Summary description of project context and objectives

The project background

The ROCARE-project is focussing on so-called Roman cements - a product designation from the 19th-century's Gründerzeit which was an era of extraordinary construction activity, of rapid industrial expansion and wealth creation. Such urban growth gave many European cities the appearance which has marked them to this day. Roman cement was the building material which realised the dreams of architects and builders for renders and mass-produced stucco elements in a wide variety of styles which could be implemented easily on façade masonry; it exhibited fast-setting, an agreeable structural consistency and colour, was extremely long-lasting, and cheaper than Portland cement at its time.

During the twentieth century Roman cements disappeared from use, displaced by the newer Portland cement, which dominated the market. The lack of appropriate binding materials - matching those available to the craftsmen of the nineteenth century - has deprived architects and conservators of objects of the original historic technology for the repair and conservation of such objects.

From a material perspective, Roman cement is the binder which bridges the gap between hydraulic lime and Portland cement: Roman cements are produced by burning naturally occurring deposits of calcium carbonate rich in clay minerals at relatively low temperatures. In distinction to hydraulic limes, the resulting Roman cement has virtually no free lime, and compared with Portland cements it is composed of a specific low-temperature assemblage of reactive clinker minerals. In this way, when mixed with water, a characteristic binder is formed which combines relatively high strength with high capillary porosity. Further typical properties of Roman cements are their rapid set and early strength followed by a relatively slow development of strength at later ages.

The above properties made Roman cement mortars an ideal material for constructions under water or in moist areas, façade renders, and run or pre-cast stucco elements, to name just their most prominent applications. According to the modern understanding of building physics, these mortars have also high potentials as breathable building materials with good capacity for moisture transport and high durability.

Knowledge about the mentioned key characteristics has been achieved mainly through the activities of the EU FP5 project, ROCEM (2003-06), which has also provided information about the process of production of these cements on laboratory and pre-industrial scales, finally leading to the reproduction of Roman cements for the purpose of trial applications. All this has raised interest of the professionals in the cultural heritage field, but in order to bring the technology to an industrial scale with Europe-wide market perspectives, more effort for the optimisation of cement manufacture and marketing was needed. The current EU FP7-project ROCARE (2009-12) is therefore focussing on those aspects. Fourteen partners from 7 European countries have joined together in the ROCARE consortium to bring the manufacture of Roman cements to an industrial level, develop the market for this binder, and investigate all necessary additional parameters needed to optimise the technology and its application. The consortium is composed of 5 SMEs, 3 universities, 3 public research centres, 2 industrial enterprises, and 1 private non-profit institution. Three of the partners are engaged in the production of Roman cements, the others are acting in the fields of R&D, marketing and practical application. More details are available at the project website www.rocare.eu.

With substantial help of the ROCARE End User Advisory Panel (EAP) comprising over 20 experts from many of the relevant European countries, the project has substantially contributed the fascinating concept of low-energy Roman cements to establish itself on the European market of building construction.

Project objectives

The principal objective of ROCARE is focused on the re-introduction of the Roman cement technology by combining knowledge of a historically well-established building material with modern aspects of its manufacture, use and marketing. The main target is the huge stock of buildings originating from the nineteenth/early twentieth centuries. Other potential fields of marketing have been identified in the restoration of historic buildings in general, and in specific areas of modern construction, e.g. high-diffusive plasterwork or floorings.

In order to reach that goal, a number of strategic issues were covered by the work plan of ROCARE, such as:

- Scaling up of the RC technology to a competitive level by optimising the process technologies at various conditions of production (Work Package 1)
- Providing data for the practical use of Roman cement mortars and a better understanding of mechanisms, by laboratory tests and studies to fully understand cement hydration and property development, as well as optimum conditions of mortar processing and handling in the conservation practice (Work Package 2);
- Enlarge the market potential of the Roman cement technology, by implementing broad dissemination measures (Work Package 3).

Main topics of work

The following topics were at the centre of interest within project duration:

- Definition of suitable raw materials for the production of Roman cements – natural stones (marls)
- Survey of potential raw materials by each producer, their analysis and pilot calcination, to identify the best raw feed and the optimum range of kiln parameters by a number of tests and analyses of the clinkers obtained
- Process optimisation of the cement production up to a pre-industrial level according to the premises of the producing partners, i.e. ranging from simple artisan shaft kilns to large PC rotary kilns. Final steps of process optimisation of the cement production up to an industrial level. Production of optimised Roman cements to supply the consortium as well as interested partners beyond with quantities sufficient to perform laboratory and on-site trials of mortar application.
- Scientific analyses to assess the composition and hydration mechanisms of the obtained cement clinkers, including studies on specific properties relevant to practical aspects of their application.
- Determination and conduction of an extensive programme to evaluate a wide range of mortars produced from optimised Roman cements, related to end-use and implementation
- Wide-spread means of dissemination, supported by an EAP – End user advisory Panel, guided by a business and market plan developed, such as constructing and maintaining a project website for internal and public use, organising high-level conferences, workshops

and seminars in a number of European countries, exchanging information with experts across Europe, performing site trials and demonstration works on various sites, encouraging and advising professionals in the use of the Roman cement technology, training scientist to identify Roman cement mortars, and presenting and publishing RTD results at various levels.

- Additional means to facilitate the marketing of Roman cements, such as producing a manual on best practice in the application of Roman cements, editing a ROCARE Standard aimed at achieving the status of an EN-standard for Roman cements, and providing data for a statistical market evaluation in the most promising regions.

Results achieved

Cement production – Work Package 1

Three partners of the consortium were in charge of manufacturing Roman cements. They represented significantly different production profiles, ranging from small-scaled, artisan style, shaft kiln calcination via small rotary kiln to large-scaled industrial rotary kiln production. Via an initial stage focussed on the identification, analysis and small-scale trial calcination of raw materials suitable for production of Roman cements, a stage of process optimisation at full-scale conditions of calcination was successfully achieved, the resulting cements were tested and analysed, and then used to perform mortar tests and eventually small on-site trials. The following production of Roman cements classified as being optimum was again successful as to the aim to provide optimum binders in sufficient quantities for a large programme of laboratory tests on mortars, further for on-site demonstration activities, for practical workshops and finally for the application to a limited group of interested end-users.

The different scales and process approaches of Roman cement calcination, a key concept of the ROCARE project, were successfully implemented, by employing the following kiln facilities: (1) a small, artisan shaft kiln fired with timber, using local marlstones as raw feed; (2) a mid-sized rotary kiln fired with oil, using several pre-selected marlstones as raw feed, and (3) an industry sized rotary kiln designed for the production of Portland cement, using one type of marlstone. In this way it was shown for the first time that Roman cements of various properties, however all within the range of Roman cements in respect to their historic performance and to the ROCARE Standard, can be produced for various sectors of the market

A full quality certification of the binders and mortars has been achieved, based on the final results of the mortar test programme performed in Work Package 2. In addition, the need to check the cements produced by the project against the historically authentic Roman cements, along with the necessity to position them on the market of hydraulic binders, required studies of several key characteristics beyond the standards of laboratory test programmes. To this end a multifold approach was followed and concluded, ranging from scrutinised methods of phase analysis for the clinkers via scientific studies of their path of hydration.

Mortars – Work Package 2

Extensive work has been undertaken to evaluate and understand two different techniques by which mortars for both castings and render may meet specified workabilities and workable lives. Chemical retardation is most applicable for casting mortars with a newly developed technology, “De-Activated Roman Cement” (DARC), being applied to renders. It was further discovered that a DARC mortar may be remixed to extend the workable life without causing a strength reduction. The base to transfer the DARC technology from mixing on-site to the industry of pre-mixed mortars has been laid by developing a technique to allow for extended storage of the de-activated mortar prior to final mortar production. A company has been approached and it is hoped that they will be able to develop the technology to produce factory-blended de-activated mortars in the near future.

The major mortar programme has generated an invaluable data-base of properties to create an envelope of expected properties for a wide range of practical Roman cement mortars and to provide a comparison with other mortars used by conservators, e.g. NHL and PC. These data clearly demonstrate the unique characteristics of Roman cement mortars They have been presented in a user-friendly manner in the Manual of Best Practice;

Further on, substantial additional work has been undertaken to support the development and revision of European Standards. Newly developed standardised production methods, suitable for the full range of Roman cements, have generated data to support a new Standard on Roman cement. A ROCARE Standard has been prepared and disclosed to the public domain.

Within various supplementary programmes specific areas of scientific interest have been investigated. They included the influence of the characteristics of the sand fraction on mortar performance, particularly on its rheological performance and on the shrinkage. Hybrid mortars of Roman cement and various forms of lime have been developed. A much greater understanding of the influence of the substrate on mortar performance has been achieved, so that the performance of a sampled historic mortar can be better related with the formulation of a repair mortar. Shrinkage cracking, a commonly observed phenomenon in historic mortars, has been studied and a model has been developed which relates unrestrained shrinkage to the tensile strength and strain at failure which has been confirmed by practical tests. The shrinkage has been found to increase with curing of the mortars which has been correlated with the development of pore structure, itself related to the hydration of the belite phases.

Hydration studies led to a refined understanding of the hydration path of various types of Roman cement, particularly, in the early stage of development. Monitoring the alkalinity of the system has been found to be a useful tool for the identification of the onset of belite hydration.

Dissemination and marketing – Work Package 3

The End-user Advisory Panel EAP, currently comprising 25 experts from various fields, who represent 13 European countries, has been providing valuable assistance to the project in their countries in a manifold way.

Activities of communication and information were organised in cooperation with interested institutions, such as meetings, workshops, information events, presentations at international fairs and conferences, and lectures. The activities were focussed to Austria, the Czech Republic Germany, France, Hungary, Italy, Poland, Romania, Switzerland and Ukraine. An international conference was organised in Paris jointly with ICOMOS-France. The number of publications related to issues of Roman cements and ROCARE and authored by consortium members or EAP delegates and other experts reached a total of 45, and 21 oral communications at conferences were given. Four half-day and three full-day information events with several lectures by consortium members as well as by invited other experts to cover all important aspects were organised, and a number of invited lectures were given in university environments. The oral presentations as well as the manuscripts of written papers were continuously made available to the public via the project website www.rocare.eu, along with other published papers on Roman cement and related issues. Workshops to attract the interest of experts and inform about techniques were organised for different groups of professionals and students, addressing aspects such as RC manufacture, calcination and grinding, mortar preparation and application on historic buildings, and scientific analysis of historic Roman cement mortars. Trial and demonstration activities on-site were performed in Austria, the Czech Republic, Germany, France, Switzerland and Ukraine. Some of these efforts were linked to a large-scaled restoration planned for the next future, which yields the chance to transfer the standards set by ROCARE to the full scale of restoration and thus set trends beyond the object itself, naturally even after the end of the project lifetime. Survey campaigns were carried out in Brno, Budapest, Prague, and Vienna, to provide sound data on the amount of buildings in areas built up in the period. The overall number of façades assessed in this way amounts to over 14,000.

A brochure with manual on best practice in the application of Roman cements was produced and made accessible on the project website at http://www.rocare.eu/. It yields guidance to the use of the Roman cement technology in the various fields of application and is a key tool of information and dissemination to approach the market. Finally, a ROCARE Standard for the classification of Roman cements has been developed to be launched to the creation of an EN standard.

