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Study on Historic Mortars Produced from Artificial Hydraulic Lime

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ABSTRACT: The building of the Augustow Canal between 1824 and 1839 was a huge and extremely important hydrotechnical construction for Kingdom of Poland. During the construction of the Canal, artificial hydraulic lime was used so extensively, probably the first time in history (with usage of more than 8,300 tons). The article presents the results of studies on mortar samples collected from walls of the Canal's locks (by chemical analysis, XRD, DTA/TGA, E-SEM and SEM/EDS). The analysis shows that in construction of lock walls the hydraulic lime with a very low hydraulic modulus of 1,7 was used. The basic functional properties of mortars as well as the description of the morphology, chemical and mineralogical content of old pastes exposed to environmental impact for approximately 180 years are presented in the article.

1 INTRODUCTION

In the early 19th century, erecting of hydrotechnical constructions in regions not plentiful in pozzolanas and limestones or other proper raw materials enabling the production of natural hydraulic lime was a challenging enterprise. The discovery of obtaining hydraulic lime through calcination of an artificially composed mix of calcareous materials and clays is attributed to Louis-Joseph Vicat. He published his results in 1817. His idea was extensively used during the building of the Augustow Canal where the artificial hydraulic lime was produced and applied (Pancer, 1829).

The waterway is located on the territory of two countries: Poland (about 80 km, 14 locks) and Belarus (21.2 km, 3 locks). The Kurzyniec Lock, the eighteenth lock, is situated exactly on the border. The canal with 18 locks, 22 sluices, 14 drawbridges and 65 simple road bridges was built between 1824 and 1839.

The Augustow Canal was the first place, where the hydraulic binder, derived from the burning process of clay and lime mixture, was used on such large scale. During construction of the canal more than 8,300 tons of artificial hydraulic lime were used (Batura et al. 2000). The hydraulic lime mortar has exhibited excellent durability through 180 years. Thanks to that, the waterway has kept almost unchanged form, the part of canal located in Poland is still operating, and the majority of locks are preserved in their original construction from the 19th century.

The present paper concerns some aspects of the hydraulic binder condition in the monumental hydrotechnical structure. The study of the manufacturing and characterization of artificial hydraulic lime mortars is rather limited.

2 HISTORY OF BUILDING AND EXPLOITATION OF AUGUSTOW CANAL

The idea to construct the canal was proposed at the beginning of the19th century. At the end of 1824, the project of the construction (over 500 sheets of maps, plans and working drawings) was finished and the construction was begun in 1825. The factories for production of building materials, metal and wood procession, necessary for realization of the project, were built on the territory bordering on the canal (Batura et al. 2000).

This process was interrupted only once, during the war in Kingdom of Poland in 1831. The canal was opened in 1839.

The canal was modern, inland water track, designed for the movement of boats of 150 t dead-weight and 1.2 m draught. The width of invert about 11.5 m was assumed.

The hydrotechnical installations were made in a very careful way. The walls of lock chambers were built of cobble-stones cemented with hydraulic lime mortars and they were faced with bricks. The facing with cut white sandstones was made in the places exposed to damages. The bottoms of locks were made of wood or stones cemented with hydraulic lime mortar, depending on subsoil type. The hand-operated lock gates were made of oak-wood and equipped with metallic accessories.

In the past the choice of material was strictly related to the building materials present near the work-areas, transport being both very difficult and expensive.

Among lots of problems concerning the canal construction, the difficulties in gaining suitable building materials were significant. The material spending was high and some problems could not be solved using standard ways. The lack of binders resistant to long-term water influence was particularly inconvenient.

For the purpose of the Augustow Canal construction the technology of artificial hydraulic lime (Pancer 1824) production was elaborated on the base of L.J. Vicat procedure. The local available raw materials were used. It was significant technological and organizing achievement in those days. Probably, it was the first case of cement manufacturing on such large scale in the world. Later, this binder was used in important buildings such as citadel in Warsaw, overbridges and others.

