



PHYSICAL AND CHEMICAL EVOLUTION OF LIME MORTARS FROM TOURNAI (BELGIUM) *

G. Mertens¹, J. Elsen¹, A. Brutsaert², M. Deckers² and R. Brulet²

Abstract

The characterization of historical mortars, ranging in age from Roman to Romanesque, was performed by a combination of microscopic, wet chemical, XRD diffraction and DTG techniques. The samples were taken from remnants of different constructions that were exposed under the present-day floor-level of the Romanesque Cathedral 'Notre Dame' at Tournai.

Roman mortars were found to differ significantly from their older homologues by the use of a high proportion of lime and the addition of ceramic fragments of well-defined size. From a mineralogical-geochemical point of view, both the lime binder and the lime lumps have evolved since their original application, but these systems must have been subjected to quite different processes.

Keywords

Historical mortars, Lime lumps, Physico-chemical evolution, Hydraulicity, DTG analysis

* © Copyright NLA Building Lime Group 2005

The views presented in this paper are solely those of the authors. The National Lime Association (NLA) and the Building Lime Group assume no liability or responsibility for any errors, omissions, or other limitations in this paper or for any products, services, or methods presented. This paper is intended for use by professional personnel competent to evaluate the significance and limitations of the information provided and who will accept full responsibility for the application of this information. NLA and the Building Lime Group do not intend to infringe on any patent or other intellectual property right or induce any other party to do so, and thus users of this document are responsible for determining whether any method, technique, or technology described herein is protected by patent or other legal restriction.

¹ G. Mertens, Prof. Dr. J. Elsen, Afdeling Fysico-chemische Geologie, Katholieke Universiteit Leuven, Belgium, Gilles.Mertens@geo.kuleuven.ac.be.

² A. Brutsaert, M. Deckers, Prof. Dr. R. Brulet, Centre de Recherches d'Archéologie Nationale, Université Catholique de Louvain, Belgium, Brulet@arke.ucl.ac.be.

1 Introduction

Since 1986, important archaeological excavations have been carried out under the present-day floor-level of the Romanesque Cathedral 'Notre Dame' at Tournai. The excavations, which have recently been integrated into a larger research program of the UCL (Université Catholique de Louvain) that is financed by the 'Direction de l'Archéologie en Région Wallonne', have exposed different levels and construction periods. The aim of this interdisciplinary project is to clarify the transition of ancient Roman cities and their rural territories to the post-Roman and the Romanesque society (Broulet & Verslype 2001). The earliest structures present, dating from the Roman Empire Period (about 3-5th century AD), are covered by more recent Palaeo-Christian (about 6-7th century AD) construction. In the Carolingian Period (about 8-10th century AD), a church was already present at this specific area. Different floor levels of the church and a relatively well-preserved baptismal font (Figure 1) can be distinguished. Later, around the year 1000, the church was rebuilt and the foundations of the new building more or less resemble that of the present-day Romanesque (about 12th century AD) Cathedral.



Figure 1: Carolingian baptismal font (external diameter $\pm 1.2\text{m}$)

In general terms, there seems to be a noticeable decline in the quality of construction methods and materials after the Roman Period (Bléazard 1981). However, only limited information is available on post-Roman construction, partly due to the frailty of the materials that were used, and partly because they are often situated on the emplacements of ancient Roman buildings. As a consequence, most excavations are oriented towards uncovering the splendor of the Roman Period, without paying much attention to overlying construction (Perkins 1996). Given the successive periods of urban activity and the material traces they left, the site of Tournai enables clarification of the transition. In addition to the archaeological methods of relative dating, based on sediments and macroscopic observations, compositional studies have been carried out on a selected set of mortar samples. These studies facilitate identification of different structures, examine the mineralogical-geochemical evolution of lime mortars, and discover the long-term processes to which the mortars are subjected.

2 Materials and methods

Mortar samples from the different construction types and time periods are listed in Table 1. After completing the inventory, one part of each sample was used to prepare a fluorescent epoxy-impregnated thin section, and the other part was preserved for chemical, thermal and XRD analysis.

Mortars are mainly composed of a binder, lime and hydraulic lime in this case, and an aggregate. Sometimes, additional ingredients are added to the mortar recipe; these are the pozzolans, which can be artificial or natural. The distinction between pozzolans and aggregates is not always straightforward, but the former may be recognised by the specific reactions that they induce with the binder (Deloye 1993). However, the deliberate use of pozzolans may not always be clear. The possible use of such additives can be recognised by combined microscopical, chemical and XRD analysis.

From observation of the thin sections using a polarizing microscope, a brief microscopic description was established and is presented in Table 1. A point-counting operation was also performed to extract more information from the thin sections.

Chemical analysis of the main elements of the binder is necessary to quantify the hydraulicity of the mortars and, if local limestone is assumed to have been used, to compare both chemical compositions and look for evolution of the binder since its application. The XRD analysis is used to identify the lime binder composition from a mineralogical point of view. Aside from possible hydrated minerals, the presence of unhydrated substances should be able to be detected. XRD analysis may also be useful to check for the use of crystalline pozzolan-like zeolites. Callebaut *et al.* (2001) and Bernard *et al.* (1975) even suggested that identification of minerals and specific mineral associations in lime can be used to retrieve the burning temperature of the limestone.