Description of the main S&T results

The production of Roman cements

Background, facilities and primary tasks of the cement producing partners

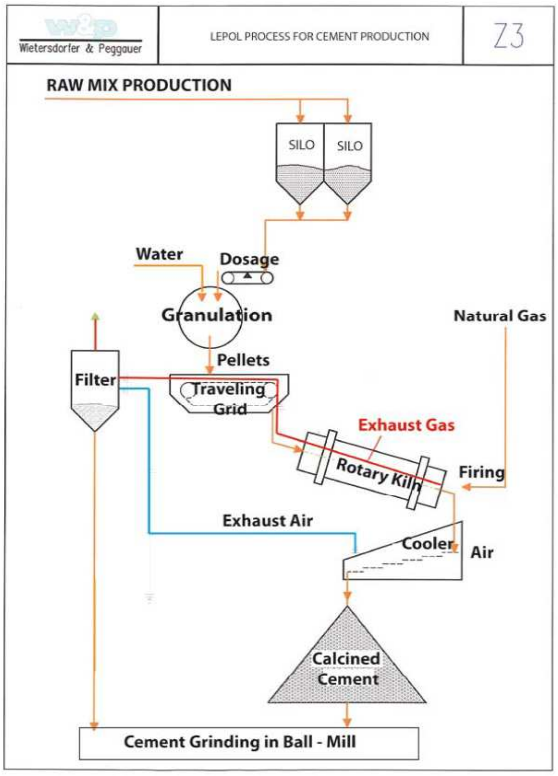
1. w&p - Wietersdorfer & Peggauer, w&p Kalk GmbH, Peggau (AT)

W&p is a privately owned industrial cement producer with a long tradition in this field. Their facilities of production are as follows:

> Rotary kilns, operated with the Lepol process: 700tons OPC/day
> Shaft kilns: 60-70 tons lime/day
> Ring shaft kiln: 120 tons lime/day

W&p had no background experience in the production of Roman cements at the onset of the project. They were prepared to use selected raw material from the company-owned quarries and to calcine them either in one of their rotary kilns or in the shaft kiln. Within the project it had to be checked, whether (1) the raw material from the company's marl deposits, and (2) the use of either of the kilns was appropriate to yield optimum Roman cement. It has to be pointed out that until then no experience was available on the possibilities to manufacture RC in a Lepol rotary kiln of an industrial scale. The success of that step of production was related to some risk of failure, which would have had no fatal consequences for the progress of the project, however, as the shaft kiln would have served as an alternative option if the rotary process had failed.

W&p acted as a supplier of their optimum binders to the scientific partners of the project to perform analyses, tests and measurements, as well as to potential end-users for reasons of testing and application trials. On a wider scale, the RC production by w&p within the project was aimed to prepare the introduction of their product to the market of hydraulic binders.



w&p rotary kiln and cooled calcined cement pellets *w&p Process flow*

2. IMBM – Institute of Ceramics and Building Materials Warsaw, Division of Glass and Building Materials in Krakow (PL)

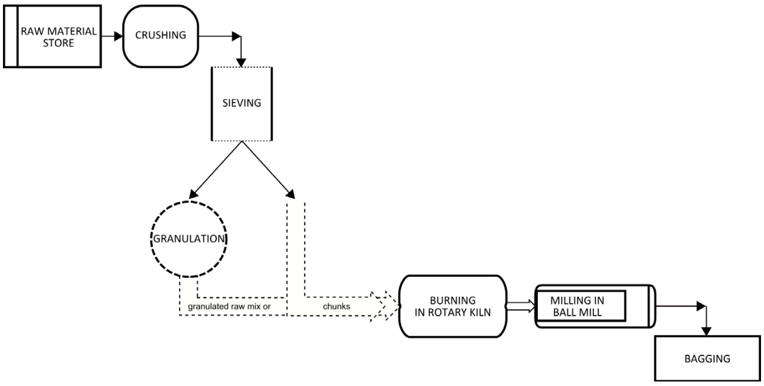
Founded in the 1950s, IMBM is a research and development institution owned by the Polish state. They started their activities in ROCARE with a strong background in the manufacture of Roman cements, which they had started to achieve as a subcontractor to the FP5-ROCEM project (2003-2006). IMBM has since then produced and delivered both RC binders and ready mixed systems based on RC, predominantly to the Polish market, but also to mortar producers abroad.

Their facilities of production are a pilot-scale rotary kiln operated in the Lepol process, with a capacity of 350 kg cement/h. This facility had already proved suitable to obtain optimum Roman cements from a number of different raw materials. In the pre-project stage, IMBM had used raw materials from different sources such as Lilienfeld (AT) and Folwark (PL), the latter being the raw feed for most of the batches produced within the past few years.

The novelty aspect in the activities of IMBM within ROCARE consisted in the use of marlstones from new sources, leading to the necessity to optimise the existing process of production to adjust for the different compositions of the marls.

Additionally, IMBM was a supplier of their optimum RC binders to the scientific partners of the project to perform analyses, tests and measurements, as well as to potential end-users for reasons of testing and application trials, and to all measures to strengthen their position on the market of hydraulic binders.

IMBM rotary kiln: dimensions: 1,25 x 16 m
capacity: 500 kg/h, kiln speed: 0.5-3.0 rpm
fuel: heavy oil



IMBM Process flow

3. VFB - Verein zur Foerderung der Baudenkmalpflege (Association for the Advancement of the Architectural Heritage Conservation), seated in Vienna-Mauerbach (AT)

Founded in 1997 by the initiative of members of the Federal Office for the Care of Monuments in Austria, VFB is as a private non-profit organisation which acts in the environment of the Office Federal Office for the Care of Monuments in Austria. Their background in respect to the ROCARE project consisted in a number of batches produced from various marls during and after the FP5 ROCEM project to which VFB had been closely linked as advisor and external scientific partner.

At the onset of the ROCASRE project, VFB had been producing and sporadically operating their shaft kiln on their own in an artisan approach, usually linked to purposes of training and demonstration, eventually also to meet specific demands in architectural conservation. They were flexibly using marls from different sources. The production capacity is approximately 0.6 tons per batch with a maximum of 1 batch per week. VFB is exclusively involved and interested in the restoration market, where they have good knowledge and excellent contacts in and beyond the borders of Austria. They are highly flexible to specific demands by users and can offer advice on practical issues of application along with the use of their cements.

The main technical development aspect in the project activities of VFB was the improvement their kiln both in size and shape, and the test of new raw materials. Strategically their role was of importance in informing, advising and encouraging the restoration community in the application of the Roman cement.

The contribution of VFB to supply their RC binders to the scientific partners for tests and analysis was limited to a number of specific data to be assessed for these cements. They were extensively used, however, for the purpose of on site trials and demonstration activities.

VFB periodic shaft kiln:
Production capacity > 600 kg/batch
Fuel: timber

Identification of appropriate marls to produce Roman cements

Marls, being natural rocks, exhibit a variety of chemical and mineralogical compositions at varying petrographic textures. In this context, the latter parameters are of higher significance for the appropriateness as Roman cement stones than their chemical composition, since the low temperatures of calcination require fain grained and optimally intermixed minerals necessary for the solid-state reactions to occur in the course of calcination.

The values given in the Table below indicate the range of compositions based on extensive screening of information in the available historic literature as well as on background empirical values assessed in earlier calcinations by the ROCEM project.

Parameter	Range	Optimum Range
Hydraulic Modulus HM	1,2 – 1,7	1,3 – 1,7
Silica Modulus SM	2 – 4	2 - 3
SiO_2	> 20%	>22 %
Al_2O_3	> 6%	> 8%
Fraction of Clays	> 13%	>15%, kaolinite, illite
Structure	homogeneous, no layer structure (no calcite or quartz layers	highly bioturbated

Conclusion: The results indicate the range of properties and composition of marls with high potential to yield optimum Roman cements. Test calcinations are always indispensable.

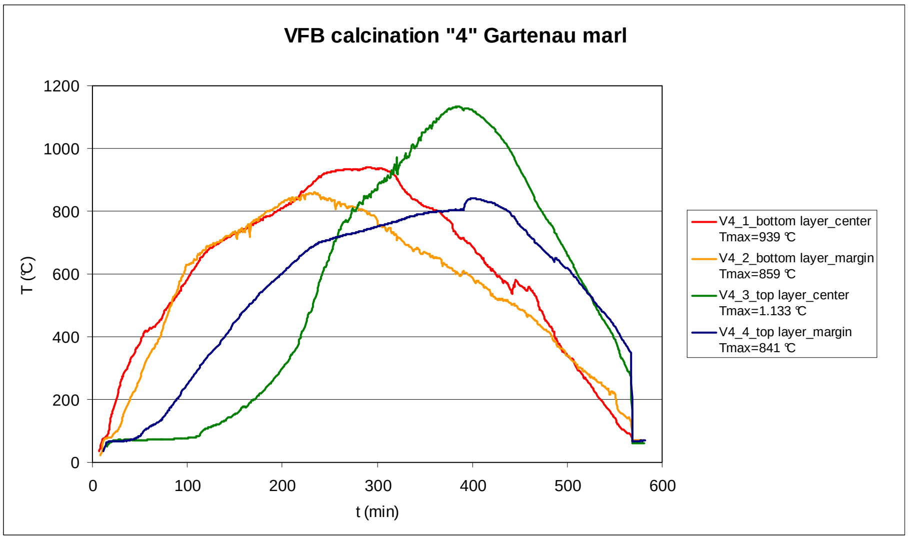
Marls from the following sources were successfully employed in RC calcinations by the three producing partners:

Producer	Origin of raw material
w&p:	> Wietersdorf marl, from the company-owned quarry at Wietersdorf, AT
IMBM	> Gartenau marl, from a subsurface quarry owned by Leube GmbH at Gartenau/Gröding near Salzburg, AT > Folwark marl, from a subsurface quarry near Folwark, PL > Rejowiec marl, from a subsurface quarry near Rejowiec, PL
VFB	> Gartenau marl, from the historic Roman cement marl mine owned by Leube GmbH at Gartenau/Gröding near Salzburg, AT

Optimum temperatures of calcination

The temperatures of calcination at which optimum Roman cements are formed have already been assessed in systematic laboratory tests conducted in the course of earlier studies, e.g. in the ROCEM project. They are in the range of about 860 – 920 °C, depending on the exact type of raw material. However, temperature gradients both within the kiln and even within each fragment of raw feed are a matter of fact, their amount depending on the type of kiln, the residence time and the way the raw feed is prepared.

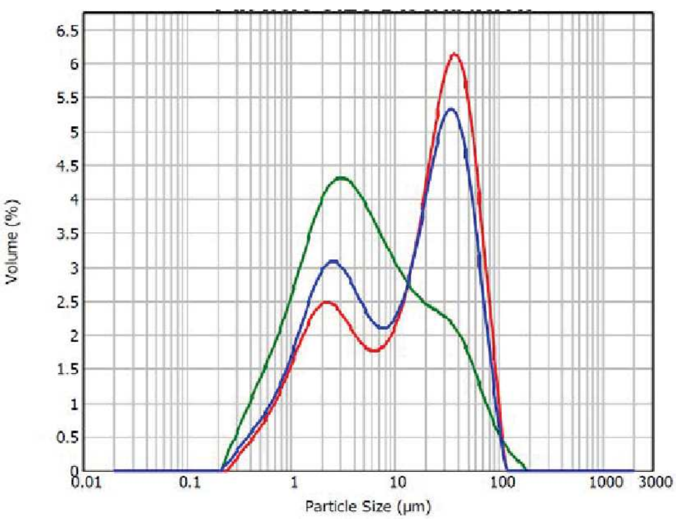
The following graph reveals the temperature curves recorded in different places of a small rectangular shaft kiln during a calcination by VFB. The obviously over-burned portion corresponding to the green temperature line in the graph would be usually be removed by hand as it can be identified by experienced workers. Lepol roraty kiln calcinations produce far less pronounced gradients of temperatures and don't require a scrutinized separation piece by piece.