Between the World Wars the canal became an important tourist attraction. Such was also the function of its Polish section after the last war.

After the World War II, the canal was restored only on the territory of Poland and since 1950 has been navigable on the length of 77.5 km. Nine out of 14 locks kept original construction of the19th century and most of the rest kept original masonry. The last unrepaired object, partly situated on the territory of Poland, is Kurzyniec Lock, built in 1829. The main reason for the hydrotechnical structures' damages was not long-term environment influence but the military operations, which caused total destruction of three locks. All locks on the territory of Belarus are out of operation and need repairing now. The project of Belarussian part of the channel restoration is being prepared, thus the plan to commence the movement on this part of the canal should be soon realized.

In 2006, passage through the full length of the canal will once again be enabled. The registration of the canal on the UNESCO World Heritage List is in progress.

3 SAMPLES AND TEST METHODS

The mortars used during construction of the walls' brickwork of locks on the Augustow Canal were the subject of the presented study. The tests were carried out for samples of mortar from the Kurzyniec Lock, the object just before reparation. The samples of mortar were collected from numerous testbore-cores drilled from the stone-brick walls of lock chamber. The shafts of walls were built of cobble-stones of different dimensions, mainly granite boulders, cemented with artificial hydraulic lime mortar.

The samples, derived from different depth of the lock wall, were indicated as follows:

- P1 – mortar from brickwork of lock, 1.0 m from wall face,
- P2 – mortar binding the cobble-stones, 3.5 m from wall face,
- P3 – mortar binding the cobble-stones, 4.0 m from wall face.

The present investigation was conducted with objective to assess the type of binder used, determination of its chemical and phase composition and evaluation of basic properties of mortars used in the Augustow Canal construction. The morphology, phase and chemical composition of products formed as the result of chemical reactions and changes of binders in contact with water and subjected to environment influence during 180 years, were described.

The chemical analysis, X-ray diffractometry (XRD), differential thermal analysis (DTA), thermogravimetry analysis (TGA) and scanning electron microscopy (E-SEM and SEM/EDS) were applied to characterize the microstructure and also to determine the hydration products of mortars. The fractured mortar specimens were used for E-SEM and SEM and the samples for chemical analysis, XRD as well as for DTA/TGA tests were dried at 40^oC and ground so that particles were smaller than 60 μm in maximum dimension (Ramachandran and Beaudoin 2001, Ramachandran et al. 2003). The properties of mortars such as absorbability and density were studied as well.

4 TEST RESULTS

4.1 Basic properties of hydraulic lime mortar

The macroscopic investigation of cores derived from lock walls showed significant differences among contemporary masonry mortars and the mortars used for the canal construction. The mortars from lock walls contain less fine aggregate (sand) than contemporary lime or cement mortars. The mortars filling the spaces among boulders are characterised by high porosity and relatively low compressive strength. In fact, because they are composed of an aggregate and a binder, often with different chemical composition, mortars represent heterogenous systems with high values of porosity and surface roughness (Sabbioni et al. 2002). The way of historic mortar putting on was particular. Probably, the wall of cobble-stones was formed and the spaces left in the pile of stones were filled with mortar of liquid consistence. The basic purposes of mortar in shafts of wall were masonry structure joining, better stress distribution assuring and sealing of wall.

The water absorbability and density of mortar were tested on specimens devoid of coarse aggregate. The average of water absorbability was 17.8% and bulk density – 1650 kg/m^3.

4.2 Chemical composition

Chemical analysis of hydraulic lime mortars included determination of CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, SO_3 and free $Ca(OH)_2$ concentration. The loss of ignition and the parts insoluble in HCl and Na_2CO_3 content was also estimated.