Table 1: List of Mortar Samples and Brief Microscopic Descriptions

Age	Construction type and code	Sample N°	Porosity Binder Porosity (BP)	Coarse "aggregates"	Fine "aggregates"
Romanesque (about 12 th century AD)	Wall 1802	RQ01	some round pores BP high		Q-sand ($\pm 250\mu\text{m}$) + glauconite
	Wall 2003	RQ02	not much but small pores BP low		Q-sand ($\pm 250\mu\text{m}$) + glauconite + 1 piece of ceramic material
	Wall 2003	RQ03	not much but small pores BP very low		Q-sand ($\pm 200\text{-}250\mu\text{m}$) + glauconite
Pre-Romanesque (about 11 th century AD)	Wall 1903	PRQ01	very low BP low	1 piece of limestone	Q-sand ($\pm 200\text{-}250\mu\text{m}$) + glauconite
Carolingian (about 8-10 th century AD)	Baptismal font	CA01	pores filled up BP very low		Q-sand ($\pm 200\text{-}250\mu\text{m}$) + glauconite
	Floor 1827	CA02	some irregular very small pores BP medium		fine ceramic (low amount) + glauconite
	Floor 1814	CA03	irregular small pores (0.2-0.5mm) BP variable	ceramic (low amount)	Q-sand ($\pm 100\text{-}250\mu\text{m}$) + 1 fragment of micritic limestone + glauconite
	Wall	CA04	irregular small pores (0.2-0.5mm) BP variable		Q-sand ($\pm 100\text{-}250\mu\text{m}$) + glauconite
Gallo-Roman (about 3-5 th century AD)	Wall 1811	GR01	well rounded macropores (0.2-1mm) BP relatively high	ceramic ($\pm 0.5\text{-}1\text{cm}$)	Q-sand fine ($\pm 200\mu\text{m}$) no glauconite ceramic (fine)
	Wall 1808	GR02	well rounded macropores (0.2-1mm) BP high	ceramic ($\pm 0.5\text{-}1\text{cm}$)	Q-sand fine ($\pm 200\mu\text{m}$) no glauconite ceramic (fine)
	Wall 1807	GR03	well rounded macropores (0.2-1mm) BP high	ceramic ($\pm 0.5\text{-}2\text{cm}$)	Q-sand fine ($\pm 200\mu\text{m}$) no glauconite ceramic (fine)

Some mortars may not be entirely carbonated, meaning that portlandite is still present in the binder. The presence of portlandite can be detected and quantified by the use of thermogravimetric methods. In addition, thermogravimetry may have the potential to better quantify the hydraulicity of mortars, because it is more related to the intrinsic presence of specific hydraulic compounds than to the general chemical composition that is classically used for this purpose.

3 Results

3.1 Microscopy

The results of the point-counting operation are presented in Figure 2. These data should not be interpreted as real quantitative results, but rather as a semi-quantitative estimation because some objects like lime lumps or ceramic fragments may be very large and occupy a significant portion of the thin section. As a result, no margin of error has been calculated because it only has significance if objects are counted not more than once. In spite of this limitation, we can clearly see that the Roman mortars have a quite similar composition, with a very high binder proportion and ceramic fragments as the main 'aggregate'. The few quartz-grains that were counted have probably been torn away from the ceramic fragments while they were crushed to be put into the mortar. Their provenance is often revealed by small slices of burned clays still sticking to them. Another peculiarity is the presence of bright red grains. These grains have probably also been detached from the ceramic fragments that are present, and are probably quartz grains (transparent) covered with a thin layer of hematite (red).

