Non-cement hydraulic binders in preindustrial architecture of Prague

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Abstract: Portland cement presents the dominant inorganic hydraulic binder used in the building industry since the 19th century. Non-cement hydraulic binders played an important role from antiquity as indicated by the use of Roman cement in ancient Rome, pozzolanic additives to lime binders for marine constructions in the Mediterranean, and hydraulic limes for engineering works in medieval Europe.

Historically, some areas of Bohemia (Czech Republic) are known to have produced hydraulic limes of excellent quality. Limestones suitable for burning excellent hydraulic limes were quarried in the surroundings of the Bohemian capital, Prague. Their use can be documented from Romanesque period (Judita Bridge construction) through Gothic (Charles Bridge construction) and Baroque (construction of churches) periods until the 19th century. According to written records, Czech hydraulic limes were exported to many places in Europe, including Italy where they was known as "pasta di Praga". This study gives a description of the resource used for the production of hydraulic lime in the Czech Republic and presents some typical examples of the use of limes in historical architecture. The analytical problems connected with the detection of hydraulic phases in ancient mortars are also discussed.

Résumé: Le ciment de Portland offre le liant hydraulique inorganique dominant, utilisé dans l'industrie de la construction depuis le XIXe siècle. Les liants hydrauliques qui ne sont pas en ciment ont joué un rôle important depuis l'Antiquité, tel que cela a été démontré par l'usage du ciment romain dans l'ancienne Rome, les additifs de pouzzolane aux liens de chaux pour les constructions marines en Méditerranée, et les chaux hydrauliques pour les travaux d'ingénierie en Europe médiévale.

Historiquement, certaines régions de Bohême (République tchèque) sont connues pour la production de chaux hydraulique d'excellente qualité. Les roches de calcaire, appropriées pour faire cuire d'excellentes chaux hydrauliques, ont été extraites dans les alentours de la capitale de la Bohême, Prague. Leur utilisation remonte à la période romane (la construction du pont Judita), gothique (la construction du pont Charles) et baroque (la construction d'églises) jusqu'au XIXe siècle. Selon certains documents écrits, les chaux hydrauliques tchèques avaient été exportées dans beaucoup d'endroits en Europe ; à savoir en Italie où elle était connue sous *pasta di Praga*. Cette étude donne une vue d'ensemble des ressources utilisées pour la production de chaux hydraulique en République tchèque et présente quelques exemples typiques de leur utilisation dans l'ancienne architecture. Les problèmes analytiques liés à la détection des phases hydrauliques dans l'ancien mortier sont également abordés.

Keywords: limestone, hydraulic binders, plasters

INTRODUCTION

Limes, produced by burning of limestones, were the dominant inorganic binders used in construction before the industrial production of Portland cement. Based on their ability to harden on contact with air or in water, the limes were traditionally classified (Vicat 1997) as:

- **fat limes** which set on air only and double volume by slaking;
- **lean limes** which set on air only and do not increase volume by slaking;
- **moderately hydraulic limes** which set immersed in the water in 15-20 days;
- **hydraulic limes** which set over 6-8 days immersion period; and
- **eminently hydraulic limes** which set in 2-4 days immersion and after 28 days are very hard and insoluble.

The behaviour of limes is mainly influenced by the mineralogical and chemical composition of limestones from which the limes are burnt. This can be expressed by the hydraulic index (Cowper 1998), defined as:

(SiO_2 wt % + Al_2O_3 wt. %) / CaO wt. %.

The percentage of individual oxides is determined by chemical analysis. For ordinary limes, the hydraulic index is below 0.1, for moderately hydraulic limes between 0.1-0.2, and for hydraulic limes and eminently hydraulic limes 0.2-0.4. Values for Portland cement and natural cements should be from 0.4 to 1.5 (Cowper 1998). The increased content of clay minerals and silica generally improves hydraulic index of limestones. Along with natural hydraulic limes (Maravelaki-Kalaitzaki *et al*. 2005), numerous inorganic and organic admixtures were applied to increase the hydraulic index and to control setting rates (Moropoulou, Bakolas & Anagnostopoulou 2005).

