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Nineteenth century hydraulic restoration mortars in the Saint Michael's Church (Leuven, Belgium) Natural hydraulic lime or cement?

K. Callebaut[a,*], J. Elsen[b,1], K. Van Balen[c], W. Viaene[a]

[a]Fysico-chemische geologie, Katholieke Universiteit Leuven, Leuven, Belgium
[b]Belgian Building Research Institute, Limelette, Belgium
[c]Departement Burgelijke Bouwkunde, Katholieke Universiteit Leuven, Leuven, Belgium

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Abstract

This research focuses on the characterization of nineteenth century hydraulic restoration mortars used in the Saint Michael's Church in Leuven (Belgium). The mortars were used as restoration mortars for weathered mortar joints. A historical study of old work descriptions and mineralogical, petrographical and chemical analyses have been used to characterize these hydraulic mortars. The different hydraulic phases are identified using petrographical analysis, X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometer (EDX) and chemical analyses. Based on the presence of gehlenite (C_2AS), the dominance of C_2S, the large amounts of portlandite, the chemical analyses and on the historical sources, these hydraulic mortars are characterized as natural hydraulic lime mortars. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Petrography; X-ray diffraction; Microstructure; Hydraulic lime

1. Introduction

Hydraulic mortars have already been used from Greek and Roman periods. Air-hardening lime was mixed with pozzolanas (natural or artificial) to obtain a mortar or concrete that could harden under water. Only from the end of the eighteenth century and the beginning of the nineteenth century on, a major change in binder type used for mortars is observed. Until then, air-hardening lime was the most popular binder used in the construction of buildings. From the end of the eighteenth century on, people began to experiment with the hydraulicity of binders. Smeaton discovered in 1756 the hydraulic properties of products obtained by burning limestones contaminated by clay, and Vicat proved in 1812 that the hydraulicity of these binders was the result of the simultaneous burning of limestone and clay. In 1824, J. Aspin discovered the first cement, and from 1835 (L.C. Johnson), Portland cement becomes the dominant binder in the building industry [1]. Natural hydraulic lime was used mostly during the nineteenth century and was the precursor of Portland cement. Belgium was well known for the export of natural hydraulic lime produced in the region of Tournai (southwest Belgium) during the nineteenth century [2]. From the end of the nineteenth century on, Portland cement and its derivatives became the major binding material in construction, mostly due to the standardization of its production. All the properties of specific cements are set, thus providing specific types of cement for specific purposes. During the production of air-hardening lime and natural hydraulic lime, parameters were not standardized, resulting in large variations in properties of the lime.

The main difference in the production of natural hydraulic lime and cement is the burning temperature. Natural hydraulic lime is produced from limestones containing a certain amount of clay impurities *below the sintering temperature*. When limestones containing silica and clay are burnt, the clay decomposes at temperatures between 400°C and 600°C and combines at 950–1250°C with some of the lime, forming silicates and aluminates. The top end of burning

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* Corresponding author. Belgian Building Research Institute (BBRI), Avenue P. Holoffe 21, B-1342 Limelette, Belgium. Tel.: +32-2-6557868; fax: +32-2-6530729.

E-mail address: kristof.callebaut@bbri.be (K. Callebaut).

[1] Current address: Fysico-chemische geologie, Katholieke Universiteit Leuven, Leuven, Belgium.

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temperatures for natural hydraulic limes is 1250°C; sintering occurs at higher temperatures. Cement is produced from mixtures of limestone and clay burnt at temperatures exceeding 1400°C when sintering occurs and a clinker is formed. The composition of the hydraulic phases thus differs: C_2S is the major hydraulic phase in natural hydraulic lime, with some C_3S due to local "hot spots" in the lime kiln, while C_3S is the major phase in cement. Gehlenite (C_2AS), which is formed at temperatures below 1200°C, can still be observed in natural hydraulic lime [3] but not in the final product in the cement production. In natural hydraulic lime, a certain amount of free CaO remains that will convert to free $Ca(OH)_2$ after slaking. In cement, all the CaO is combined in Ca silicates (mainly C_3S) and Ca aluminates (ferrites) during sintering. The study of the production and characterization of natural hydraulic lime and hydraulic lime mortars is rather limited. Nevertheless, these mortars can be very important for the conservation of historic buildings where conservators mostly do not want to use cement. Several damage cases are known to have been caused by the use of cement in the conservation of historic buildings because cement is too hard, rigid and impermeable [4]. Cement also contains more soluble salts, which can be harmful for the historic building. These salts not only produce unaesthetic layers on the building but can also develop large crystallization pressures, thus damaging the historic building.