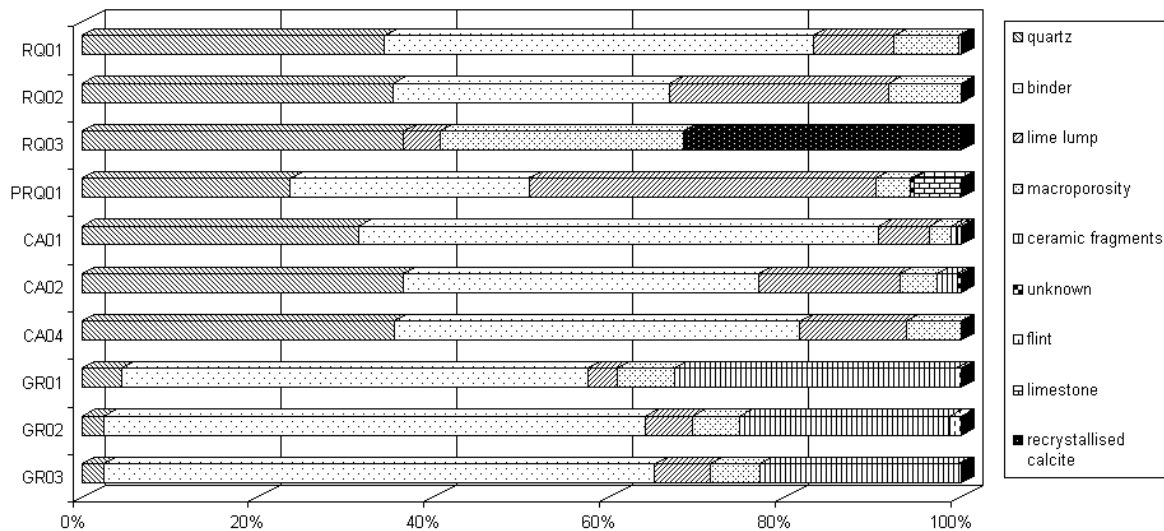


Figure 2: Point counting results

Because of their exclusive and well-proportioned presence, the ceramic fragments are thought to have been added as a pozzolan. Even if no reaction rim could be observed in these samples, a few were identified in a previous study of similar Roman mortars from Tournai (Elsen *et al.*, 2003). There is a possibility that potsherds, which are characteristic for the Roman Era (Coutelas *et al.*, 2000), were first sieved and further crushed, if necessary, before they were added to the mortar (Perkins 1996). These mortars confirm what is stated in the literature (Furland and Bissinger 1995) and show that, after the Roman Era, ceramic fragments were less-frequently used. The initial purpose of their addition by the Romans, which was to make strong, hydrophobic mortars, fades away through time and their use possibly becomes limited to that of an aggregate. As an aggregate, the pozzolanic

properties no longer matter but perhaps they ensure fast carbonation by entraining additional air through pore spaces.

The Roman mortars generally present remarkable round macropores with radiating shrinkage cracks (Figure 3). These cracks are probably the result of very high matrix density combined with the 0.35% shrinkage to which lime mortars are subjected (Adams *et al.*, 1992). Due to the process of dissolution and re-precipitation of the binder (Hofkens 2003) in the vicinity of these more permeable zones, the binder around the pores and cracks is darker and denser compared to the remaining part of the matrix. Some pores are coated with 10 micrometer-long calcite crystals that are more or less perpendicular to the pore surface (Figure 4), which confirms the dissolution-re-precipitation hypothesis.

Another common feature of the Roman mortars is that the mainly well-rounded lime lumps, with dimensions up to 4 mm, cannot always be clearly distinguished from the matrix. Often, they present a well-defined central zone with a lighter, darker or sometimes intermixed white-black tint (Figure 5). These tainted zones may have dimensions up to 200 μm and are also observed in the lime lumps of post-Roman mortars. The lime lumps do not contain any aggregate. Previous microprobe results (Elsen *et al.*, 2003) pointed out that certain parts of these zones are made up of hydraulic minerals. However, Bakolas *et al.* (1995b) observed homogeneous lime lumps, but could also detect the presence of both silicon and aluminum, which they concluded to be from the hydraulic minerals. The lime lumps in the post-Roman mortars don't have the regular forms and dimensions of those observed in their slightly older homologues, but are quite similar in other aspects.

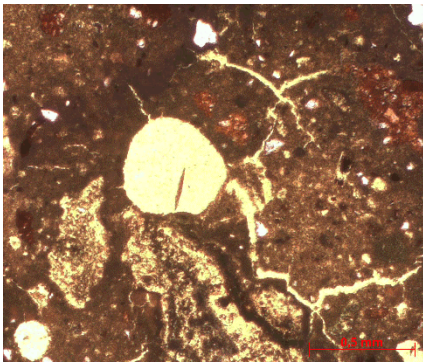


Figure 3: Radiation of cracks from pores

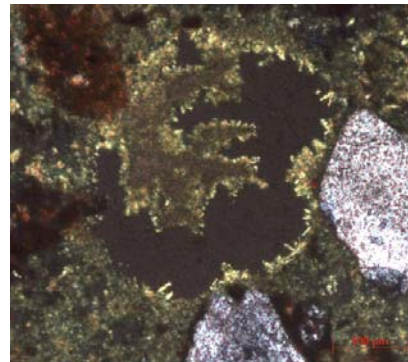


Figure 4: Calcite crystals on the pore surface

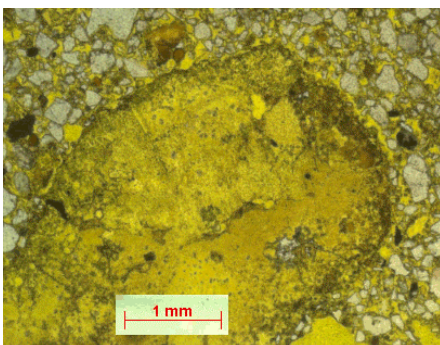


Figure 5: White zone in lime lump (above right of the scale bar)

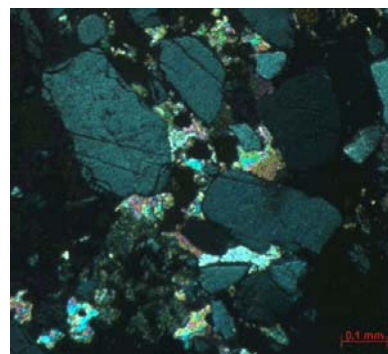


Figure 6: Re-crystallized calcite matrix (crossed polars)

From the limited set of post-Roman samples examined in this preliminary study, it is not clear whether any specific, common recipe was used during a certain period of time. However, the point-counting results make it evident that the binder-aggregate ratio is considerably lower, and that ceramic fragments no longer make up an important part of the mortars. Moreover, the proportion of potsherds (if any) seems to be quite variable and the concern for using a well-defined size of fragment is less apparent or even absent. The aggregate is probably of local origin, and consists of a glauconite-rich marine sand. Microscopically, three to four different grain-size distributions can be distinguished. The binder in these mortars is generally less dense. Their porosity mainly consists of small pores with dimensions ranging from about 0.2 to 1 mm with an irregular and less rounded appearance. Exceptions to these general rules, like samples RQ01 and CA01, may occur.