Temperature curves recorded in different sections of a small shaft kiln

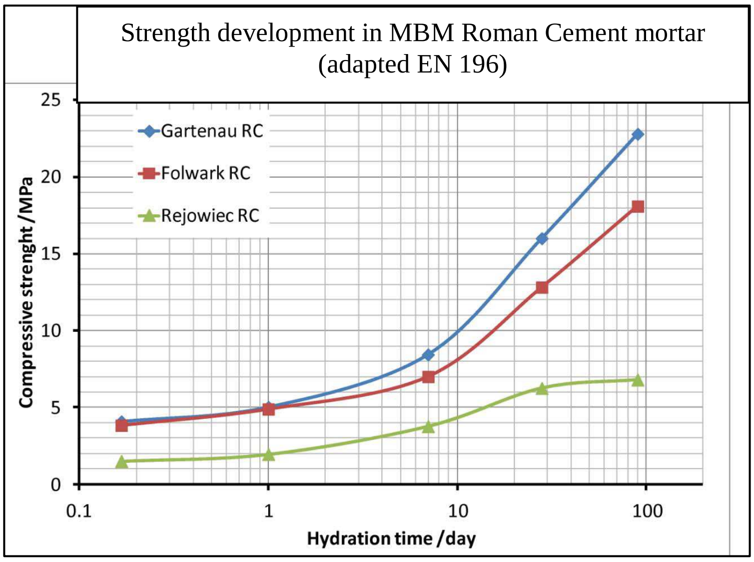
Grinding

To grind a RC clinker to a fine powder is a necessary prerequisite, since RCs do not slake with water, in contrast to lime. Although it is known from analyses of historic mortars that the average 19th century RC has always contained surprisingly large cement grains of up to 1 mm, the producers of the ROCARE consortium decided to produce more fine-grained



powders for the sake of quality consistency of their products – despite a few batches of FVB which were coarsely ground on purpose.
The grain size distribution measured for three of IMBM's Roman cements are plotted below as an example.

Strength
Compressive strength values of a cement paste or mortar and their development at increasing ages are the most useful approach to check or assess the quality of a binder.
As expected, the respective strength values of ROCARE cements differ between RC batches produced from different raw feeds under different process conditions. This is in full agreement with the historic conditions where different brands of Roman cement from across Europe covered a wide range of strength regimes. The ROCARE Standard for the classification of Roman cements has well considered this natural spread by creating three



classes which specify three regimes of early strength, useful for the end-user who wants to select a product for a specific mode of application.
Much more data describing important properties of the Roman cements produced in the project are given in the following section. At this point, just an example is given to illustrate the development of strength for the three RC binders by IMBM. They curves define the brackets of strength at a mature age of 3 months as being between 7 and 23 MPa. One can estimate the further increase in strength at later ages.

Composition
Optimum Roman cement comprises two reactive silicate phases, i.e. β and $\alpha^{/}$ belites with the latter being dominant. These are formed from both the lime and silicates within the clay fraction of the marl and the inward migration of lime into the quartz crystals. The latter can be

easily identified by microscopic techniques as reactive rims around quartz remnant cores. Under kiln conditions in which carbon dioxide is present in high concentrations, a carbonated belite may form and this is less reactive. The other reactive phase is that labelled amorphous which largely comprises calcium aluminates. The amorphous phase forms a very finely grained matrix within which the crystalline belite is embedded. An unreactive alumina-silicate, gehlenite, is present in small quantities.

As the calcination temperature increases, the amount of β belite increases at the expense of α' belite, the amount of amorphous material reduces and the gehlenite increases. The unburned remnants also decrease; these are a characteristic feature of optimum Roman cements

At calcination temperatures below that of optimum conditions, the proportion of unburned material increases and the calcium silicate may be present as wollastonite.

These characteristics can be used as a Quality Control device during calcination since, with their knowledge and regular XRD analysis, the progress of calcination can be assessed. Studies of calcined clinkers have shown that it is beneficial to use both XRD and microscopic techniques to fully understand the progress of calcination. This is particularly advantageous in assessing non-crystalline fractions as well as the presence of quartz remnants and their reaction rims.

Current availability of Roman cements by ROCARE

At the time of editing this document, the cement producers can supply their products on the following terms – the Classes refer to the early strength regime as specified by the ROCARE Standard:

w&p Peggau

w&p RC, of a reddish colour; about 10 tonnes are currently on stock, and 100 tonnes are available on request before the next batch will be produced

IMBM Krakow:

Folwark: RC Class A, of pale colour; limited quantities are usually on stock, larger amounts are produced on request. A Class B version has also been produced and purchasers should discuss their requirements with IMBM.

IMBM Gartenau: RC Class B, of pale colour; only limited amounts are available, there will probably be no further production of this brand.

IMBM Rejowiec; RC Class C, of light pale colour, limited quantities are usually on stock, larger amounts are produced on request.

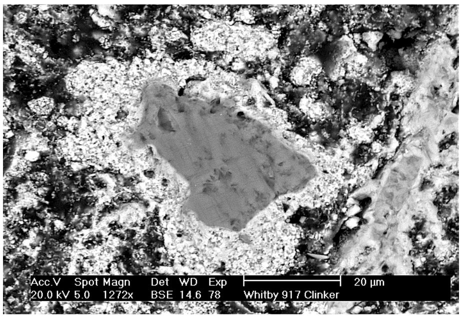
VFB Vienna-Mauerbach:

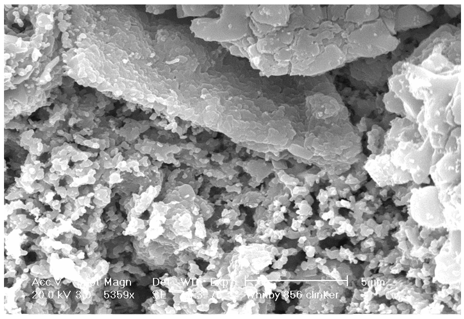
Small batches up to 1-2 tons per week, exclusively produced on request, specific demands of customers are met if possible.

Hydration

Roman cements contain two reactive phases; aluminates responsible for early age strength and silicates responsible for the long-term development of the microstructure influencing strength and moisture transport. The aluminates are generally present in an amorphous phase making their identification difficult. The silicates, polymorphs of belite, are found both within the background matrix as well as in reaction rims surrounding quartz remnants.

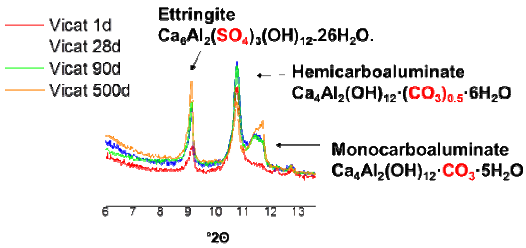
The reaction rim can be clearly seen in the BSE micrograph on the left whilst the SE image on the right shows the very fine nature of the belites making SEM analysis difficult. XRD Rietveld analysis indicates two polymers of belite, i.e. β and α′; a belite might also exist although differentiation from α′ belite is uncertain due to the wide spectra of crystalline structure possibly formed below 900°C. Carbonated belites, Spurrite and Tilleyite, may also be present representing unreactive phases. The presence of Gehlenite indicates high calcination temperatures which may be found in local "hotspots" within the kiln.



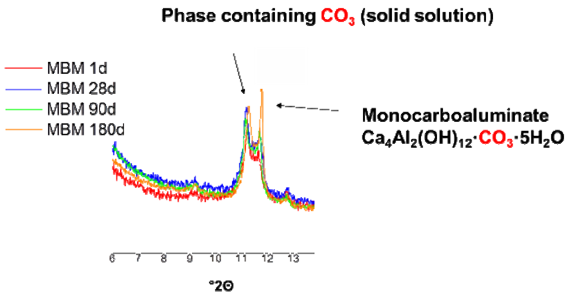


In considering the aluminates it is useful to differentiate three types of Roman cement:

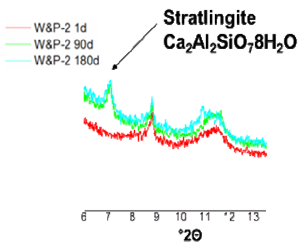
Cements containing sulfate and carbonate - The initial hydration products are the AF_m phase hemi-carboaluminate ($Ca_4Al_2(OH)_{12}.(CO_3)_{0.5}.6H_2O$) and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26\ H_2O$). Unlike Portland cements the ettringite does not convert to the monosulfate form but rather additional precipitation is observed as hydration progresses. The hemi-carboaluminate remains prominent and is joined by the precipitation of mono-carboaluminate ($Ca_4Al_2(OH)_{12}.(CO_3).5H_2O$.

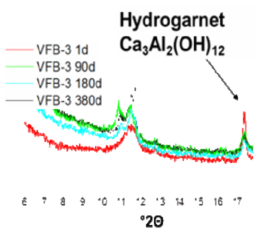


Cements containing carbonate but no sulfate - Without sulfate being present no ettringite is produced. Two AF_m phases are produced. Initially a carbonated AF_m (CO_3-AF_m) dominates over the mono-carboaluminate. However, with further hydration both hydrates are prominently visible.



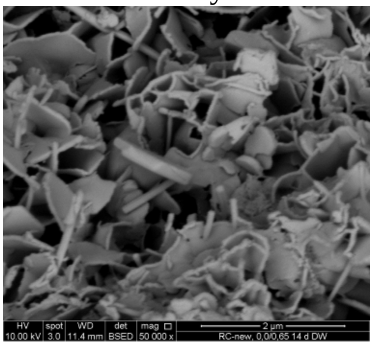
Cements containing neither carbonate nor sulfate - This group of cements are rare and may represent over-burned clinker. In addition to the previous phases, which may be not so well formed, stratlingite ($Ca_2Al_2SiO_7.8H_2O$) and hydrogarnet ($Ca_3Al_2(OH)_{12}$) have been observed. Being a calcium-alumino-**silicate**, the



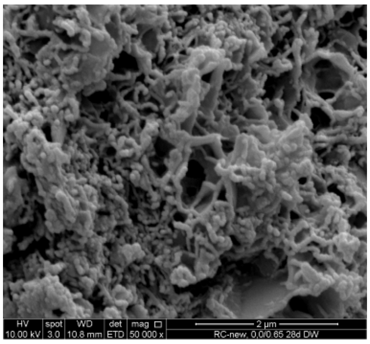


stratlingite is not observed at the earliest age of hydration. The peak present at ~9^o 2theta represents muscovite, a remnant from the original marl.

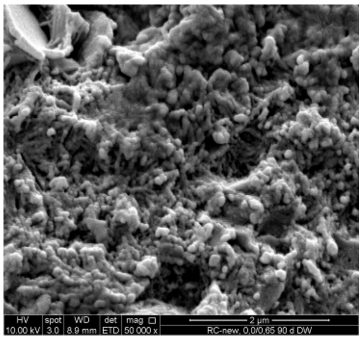
The hydration of the belites produces CSH. The following micrographs show the development of microstructure. The early hydration of the aluminates creates a very open structure which is subsequently infilled by the CSH. This can be seen below by both SEM and pore structure analysis.



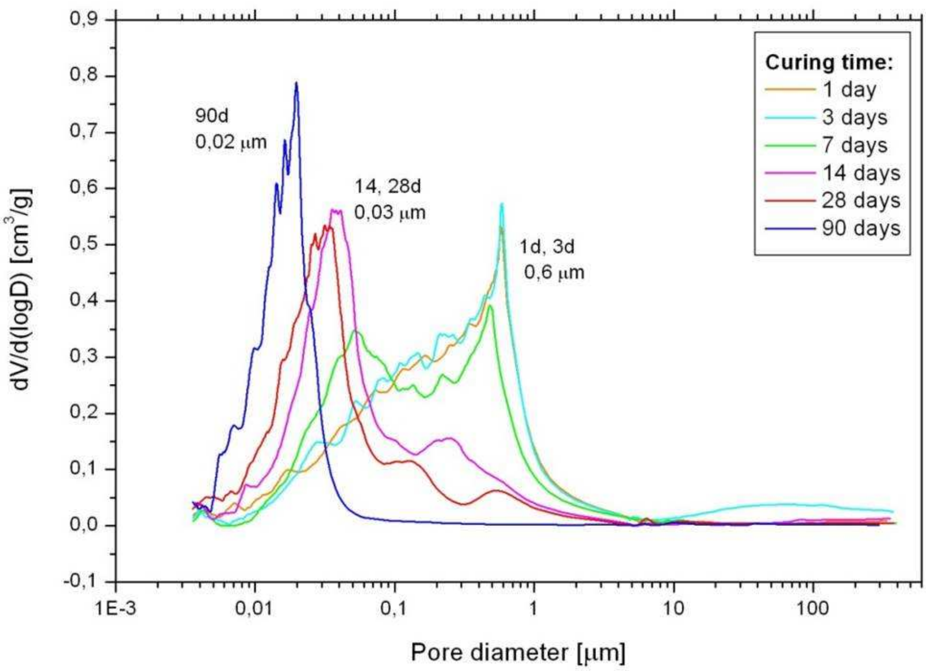
Young paste – a 'card house' structure built of the AF_m platelets.