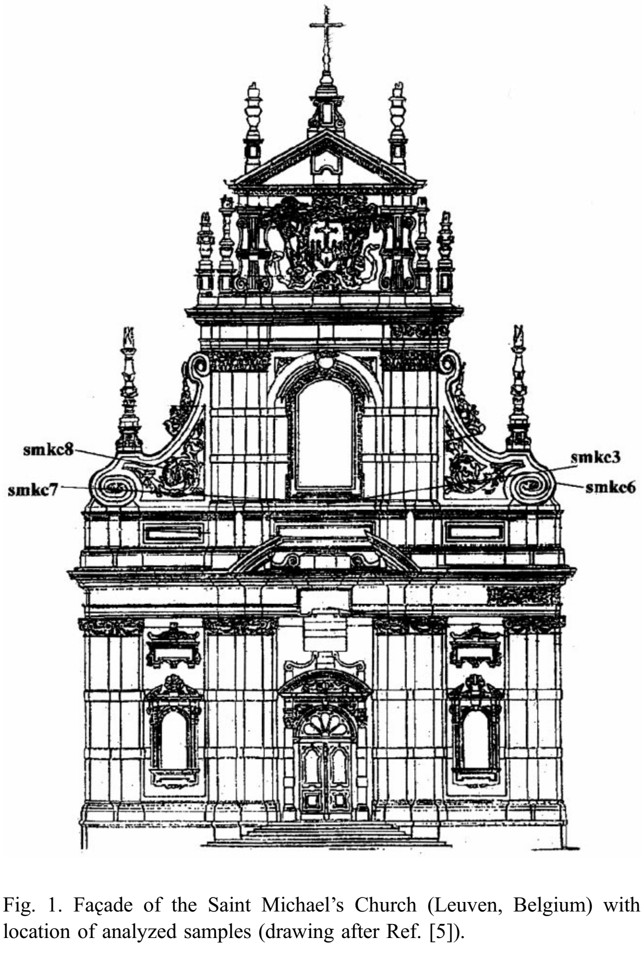

Fig. 1. Façade of the Saint Michael's Church (Leuven, Belgium) with location of analyzed samples (drawing after Ref. [5]).

This study is a part of a greater research on historical lime mortars in Belgium, which focuses on the characterization of hydraulic lime mortars used during the nineteenth century and on the distinction between natural hydraulic lime and cement. The analyzed hydraulic mortars are sampled from the Saint Michael's Church in Leuven (Belgium; Fig. 1). This church is situated in the heart of the city and is an important example of Jesuit architecture influenced by the Flemish baroque in Belgium. It was constructed during the seventeenth century (1650–1666), and the most important interventions were done during the nineteenth century. During the restoration phase at the end of the nineteenth century (1853–1880), natural hydraulic lime from Tournai was used. This is described in the old work descriptions that give information about the materials used during the different building phases [5].