The binder content in mortar was determined by assuming that all the acid-insoluble parts account for aggregate (Ramachandran and Beaudoin 2001). The remain parts of the material analysed are the products of binder reactions with water, carbon dioxide as well as with aggressive environmental media (salts and acids dissolved in water). The determination of insoluble parts and loss of ignition content makes it possible to estimate chemical composition of burned binders. In order to make the evaluation correct two conditions should be complied: the lack of significant amount of aggregate constituents soluble in HCl and not very advanced corrosive processes in mortar. The mortars tested kept both conditions mentioned. The chemical compositions of mortar and binder are given in Table 1.

As it is shown in Table 1 the water resistant lime used in the Augustow Canal construction was a binding material of strong hydraulic properties and high content of acidic oxides: SiO_2, Al_2O_3, Fe_2O_3. The hydraulic modulus (HM = $CaO[\%]/SiO_2, Al_2O_3, Fe_2O_3[\%]$) of binder was 1.7. The weight ratio of ignited binder and sand is very close to 1:1. Considering the test results presented in Table 1, the description of hydraulic lime manufacturing (Landsberg 1999, Moropoulos et al. 2005) and the data about the processes occurring in quaternary system $CaO–SiO_2–Al_2O_3–Fe_2O_3$ (Gosh 1983) with temperature changes, it can be supposed that the binder tested contained relatively little amount of free CaO, and belite C_2S, gehlenite C_2AS were probably its basic components (Callebaut et al. 2001). The significant amount of periclase, calcium aluminates CA, $C_{12}A_7$ and calcium aluminoferrite $C_2(A,F)$ also occurred in hydraulic lime.

Table 1 : The results of chemical analysis.

Component	Content in sample tested (% by mass)					
	P1		P2		P3	
	mortar	binder	mortar	binder	mortar	binder
Insoluble parts	32.31	-	40.34	-	40.11	-
Loss of ignition	23.28	-	18.22	-	18.09	-
SiO_2	11.38	25.62	10.04	24.23	10.12	24.21
Fe_2O_3	1.75	3.94	1.67	4.03	1.70	4.07
Al_2O_3	3.80	8.56	3.45	8.33	3.58	8.56
CaO	23.24	52.33	21.40	51.64	21.98	52.58
MgO	4.11	9.25	4.06	9.80	4.07	9.74
SO_3	0.05	0.11	0.06	0.14	0.04	0.10
$Ca(OH)_2$	0.04	-	0.04	-	0.05	-

It is not possible to determine precisely binder composition, because the proportion among particular components is dependant not only on its chemical composition but also on the conditions of lime manufacturing (Konow 2003). It should be considered that the part of CaO and products of clay minerals dehydration and dehydroxylation were not able to react with each other because of the conditions of hydraulic lime homogenisation and burning process. In this case, the binder was enriched in free CaO as well as in hydraulic active product of thermal decomposition of clay raw materials – methakaoline.

4.3 X-ray diffractometry

The X-ray diffraction analysis was done using Philips X'PERT PRO diffractometer, according to Debye-Scherrer-Hulle powder diffraction method. The CuKα radiation was used, the measuring angle range was as wide as 5 to 70° 2Θ, the tube voltage and currant were 40 kV and 30 mA, respectively. The patterns obtained were compared with PDF database (ICDD) – the component of diffractometer software system.

The X-ray patterns of all mortars tested are similar. The main component of mortars is fine calcium carbonate (calcite), formed as a result of carbonation of binder constituents reaction with water (Callebaut et al. 2001). The strong peaks of quartz – basic crystalline phase of aggregate – and feldspars (microcline and orthoclase) were observed. Other components identified in mortar were scawtite $Ca_7[(Si_6O_{18})(CO_3)]\cdot 2H_2O$, nesquehonite $MgCO_3\cdot 2H_2O$ as well as calcium hydrosilicates containing substantial amounts of aluminium and magnesium ions. There was some slight content of gypsum in P2 and P3 samples. In any samples tested there were no lines that can be ascribed to portlandite, typical forms of C-S-H phase, hydrogehlenite, hydrogarnets or $C_3A\cdot CaCO_3\cdot 12H_2O$. The remains of primary constituents of binder were not observed, either.

