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Hydraulicity in Historic Lime Mortars: a Review

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Abstract Natural hydraulic limes were used in ancient times and are still produced nowadays. A comparison of the chemistry and mineralogy of currently available NHL2 and NHL5 limes indicate that there are no clear differences except for the amount of 'undefined material', mainly consisting of an amorphous phase. The chemical composition of these different limes is nearly identical. However, the classification of ancient hydraulic limes is mainly based on their chemistry, obtained from the analysis of ancient mortar binders. Moreover, it is shown that the phase composition of these limes evolves with time. This makes their classification uncertain and difficult.

1 Introduction

A variety of binders have been used in the past (Fig. 1). The oldest types; clays and bitumen, were readily available. Materials needing heating and subsequent mixing with water before application were used subsequently. The use of plaster (hemi-hydrate: $CaSO_4 \cdot 0.5H_2O$) probably dates back earlier than the use of lime since its production from gypsum requires lower temperatures compared to the production of lime from limestone and was therefore easier to obtain. Both binders harden in air.

A next step in the development was the manufacture of `hydraulic' binders obtained by mixing lime with pozzolans. `Hydraulic' refers to the ability of the binder to harden under water [1]. More recently, other types of hydraulic binders are obtained; either by burning an impure limestone or by mixing Si- and Al-bearing materials with a pure limestone and burning them together.

Although the hydraulicity of ancient mortars provides us with technological information or with indications for their restoration, it appears very difficult to measure. This article starts with a tentative definition of hydraulicity and then discusses the chemistry and mineralogy of some commercial hydraulic limes that are presently available on the market. Afterwards, a survey will be provided on the current knowledge about ancient hydraulic mortar technology and finally an overview of the methods that have been used to identify and measure this hydraulicity in ancient mortars will be given. The last part of the paper shows, with an example, that the hydraulicity of ancient mortars cannot always be determined unambiguously. Less attention will be paid to the addition of pozzolanic materials to lime. This subject was treated by for instance Charola and Henriques [2].

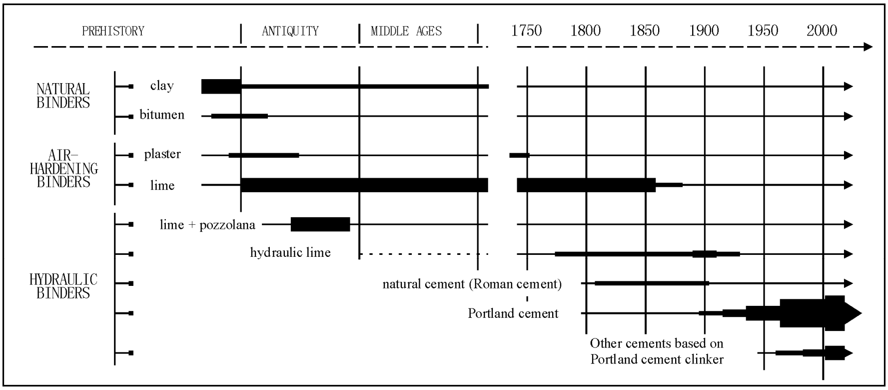

Fig. 1 Use of binders during history (Adapted from [3])

2 Definitions

Hydraulic limes are limes containing enough free CaO to be slaked with water and capable of setting under water. A minimum amount of free CaO must be present in the calcined product to reduce the entire mass to a powder when it is slaked [4]. The combination of the free CaO with water induces an expansion that leads to the disintegration of the freshly burnt limestone. The maximum amount of free CaO is determined by the second condition. If too much free CaO is present, the product will not be able to harden under water. There is a large range of products complying with this definition. They are most commonly classified according their chemical composition and more specifically to their Cementation Index 'CI' (Equation 1) or Hydraulicity Index 'HI' (Equation 2). Boynton [5] proposed a classification into 'feebly', 'moderately' and 'eminently hydraulic' limes based on their Cementation Index. In the actual European norm (EN459-1:2001), the following classes of natural hydraulic limes with pozzolanic additives are defined; NHL2, NHL3.5 and NHL5. However, they do not correspond to