2. Material and methods

Four samples of the hydraulic restoration mortar are sampled at the façade of the church (Fig. 1). The selected samples are taken with hammer and chisel and cut in two halves. One-half is used for the preparation of thin sections. Samples are impregnated with a resin dyed blue and thin sections are polished with an oil and silicon–carbide mix to avoid dissolution of phases and further hydration. The polished thin sections are analyzed with a microscope with both transmitted and reflected light (Olympus BX60-type). This way, the nonhydrated hydraulic phases can be distinguished and identified [6], and the aggregate can be characterized. With X-ray diffraction analysis (XRD) on crushed sample, the mineralogical phases can be characterized. A Philips PW3020 X-ray diffractometer using Cu $K\alpha$ radiation (45 kV, 30 mA) is used. A scanning electron microscope (SEM) is used to characterize the microstructure of the hydraulic mortars. Broken surfaces of mortar coated with gold are analyzed with a type JSM-6400 scanning microscope (JEOL) to characterize the microstructure of the different phases. With energy dispersive X-ray spectrometer (EDX) spot analysis, the different atomic ratios of the hydraulic phases can be identified. SEM analysis in the backscatter electrons (BSE) mode on polished sections coated with gold was used to identify the different hydraulic phases in more detail. Analysis with EDXA identified the atomic ratios in the different hydraulic phases. A type Philips XL30i SEM was used. For the chemical analysis, part of the crushed mortar is attacked with HCl (1:9; one part of concentrated HCl to nine parts of distilled water). The major elements (CaO, MgO, Al_2O_3 and Fe_2O_3) are analyzed with atomic absorption spectrometry (AAS), whereas the amount of insoluble residue (IR) and SO_3 is determined by a gravimetric method. For the determination of the amount of soluble SiO_2, a measure for the hydraulicity of the mortar, the sample is attacked with HCl (10%), and SiO_2 in the filtrate is analyzed by atomic emission spectrometry (AES) [7]. Based on the chemical analyses, two "hydraulicity indexes" can be calculated: the hydraulicity index "i" [Eq. (1)] and the cementation index according to Boynton [8] "CI" [(Eq. (2)]. The higher the index, the more hydraulic properties the mortar has.

$$i = \frac{\%Al_2O_3 + \%Fe_2O_3 + \%SiO_2}{\%CaO + \%MgO} \tag{1}$$

$$CI = \frac{2.8 \times \%SiO_2 + 1.1 \times \%Al_2O_3 + 0.7 \times \%Fe_2O_3}{\%CaO + 1.4 \times \%MgO} \tag{2}$$

3. Results and discussions

3.1. Petrography

The mortars are characterized by a very fine-grained matrix consisting of hydraulic phases and calcite, but the particles are too small to be identified by petrography. XRD analysis of the binder characterizes these phases. The aggregate consists of siliceous sand with a small amount of glauconite (quartz and glauconite grains). Nonhydrated hydraulic phases can be observed (Figs. 2 and 3) in minor quantities: yellowish, rounded C_2S grains and more angular, white C_3S grains. The rounded C_2S grains showed yellow first-order interference colors, while the C_3S grains have grey first-order interference colors. According to Furlan and Pancella [6], C_2S grains can present striations in different directions. These striations however are not observed in the analyzed samples, which indicate that C_2S may exist in the α-form. Hydration rims can be observed around individual hydraulic phases as a colorless rim. The dominance of C_2S is observed in all these mortars, C_3S being only present in "clinkers" (Fig. 2). According to Gödicke-Dettmering and Strübel [3], a part of the hydraulic phases can form such "clinkers" that result from local higher temperatures ("hot spots") in the lime kiln. This has been observed in several natural hydraulic limes [3]. Characteristic for these clinkers due to an overheating is the inhomogeneous formation of large C_2S and C_3S phases in a small amount of a brown matrix consisting of C_3A and C_4AF. In clinkers formed in cement, the distribution of idiomorphic C_3S and C_2S and a larger amount of the brown matrix is more uniform [9]. Portlandite is observed in some pores as a rim in these hydraulic lime mortars. These hydraulic lime mortars are very dense, and with a petrographical analysis, only a small amount of pores is observed. In some samples, a carbonation rim is observed at the exterior of the sample. This rim is denser than the interior of the sample and is characterized by more calcite (observed by the typical carbonate interference colors). In the smaller samples (due to the limitations of sampling historical mortars), mainly the interior of the mortar was sampled to have a noncontaminated sample. The results from all analyses present mainly this interior part.