4.4 Thermal analysis

The Differential Thermal Analysis and Thermogravimetric Analysis were carried out using Universal V2.5H TA Instruments. The measurements were conducted in the range of temperature changes from 20 to 1000°C. The rate of temperature increase was 10°C/min and the weights of samples tested fluctuated from 60 to 100 mg.

The DTA and TGA curves of samples tested are characterized with similar course. The example of tested mortar thermogram is presented in Fig. 1.

The DTA curves showed two endothermic peaks at 500 – 1000°C. The first one, with maximum at 573°C, is associated with polymorphous transformation of β-SiO_2 in α- SiO_2 (quartz is a main component of sand presented in mortars). The other one, with extreme between 720 and 780°C, is attributed to decarbonation of $CaCO_3$, formed in the process of CO_2 reaction with binder hydration products. The process of $CaCO_3$ decarbonation is connected with significant samples weight loss, recorded at TGA curve at the same temperature range.

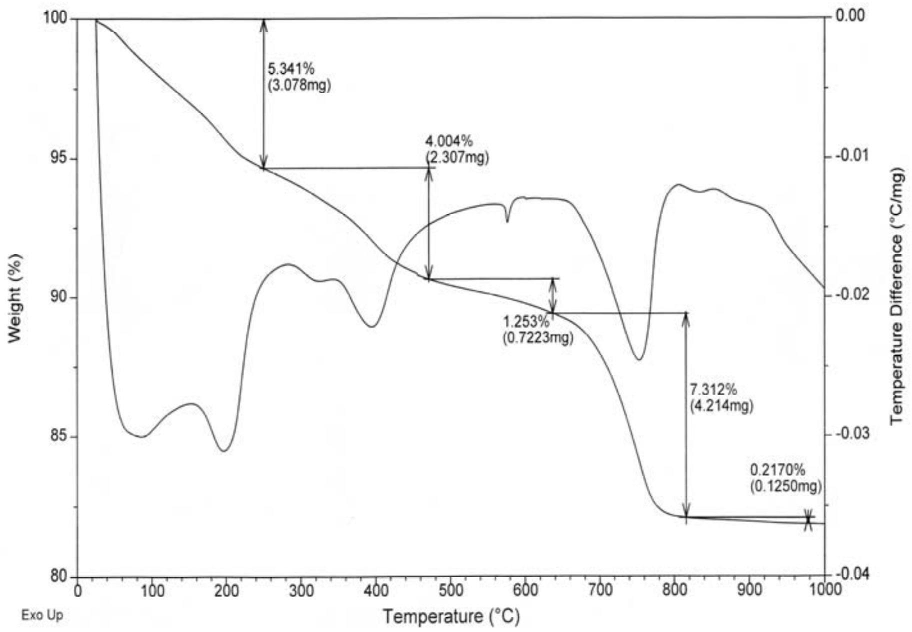

Figure 1 : Thermal analysis of P2 sample.

The TGA curves, recorded at temperature below 500^{o}C for all samples tested, show nearly linear weight loss with temperature increase. Whereas, at the DTA curves several endothermic peaks occur, with maximum at 80-100^{o}C, about 180^{o}C, 330^{o}C and 380-400^{o}C.

The polymineral composition of the material tested, the lack of well-formed crystalline structure of major components, the presence of a number solid solutions and multi-stage of processes occurred such as dehydration, dehydroxylation and decarbonisation make it difficult to attribute univocally the peaks indicated at the DTA curves.

Probably, the peaks at temperature below 200^{o}C should be attributed to the dehydration of unidentified semicrystalline products of hydration of gehlenite, C-S-H phase, magnesium-aluminium hydroxide and their solid solutions. The peaks observed on the DTA curve at higher temperature are mainly connected with scawtite and nesquehonite decomposition.