Not only the age and initial composition, but also the relative position inside a construction influences the appearance of mortars. Samples RQ03 and RQ02 were taken from the same construction; RQ03 from the exterior part of the wall and RQ02 from an interior part that was not exposed to varying weather conditions. We can consider that both samples were initially identical, since they originated from the same construction. In addition, we can clearly see that they are made up of the same aggregate that is present in the same proportion (see Figure 2). Whereas the matrix in sample RQ02 consists of cryptocrystalline (micritic) calcite, it is rather microcrystalline (Figure 6) in sample RQ03. The large calcite crystals are cementing the quartz grains together, analogous to a sandstone with calcite cement. The macroporosity of RQ03 is also more significant than in RQ02, although the volumetric percentage of lime lumps in the former is considerably less. In their study of ancient Gallo-Roman mortars, Rasineux et al. (1985) already concluded that there was a considerable decline in the quality of the mortars due to dissolution and leaching away as a result of their atmospheric exposure. These microscopic observations clearly show that the exposure had an important influence on the characteristics of the mortars, but a decline in their quality could not be observed. On the contrary, their consistency seems to have increased. This information cannot be generalized, however, since the observations are restricted to only two samples.

A general feature of all mortars is the presence of flint, with dimensions up to 1 cm. The flint is rather spherical, but certainly not rounded. Their presence in the matrix points towards the burning of local limestone, which is rich in these inclusions.

3.2 X-ray diffraction

After gently crushing the remaining part of the mortars and sieving the <63 μ m fraction that is assumed to be enriched in the binder fraction (Bakolas *et al.*, 1995a; Middendorf *et al.*, 2000), an XRD pattern was recorded of all samples except CA02, GR01 and GR02. From sample RQ02, some lime lumps were removed and crushed separately (sample RQ02II). In all patterns, calcite and quartz seem to be the main components. Portlandite could not be identified in any of the samples, meaning that all mortars are entirely carbonated. Calcite comes from the transformation of burned lime, and the quartz peaks must originate from the aggregate that is smaller than 63 μ m. However, from the XRD analysis of the removed lime lumps, where no aggregate is present (microscopy), quartz peaks can clearly be identified. In addition, two hydrated minerals, tobermorite (14Å) and hibschite, are present in non-negligible quantities (Figure 7). The broader 14 Ångstrom peak of tobermorite could be due to a limited crystallite size, or to a variable amount of water in the 001-direction. The former cause seems more probable since the other characteristic peaks are also slightly broader compared to those of well-crystalline materials. Hydrogrossular or hibschite is present in lesser amounts, but its peaks are clearly identifiable, with exception of the 3.03Å peak that overlaps with that of calcite and tobermorite.

Sample CA01 shows the presence of additional hydrated minerals. In CA01, a broad diffraction band without discrete peaks is present in the zone from about 2.85Å to 3.03Å. According to Ito *et al.* (1992), this is the zone where poorly-crystalline CSH is diffracting. Additionally, hydrocalumite, a hydrated aluminium-rich salt collectively known as one of the Afm phases in the cement literature (Taylor 1997), could be identified in this sample. Microscopic observations confirm its presence, which is apparently limited to filling of pore spaces.

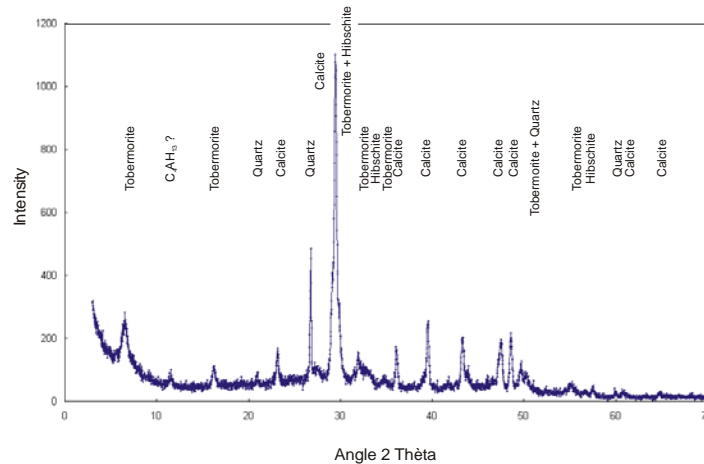


Figure 7: XRD pattern of sample RQ02II

If we logically consider the local hydraulic limestone to be the source of the lime, then hydraulic compounds should be identified in the binder, just as in the study of 19th century mortar samples from Leuven (Central Belgium), which contained burned lime from Tournai (Callebaut 2000). However, with the exception of a few samples, this seems not to be the case, and minerals like C₂S, C₃S and gehlenite could not be recognized. Therefore, there might be an important evolution of the binder mineralogy associated with aging of the mortars. Because of this evolution, estimation of the burning temperature of the lime, based on specific mineral associations, cannot be applied in this case.