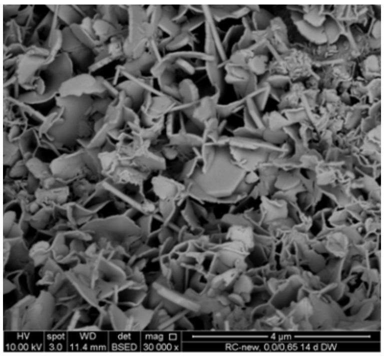
Intermediate curing – the C-S-H gel generated in the belite hydration process gradually fills in large pores of the early structure.



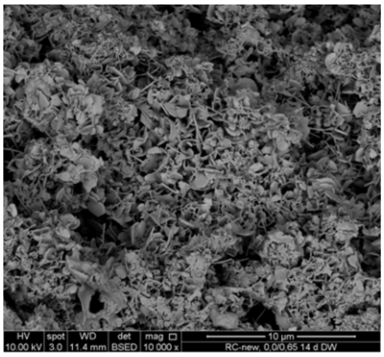
Mature paste – dense homogenous microstructure.



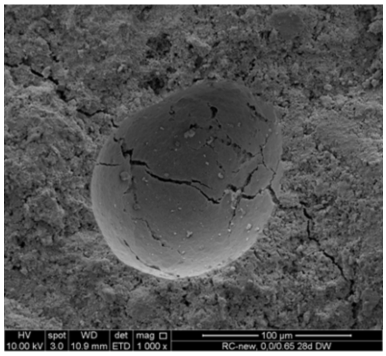
Knowledge of micro-structures formed under ideal conditions allows us to interpret data from historic mortars. Historic Roman cement mortars, representative of different application techniques from architectural castings to *in situ* formed renders and profiles, show even more complex pore structure as they were applied and cured at the construction sites under conditions far less controlled than in the laboratory. Three different types of pores are observable in the SEM as illustrated below. It is the “matrix pores” which are quantified in mercury intrusion analyses.



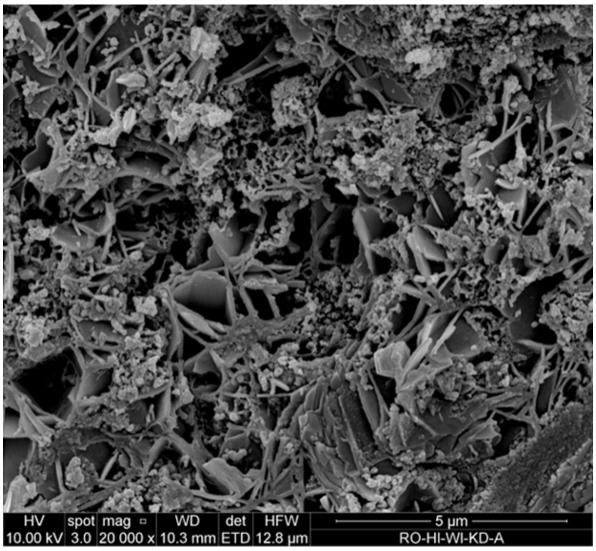
„Matrix“ pores – mainly in the range of 0,1 – 0,5 µm

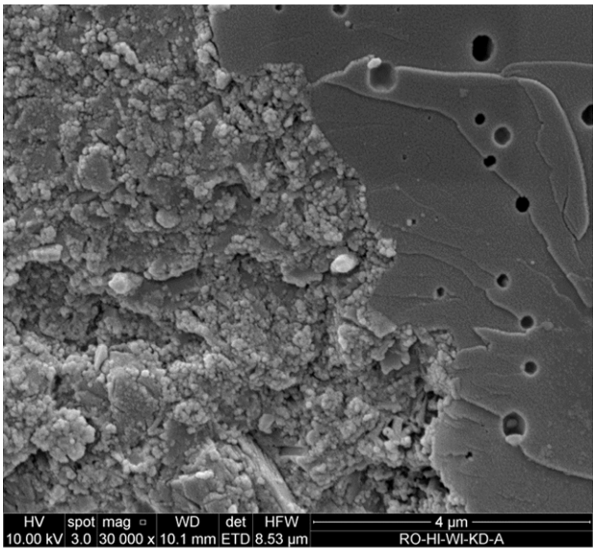


„Air-void“ pores – mainly in the range of 1 – 5 µm



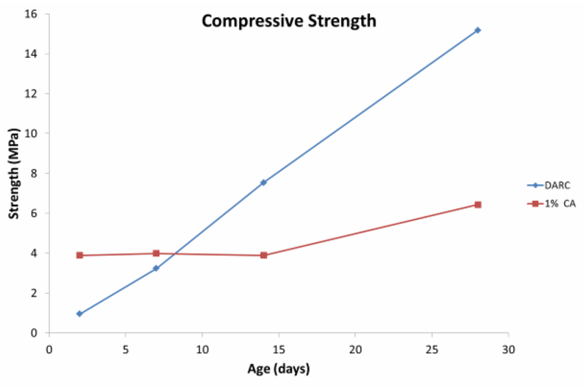
Air bubbles – up to 500 µm

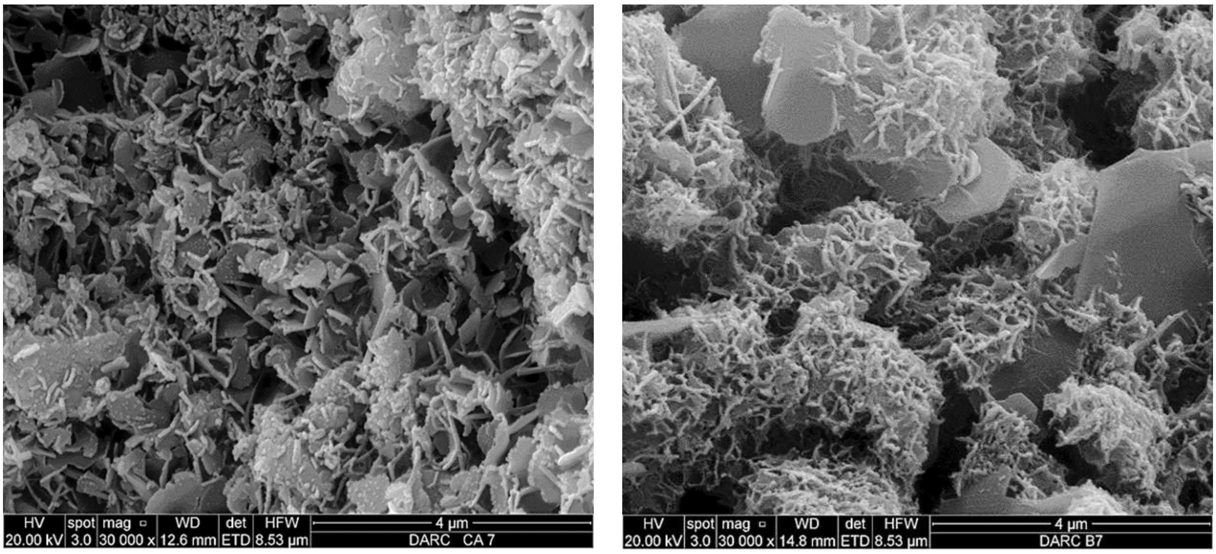




The micrographs above are from a Viennese render dating to 1870. It is clear that within the same render microstructures associated with both good curing and early age hydration are observed. This may reflect either differential “workmanship” in the original construction or variable exposure conditions on different sections of the façade.

As discussed in the next section a new retardation technique based on pre-hydration of the cement has been developed. This has permitted an assessment of the impact of the use of citric acid as a retarder on the hydration of Roman cement. Use of SEM (below) and XRD indicate that the hydration of the belite phases is retarded by the use of citric acid. This is also reflected in the development of strength within the first 28 days.



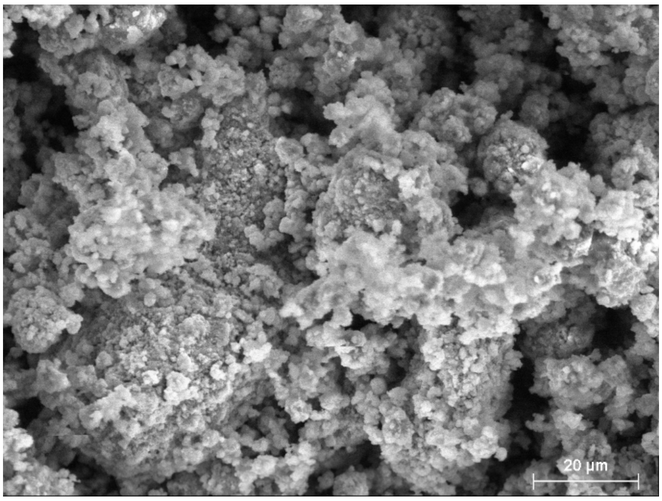


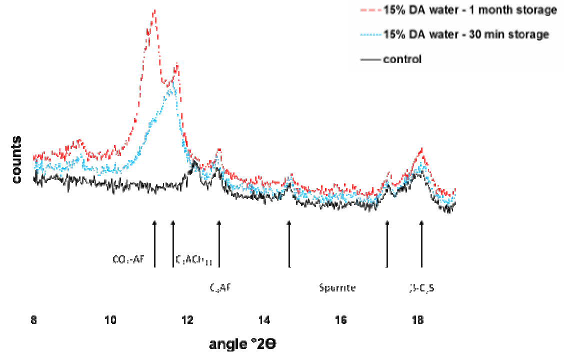
Citric acid has produced a more open structure (left) than DARC (right) at an age of 7 days

Retardation

At the outset of the project performance criteria were agreed for mortars for both cast elements and renders. Principal among these were requirements of workable lives of 15 – 30 minutes for cast elements and 1 – 2 hours for renders. It had originally been expected that chemical retarders such as citric acid could be universally applied. However, whilst these worked well for cast elements it was a different matter for renders. Some retarders would not deliver the workable life whatever dosage was used whilst others, such as sodium gluconate, delivered the required workable life but only at the expense of a major reduction in strength. Following suggestions made at a ROCARE workshop a technique has been developed in which the cement is pre-hydrated before the mortar is produced. This is a more refined version of the historic practice of leaving the cement in the open air before being placed into barrels for transport. The process has been termed De-Activated Roman Cement (DARC).

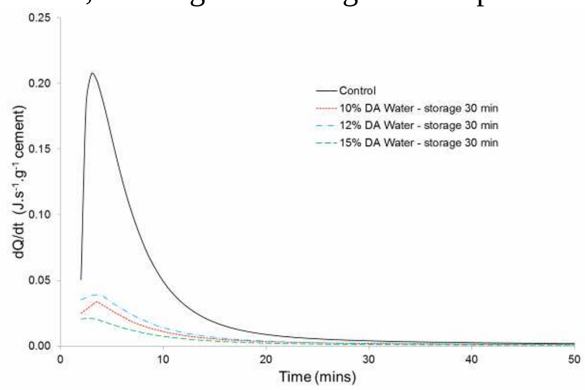
The deactivation water is expressed as a percentage of the cement weight within any mortar. In order to obtain a uniform distribution of the deactivation water amongst all cement grains the water is first added to the oven dry sand and mixed for 2 min at 62 rpm (a Hobart mixer was used for all mortar production). Subsequently, the cement was added to the wet sand and the whole mixed for a further 2 minutes at 62 rpm. The resulting free flowing mixture was then stored in an air-tight container for various periods (storage times) until required for preparation of the mortar. Throughout this paper the deactivation parameters are principally defined by % deactivation water and time of storage.