Boynton's classes and tend to neglect the 'feebly hydraulic limes'. As the strength of the binders is tested at 28 days, according to the norm, 'feebly hydraulic' limes tend to be omitted because their final strength is only attained at longer curing times. The main reason is that carbonation plays a major role in their hardening. Carbonation is generally a much slower process than the hydration reactions that are dominant in the more hydraulic binders. This has important implications for the restoration of constructions where 'feebly' or even more feebly hydraulic binders have been used. Lindqvist [6] therefore defined the class of sub-hydraulic mortars, having a hydraulic character between that of the pure air limes and the 'feebly hydraulic limes' defined by Boynton [5].

$$CI = \frac{2.8SiO_2 + 1.1Al_2O_3 + 0.7Fe_2O_3}{CaO + 1.4MgO} \tag{1}$$

$$HI = \frac{SiO_2 + Al_2O_3}{CaO} \tag{2}$$

The term `hydraulic lime' was first suggested by Vicat. `Lean lime' and `water lime' were terms used previously.

Hydraulic limes can also be produced by adding pozzolans to non-hydraulic limes. This technique was known since ancient times and was revalued during the Renaissance. However, only since the 18th and mainly during the 19th century, the use of pozzolans in lime for water-related structures or foundations became common practice. Pozzolans react with the $Ca(OH)_2$ in the lime to form reaction products similar to those formed in the previously defined natural hydraulic limes (NHL2, NHL3.5 and NHL5).

3 Present-day Natural Hydraulic Limes

Currently, natural hydraulic limes (NHL's) are only produced in a few places in Western Europe. Actual production is for instance done by Otterbein and Hessler-Kalkwerke in Germany, by CIMPOR in Portugal, by Singleton Birch and Roundtower in the UK, by the SOCLI-group, Lafarge, Boehm and St. Astier in France and by Tassullo in Italy. Some of these, as well as some other companies as Unilit, sell pre-mixed mortars and concretes based on natural hydraulic lime. The mineralogical composition of some of these limes has been plotted in Fig. 2. Part of the data in this figure were obtained from the Rietveld refinement of the X-Ray Powder Diffraction (XRPD) patterns of the natural hydraulic limes after mixing them with an appropriate crystalline standard (10wt.% ZnO). The other part of the data, marked with an asterisk, was obtained from Kraus et al. [7]. Their quantitative phase analyses were obtained from the chemical and XRPD data.

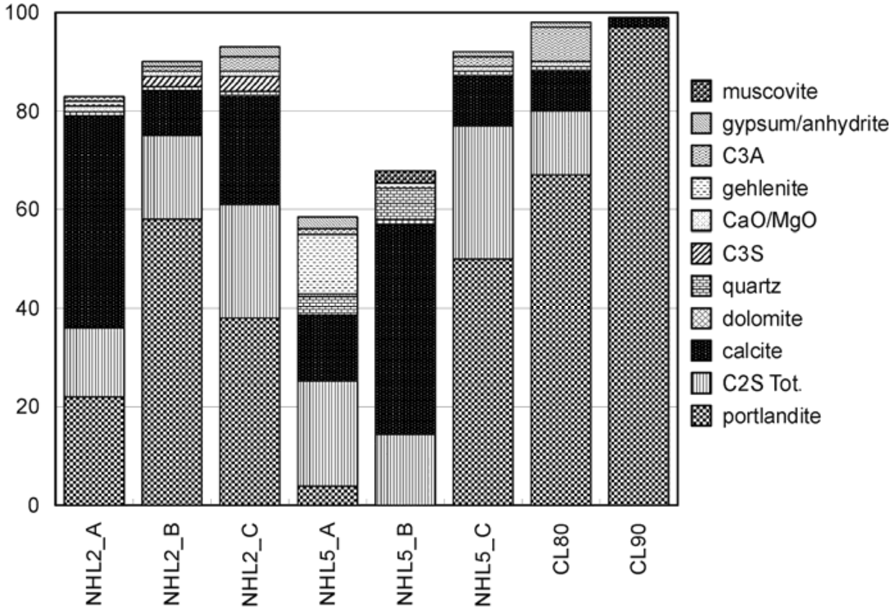

Fig. 2 Mineralogical composition of the studied limes: NHL2 and NHL5 samples are classified as hydraulic, CL80 and CL90 as non-hydraulic.