3.3 Geochemistry

The sieved fraction, smaller than 63µm and enriched in binder, was analyzed according to the RILEM procedure (Middendorf *et al.*, 2000) for Ca, Fe, Mg and Al by AAS. CO₂ was determined using a Ströhlein apparatus, and the soluble silica concentration was measured by AES from the filtrate after dissolution of 0.5g of sample in 25ml HCl 10% (Callebaut 2000; Degryse 2001). The results are presented in Table 2. From the oxide concentrations, the Cementation Index (CI) was calculated according to Boyton (1980). Most samples, except RQ01, RQ02II and CA01, can be classified as non hydraulic (NH). These results seem to be consistent with the constitutive mineralogy of the samples. CA01 can be classified as eminently hydraulic, and is situated at the border of the natural cements (CI>1.1). Table 2 makes it apparent that hydraulic mortars (H) with high SiO₂ and Al₂O₃ concentrations contain only small amounts of CO₂.

Similar to the results of the XRD analysis, most of the mortars do not present a hydraulic character. For most samples, there is a rather limited correspondence between the mean composition of the Tournaisian Limestone (Table 2) and the composition of the lime binders. The same conclusion can be reached by comparing these binder compositions with that of Callebaut *et al.* (2001) from 19th century mortars containing lime from Tournai. If we again consider the local hydraulic limestone as

the source of the binder, an evolution during the aging process is clear from the chemical point of view. On the other hand, if we consider the composition of the lime lumps (RQ02II), the correspondence with the limestone and the 19th century mortar binder is better.

The elemental composition of the lime lumps was not obtained by a total-analysis, however, but by analysis of the HCl-soluble fraction. An XRD analysis of the insoluble residue after reaction showed a broad maximum rising from the background, which is attributable to an amorphous silica gel, meaning that at least a part of the SiO₂ content in the lumps was not measured. Franzini *et al.* (1999) already noticed that lime lumps can provide invaluable information about the initial composition of the binder and about the evolution that takes place during the hardening process. If we compare the composition of the binder from sample RQ02 with that of its lime lumps (RQ02II), we can easily see that there is an important difference, especially when we consider the SiO₂ concentration. Making the assumption that both compositions were initially identical, we must conclude that the two systems have evolved separately. Since the binder is a less closed, less dense and more permeable material compared to the lime lumps (Hughes *et al.*, 2001), it has a higher susceptibility to change. One of these changes is the leaching of mainly SiO₂, but probably also MgO. Another change is relative enrichment in calcite, which represents only about 40%wt of the lime lumps but is present up to about 72%wt in the binder fraction of RQ02. Binders and lime lumps from other mortar samples should, however, be analyzed to confirm these assumptions. Furthermore, efforts to more precisely determine the provenance of the source rock are being made, in order to get a narrower compositional range of the limestone. Experimental burning of that limestone will enable us to look at the mineral phases that are formed and their repartition in the burned rock by means of thin sections. We assumed that the lime was initially homogeneous, but the hydraulicity could also be concentrated in specific zones; for example, in the immediate vicinity of former clay flakes or flint nodules, possibly leading to an inhomogeneous slaked lime.

Table 2: Results of the chemical analysis

	% CaO	% MgO	%Fe2O3	%Al2O3	% SiO2	% CO2	Cementation Index*	
RQ01	45.79	1.05	2.51	4.13	4.37	29.57	0.392	H
RQ02	44.84	0.67	2.11	2.07	2.05	31.57	0.207	NH
RQ02II	48.59	1.47	1.31	4.61	10.48	17.39	0.698	H
RQ03	48.63	0.66	2.57	5.07	1.68	36.47	0.244	NH
PRQ01	50.13	0.33	0.85	1.88	0.79	37.07	0.096	NH
CA01	41.80	0.80	1.50	3.45	15.07	13.22	1.096	H
CA03	45.88	0.50	1.08	3.10	1.13	36.28	0.157	NH
CA04	41.61	0.52	1.78	2.98	0.86	35.77	0.164	NH
GR03	48.78	0.30	0.57	1.70	0.94	37.88	0.100	NH
Limestone from Tournai (range from basin)	35.6 - 51	0.7 - 1.9	0.4 - 1.8	0.8 - 4.8	7.5 - 24			
19th century binder with lime from Tournai (Callebaut <i>et al.</i> , 2001)	47.76	0.85	2.59	3.95	15.66			