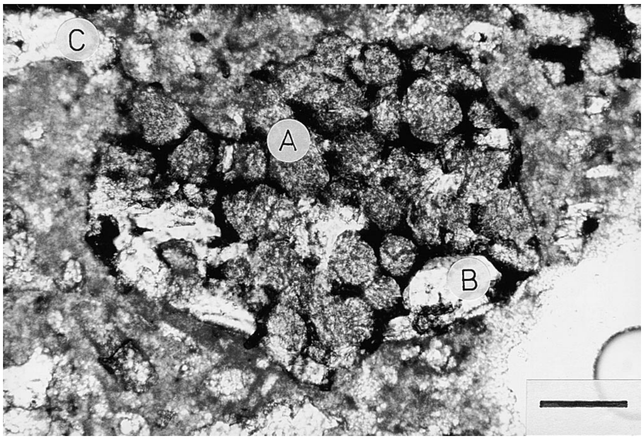

Fig. 2. Nonhydrated hydraulic phases (A and B) and quartz grains (C) in fine-grained binder of nineteenth century hydraulic mortars. Rounded C_2S grains (A) and more angular C_3S grains (B) are observed in the "clinker" Scalebar = 0.067mm.

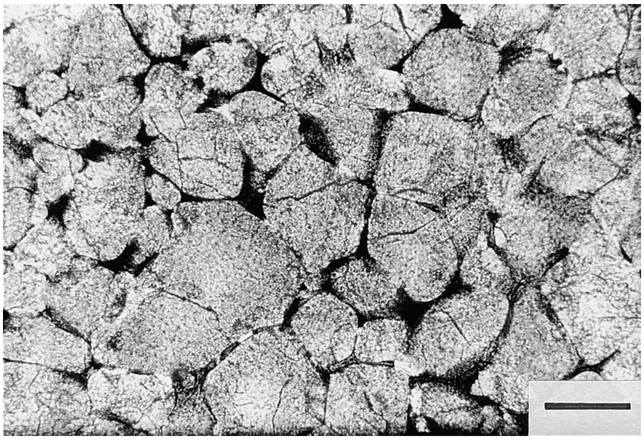

Fig. 3. Detail of rounded, nonhydrated C_2S grains (SMKC8). Scalebar = 0.067mm.

3.2. XRD analysis

The results of the XRD analyses are presented in Table 1. An example of a representative XRD chart is given in

Table 1
Results of XRD analyses on the nineteenth century hydraulic mortars

Sample	cc	Q	C_2S	C_3S	C_2AS	CSH	C_3A	port	glauc	fsp	gy	ettr
SMKC3	++	++	+++	++	++	++	++	+++	?	?	+	+
SMKC6	++	++	+++	++	++	++	++	+++	?	+	+	+
SMKC7	++	++	+++	++	++	++	++	+++	+	+	+	+
SMKC8	++	++	+++	++	++	++	++	+++	+	+	+	+

+++ = dominantly present, ++ = present, + = traces, − = not present, ? = possibly present. cc = calcite, Q = quartz, port = portlandite, glauc = glauconite, fsp = feldspar, gy = gypsum, ettr = ettringite.

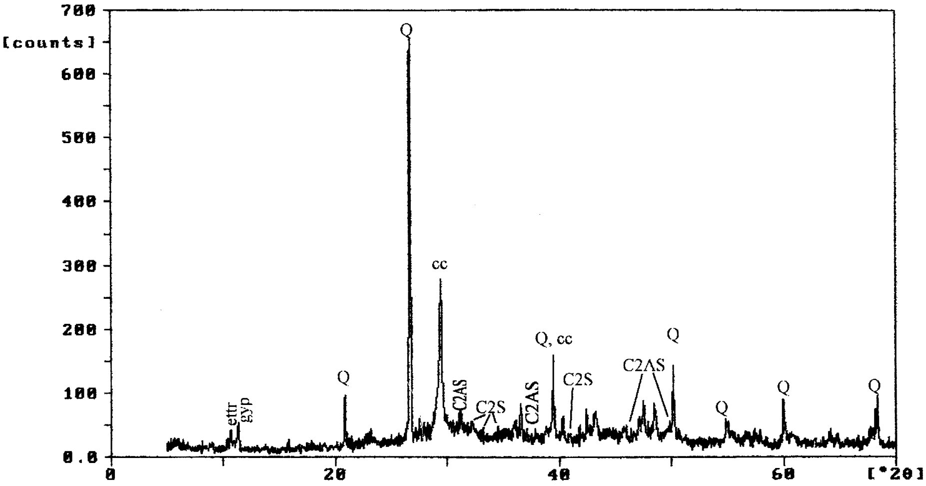

Fig. 4. XRD chart of a hydraulic lime mortar (SMKC6). Ettr = ettringite, gyp = gypsum, Q = quartz, cc = calcite.