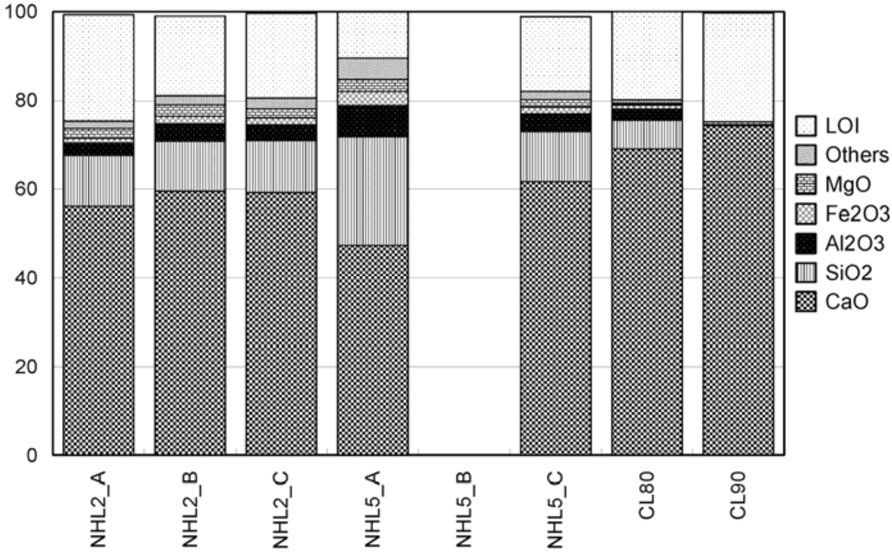

Fig. 3 Chemical composition of the studied limes: NHL2 and NHL5 samples are classified as hydraulic, CL80 and CL90 as non-hydraulic.

The chemical composition of the NHL's can be found in Fig. 3. For comparison, the composition of two non-hydraulic limes ('CL80' and 'CL90') is plotted in the same figure.

From these data it appears that there is no clear correlation between the mineralogy and the type of lime. However, the portlandite content in the non-hydraulic limes is higher than that in the hydraulic limes. Although 'CL80' is classified as non-hydraulic, Kraus et al. [7] identified considerable amounts of C_2S and C_3A. These minerals are mostly characteristic for hydraulic binders. Nevertheless, the concentration of C_2S and C_3S in the non-hydraulic limes is lower than in the hydraulic ones. In accordance with this, higher SiO_2 contents are observed in the hydraulic limes compared to the non-hydraulic limes.

The only clear difference between the NHL2 and the NHL5 samples lies in the amount of 'undefined material'. Most of it consists of amorphous material, although it possibly includes a small amount of undefined minerals that could be overlooked in the XRD spectra. Nevertheless, the amount of 'undefined material' appears to be generally higher in the more hydraulic NHL5 samples compared to the NHL2 samples. No clear difference could be observed between the chemistry of the NHL2 and NHL5 samples. The content of the main elements in NHL5_C for instance is similar to that in NHL2_B and NHL2_C. This is an indication that the chemistry alone is probably insufficient to give a clear indication about the hydraulicity of the sample.

4 Historical use of hydraulic lime mortars

4.1 Pre-Middle Ages

The Greek knowledge of the use of highly siliceous, volcanic Santorin Earth (pozzolans) goes back to 500-300BC [8]. The use of pozzolanic materials in mortars used in the construction of draining canals dated 400BC, has also been noticed in Olynthos, on the continent more to the north of island of Santorin [9]. In Eastern civilizations, rice husk ash was used as a pozzolan [10]. Other Greek mortars, in which no pozzolans were used, were found to be extremely hard. This is perhaps due to the quality of the limestone, which was of lower purity compared to that used by the Romans [11]. To the Romans, the best lime was that produced from pure limestone.