*H denotes hydraulic, NH Non -hydraulic

The lime lumps are less permeable and more closed structures. This is the reason why they may contain hydraulic components such as tobermorite and hydrogrossular. The main condition for the long-term conservation of these hydraulic minerals is their confinement to a zone of low permeability (Rassineux *et al.*, 1989). However, this is clearly not the case for the binder in most mortars. Most of the aluminum present in the lime lumps is included in hydrogrossular. Ettringite, another aluminium-

rich phase, could not be identified and is probably only present when SO₂ concentrations are higher (Rassineux *et al.*, 1989). Tobermorite probably results from crystallization of a more amorphous CSH-phase. This poorly-ordered material has a chain structure (Boch 2000; Brough *et al.*, 1994a), the length of which is dependant on the proportion Ca/Si. The mean chain length is longer when the proportion of Ca/Si is lower. Other studies (Brough *et al.*, 1994a; Brough *et al.*, 1996) pointed out that polymerization of the hydrated gel increased through time, even if no discrete diffraction peaks could be observed in a two-year-old CSH-paste, meaning the substance was still amorphous. More than once, the link with tobermorite has been made with respect to the structure of the material (Brough *et al.*, 1994a). This link is emphasized by the consideration that thermal treatment (110-150°C) of synthetic CSH-gels leads to formation of crystalline tobermorite (Boch 2002; Kurdowski and Nguyen 1990). However, when tobermorite is in contact with CO₂, it will transform to vaterite and an amorphous silica gel (Goto and Ikeda 1990), confirming the need for a confined environment for its conservation. Tobermorite that is present in these lime lumps is probably the result of a prolonged crystallization from a well-protected amorphous CSH gel.

3.4 DTG-Study

Thermogravimetry is a technique in which a relatively small amount of sample is heated while the weight loss is measured. This technique is often combined with a differential thermal analysis that allows differentiation between endo- and exothermic processes. Compounds that have low crystallinity and, therefore, cannot be identified with X-ray diffraction techniques, can be conveniently identified (Adams *et al.*, 1992) and quantified (Brough *et al.*, 1994b). An advantage of this technique is that more than the total amount of the compound can be determined because water is released at different temperatures. A disadvantage is that some transformations may overlap so that individual processes can not always be clearly distinguished and quantified. As a consequence, the boundaries between processes are often arbitrary and may be rather variable for different mortars. In the literature, proposed limits for analysis of historic mortars are not only dependant on the nature of the mortars, but also on the discretion of the authors (Figure 8).

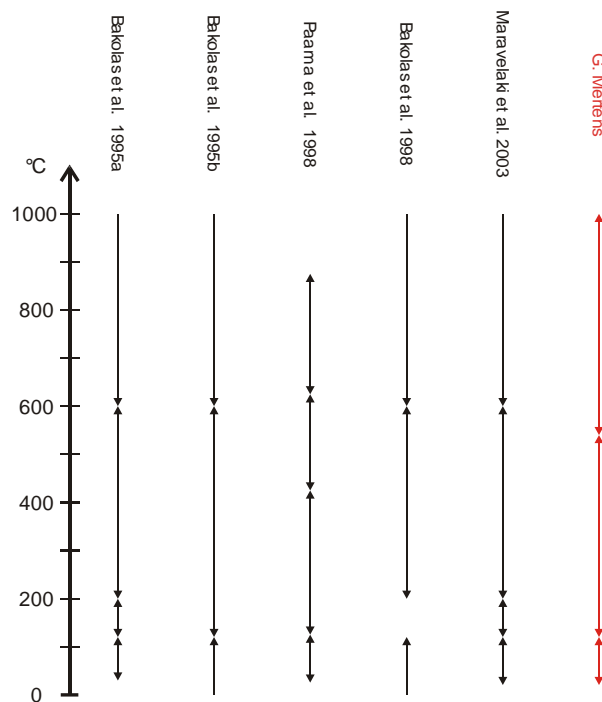


Figure 8: Repartition of temperature ranges from the literature

Thermogravimetric measurements were applied to a small sample (30mg) of the <63 μ m fraction of the mortars, and heated under a N₂ atmosphere at a rate of 10°C/min from room temperature to 1000°C. The results are presented in Table 3.

Table 3 Results of DTG Analysis

Mortar Sample	TG%<120°C	TG%120-540°C	TG%>540°C
	Hygroscopic water	Hydraulic water	Decarbonation
RQ01	2.67	4.96	16.51
RQ02	1.86	3.51	14.73
RQ03	1.69	1.95	9.46
PRQ01	1.17	3.37	25.46
CA01	5.45	8.26	11.16
CA03	1.73	3.13	14.89
CA04	1.68	2.72	14.57
GR03	1.18	2.84	22.46

All mortars seem to be well carbonated, since no peaks could be attributed to dehydroxilation of portlandite, and the loss of CO₂ from decarbonation of calcite is well developed in most samples. Some of the samples show additional loss of water in the lower temperature range. Generally, the CO₂, being bound to carbonates, and the water, being bound to hydraulic components, discern two groups of mortars, the typical lime and the hydraulic, respectively (Paama *et al.*, 1998). The weight loss has been divided into different parts. Below 120°C, the change in weight is attributed to the loss of hygroscopic water, from 120°C to 540°C to the loss of hydraulic water, and above 540°C to decomposition of the calcite. The loss of weight in the different temperature ranges can help to differentiate between hydraulic and non hydraulic mortars. However, this repartition has to be cautiously considered for mortar sample CA01, since hydrocalumite was identified from its XRD pattern. Even if the corresponding diffraction peaks of this layered Ca-aluminate hydrate are very weak, the weight loss associated with its decomposition is considerable, and can clearly be recognized in the zone around 280°C, where dehydroxilation is taking place (Vieille *et al.*, 2003). This shows that thermal analysis can be very helpful in unraveling or in validating the mineralogical composition of mortar samples.