Fig. 4. The dominant phases are C_2S together with portlandite. Calcite is found due to the carbonation of portlandite. The latter is formed by slaking of the free lime or by the hydration of hydraulic phases. C_3S is present in all samples but in small quantities compared to the amount of C_2S. A more crystalline type of CSH is observed, but further analysis with SEM is needed to characterize the CSH phases. Gehlenite (C_2AS) is present in all these hydraulic mortars and is characteristic for natural hydraulic lime [3] that is burnt at lower temperatures (< 1200°C). The stability range of gehlenite is situated between 900°C and 1150°C [10]. Gehlenite can be considered as an indicator for lower burning temperatures. According to Taylor [9], gehlenite possibly forms as an intermediate compound during the production of Portland cement clinker but does not occur in the final product. In natural hydraulic lime and in mortars produced with natural hydraulic lime, gehlenite is still present [3]. The presence of gehlenite therefore can be considered to be a valuable indicator for the distinction between cement and natural hydraulic lime. Quartz and glauconite are the main phases in the aggregate fraction. Portlandite will later react with CO_2 from the air to form calcite by carbonation. Due to the dense structure of the hydraulic mortars, part of the portlandite from the interior will not be converted to calcite since moisture and CO_2 will not reach the interior of the mortar. Since carbonation proceeds from the surface to the interior and porosity decreases during this process, the interior will be less carbonatized. This is also observed in air-hardening lime mortars. A carbonated rim that is denser is observed macroscopically and with a petrographical analysis. This denser rim will prevent the CO_2 and moisture to reach the interior of the mortar. The presence of gypsum and ettringite probably results from the secondary salt formation with pollutants in the air, as has been demonstrated by the Environmental Deterioration of Ancient and Mod-

Fig. 5. Detail of the microstructure of CSH phases in the matrix of the nineteenth century hydraulic mortars (SMKC7). Scalebar = 10μm.

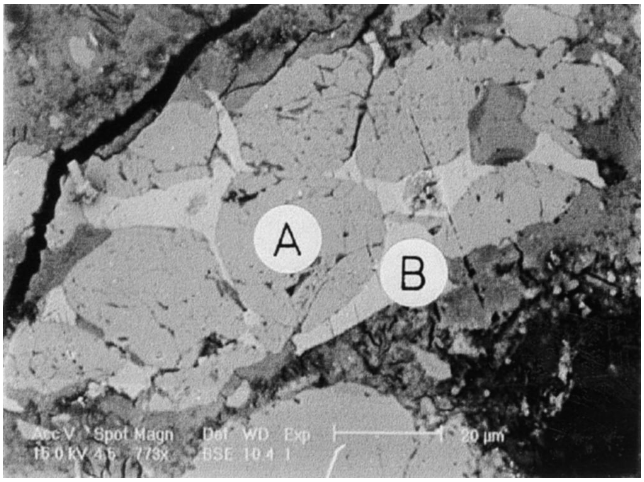

Fig. 6. BSE image of unhydrated C_2S phases (A) and Fe-rich phases (B). SMKC6.

ern Hydraulic Mortars (EDAMM) research project (ENV4-CT95-0096). The formation of ettringite needs gypsum, hydrated calcium aluminates and moisture [11] present in the lime mortars. The gypsum can be formed from the $Ca(OH)_2$ present in the mortar and sulphate in the air. C_3A is present in the mortars (Table 1) and probably also a hydrated calcium aluminate, but that could not be confirmed with XRD.

3.3. SEM analysis

With SEM analysis on broken samples of mortars coated with gold, the microstructure of different phases can be clearly visualized. Needle-shaped CSH phases are observed in clusters in the matrix (Fig. 5) and as a felt-like mat covering the quartz grains. According to Lewin [12], SEM analysis of a mixture of hydraulic lime and sand reveals that the surfaces of the quartz grains are covered with a felt-like mat of hydration products of the hydraulic binder, out of which grow the fibers and needles typical of CSH phases. Hexagonal portlandite plates are observed in pores and in the matrix of the hydraulic mortars. This portlandite occurs as bouclets of hexagonal plates in the matrix. In pores, ettringite and gypsum needles can also be observed, resulting from a reaction of components from the mortar with sulphates present in air pollutants. The small amounts of these phases however are not damaging the mortars.