Around the 3rd century BC, Roman builders discovered how to make hydraulic mortars [12]. A natural deposit of reactive 'sand', similar to that found by the Greek on the Island of Santorin, was discovered near the Mount Vesuvius. This 'pulvis puteolanus' ('earthy material from Puteoli') survived in many languages as 'pozzolana'.

Hydraulic mortar and concrete was used on land by the later 3rd century BC [13]. Whenever pozzolanic materials were not available and a mortar insoluble in water was needed, the Romans used a mixture of hydrated lime and crushed ceramics. Many names have been used to designate these crushed ceramics over the world; Horasan in Turkey, Surkhi in India, Homra in arabic countries and cocciopesto in Italy [14, 15]. The most common name for this type of mortar is `opus testaceum' [16, 17].

In a few areas, `sands' resembling those found near the Mount Vesuvius, such as for example Trass, were used to produce hydraulic mortars. During Roman dominion, little seems to have changed to preparation techniques and mortar composition [18]. After Roman times, a clear uniform mortar and lime composition is lacking.

Even though studies about medieval mortars are scarcer than those treating of mortars and mortar technology from classical antiquity, it appears that great differences exist in their composition. Whereas medieval mortars from Pamplona (Spain) appear to be non-hydraulic [19], others from Crete (Greece), for instance, show a clear hydraulic character [20]. Even in the same area, such as for example in the city of Pisa, both mortars with a marked hydraulic character as mortars prepared from non-hydraulic lime have been used alternatively without any apparent reason [21].

However, studies from a 16th century dockyard in Venice (Italy) indicate the deliberate use of hydraulic lime for foundations and air-lime for indoor masonry [22]. Mortars made with hydraulic lime also seem to be used deliberately in Ottoman baths in Budapest during the same period [23]. Whereas the only hydraulic mortars known from the Roman era are those made from pure lime mixed with pozzolans, medieval hydraulic mortars appear to be prepared either from the addition of pozzolans or from burnt and slaked clay-bearing limestone [24]. Moreover, there are indications of the use of a variety of pozzolanic additions, ranging from the classical crushed ceramics [22, 25] over volcanic ashes [25, 26] or metamorphosed soils (agghiara; see [27]) to the addition of fine opal-A ($SiO_2 \cdot nH_2O$) from unclear origin [28]. The use of specific deposits with pozzolanic properties, known from Roman times, such as for instance Trass - knows a certain revival during the Middle Ages [29, 30].

Blezard [31] identifies a gradual decline in the quality of the mortar after Roman times, throughout the Middle Ages and notes that mortars in Saxon and Norman buildings often show evidence of bad mixing and the use of imperfectly burnt lime. By contrast, some authors [26] claim that the use of particular sands, rich in volcanic ashes, in south-Italian mortars from the 10th-11th century testify a deep knowledge of the raw materials and a deliberate selection of building materials.

During the Renaissance, the ancient techniques are revalued [17, 31]. Moreover, contemporaneous writings testify of the deliberate use of hydraulic limes prepared from impure limestone. Beside the `white lime' (pure lime), `dark lime' (hydraulic lime) was obtained from the calcination of grey and dark limestones as substitutions of pozzolans (Palladio, 1570 and Scamozzi, 1615 in [32]).

From this, it appears that conflicting ideas and perceptions about the technological knowledge and practices in the Middle Ages exist.