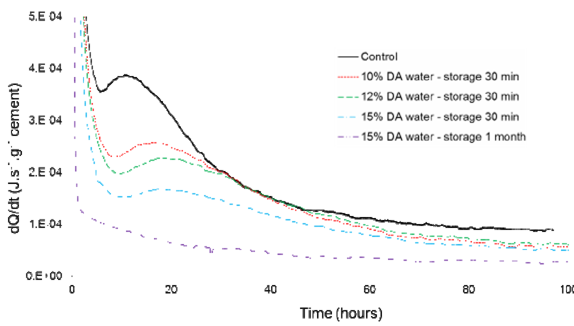




Pre-hydration products on the surface of cement grains (left) and influence of storage on mineralogy (above). The packing density of the products increases with % de-activation water and age.

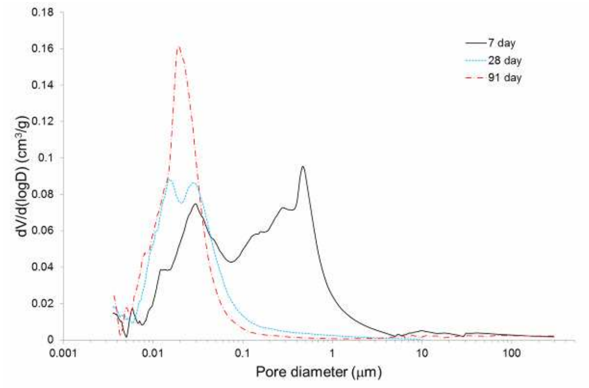
XRD analysis shows the pre-hydration products to be initially dominated by monocarboaluminate ($C_4A\dot{C}H_{11}$), with comparable amounts being generated for deactivation water contents in the range 10 – 15% and storage times between 30 – 60 minutes. It can be seen that the left side of the monocarboaluminate peak is broad suggesting a minor phase may also be present. Following a prolonged storage of 1 month the monocarboaluminate has been augmented by the development of a carbonated AF_m phase, suspected to be the previously identified minor phase. Additionally, no pre-hydration of the belite phases or production of calcium hydroxide is observed suggesting that, whilst the initial strength would be expected to be low, the long term strength development should not be influenced.



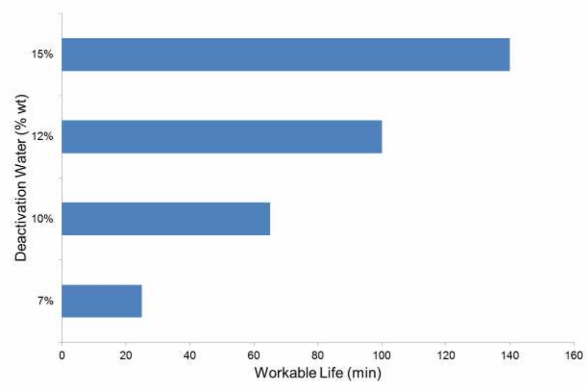


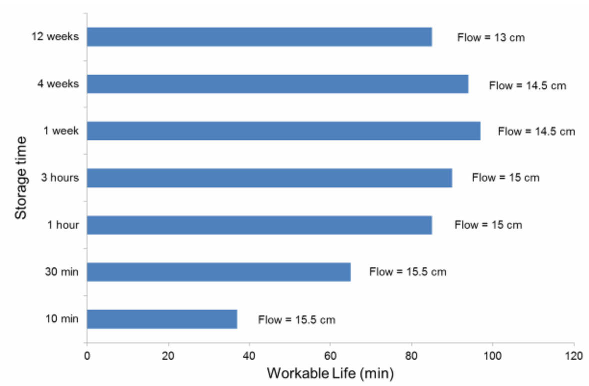
The Figures above show the heat evolution of DARC pastes as a function of the amount of de-activation water and storage time which indicates that substantial retardation has occurred.

The pore structure development of a DARC 1:2 mortar (10% DA water and 30 mins storage) is shown on the right. The traditional refinement of the pore structure is observed. Even at an age of 7 days there is evidence of belite hydration with the presence of pores in the fine range (~0.03 µm). Increasing the de-activation water and storage time yields a coarsening of the pore structure and an influence on strength would be expected.

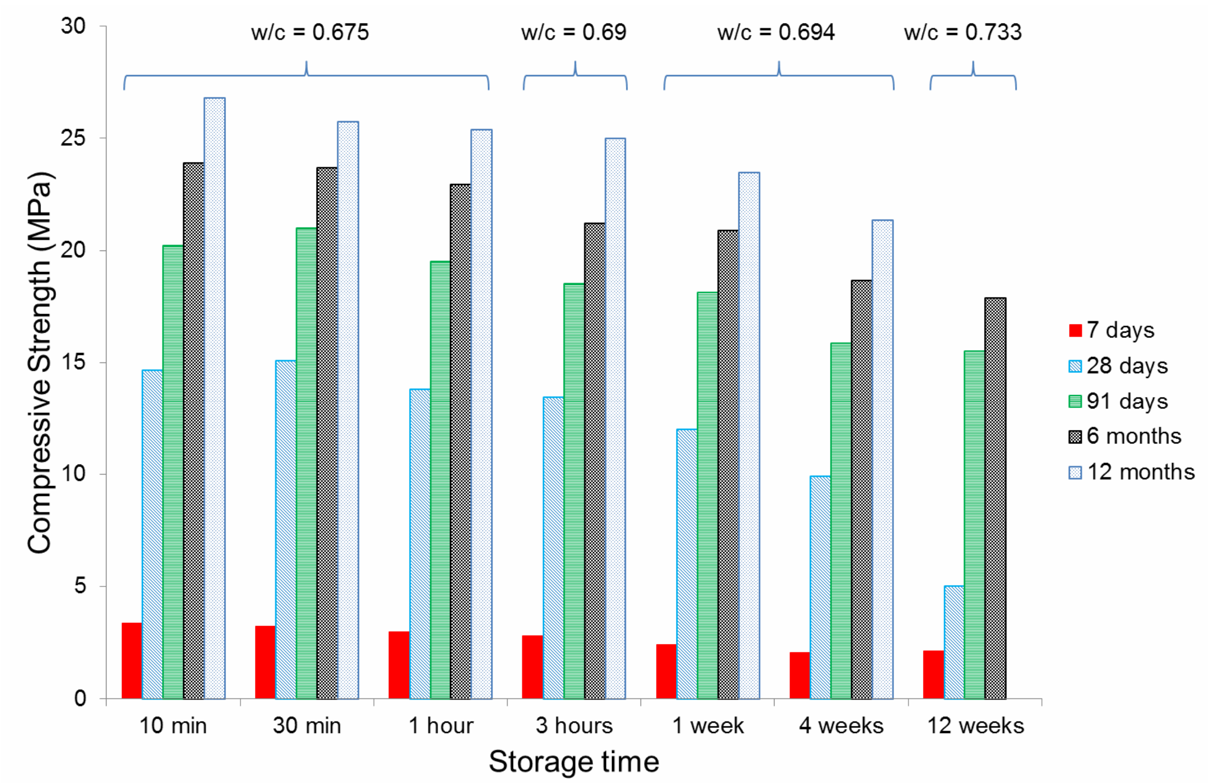


Measurements on DARC mortars (below) show that the workable life is influenced by both parameters as predicted by the calorimetry data. Not only that, but the target workable life is achievable by the use of short storage times.





The remaining question was the influence of DARC on strength development. A 1:2 DARC mortar was produced with cements which had been stored in the range 10 minutes to 12 weeks. The strength data (below) is characterised by a short plateau of up to 1 hour storage time before a strength decrease as the storage time increases; by way of example, the strength of the 12 week storage mortars being some 63% at 7 days, 34 % at 28 days, 76% at 91 days and 74% at 6 months of those stored for 10 minutes. It is supposed that the degradation is caused by the presence of free water in the stored material. This may be removed by one of two means – the application of heat or the addition of quicklime to the mix in the correct proportion. This reacts to produce slaked lime and heat which also evaporates water. Both techniques have been successfully applied to a single mix with quicklime yielding the most interesting result.

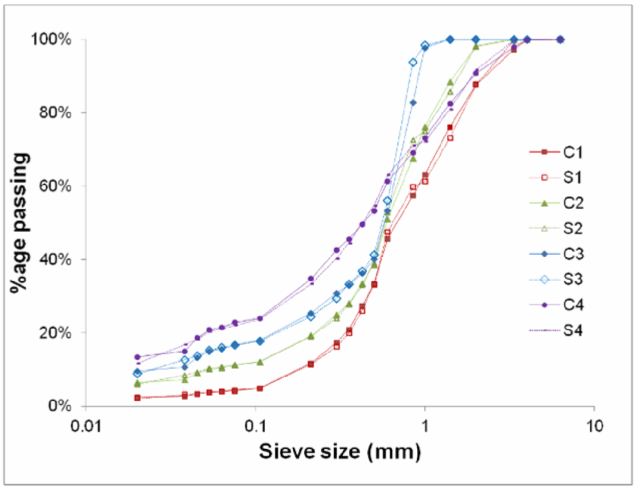


An interesting feature of DARC mortars is that they can be re-mixed when they approach the end of their workable lives. This not only greatly increases the workable life but also without any reduction in strength. Finally, workable life can be extended by prolonging the time of mixing the mortar.

Thus, the DARC technique has proved itself for both use on-site and for the production of factory-blended dry mortars and it is hoped that a company will soon undertake trials of this technique.

Influence of sand type

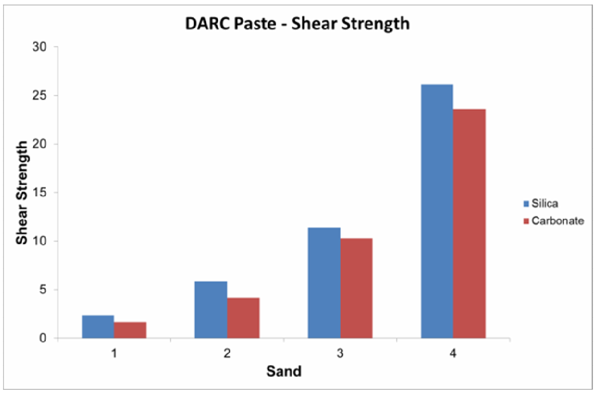
Sand is the often forgotten element in mortars. Four gradings of silica and carbonate sands have been used. Microscopic observation reveals that the particle shape of both minerals is similar although the silica sand has more rounded edges. The surface of the carbonate sand is rougher than the silica sand. SEM analysis of the fine fractions (<106 μm) shows the carbonate sand to comprise small, mainly micritic crystals which tend to agglomerate to larger particles; this agglomeration is not so apparent in the silica sand. The difference in surface texture is apparent even on the fine grains. Nitrogen adsorption yields surface areas of 2.2 m^2/g and 1.2 m^2/g for the carbonate and silica sands respectively. The Table below shows the

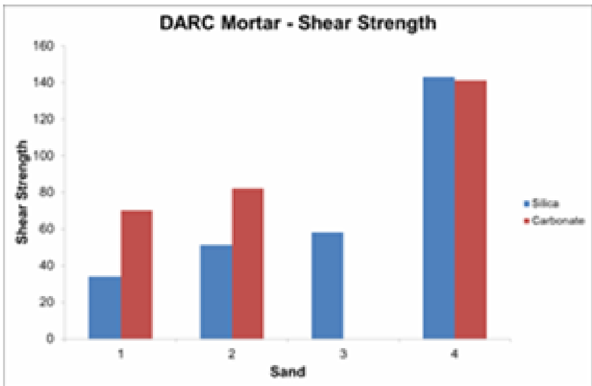


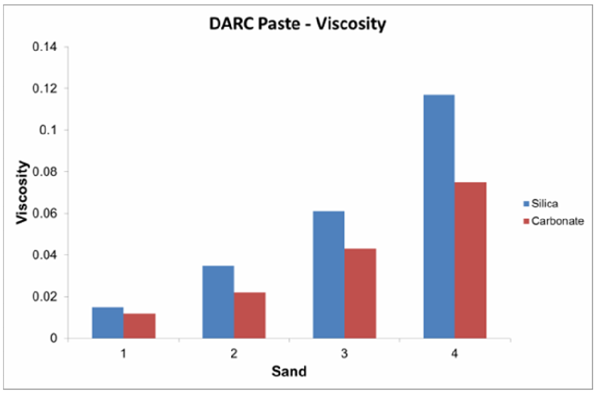
physical properties of each of the eight sands. The specific gravity of the two sources is similar but the density of sands of identical grading is different with the carbonate sands possessing the lower values. Two densities are cited for each sand, one being for the complete grading whilst the second is for that fraction of the grading greater than 106 μm, i.e. the coarse fraction. Thus, the voidage ranges between 31% and 44%. The rheology of the mortar is governed by that of the paste fraction (cement, fine sand and water) and the inter-particle interaction, particularly affected by the thickness of a pste layer around the coarser sand fractions. It is the density value >0.1 mm which is subsequently used in the calculation of the excess paste thickness.