CZECH HYDRAULIC LIMES

Historical background of lime production

In Bohemia, a need for inorganic building binders appeared due to the growing construction activity arising from Christianisation and the development of the city of Prague (the Bohemian capital). Preindustrial lime production dramatically increased in two distinct historical periods as a result of increased construction activity. The first peak occurred in the mid-14th century under the reign of the Czech King and Roman Emperor Charles IV the Luxembourg, who founded the University, built the New Stone Bridge (now called Charles Bridge) and allowed major expansion of the city. The second peak of production was part of the Baroque renewal of the country after several decades of destruction during 30 years of war in the first half of the17th century.

Limestones for quick lime and hydraulic lime burning were quarried at several places away from the historical centre of Prague (Bráník, Podolí, Zlíchov, Smíchov, Barrandov, Radotín, Hlubočepy). The beginning of limestone extraction is not documented in the literature – the first written documents on quarries are the mineralogists' records of fossil sampling (e.g. Zeno 1770). The limestone was not burnt at the quarry but was transported in its raw state by ships on the Vltava River to limekilns located in the centre of Prague (e.g. Herget's lime works at Little Quarter just below Prague Castle). Lime burning in the city was prohibited after 1857 and then had to be carried out at the quarry sites. In the same period (1860), the first lime works started to produce ordinary Portland cement and the production of non-cement hydraulic binders started gradually declining. After the Second World War, hydraulic lime was no longer produced in the Czech Republic.

During the Middle Ages, the high reputation of lime produced in Prague resulted in its export to foreign countries. It is supposed that Prague lime was exported in Italy where it was known under the name "Pasta di Praga" (Láník & Cikrt 2001). The excellent quality of the lime produced in this period is mentioned in the literature (Balbín 1679-1687).

Geological position and properties of limestones

Part of Prague and its SW environs lies on the geological unit called the Barrandian basin. This large oval syncline structure extending SW-NE comprises non-metamorphosed and low-metamorphosed sedimentary and volcano-sedimentary rocks belonging to the Upper Proterozoic and Lower Palaeozoic periods (Cambrian to mid-Devonian). In terms of limestone occurrence, the Ordovician to Devonian beds of the Prague subbasin are the most important. Especially during the Lower Devonian, the area of Prague lay in an equatorial position with a warm climate. This resulted in the development of coral reefs and sedimentation of pure limestones rich in fossils (brachiopods, corals, bryozoa, sea-lilies and trilobites) for which the area was well known amongst palaeontologists of the 18th century. Muddy limestones and limy mud were deposited offshore and from these non-pure limestones originated. These limestones, locally called Dvorce-Prokop limestones, were prospected for non-cement hydraulic binders in the past (Braník quarry, Dvorce Quarry, Prokop Valley, Radotín valley) and are currently used for cement production (Hvížd'alka quarry at Radotín). These grey, fine-grained micritic limestones were deposited in the deepest part of the basin and are characterised by increased volume of clay minerals. Due to higher proportion of clay minerals and thus of Al_2O_3 and SiO_2 (see Table 1), these limestones exhibit excellent hydraulic properties classifying them as eminently hydraulic limes according to Vicat (1997) and Cowper (1998).

Table 1. Representative chemical composition of main limestone types used in Prague for lime, hydraulic lime and cement production (chemical data after Brunnerová 2001). Hydraulic index (HI) calculated according to Cowper (1998)

	Dvorce-Prokop limestone (Prag stage)	**Řeporyje limestone (Prag stage)**	**Slivenec limestone (Prag stage)**	**Kosoř limestone (Lochkov stage)**	**Radotín limestone (Lochkov stage)**
SiO_2	12.61	9.09	3.59	4.05	4.90
Al_2O_3	3.57	2.93	1.25	1.10	1.29
Fe_2O_3	1.60	1.48	0.76	0.62	0.52
CaO	43.45	46.04	48.81	41.48	40.58
MgO	1.37	1.28	2.65	6.13	8.62
HI	0.37	0.26	0.10	0.12	0.16

