates and calcium carbonate, and a porosity test, considered with the quantitative soluble silica test results combine in making an informed assessment of binder type. Only by determining whether unhydrated C3S is present can Portland cement be confirmed, although there is an indicative calcium oxide : soluble silica ratio. The experience of the person interpreting the results is almost as important as the results themselves. In one recent project the same mortar was tested by four laboratories, and each interpreted differently. Conclusions ranged from a cement/lime blend, a hydraulic lime (possibly in the form of a natural cement), a hydraulic lime/non-hydraulic lime blend, to a 'hydraulic or cementitious' binder.

On another occasion, a fresh lime putty plaster sample had been tested because gypsum gauging was suspected. The testing laboratory, using XRD found no gypsum but identified C3A, a constituent of cement, and some hydraulic limes. Cement or hydraulic lime gauging was immediately identified ignoring the facts that the wet putty plaster was not setting and that calcium silicate hydrates had not been identified. This resulted in a high level meeting of client, architects, analysts, main contractor, and plastering sub-contractor, most of us flown in at great expense. DTA was able to prove conclusively that hydrated calcium aluminates were not present. The outcome was that the XRD reflection had been incorrectly identified as C3A, and it was in fact a constituent of the complex igneous aggregate.

The area most underestimated is how mortars age and the complex chemical reactions and changes that occur with time. The fact that the binder in an aged sample is now principally calcium carbonate does not indicate that it was lime originally, as much of the hydrated hydraulic compounds in cement and hydraulic lime will themselves react with CO2 (carbon dioxide), and carbonate. To complicate further, lime still present in a 40-year old sample for example, does not necessarily indicate a lime mortar originally, as lime is a reaction product of the hydration of C3S and C2S. Indeed, the presence of lime in such a sample is more likely to indicate a cement mortar as its non-permeable nature would have impeded or prevented the access of CO2, and carbonation of the reaction product has therefore not taken place.

Mortar analysis is now a very sophisticated business. However, any examination that measures only part of the components, characteristics or properties of a mortar and their relationship with durability or performance must be viewed with caution. As with everything, a little knowledge can be a dangerous thing.

BINDERS

Ordinary Portland cement OPC is prepared by intimately mixing limestone and clay, burning them at above clinkering temperature ( >1,260 degrees C), and grinding the resulting clinker. The compounds present are formed by the interaction during burning of the lime, silica, alumina and ferric oxide compounds. The principal setting compounds in OPC are tricalcium silicate (C3S), dicalcium silicate (C2S), tricalcium aluminate (C3A), and tetracalcium
aluminoferrite (C4AF). These compounds are present in known controlled proportions. In the 20th century, the desire for a higher strength product led to increased C3S and reduced C2S proportions. The setting process is the hydration of these four compounds, but it is the C3S that has all the essential properties of OPC.

Hydraulic lime The essential difference between modern hydraulic limes and OPC is that hydraulic lime should not contain C3S and should contain lime. Various types are available and they are produced in various grades. Limestone containing clay and/or silica is burnt in a kiln at below clinkering temperature (<1,200 degrees C) and the resultant product is hydrated with only sufficient water to convert the calcium oxide to calcium hydroxide, but not to hydrate the C2S, which in any case is slow to hydrate. The setting process is a combination of the hydration of C2S and carbonation of the lime. In most hydraulic limes, a proportion of uncombined reactive silica and alumina is also present, and these will react with lime in the mortar to also produce calcium silicate hydrates and calcium aluminate hydrates. In the United Kingdom hydraulic limes are classed as:

Feebly hydraulic

NHL 2

Moderately hydraulic

NHL 3.5

Eminently hydraulic

NHL 5

Pozzolanic lime Pozzolanas are defined as materials which though not cementitious in themselves, contain constituents which will combine with lime at ordinary temperatures in the presence of water to form stable insoluble compounds possessing cementing properties. Natural pozzolanas are mainly materials of volcanic origin, for example Rhenish trass and Santorin earth. Artificial pozzolanas are mainly products obtained by the heat treatment of natural materials, such as china clay. The precise reasons for pozzolanic properties is still a subject of controversy and various explanations have been advanced to explain the reaction. Pozzolanas do in fact vary, and there is probably more than one explanation. Indeed more recent volcanic ashes of similar composition from Vesuvius for example are (at best) of very low reactivity. It is generally accepted however that two reactive products, a silica glass and fine grained clay minerals, activated by heat, are of paramount importance. These materials can combine with lime to produce calcium silicate hydrates, calcium aluminate hydrates and calcium alumino-silicate hydrates.
Non-hydraulic lime Limes (>95% calcium hydroxide) made by hydrating or 'slaking' the quicklime of relatively pure limestones which set by 'carbonation', a reaction with atmospheric carbon dioxide to form calcium carbonate. Two forms are available:

Lime putty Ordinary (non-hydraulic) lime produced by slaking quicklime in an excess of water to form a putty. Lime putty is matured for several months in pits or under a thin film of water to prevent carbonation, and during this process the portlandite (lime) crystals change shape, becoming smaller and flatter, thus aiding workability. It is used for the production of lime plasters, mortars, and limewash. Also known as 'air' limes, 'fat' limes and 'high calcium' limes.

Dry hydrated lime Ordinary (non-hydraulic) lime produced as a dry powder by hydrating the quicklime with sufficient water only to convert calcium oxide to calcium hydroxide. Also known as 'bagged' lime