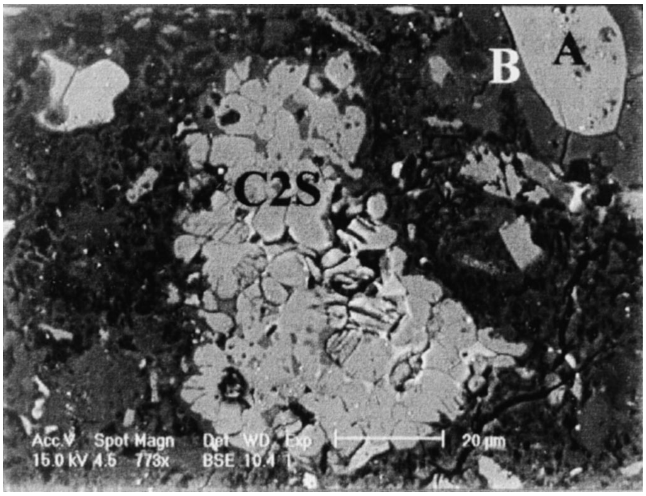

Fig. 7. BSE image of a unhydrated core of C_2S (A) and a hydration rim (B). SMKC6.

With a SEM-EDX analysis in the BSE mode on polished sections, the individual hydraulic phases have been identified in more detail. Atomic ratios of the different elements present in these hydraulic phases have been determined quantitatively. Due to the differences in atomic number that correspond with a difference in grey level displayed on the monitor, the different hydraulic phases can be visually distinguished (Fig. 6). The phases containing more Fe are lighter colored, so ferrite phases are clearly distinguished. The combination of EDX, the shape of phases and their grey levels allows us to identify the different hydraulic phases. C_2S grains have a typical analyzed Ca/Si atomic ratio of 64:36, while C_3S grains show a typical Ca/Si atomic ratio of 72:28. The hydration rim around the unhydrated cores (Fig. 7) displays the same atomic Ca/Si ratio as the core. The lighter zones between the C_2S and C_3S grains in the "clinkers" contain a larger amount of Fe and Al and are possibly brown millerite phases.

3.4. Chemical analysis

The results of the chemical analyses are presented in Table 2. The wt.% of $CaCO_3$ is calculated from the $\%CO_2$ and %CaO and distinguishes these hydraulic mortars from air-hardening lime mortars that have a much larger amount of calculated $CaCO_3$. The remaining CaO is combined with SiO_2 in Ca silicates (hydrates). Al_2O_3 and Fe_2O_3 are mostly found in the hydraulic Ca aluminates and Ca ferrites. The hydraulic properties of these mortars are clear from both hydraulic indices (*i* and CI): the cementation index according to Boynton [8] classifies these mortars as highly hydraulic ($0.7 < CI < 1.1$). The disadvantage of these chemical analyses is that only a bulk analysis is possible, individual hydraulic phases cannot be identified. In comparison with a Portland cement composition, these mortars contain a lower amount of Al_2O_3 and Fe_2O_3, typical for natural hydraulic limes that contain a lower amount of C_3A and C_4AF. Also, the amount of SiO_2 is lower in natural hydraulic limes in comparison with cements [13]. No real standards exist concerning the analysis of the soluble SiO_2 content [14], making it difficult to compare the analysis results of different laboratories. The binder/aggregate ratio corresponds with the ratio given in the historic sources and

Table 2
Results (wt.%) of chemical analyses on the nineteenth century hydraulic mortars

Sample	CaO	MgO	Al_2O_3	Fe_2O_3	Sol. SiO_2	Free $Ca(OH)_2$	CO_2	$\%CaCO_3$	B/A	*i*	CI
SMKC3	47.76	0.85	3.95	2.59	15.66	6.66	4.75	8.69	1:1	0.492	1.100
SMKC6	46.75	0.88	3.87	2.53	15.21	11.20	3.38	5.50	1:1	0.496	1.018
SMKC7	46.37	0.84	3.79	2.48	13.80	10.11	4.38	7.87	1:1	0.466	1.026
SMKC8	49.52	0.86	3.82	2.51	14.76	9.01	6.62	12.92	2:1	0.453	1.009