LABORATORY ANALYSIS

St. Nicolas Church in Prague

St. Nicholas Church in the Prague Little Quarter is one of the finest Baroque buildings (architects K. Dienzenhofer, K. I. Dienzenhofer, A. Lurago) constructed during first half of 18th century. This huge building (60 m long, 40 m wide, cupola 50 m high) was constructed with brick masonry and its facade covered by plaster of excellent quality. In spite of numerous restorations (1888-1890, 1925-1928, 1955-1964), the original plaster still dominates the facade of the Church (Široký *et al*. 2002).

The study was focused on the original Baroque plasters used on the western facade of the church. During the research, the extent of used plasters was mapped. Sampled plasters were then analysed by several analytical methods

to obtain detailed information on their composition. The research was conducted as a part of complex pre-restoration research (Široký *et al*. 2002).

Analytical approaches

The composition of sampled plasters was studied by the following methods:

- optical microscopy of polished cross-sections (colour scheme of surface layers, stratigraphy of plasters, composition)
- optical microscopy of thin sections (mineralogy of fillers) equipped with image analysis (quantitative determination of filler: binder ratio, grain size distribution of fillers)
- X-ray diffraction (phase study of binders' mineralogy)
- FTIR spectrometry (organic substances in binders)
- electron microanalysis (chemical composition of inorganic phases in binders)
- silicate analysis (chemical composition of binders).

Results and their interpretation

Fillers

Mineralogical and petrographical composition of fillers is very homogeneous in studied samples showing dominance of quartz and rock fragments, and less proportion of feldspars (Table 2). Due to relatively high angularity of fillers, the local provenance can be assumed. Fillers of individual samples exhibit similar grading (Figure 1).

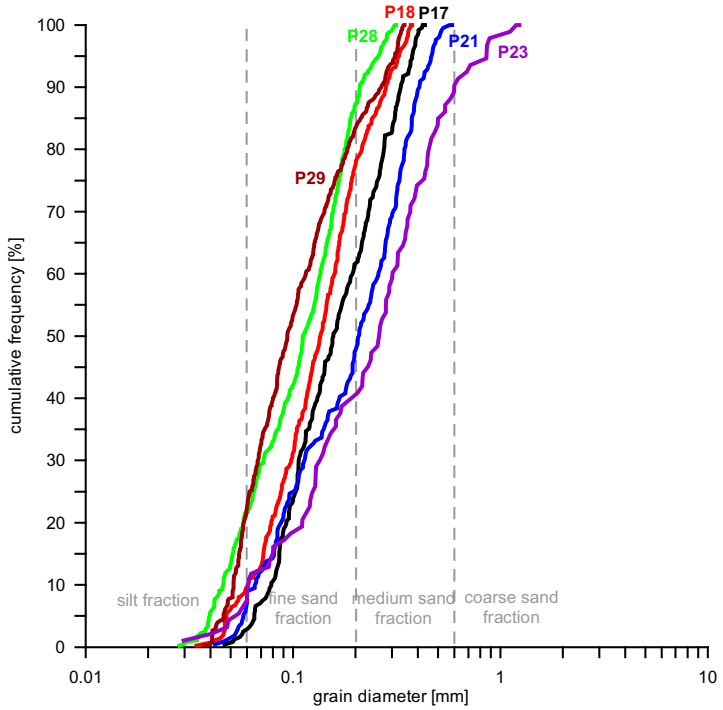

Figure 1. Grading of fillers in studied samples of plasters at the western facade of St. Nicholas Church in Prague (adopted from Široký *et al*. 2002)