4.5 SEM images analysis

The morphology of mortar was investigated using the scanning electron microscope JEOL 5200 equipped with the energy dispersive X-ray analyser EDS Link ISIS and the environmental scanning electron microscope E-SEM Philips XL 30 operated with a poor vacuum in specimen chamber. The observations were conducted with magnification from 50 to 1000 times. The selected micrographs and EDS results are presented in Figs. 2-4.

The SEM and E-SEM micrographs do not indicate significant differences among the mortars analyzed. The dense microstructure without any crystals, apart form the aggregate grains, is observed. The pastes, which are ingredients of mortars, contain randomly oriented, irregular forms of secondary calcite, originated in carbonation process. In some samples the fibrous parts of plants are presented. There are not the forms of CSH phase typical for present hardened binders. The areas with well-formed crystallites are unusual (Fig.4).

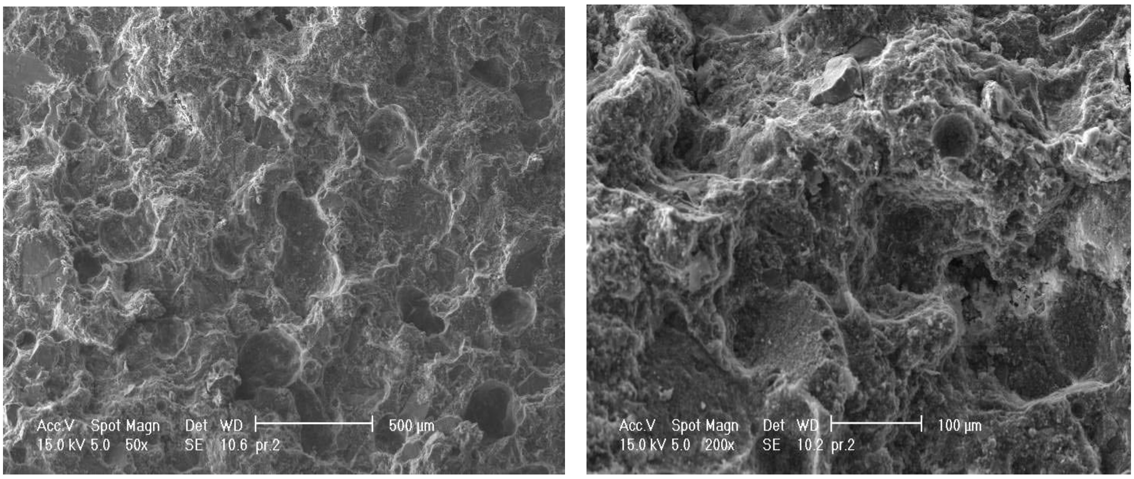

Figure 2 : SEM micrographs of historic mortars derived from the wall of the Kurzyniec Lock.