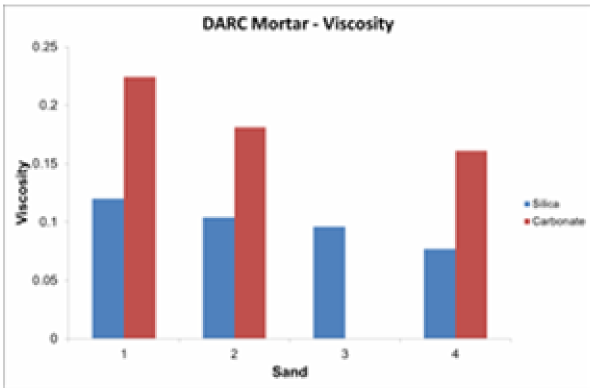
Sand	**Median size**	**Densities**		**SSA**		**Voidage**	
	(mm)	**Total**	**>0.1**	**Total**	**>0.1**	**Total**	**>0.1**
C1	0.69	1648	1625	23.65	10.55	39.0%	39.8%
C2	0.59	1637	1566	45.22	10.63	39.4%	42.0%
C3	0.58	1657	1516	61.99	10.71	38.6%	43.9%
C4	0.43	1673	1676	81.56	10.60	38.0%	37.9%
S1	0.65	1814	1748	23.36	10.44	32.3%	34.8%
S2	0.58	1826	1765	45.19	10.58	31.9%	34.1%
S3	0.56	1755	1655	62.23	10.88	34.5%	38.2%
S4	0.43	1791	1855	78.64	10.46	33.2%	30.8%

Physical properties of the sands. SG silicate – 2.68; SG carbonate 2.70.









Pastes and mortars were produced at constant w/c ratio and assessed for shear strength and viscosity in the fresh state (above). For both sand types the shear strength and the viscosity of the pastes increases with increases in fine sand content. The silica fines consistently yield higher shear strengths and viscosities than the carbonate fines despite their lower surface area. This is possibly a reflection of the lower bulk density of the silica fines and the higher associated volume of fine sand for each mix. The paste shear strength of the silica sanded pastes is similar to or higher than that of their carbonate counterparts whilst the shear strength of the carbonate sanded mortars is higher. This is obviously a reflection of differing characteristics of the coarse sand fractions and may be partly related to the smoother surfaces of the silica sand. The behaviour of the mortars does not replicate that of the pastes. The highest shear strength is obtained for grading 3 with the carbonate sand. If this outlier is put to one side, the trend is for increasing shear strength with increased sand fineness; in contrast the viscosity tends to decrease despite the viscosity of the paste increasing.

The Table right shows the relative values of rheological properties of mortar to their paste fractions. It is apparent that for both binders the ratio decreases with increasing fineness such that the properties of mortars with grading 4 sands approach that of their paste fraction, most apparently for viscosity.

	Ratio DARC Mortar / Paste	
Sand	**Shear Strength**	**Viscosity**
C1	42.2	18.7
C2	19.9	8.2
C3	-	-
C4	6.0	2.1
S1	14.5	8.0
S2	8.8	3.0
S3	5.1	1.6
S4	5.5	0.7

It is often stated that the basis of mortar design is to fill the voids between the sand particles with paste. In that extreme case there would be insufficient paste to prevent inter-particle contact and an unworkable mortar would result. In order to separate the particles and to provide a lubricating layer a thickness of excess paste (T_p) is required. Using the assumption that all the sand particles are spheres, which is obviously not the case, the value of T_p may be calculated for each mortar (Table right). It can be seen that as the fine sand content is increased the value of T_p also increases reflecting the increased paste fraction within the mortar. Viewing this data with that of the relative performance of mortar and paste shows that as the paste layer becomes thicker, its influence

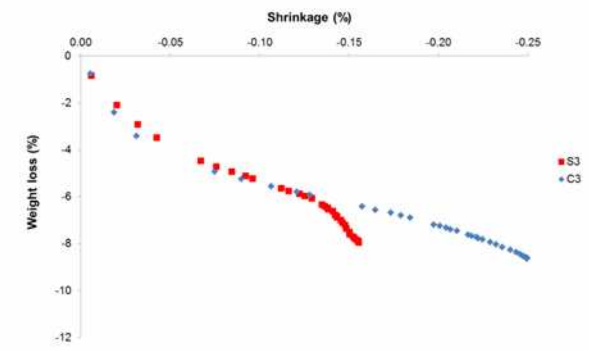
	T_p (µm)
C1	13.8
C2	22.9
C3	23.4
C4	44.8
S1	13.7
S2	24.3
S3	25.1
S4	49.5

over the performance of the mortar increases and the mortar performance approaches that of the paste.

	Strength (MPa)	Shrinkage (%)	S/C
C1	11.4	0.16	1.00
S1	10.6	0.16	
C2	13.3	0.262	0.64
S2	10.8	0.167	
C3	13.8	0.252	0.62
S3	11.6	0.155	
C4	12.7	0.224	1.04
S4	13.5	0.234	

The sand type and grading does not have such a large influence of strength and water absorption coefficient. The carbonate sands yield the slightly higher strength (Table left). However, if the mortars had been produced at the same workability then the differences would have been minimised. There is no consistent influence of sand on WAC.

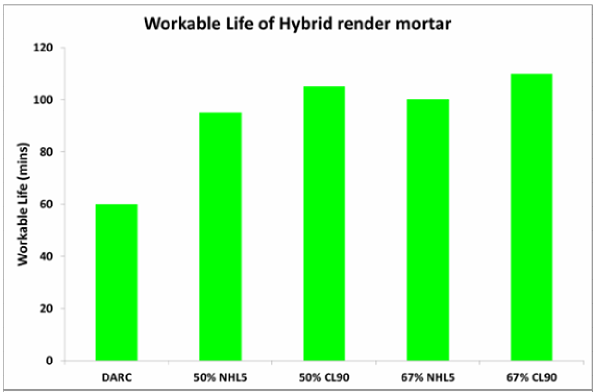
In contrast, the shrinkage of the mortars is strongly influenced by grading and sand type but not in a consistent manner. The S/C column represents the ratio of shrinkage in silica mortars to carbonate mortars of identical grading. The differences in performance can be related to different responses of weight loss to shrinkage. Examples are shown below.

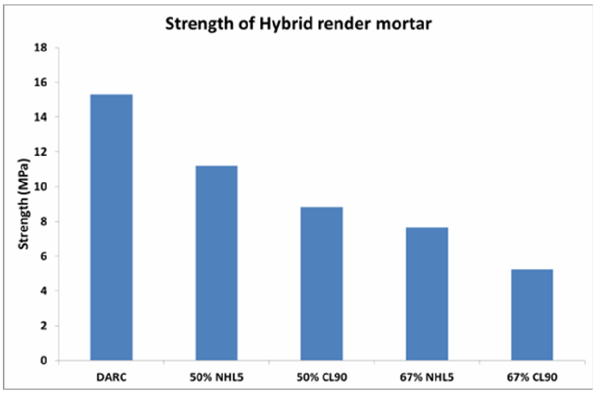


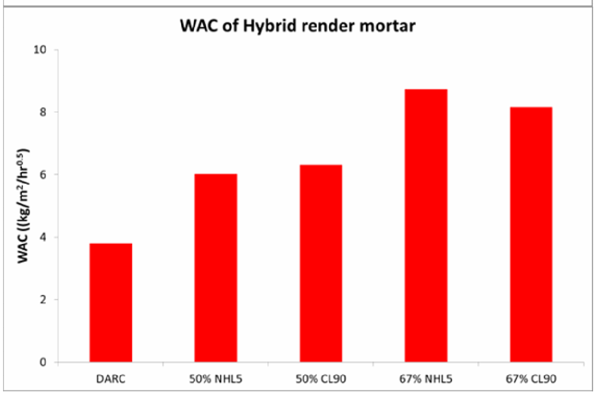
As the difference between the responses grow so does the difference in shrinkage. In the case of the DARC mortars the relevant feature is the reduction in rate of shrinkage increase despite the continuing weight loss found in the S3 mortar. This response may resemble what might be expected if water was being removed from the bodies of large ink-bottle pores which would contribute to water loss but little shrinkage. However, the reasons for these differences remain to be confirmed. XRD analysis does not reveal any significant influence of sand mineralogy or grading.

Hybrid mortars

It is known that 19th century mortars could contain lime; however, there is little contemporary data available. Initial work on hybrid mortars containing both lime and Roman cement showed that lime does not retard the setting of Roman cement and that retardation is essential, in this case by DARC but citric acid may be successful for some mortar applications.







It is apparent that the hybrid mortars have a longer workable life than the DARC mortar with 100% Roman cement as the binder. The type of lime and its quantity do not have a large effect on the increased workable life.

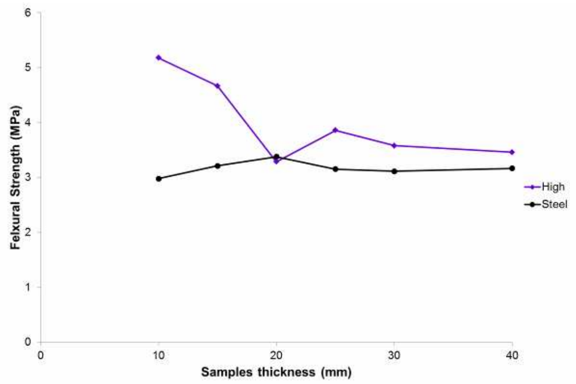
As expected, the use of lime decreases the strength with 50% NHL5 >50% CL90 >67% NHL5 >67%CL90.

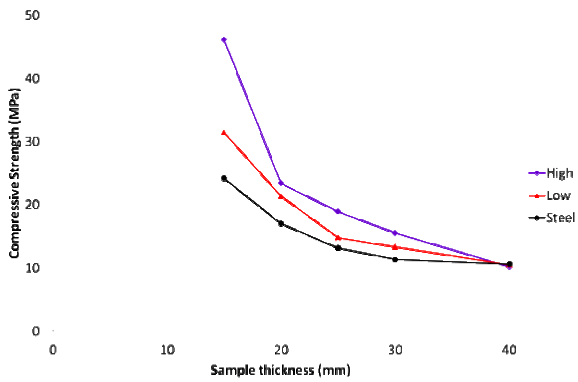
The hybrid mortars possess higher values of Water Absorption Coefficient such that it is possible to double the WAC in comparison to the original DARC Roman cement mortar. Shrinkage of DARC hybrid mortars exposed to 65% rh was independent of the lime type and proportion in the mix. The mix with 67% CL90 registered a more rapid initial rate of shrinkage.

The appropriate use of lime permits the refinement of properties of the mortar to achieve specified properties. If Natural Hydraulic Lime is to be used then it is recommended that trials are conducted since the limes vary in performance just as do Roman cements since they reflect the characteristics of the limestone from which they were calcined.