Table 2. Mineralogical characteristics of fillers in studied samples of plasters at the western facade of St. Nicholas Church in Prague. Number of + signs denotes relative abundance of individual phases (data adopted from Široký *et al*. 2002)

	quartz	feldspars	rock fragments
P17 core	+++++	++	+++
P18 core	+++	++	+++
P21 core	++++	++	+++
P21 stucco	+++++	+	-
P23 core	++++	+	++++
P28 core	++++	+	+++
P28 stucco	++++	+	-
P29 core	+++	++	++++

Binders

The XRD technique confirmed presence of calcite, larnite, quartz and gypsum (Table 3). Calcite is the most common crystalline phase detected. Larnite (dicalcium silicate, Ca_2SiO_4 or C_2S) is the only hydraulic phase analysed by XRD. C_2S evidently indicates hydraulic lime. Traces of quartz can be linked to the fine fractions of filler. Gypsum was observed in both stucco layers and in the core of the mortar, and probably was used as an admixture controlling setting rates of mortar.

Presence of hydraulic phases can be also assumed from the electron microanalysis. Using this technique, other minor phases like C_3S and non-stoichiometric Ca^{2+}-Si^{4+}-rich phase were detected. The proportion of these fractions is below the detection limit of XRD and electron microscopy offers the excellent possibility to detect them.

Detected organic phases – oils (unspecified) and proteins (glue) probably represent admixtures improving the rheological properties of plaster. FTIR spectrometry was employed for the study of the organic phases and was not used for inorganic hydraulic phases.

Increased volume of SiO_2 and Al_2O_3 as shown by silicate analysis partly confirms the hydraulic character of the binder. The major problem in interpretation is the separation of SiO_2 that can be attributed to the binder and that due to the fine filler fraction.

Table 3. Phases detected in plasters from western facade of the St. Nicholas Church in Prague. Calcite (trig. $CaCO_3$), quartz (SiO_2), gypsum $CaSO_4.nH_2O$, larnite - dicalcium silicate (Ca_2SiO_4), vaterite (hexag. $CaCO_3$). Number of + signs denotes relative abundance of individual phases (data adopted from Široký *et al*. 2002)

	calcite	quartz	gypsum	larnite	vaterite
P4	++++++	+	++	-	-
P17	+++++	+	-	++	-
P18	+++++	+++	+	-	-
P21	++++++	+	+	-	-
P23	++++++	+	-	++	-
P28	++++++	+	-	-	-
P29	++++++	+	-	-	-
P30	+++++	+	+	-	-
P31	+++++	+++	++	-	-
P32	+++++	++	+	++	-
P19	++++++	+	+	-	-
P20	++++	++	+++	+	-
P22	++++++	+	-	-	-
P24	+++++	+	+++	-	-
P25	++++	++	+++	+	tr.
P26	+++++	++	+	+	-
P27	++++++	++	-	-	-

Filler:binder ratio

Proportion of filler and binder has been determined from quantitative image analysis of thin sections. Based on this parameter, the studied samples can be subdivided into two groups: (I) those showing a filler:binder ratio of 1:1, and (II) samples showing a ratio 1:2-3.

CONCLUSIONS

Hydraulic limes range to the historically important binders used in the Czech Republic. Their production was facilitated by the presence of impure limestones in Prague environs. These limes were probably produced from Gothic times till the beginning of the 20th century and were widely used in construction. The two peak periods of lime production coincided with periods of peak construction in the Czech lands during the Gothic and Baroque periods. During the Baroque period, hydraulic limes were not only used as mortars for engineering work, but also as binders for plaster applied to prestigious buildings for example St. Nicholas Church in Prague.

There is no universal analytical technique for the determination of hydraulic phases in hydraulic lime mortars. Combination of two techniques, X-ray diffraction and electron microanalysis, seems to produce reliable results. The first method is applicable as long as the content of hydraulic phases in the analysed sample exceeds the detection limit of the instrument (about 2-3 wt. %). Electron microscope allows detection of smaller amounts. The measured data on concentration of certain chemical elements must be extrapolated to the phases which can introduce uncertainty in certain cases.

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