4.2 Post-Middle Ages

The first detailed investigations carried out in the field of hydraulic limes made from impure limestone were those of John Smeaton. His investigations in 1756 led to the discovery that mortars with limes made from impure limestone gave the best results. By dissolving the limestones in nitric acid he obtained an insoluble residue of quartz SiO_2 and clayey material to which he attributed the hydraulicity. At about the same time in Sweden, Bergmann (1735-1784) attempted to discover why some limes harden when immersed in water [33]. The hydraulic limes he analysed, all contained manganese. Therefore he attributed their hydraulicity to the presence of this element. In France, at the beginning of the 19th century, Guyton de Morveau analysed the properties of an artificial mixture with the same composition as the natural limes studied by Bergmann. He calcined it and found that the lime obtained was an excellent `water lime'. He also attributed this property to the manganese (4%) and not to the clay, which had been added in a proportion of 6% to the lime carbonate [34]. In Switzerland, Saussure (1740-1799) also dissolved `meagre limes' in acid and found that the residue was composed of quartz and clay. However, he adds that "the manganese would appear to have greater influence than the siliceous content". Vitalis (in 1807), among others, found that some good quality hydraulic limes contained no manganese, and stated that "clay was the chief source of their water setting properties" [34].

The French engineer Collet Descotils (in 1813) was the first to relate clearly the properties of the meagre limes to the presence of silica. He stated that an intimate combination of silica with lime is produced when these limes are slaked. He found that the silica in the used limestones was insoluble in acid, whereas it became soluble in the lime derived from it. His conclusions were correct in that a high quality meagre lime must contain a high quantity of finely disseminated siliceous matter.

The hydraulicity of binders is highly variable. The first attempt to classify hydraulic binders was made by Louis Vicat [35], who introduced the Hydraulicity Index (see Equation 2)

In this formula, Vicat compiled all knowledge then available and directly related the hydraulicity to the SiO_2 and Al_2O_3 contents. However, equal importance was incorrectly attributed to the two constituents. Gradually it was found that Fe_2O_3 and MgO also had an influence on the hydraulicity. An adapted formula was therefore developed about a century later by E.C. Eckel [4]. The formulation of this Cementation Index is shown in Equation 1.

It was conceived to be a direct expression of the quantity of CaO combined with the other constituents to form hydraulic minerals. The use of this cementation index is based on a number of assumptions. Firstly, it is assumed that all available SiO_2 combines with CaO to form C_3S (Ca_3SiO_5) and that all Al_2O_3 combines to form C_3A ($Ca_3Al_2O_6$). MgO is considered equivalent to CaO and Fe_2O_3 to Al_2O_3. This is clearly an oversimplification, since the mineralogy of hydraulic binders is more complex than assumed here. Eckel emphasized that the properties of hydraulic binders not only depend on their composition ('CI'), but also on the conditions of their manufacture. The hydraulic properties are indeed indirectly related to the burning temperature and time, since these influence the mineralogy of the final product [36].

A more detailed discussion on the origin of modern hydraulic binders and their classification can be found in [37].

5 Determining the hydraulicity of ancient mortars

5.1 Remaining hydraulicity in ancient mortars

A characteristic property of ancient calcareous binders is their hydraulicity. To determine this hydraulicity, which can be deduced from microscopic observations only in some rare cases, a chemical analysis is useful. However, the main difficulty resides in separating the binder from the other mortar constituents. Generally, this is achieved by dissolving a part of the mortar, or a previously disaggregated fraction of the mortar, in a dilute acid [20, 26, 38-42]. Other studies [16, 43, 44] mention the analyses of the entire mortar or a smaller grain size fraction after disaggregation and sieving. However, the results of such analyses are not helpful to obtain any information on the binder, because a significant contribution of the aggregate can never be ruled out.

A wide range of analyses methods to determine the chemistry of mortars or the binder fraction more in particular have been used. Difficulties arise when trying to compare the results of these analyses. In an attempt to obtain uniformity in the procedure for the chemical analysis of binders, Middendorf et al. [45] introduced a standardised methodology.

However, difficulties were previously observed during the implementation of the method [46]. Hofkens [46] made an evaluation of different analysis procedures and concluded that the treatment of the sample with HCl (10%) appears most straightforward. Many other authors [19, 39, 47-49] have adopted for the determination of the soluble silicic acid content. Specifically, 1g of sample is dissolved in 50ml HCl (10%) and the suspension is filtered after 5 minutes of reaction. The filtrate is used for the determination of Si by ICP-OES or AAS.