Influence of substrate

Renders are applied to masonry substrates yet their properties are measured in the laboratory on mortars manufactured in steel sided moulds. Further, renders are rarely available as 40 mm thick samples. Hence, a study was undertaken on a DARC mortar cast between bricks to produce samples of varying thickness. Two brick sources characterised by low (4.11 $kg/m^2/hr^{0.5}$) and high (20.16 $kg/m^2/hr^{0.5}$) water absorption coefficient have been evaluated. Fifteen mm brick slips have been carefully produced to form the sides of beam moulds of sizes 40, 30, 25, 20, 15, 10 mm; the faces of the slips were sanded to a smooth finish. Special moulds have been manufactured to accommodate the slips (upper Figure) and also to yield steel sided control moulds. The experimental set-up facilitated composite moulds with a brick slip as one face and steel as the other (lower Figure). Mortars were produced at a cement:sand ratio of 1:2.5 by volume and a constant w/c ratio of 0.87; the 8 sands previously described were used in this study. Various parameters of strength, WAC, shrinkage, water extraction and pore structure have been investigated but not in all combinations of mortar and substrate.



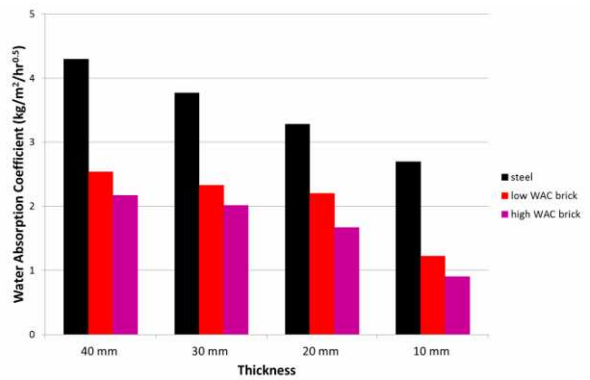


A typical example of flexural strength and compressive strength is shown above. Whilst the flexural strength is independent of sample thickness for mortars cast in steel moulds the compressive strength increases as the samples become thinner. This is a reflection of the tri-axial compression produced in the sample by the restraints of the test machine. Mortars cast between brick slips show both an influence of sample thickness and the WAC of the substrate. The influence of the substrate is greater for thinner samples and for mortars manufactured with sands of lower fines content. The latter is particularly noticeable in the 15 mm samples where the workability of the mortar is key to being able to fill the moulds before the substrate has de-watered the mortar. Thus, as the shear strength of the mortar increases (see above) the influence of the substrate decreases. The influence of sand grading in 15 mm thick samples is more pronounced for the silica sand than the carbonate sand; the inference being that the water retention of the carbonate sanded mortar is greater than that with silica sand.

All of the previous tests were undertaken using dry brick substrates, which is contrary to frequent guidance on best practice. Mortars were made between slips which had been immersed in water for 35 and 45 seconds prior to mortar manufacture. The soaking generated a small reduction in the compressive strength value and a small increase in the flexural strength.

The moulds in which both faces use brick as the substrate is representative of a mortar bed between two bricks. In order to replicate a render a steel slip was used on one face and a brick on the other. The compressive strength of 15 mm thick samples showed an 8% strength reduction over samples cast between two bricks. The strengths remain substantially higher than for samples cast in steel moulds. The flexural strength of the face in contact with the brick was higher than that of the opposite face; the difference increases with thinner samples. It is interesting to note that the flexural strength of mortars cast between steel moulds is higher than that measured with the "steel" face in tension of the composite moulded samples. It is possible that whilst the brick has removed water from the mortar, densification has occurred on the brick face whereas the removal of water on the steel face has simply reduced effective hydration.

Shrinkage was measured for samples cast between steel slips, brick slips and steel-brick opposite faces. As expected, the highest shrinkage is found in the steel moulded samples with the lowest shrinkage in the brick-brick samples.



The Figure opposite shows the influence of substrate on the WAC of the mortar as a function of substrate WAC and sample thickness. As expected the substrate reduces the WAC and is more pronounced as the sample becomes thinner. It was not expected that the same relation to thickness would be observed in samples cast in steel moulds. An obvious explanation is not forthcoming.

Mortars produced with the coarser sands (S1 and C1) and cast in both brick and control steel moulds show a clear WAC reduction trend as the sample thickness decreases, independent of their mineralogy. When finer sand is used (S3 and C3) the WAC reduction with thickness is less evident and restricted to the 10 mm samples. The WAC of the carbonate sand mortars tends to be higher than that of their silica counterparts when cast between brick faces. This trend is not the general case when cast in steel moulds and the desorption of the mortars by the brick substrate is critical.

Substrate	Sand	Threshold pore (µm)	Porosity (%)
High WAC brick	S4	0.023	14
Low WAC brick	S4	0.025	17
Steel	S4	0.044	19
High WAC brick - steel	S4	0.021	16
High WAC brick	S4	0.023	14
High WAC brick	C4	0.036	16

The influence of substrate and sand mineralogy on pore structure is summarised in the Table (left). The largest threshold pore size and highest porosity occurs in mortars made in steel moulds. The influence of increasing the WAC of the substrate is to reduce both parameters. Carbonate sand yields higher values of the same parameters. A reduction in sample thickness of samples cast between high WAC bricks is accompanied by a small reduction in the threshold diameter.

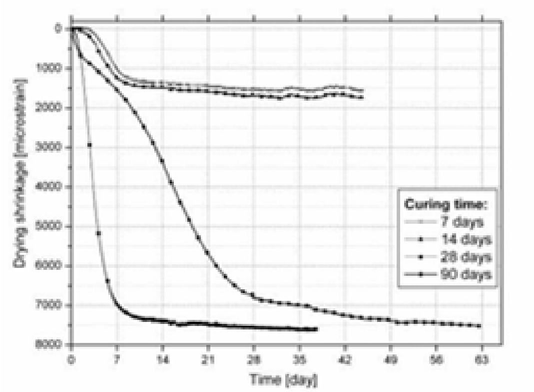
The outcome of this work is that a much better correlation can be made between mortars "on the façade" and the performance and specification of conservation mortars produced in the laboratory.

Shrinkage

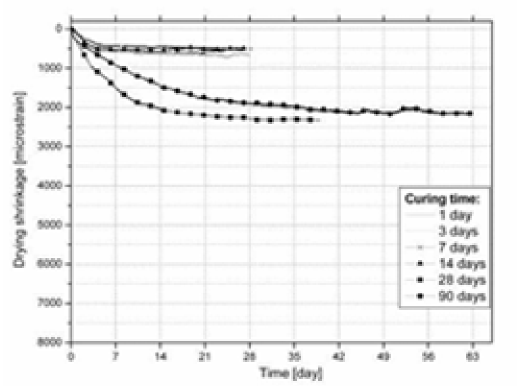
Fine surface cracks, forming an irregular network not related to building features, are a distinct characteristic of all Roman cement renders and architectural castings. Though usually they do not lead to damage, their formation is one of important barriers preventing broader acceptance of Roman cements as a cultural heritage material by the contemporary restoration and construction sector.

The fine cracking of Roman cement mortars is caused by their restrained shrinkage during the drying process. Uniform, free drying shrinkage does not induce stress in the material. However, drying shrinkage in repair mortars is restrained by the existing substrate, which induces tension leading to irreversible stretching and eventual cracking. The repair mortar can also experience internal restraint as the moisture transport is not instantaneous and, with a reduction in relative humidity, the outer part of the repair will dry more quickly than the interior and will be restrained from the shrinkage.

The aim of the work was to study the mechanism of cracking of Roman cement mortars. In the first stage of the research, two fundamental properties of the materials controlling its potential for cracking were determined: drying shrinkage in response to a range of relative humidity (RH) levels in the environment, and relationships between tensile stress and strain, especially the critical levels of strain at which the materials fail mechanically. These properties were determined at various curing times, as restricted hydration also can be expected in freshly prepared Roman cement repair mortars, which are exposed to dry real-world external environments.

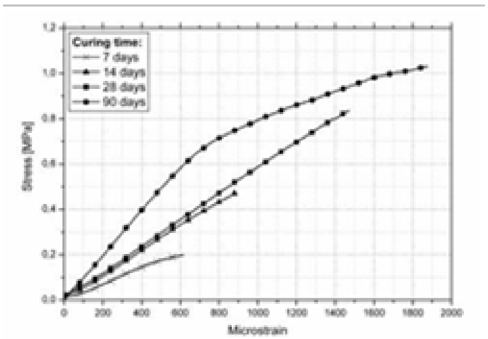


Drying shrinkage at 45% rh of the cement pastes cured at various ages (w/c=0.65)

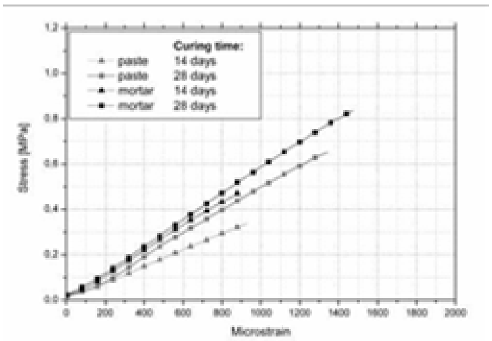


Drying shrinkage at 45% rh of the mortars cured at various ages (w/c=0.65. a/c=3:1 by vol.)

The Figures above show the evolution of shrinkage in the specimens as a function of time after a given curing time. By 65 days the shrinkage in all cases was observed to level off. There is a characteristic evolution of the shrinkage curves with the time of hydration. Young pastes and mortars, i.e. cured for less than 14 days, show much lower shrinkage than matured materials, the reduction factor being five for the pastes and four for the mortars. The observation can be correlated with the radical change in the pore structure, which occurs in the pastes with increasing curing time: a relatively open porosity structure at an early age changes to a more dense structure as larger pores are filled with the C–S–H gel formed. Because narrower pores lead to an increase in capillary suction, which is the primary cause of paste shrinkage, matured pastes will have higher shrinkage. As expected, the addition of aggregate considerably reduces the shrinkage, the asymptotic values for the matured pastes being 7500 µm/m when compared to just over 2000 µm/m for the mortars.



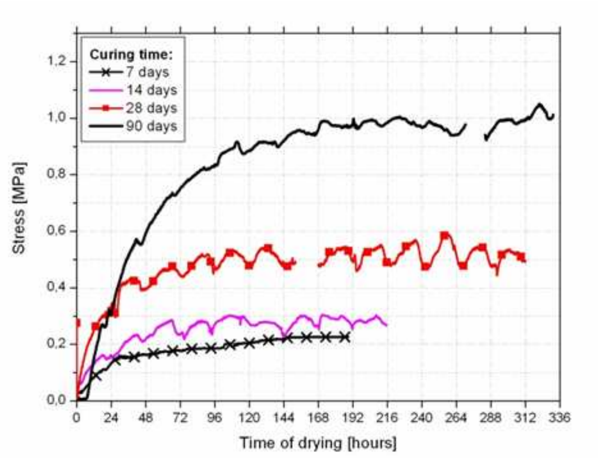
Tensile stress-strain relationships of the mortars



Tensile stress-strain relationships of the cement pastes and mortars cured for 14 and 28 days

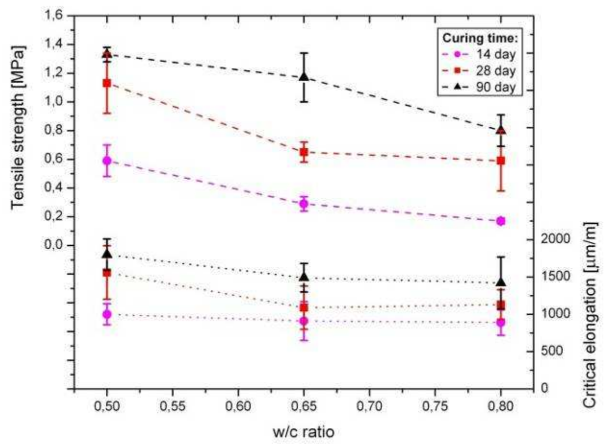
The Figure (above left) shows the tensile stress-strain relationships for wet mortars cured at four different ages whilst the Figure (above right) compares the stress-strain relationships for wet pastes and mortars cured for 14 and 28 days. The most important observation from the tensile testing is that breaking strain of the mortars considerably increases with the curing time, the range being from 600 µm/m at 7 days, to almost 2000 µm/m at 90 days. Also the modulus of elasticity of the mortars, expressed by the ratio of stress to strain in the elastic region, increases with the curing time. Pastes have slightly lower modulus of elasticity than mortars, but their breaking strains do not differ significantly from those of the mortars.