Sol. SiO_2 = soluble SiO_2, B/A = binder/aggregate ratio, *i* = hydraulicity index, CI = cementation index according to Boynton [8] ($0.3 < CI < 0.5$ = weakly hydraulic, $0.5 < CI < 0.7$ = moderately hydraulic, $0.7 < CI < 1.1$ = highly hydraulic).

shows a rather low amount of aggregates. The higher amount of free $Ca(OH)_2$, in comparison with the air-hardening lime mortars, points to the formation of portlandite in the hydraulic mortars.

4. Conclusions

The hydraulic mortars used during the nineteenth century restoration in the Saint Michael's Church in Leuven have been characterized using petrographical, mineralogical, SEM-EDX and chemical analyses. From historical notes, it is known that *natural hydraulic lime* from the region of Tournai (southwest Belgium) has been used for these hydraulic restoration mortars. From 1853 to 1880, the old work descriptions mention the use of "lime from Tournai" and even a "*chaux hydraulique: 1/2 chaux de Tournai et 1/2 sable rude et sec*" (hydraulic lime: 1/2 lime from Tournai and 1/2 dry, crushed sand) [5]. The use of natural hydraulic lime is thus already clear from historical sources. With this study, a distinction between natural hydraulic lime and cement is made with petrographical, mineralogical, SEM-EDX and chemical analyses. The dominance of C_2S, the presence of gehlenite (C_2AS), the large proportion of free $Ca(OH)_2$ and the lower quantities of SiO_2, Al_2O_3 and Fe_2O_3 in chemical analyses point to the use of natural hydraulic lime for these mortars. The presence of gehlenite (C_2AS) can be used as a valuable and useful indicator for the maximum temperature reached in the lime kiln during the burning process. Gehlenite is formed at temperatures below 1250°C [3] together with C_2S. Nevertheless, C_3S is also present in smaller quantities in these mortars. According to Klenner et al. [15], C_3S can be formed due to an overheating of the raw materials during the production of natural hydraulic lime. Calcite ($CaCO_3$), which is found in these samples, is also present in natural hydraulic limes but is not found in cements [3]. The presence of gehlenite (C_2AS) and calcite ($CaCO_3$) therefore is an important indication for the use of natural hydraulic lime. Moreover, the dominance of C_2S is also an indication for the use of natural hydraulic lime in mortars, however, less valuable since C_3S hydrates faster than C_2S, which results in a relative higher proportion of C_2S crystals in the binder.

Petrographically, the nonhydrated hydraulic phases (C_2S and C_3S) are clearly differentiated by their shape and color. The dominance of C_2S and the inhomogeneous distribution of C_2S and C_3S grains in a small amount of brown matrix (C_3A and C_4AF) characterize these mortars as natural hydraulic lime mortars. The morphology and atomic Ca/Si ratios of the hydrated products are studied with SEM analyses on broken surfaces of mortars. The needle-shaped CSH and the hexagonal portlandite plates typical for natural hydraulic lime are observed. The atomic ratios of the different elements present in the hydraulic phases are determined quantitatively with SEM-EDX analyses in the BSE mode on polished sections. Constant atomic Ca/Si ratios are found for C_2S (64:36) and for C_3S (72:28). Hydrated phases, present as rims around nonhydrated cores, showed similar atomic Ca/Si ratios as the cores.

The compatibility of restoration mortars and original mortars is the greatest concern of conservators, so the correct identification of original material (especially the type of binder) is important [16]. With a combination of a historical study and scientific analyses, the use of natural hydraulic lime in the restoration mortars from the nineteenth century in the Saint Michael's Church in Leuven is recognized. The composition is different from recent Portland cement. The change in technology from natural hydraulic lime to Portland cement cannot be seen as a constant point in time, but as a gradual evolution. Variations in composition of raw materials and in the production processes are responsible for a large variation in types of natural hydraulic limes. Later on, the production became much more controlled in a standardized way so that the difference between hydraulic lime and Portland cement is clearly differentiated.

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