From the amounts of the main elements, the hydraulicity (Equation 1) and cementation indices (Equation 2) can be calculated. However, high acid-soluble silicic acid contents, resulting in a high 'HI' and 'CI', might not provide clear evidence for the use of hydraulic lime as binder material [45]. The silica might as well originate from pozzolanic additives that reacted with a more or less pure lime binder.

In general, the contribution of acid soluble SiO_2 from the aggregates is considered to be limited [50]. However, the use of hot HCl in mortar analyses revealed that part of the aggregate fraction may dissolve, especially clays such as smectites and kaolinites [40].

If the previously described methodology is considered to be suitable to assess the bulk chemistry of the binder, microprobe analyses are useful to provide more detailed information of points or areas in the polished (thin) sections. Moreover, information about individual mineral phases can be obtained. However, the main restriction is that no volatile components like CO_2 and H_2O can be measured. In spite of this limitation, microprobe has previously proven to be useful for the analyses of ancient mortars [21, 25, 39].

Additional information on the mineralogy of the mortars can be obtained by X-ray diffraction. The data complement the results of the petrographical and chemical analyses. The identification of the nature of the binder is easily made with X-ray diffraction. Hydrated calcium silicates or -aluminates can point towards the use of hydraulic binders. Some authors [47] state that a mineralogical analysis can make a distinction between different types of hydraulic binders possible. X-ray diffraction also enables to identify possible pozzolanic admixtures, which are sometimes too fine to be recognisable in thin sections.

The Thermo-gravimetrical (TG) patterns of ancient mortars are often subdivided in temperature ranges that allow making a more or less accurate delineation of characteristic transformations. For calcareous binders, most authors [14, 18, 20, 52-54] make a distinction between hygroscopic water (temperature range from 30°C to 120°C), water from hydrated salts (temperature range from 120°C to 200°C), the loss of water bound to hydraulic compounds (temperature range from 200°C to 600°C) and the loss of CO_2 (>600°C).

More in particular, TG reveals to be useful for the differentiation between hydraulic and non-hydraulic mortars [52]. Most often [20, 25, 52-56] a plot is made of the weight loss >600°C and of the ratio of the weight losses >600°C and from 200°C to 600°C. Samples with high amounts of water bound to hydraulic compounds and proportionally low amounts of CO_2 are considered to be hydraulic.

Many studies reveal the presence of crushed ceramics in Roman mortars [44, 57-60] but also in younger mortar samples [14, 61, 62]. In addition to these fired clayey materials, other types of pozzolans have been found in ancient mortar samples, being either natural or artificial. Some authors make mention of slag fragments [63], charcoal [57] and flint [8, 64] particles. However, in many cases it is difficult to distinguish between the deliberate use of these mineral admixtures and their accidental addition.

It is however difficult to determine whether the hydraulicity of a mortar is induced by the addition of the supplementary materials or by the use of natural hydraulic lime. An analysis of the Binder Related Particles can be therefore be useful [65, 66]. The chemistry of the binder related particles is expected to be identical to that of the limestone used to prepare the lime.

5.2 Vanishing hydraulicity of ancient mortars

It was previously indicated that making a chemical analysis of the binder alone and as a whole is probably impossible, because it is closely intermixed with the aggregate. Moreover, different dissolution techniques are likely to yield distinct results. Therefore, the authors [67] analysed the binder fraction in a selected set of thin sections from mortars excavated at the Cathedral of Tournai [39] with the microprobe (CAMECA SX 50 at 15kV and 6nA). Small areas of approximately 15µm x 12µm (depth of a few µm) were quantitatively analysed (Table 1).

A first important observation is that the binder can be very heterogeneous within one mortar sample. If some analysis reveals compositions near to that of pure C-S-H, other analyses within the same mortar reveal areas that are much poorer in SiO_2 and with a Cementation Index (Equation 2) of only 0.09.