The boundary between decarbonation (>540°C) and loss of hydraulic water (120-540°C) was established by comparing the weight loss above different temperatures (DTG) to the amount of CO₂ measured with the Ströhlein apparatus for each sample. The correlation between weight loss above 540°C and CO₂-content measured by Ströhlein is a one-to-one correlation, and has correlation coefficient of 0.96. For mortar sample RQ03, decarbonation starts at a higher temperature than for the other samples. This may be due to the recrystallized nature of the binder (Moropoulou *et al.*, 2003), which is also confirmed by the microscopic observations.

From the table of results, a correlation appears to exist between the amount of water released below 540°C and the CO₂ lost at temperatures higher than 540°C. If a lot of water is present in the mortars, only a limited amount of CO₂ is lost at higher temperatures, meaning that only a little calcite is present compared to a higher amount of hydrated substances. However, given the presence of hydrated salts, an estimation of hydraulicity from the DTG-curves is not appropriate in this case.

An attempt has also been made to establish a correlation between the loss of water and the elemental composition of the <63 μ m fractions. Both the SiO₂ and the CaO (that remains after combination with CO₂) concentrations show a quite good correlation (correlation coefficients of 0.96 for both), whereas the correlation for other elements such as Al, Mg and Fe is very poor (correlation coefficients of 0.04, 0.29 and 0.01 respectively). This could indicate that the latter three elements have a more limited importance with respect to the hydraulic character of mortars.

4 Conclusions

There are considerable differences in the composition of Roman and post-Roman mortars. Roman mortars have more binder and the intentional addition of ceramic fragments of a well-defined size. The post-Roman mortars contain less binder and a glauconite-rich sand as the main aggregate. The use of ceramic fragments is more sporadic.

The position of the mortar samples in a building seems to greatly affect their appearance and physico-chemical evolution. Prolonged exposure to atmospheric conditions can cause the binder to re-crystallize to a microcrystalline matrix.

There are important mineralogical and chemical differences between the lumps and the binder in the mortars. The difference could arise from a distinct evolution starting from an initially-identical composition. Future work will be designed to unravel the long-term processes affecting this evolution.

This study also shows that a combination of different techniques is necessary to characterize historic mortars. Nevertheless, difficulties exist in determining the hydraulicity of the binder fraction. Use of the Cementation Index, based on chemical analysis, does not consider the contribution of salts or additives like fine ceramic powder. Thermogravimetric methods, XRD and microscopic investigations help to identify the salts or additives, but cannot enable taking their contribution to the chemical analysis into account.

References

- Adams, J., Kneller, W. and Dollimore, D., 1992, Thermal analysis (TA) of lime- and gypsum-based medieval mortars, *Thermochimica Acta*, 211, 93-106.
- Bakolas, A., Biscontin, G., Contardi, V., Franceschi, E., Moropoulou, A., Palazzi, D. and Zendri, E., 1995a, Thermoanalytical research on traditional mortars in Venice, *Thermochimica Acta*, 269/270, 817-828.
- Bakolas, A., Biscontin, G., Moropoulou, A. & Zendri, E., 1995b, Characterization of the lumps in the mortars of historic masonry, *Thermochimica Acta*, 269/270, 809-816.
- Bakolas, A., Biscontin, G., Moropoulou, A. and Zendri, E., 1998, Characterization of structural byzantine mortars by thermogravimetric analysis, *Thermochimica Acta*, 321, 151-160.
- Bernard, A., Millet, J., Hommey, R. and Poindfert, A., 1975. Influence de la température de cuisson et de la nature du calcaire sur la minéralogie des chaux vives. *Bull. Liaison Labo. P. et Ch.* 79, p. 45-50.
- Bleazard, R.G., 1998, The history of calcareous cements, In: *Lea's Chemistry of Cement and Concrete*, Peter C. Hewlett (editor), New York.
- Boch, Ph., 2002, Ceramics and cements: two sides of one medal, *International Lecture; ECERS VII*, 9-14.
- Boyton, R.S., 1966, *Chemistry and technology of lime and limestone*, John Wiley & Sons, New York.
- Brough, A.R., Dobson C.M., Richardson, I.G. and Groves, G.W., 1994a, Application of selective ²⁹Si isotopic enrichment to studies of the structure of Calcium Silicate Hydrate (C-S-H) gels, *J. Am. Ceram. Soc.*, 77, 593-596.