The results of the drying shrinkage analysis and the tensile strain testing clearly show that the high final shrinkage values for pastes dried at 45% RH exceeds the breaking strain irrespective of the curing time, although the difference is particularly pronounced for the matured pastes. Therefore, pastes, and in consequence cement rich mortars, will be particularly susceptible to cracking on drying. The considerably reduced drying shrinkage in the mortars is comparable to the breaking strain in matured mortars and is even lower than the breaking strain in mortars at young ages. The data indicate that an optimum curing time of around 14 days produces mortars which should have the least susceptibility to cracking, as they have a low shrinkage that is also well below their breaking strain.

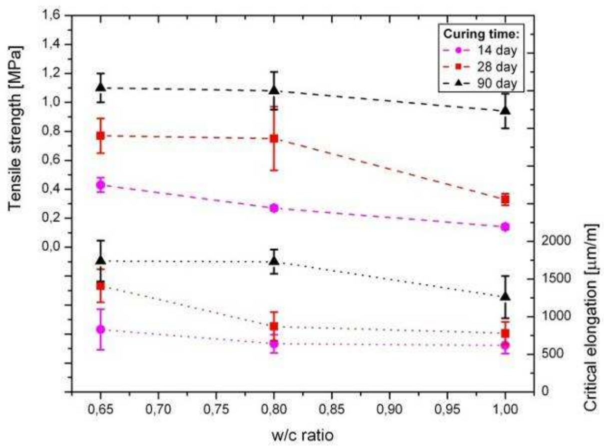


Whilst the first stage of work involved shrinkage in unrestrained conditions the cracking sensitivity of Roman cement mortars is directly illustrated by stress development caused by drying shrinkage - at 45% RH - under restrained conditions (see opposite). No mortar failed, irrespectively of the curing time and related ultimate drying shrinkage, confirming the earlier analysis based on the comparison of the ultimate shrinkage and the elongations at break. The ultimate stress levels observed are reduced to varying extent when compared with the short-term tensile strength.

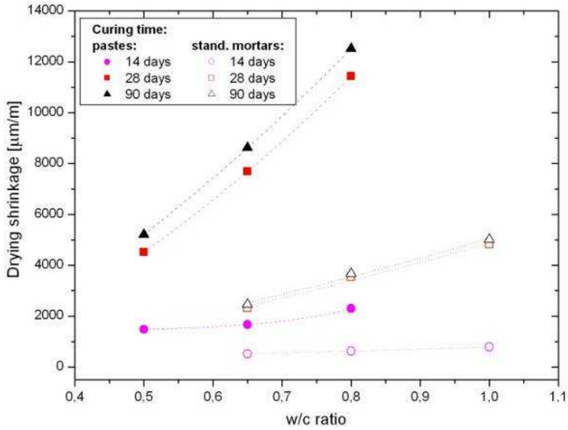
Susceptibility to cracking is a function of shrinkage and the ability to accommodate the strain developed. Obviously, the w/c ratio of the mortar will have a substantial influence.



Tensile strength and critical elongation values for the pastes

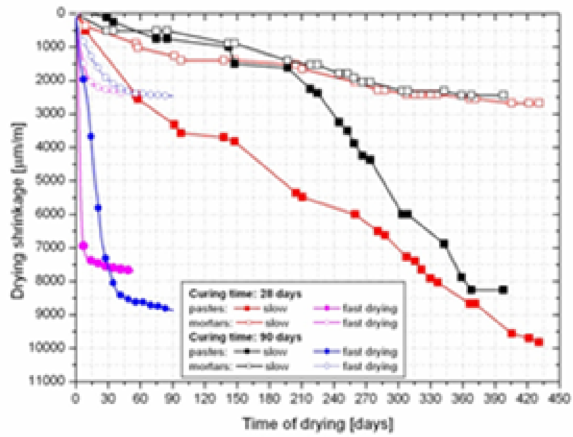


Tensile strength and critical elongation values for the standard mortars



Ultimate drying shrinkage for the pastes and standard mortars

The shrinkage values increase with increasing w/c ratio as higher w/c leads to an increase in the capillary porosity and a decrease in a solid volume on which the capillary pressure acts. The results of the tensile mechanical properties analysis for specimens produced at varying w/c ratio show that increasing content of water in the mortars reduces the elongation at break and also the tensile strength for given curing times.



Shrinkage is conventionally measured by exposing samples to a low rh, in this case 45% rh, producing a fast rate of drying. In order to assess the influence of the rate of drying a series of tests were undertaken in which the environmental rh was gradually reduced in steps to 45% rh. Different shapes of the shrinkage curves are evident. A fast shrinkage development is observed during the fast drying and the ultimate shrinkage levels are attained practically after around 100 days. In contrast, the shrinkage changes linearly with time during the slow drying process as the ultimate shrinkage levels are attained in more than 300 days.

Fast drying produces dramatic fall in the tensile strength of the pastes due to microcracking induced by moisture gradients and differential shrinkage across the specimens. Conversely, slow drying produces an increase in the tensile strength of the materials (especially, the mortars).

In order to validate the approach developed above samples of cast elements and render were exposed to realistic conditions following curing for various periods. The observation of crack formation was in line with the model proposed and gives confidence in being able to provide valuable guidance on mix formulations and curing in order to minimise drying shrinkage cracking in practical mortars.

Data for Standards

Work has been undertaken to produce data both for a Standard on Roman cements and to identify appropriate curing conditions for the testing of conservation mortars, currently specified in EN 1015-11.

A ROCARE Standard has been produced and the full text is available at www.rocare.eu. The opportunity has been taken to develop it along similar lines to those for Portland cements and Building Limes although key modifications have had to be made to allow for the special characteristics, production and uses of Roman cements. To account for use as a cement for the production of cast elements as well as for its calcination by small-scale artisan producers strength has been specified at an age of 3 hours. However, a specification at later ages would be more appropriate for specifiers of render mortars. Thus, an Informative section is included with a specification at 91 days. Both are shown below.

Classification	**3 hours**
A	≥5.0
B	<5.0 ≥1.0
C	<1.0

Types of Roman cement

Classification	**3 hours**	**91 days**
I	≥5.0	≥25
II	<5.0 ≥1.0	≥15
III	<1.0	≥10

Extended classification of Roman cements

EN 1015-11 specifies two different production methods for mortars "*Mortars with hydraulic binders, and air-lime/cement mortars with mass of air-lime not exceeding 50 % of the total binder mass*" and "*Mortars based on air-lime, and air-lime/cement mortars with cement mass not exceeding 50 % of the total binder mass*". The method for the second group involves casting the mortar between sets of absorbent filter papers and applying weight to ensure hydraulic contact is maintained. Apparently, this was prescribed in order to generate mortars with adequate strength for stripping in a reasonable time. As has been demonstrated in this report such de-watering is likely to have an impact on the strength of the mortar.

The specification for early curing is for a period under high humidity in the range above 90% rh or in a polythene bag. Following this, the mortars are stored under 65% rh. Testing is at an age of 28 days. There has been much debate around testing at 91 days for lime mortars which both carbonate and rely on the slow hydration of belite. Such concerns also apply to Roman cement and hybrid mortars.

Four lime mortars investigated have been based on two NHL 5, one NHL 3.5 and one NHL 2 and subject to curing as shown in the following Table. These binders were selected to encompass a wide spread of mortar performance. Regimes F, G and H were introduced to try to obtain early de-moulding of weak mortars without resort to artificial de-watering.

Curing regime	**Mould in bag**	**Mould in 65% rh**	**Samples in bag**	**28 day test Samples in 65% rh**	**91 day test Samples as shown**
A	5		2	21	+63d 65%
B	5		9	14	+63d 65%
C	5		16	7	+63d 65%
D	5		23		+63d 65%
E	5		23		+63d bag

F	1	1	5	21	+63d 65%
G	1	1	26		+63d bag
H	1	1	19	7	+63d 65%

In addition, DARC hybrid mortars using NHL 5 and CL90 have also been assessed and cured as below. The upper part of the Table relates to the mortars with 50% lime and the lower part to 67% lime.

Curing regime	Mould in bag	Samples in bag	28 day test Samples in water	28 day test Samples in 65% rh	91 day test Samples as shown
a	3		25		+63 water
b	3	25			+63 bag
c	3	18		7	+63 65%
d	3	4		21	+63 65%
Curing regime	**Mould in bag**	**Samples in bag**	**Samples in water**	**28 day test Samples in 65% rh**	
a	5		23		+63 water
b	5	23			+63 bag
c	5	16		7	+63 65%
d	5	2		21	+63 65%

Immediately upon floating off the fresh mortar, each mould was placed in a polythene bag together with a wet tissue to ensure a high humidity. The open end of the bag was not heat-sealed but rather tucked under the mould. Weight measurements indicated very low weight loss whilst the moulds remained in the bag. The humidity in the bags is unknown; however, condensation was observed in the bags and it is assumed that the rh was close to 100%.

The NHL 5 mortars required between 2 and 5 days in the moulds stored in the bags before being strong enough to remove safely. This period was extended to 13 days and in excess of 14 for the NHL 3.5 and NHL 2 respectively. However, all mortars subject to regimes F, G and H could be de-moulded after only 2 days.

	NHL 5(1)	NHL 5(2)	NHL 3.5	NHL 2
G/E	1.13	1.31	2.69	2.61
H/C	0.97	1.40	2.63	3.16
F/A	1.05	1.59	1.89	2.27

This Table shows the ratio of strength for mortars subject to equivalent curing regimes tested at an age of 28 days. It can be seen that the early de-moulding of regimes F, G and H have led to higher strengths than if the mortars were kept at high humidity until they could be transferred. The proportional increase in strength increases as the hydraulicity of the binder decreases.

Binder	28 days	91 days
NHL 5(1)	C	E
NHL 5(2)	H	G
NHL 3.5	G	G
NHL 2	H	G
DARC Hybrids	c	c

This Table shows the curing regime which generates the highest strength at both 28 and 91 days. It is clear that a specification of any curing regime can only be a compromise given the variation of optimum regimes. It should be noted that in all cases the regime which yielded the lowest strength for all mortars was that specified in EN 1015-11. Not all curing regimes showed the expected strength gain between 28 and 91 days.

As stated earlier, the EN specifies that the early curing should be in the range 90 – 100% rh. The two NHL 5 mortars were subject to early curing at 93% and 97% rh as well as in the bags; this lasted 21 days before transfer to 65% rh for the remainder of the curing period. For the NHL 5(1) mortar there was a distinct ranking for both 28 and 91 day strengths of Bag>97%>93% curing. Thus, the EN guidance is too broad.

Two additional programmes have been undertaken. The first involved the use of a humidity cabinet which was controlled to cycle between 60% and 90% rh with each humidity being held for 12 hours. DARC, DARC hybrids, NHL 5(1) and NHL 5(2) mortars were subject to this regime. Only NHL 5(2) yielded strengths that were stronger than those resulting from the EN 1015-11 regime which has already been identified as a poor regime.

The second programme was to expose the same mortars to external curing at a location on the roof of the University. During this period the temperature and humidity varied widely. Compressive strength was measured at an age of 91 days and in all cases was either comparable with or greater than the highest strength obtained by the optimum laboratory curing.

It is clear that the current specification for curing is yielding the lowest strength and does not reflect that which can be achieved in practice. Any revision to EN 1015-11 first needs to define the purpose of testing mortars according to its regimes. This data has already been discussed at 3 British Standards Institution with an interest in the EN.

Roman cement paints

Some work has been conducted to develop a ROCARE paint. Following various trials a successful paint was produced which included a super-plasticiser (Peramin SMF – sulfonated melamine polymer) and a water retaining agent (Culminal) as well as ROCARE cement and a fine carbonate powder. High shear mixing was used to ensure uniform mixing. The resulting paint has a pot-life of more than 1 hour in addition to being easily applied by brush – a sprayable version could relatively easily be developed. This showed that a long workable life might be attainable with a super-plasticiser rather than relying on a retarder.