Secondly the results reveal that the Cementation Indices of the binder calculated from the microprobe results are systematically higher (with one exception out of 12 samples) than those calculated from the chemical analyses obtained by acid dissolution used for the determination of the bulk chemistry.

By looking on a smaller scale, it appears that the binder in many samples does not consists of a single phase, but appears to be composed of at least two distinct components that are intimately intermixed (Fig. 4). In several samples, a lightly coloured zone (in BSE mode) with a composition close to that of pure Ca-carbonate is intermixed with darker material rich in Si and having an average composition of 8 wt.% CaO, 16 wt.% SiO_2 and 2 wt.% Al_2O_3 at this specific location. The composition of the latter phase is however variable and ranges between CaO contents of 0-10 wt.% and SiO_2 contents of 15-70 wt.%. These specific point analyses (volume of approximately 5-10 μm^3) reveal the heterogeneous nature of the binder that has an average composition of 18 wt.% CaO, 14 wt.% SiO_2, 2 wt.% Al_2O_3 as determined by the analyses of larger areas (15 µm x 12 µm and a depth of a few µm). Because of the porous nature of the binder, these analyses are only suitable to establish the concentration ratios between different oxides. The ratios of Ca/Si=1.3 and Si/Al=7.5 are similar to those found in C-S-H [67]. It is therefore suggested that segregation has occurred in the C-S-H phase, whereby Ca and Si are moving into separate phases. The lightly coloured zones correspond to that of nearly pure Ca-carbonate and are an indication that a carbonation reaction of the C-S-H has occurred. The spatial distribution of the two phases confirms these results as the lightly coloured material in Fig. 3 is consistently located on the outside, adjacent to the pores and enclosing the darker zones that are richer in silica.

Table 1 Microprobe analyses of the binder for a selection of mortar samples from Tournai. Analyses inside one zone (z) are made at a distance of less than approximately 1mm from each other. The distance between two zones in one thin section is at least 1cm.

sample name	numbre of analyses		SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	CI
D03B	4	average	4,2	0,6	0,0	0,1	47,6	0,26
		stdev.	1,3	0,3	0,0	0,1	2,8	0,09
D06B (z1)	3	average	16,6	3,0	0,1	0,2	24,6	2,03
		stdev.	2,3	0,3	0,1	0,0	1,2	0,38
D06B (z2)	4	average	8,6	1,3	0,3	1,4	39,1	0,63
		stdev.	1,7	0,3	0,2	0,7	2,4	0,15
D07B (z1)	2	average	12,3	1,4	0,7	0,2	39,5	0,92
		stdev.	0,2	0,4	0,7	0,2	0,7	0,02
D07B (z2)	3	average	0,1	0,1	0,1	0,1	0,1	0,11
		stdev.	0,1	0,1	0,1	0,1	0,1	0,05
D08B	3	average	3,1	0,4	0,4	0,2	50,6	0,18
		stdev.	0,8	0,1	0,0	0,1	1,2	0,05
D09B	4	average	5,7	0,7	0,1	0,1	47,2	0,36
		stdev.	0,9	0,2	0,1	0,0	1,1	0,07
D19B	6	average	5,4	1,3	0,6	0,3	41,9	0,40
		stdev.	2,1	0,7	0,8	0,3	2,9	0,16
D20B	5	average	6,7	1,0	0,5	0,2	44,3	0,46
		stdev.	1,5	0,2	0,3	0,0	1,7	0,12
D22B	3	average	3,4	0,3	0,1	0,1	45,0	0,22
		stdev.	0,5	0,1	0,2	0,0	1,7	0,03
D23B	5	average	5,7	0,8	0,6	0,3	47,4	0,36
		stdev.	2,4	0,4	0,4	0,2	2,1	0,15
D36B (z1)	5	average	23,4	3,7	1,0	0,7	19,0	3,57
		stdev.	1,7	1,1	0,8	0,3	3,1	0,46
D36B (z2)	2	average	1,6	0,3	0,0	0,4	53,7	0,09
		stdev.	0,0	0,1	0,0	0,1	0,5	0,00
D41B	6	average	2,9	0,4	0,4	0,2	50,5	0,18
		stdev.	1,6	0,2	0,2	0,3	4,0	0,11
D48B	6	average	6,0	0,8	0,4	0,2	40,3	0,47
		stdev.	2,1	0,4	0,2	0,0	5,9	0,20