- Brough, A.R., Dobson C.M., Richardson, I.G. and Groves, G.W., 1994b, In situ solid-state NMR studies of Ca_3SiO_5 : hydration at room temperature and at elevated temperatures using ^{29}Si enrichment, *Journal of materials science*, 26, 3926-3940.
- Brough, A.R., Dobson, C.M., Richardson, I.G. and Groves, G.W., 1996, Alkali activation of reactive silicas in cements: in situ ^{29}Si MAS NMR studies of the kinetics of silicate polymerization, *Journal of materials science*, 31, 3365-3373.
- Brulet, R., Verslype, L., 2001, Naissance et évolution de la ville: analyse du bâti antique à Tournai, In: Lodewijckx M. (editor): *Album amicorum Joseph Remi Mertens, Acta Archaeologica Lovaniensia, Monographiae*, 13, Leuven, Belgium, 101-109.
- Callebaut, K., 2000, Characterisation of historic lime mortars in Belgium: implications for restoration mortars, PhD thesis, Katholieke Universiteit Leuven, Leuven.
- Callebaut, K., Elsen, J., Van Balen, K. and Viaene, W., 2001, Nineteenth century hydraulic restoration mortars in the Saint Michael's Church (Leuven, Belgium) Natural hydraulic lime or cement?, *Cement and Concrete Research*, 31, 397-403.
- Coutelas, A., Guyard, L. and David, Ch., 2000, Pétroarchéologie de mortiers gallo-romains: Application de méthodes analytiques à l'étude des thermes du Vieil-Evreux (Eure), *Les Nouvelles de l'archéologie*, 81, 31-36.
- Degryse, P., 2001, Mineral resources and their use on the territory of Sagalassos (SW Turkey), Phd thesis, Katholieke Universiteit Leuven, Leuven.
- Deloye, F-X., 1993, Hydraulicité et pouzzolanité, *Bull. Liaison Labo. P. et Ch.*, 184, 94-95.
- Elsen, J., Brutsaert, A., Deckers, M. and Brulet, R., 2003, Microscopical study of ancient mortars from Tournai (Belgium), *Proceedings of the ninth Euroseminar on Microscopy Applied to Building Materials*, Trondheim, 1-10.
- Furlan, V. and Bissegger, P., 1975, Les mortiers anciens, *Histoire et essais d'analyse scientifique*, *Revue suisse d'art et d'archéologie*, 32, 2-14.
- Franzini, M., Leoni, L., Lezzerini, M. and Sartoti, F., 1999, On the binder of some ancient mortars., *Mineralogy and Petrology*, 67, 59-69.
- Goto, S. and Ikeda, S., 1992, Effects of the carbonation on the thermal properties of Tobermorite, *Proc. 9th International Congress on the Chemistry of Cement*, 304-309.
- Hofkens, T., 2003, Chemisch-mineralogische karakterisering van de mortels van de domestic area te Sagalassos (Turkije), licentiaatsthesis, KULeuven, Leuven.
- Hughes, J.J, Leslie, A.B. and Callebaut, K., 2001, The petrography of lime inclusions in historic lime based mortars, *Proceedings of the 8th Euroseminar on the Microscopy Applied to Building Materials*, Athens, Greece, 359-364.
- Ito, S., Nishikawa, T., Ito, Y. and Suzuki, K., 1992, Thermal behaviour of synthesized C-S-H, *Proc. 9th International Congress on the Chemistry of Cement*, 151-156.
- Kurdowski, W. and Nguyen, T.T., 1992, The influence of admixtures on the crystallization of Tobermorite from C-S-H, *Proc. 9th International Congress on the Chemistry of Cement*, 591-596.
- Maravelaki-Kalaitzaki, P., Bakolas, A. and Moopoulou, A., 2003, Physico-chemical study of Cretan ancient mortars, *Cement and Concrete Research*, 33, 651-661.
- Middendorf, B., Baronio, G., Callebaut, K. and Hughes, J.J., 2000, Chemical-mineralogical and physical-mechanical investigations of old mortars, *Proceedings of the International RILEM-workshop "Historic mortars: characteristics and tests."*, Paisley, 53-61.
- Moropoulou, A., Bakolas, A. and Bisbikou, K., 1995, Characterization of ancient, byzantine and later historic mortars by thermal and X-ray diffraction techniques, *Thermochimica Acta*, 269/270, 779-795.
- Paama, L., Pitkänen, I, Rönkkömäki, H. and Perämäki, P., 1998, Thermal and infrared spectroscopic characterization of historical mortars, *Thermochimica Acta*, 320, 127-133.
- Perkins, B.W., 1996, Urban Continuity? In: N. Christie & Loseby, S.T. (est.). *Towns in transition. Urban evolution in Late Antiquity and the early middle ages*, Aldershot & Brookfield, p.4-17.

- Rassineux, F., Petit, J.C. and Meunier, A., 1989, Ancient analogues of modern cement: calcium hydrosilicates in mortars and concrete from Gallo-Roman thermal baths of western France, *J. Am. Ceram. Soc.* 72, 1026-1032.
- Taylor, H.F.W., 1997, *Cement Chemistry*, 2nd edition; Thomas Telford Publishing: London.
- Vieille, L., Rousselot, I., Leroux, F., Besse, J.-P. and Taviot-Guého, Ch., 2003, Hydrocalumite and its polymer derivatives. 1. Reversible thermal behavior of Friedel's salt: A direct observation by means of high-temperature in situ powder X-ray diffraction, *Chem. Mater.*, 15, 4361-4368.