Microprobe analyses can only reflect the chemical composition at specific locations in the binder, but does not necessarily reveal the exact mineralogy of the different components. Ca-carbonates are observed in each X-ray diffraction pattern of the binder-enriched fraction (<63 µm fraction of the gently disaggregated mortar sample). Calcite, one of the Ca-carbonate polymorphs, is indeed present in each sample. However, vaterite ($CaCO_3$) and aragonite ($CaCO_3$), other Ca-carbonate polymorphs, are also present in many samples. Remarkably, their occurrence and abundance appears to be related to the hydraulicity (read CI) of the samples determined from their chemical analyses by acid dissolution. Vaterite and aragonite are generally considered to be less stable compared to calcite at atmospheric pressures and near-room temperatures. Therefore, they do not occur upon carbonation of pure lime (portlandite). However, these two polymorphs were proven to form upon carbonation of C-S-H.

This phase evolution might have consequences for the bulk chemical analyses, since the dissolution of these neo-formed phases might differ significantly from that of the phases initially present.

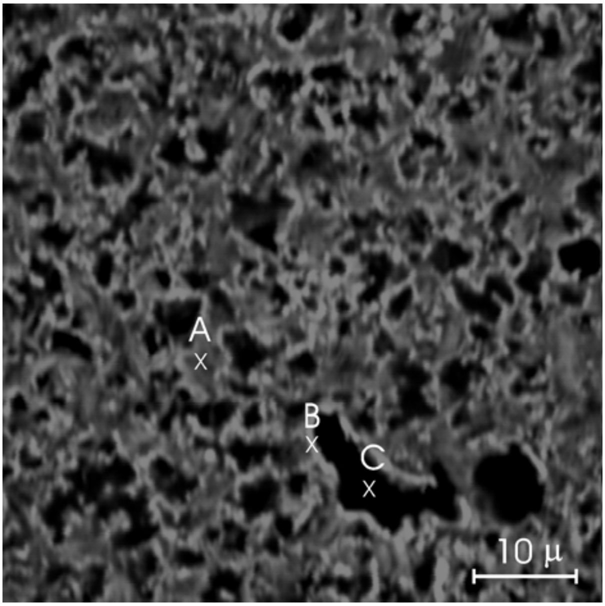

Fig 4 BSE micrograph of the hydraulic binder in a mortar sample from Tournai with a lightly coloured zone (B) rich in Ca (CaO: 49.3 wt.%; SiO_2: 1.4 wt.%; Al_2O_3: 0.2 wt.%), a darker zone rich in Si (A) (CaO: 8.3 wt.%; SiO_2: 15.5 wt. %; Al_2O_3: 1.6 wt.%) and a black zone (C) corresponding to the porosity. These are average analyses results of points (volume of approximately 5-10 μm^3) obtained at 15kV and 6nA.

6 Conclusions

From a chemical and mineralogical viewpoint, the composition of the currently available natural hydraulic limes is different from that of the non-hydraulic limes. However, the differences between samples of NHL2 and NHL5 limes are less obvious and mainly based on the amount of amorphous material. In ancient times, hydraulic limes were used in mortars. Although hydraulic binders made from the addition of pozzolans to lime are identified in many mortar samples since Antiquity, the natural hydraulic limes made from impure limestone seem to be used less frequently. Many questions remain about their deliberate use, because the theoretical knowledge of hydraulicity only dates from the end of the eighteenth century. Moreover, the analysis of ancient lime binders is not straightforward because it is difficult to separate from aggregate in ancient mortars. In addition, the identification and classification of hydraulic binders is complicated by their physico-chemical evolution through time.

7 References

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