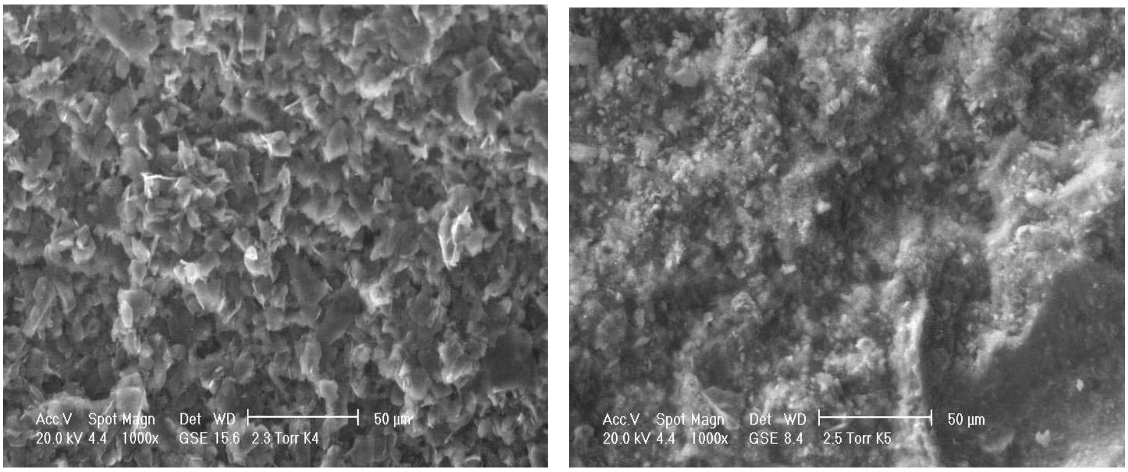

Figure 3 : E-SEM micrographs of mortars from the wall of the Kurzyniec Lock

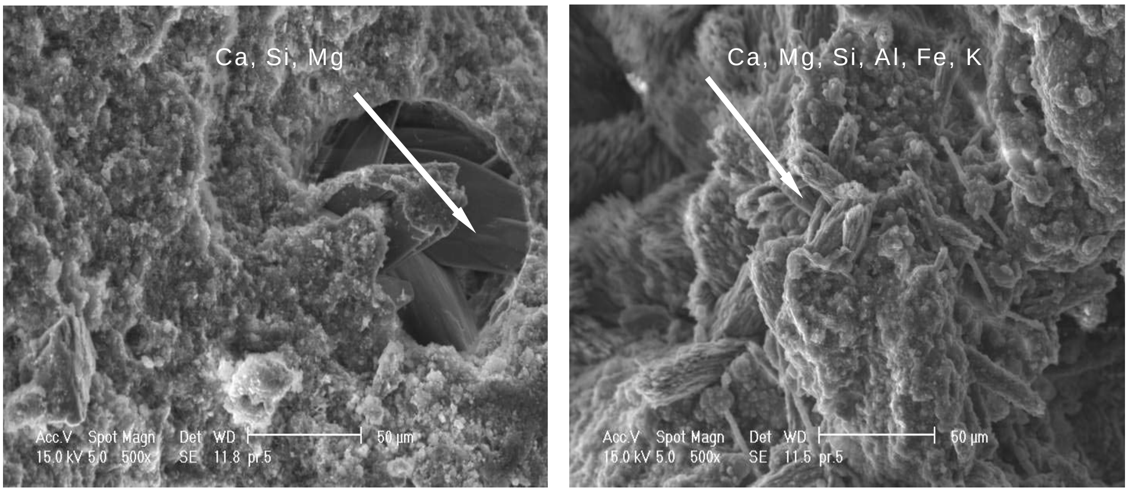

Figure 4 : SEM micrographs and EDS analysis of mortar of atypical morphology.

5 CONCLUSIONS

The analysis allowed not only to describe the present condition of mortars and pastes but also to obtain critical information about the artificial hydraulic lime used for construction of the canal, to determine the original content of the mortars, and to define their probable consistence and the method of using them during building the canal’s brickwork of locks. The study of existing mortars in historic structures is an important aspect of building conservation. From the obtained results the following conclusive remarks can be point out:

The binder used for the Augustow Canal construction was artificial hydraulic lime. The hydraulic modulus (HM) of the binding material was 1.7. This material was calcinated from dolomitic limestone and clay. The analysis of the data given in Table 1 points to the fact that the main components of the material were probably belite ($2CaO \cdot 2SiO_2$) and gehlenite ($2CaO \cdot 2SiO_2 \cdot Al_2O_3$) although a considerable amount of uncombined lime (10%) and MgO (above 9%) also occurred, as well as smaller amounts of calcium aluminate and calcium ferrite. Probably, the hydraulic lime used had characteristic of non-shrinking or expanding material.

The pastes, which are ingredients of mortars, tested after 180 years of exploitation, differ significantly in microstructure and phase compositions from modern binder pastes. The microstructure of pastes is compact and homogenous, without well-formed crystallites. The main component of the paste is fine calcium carbonate (calcite) obtained in reaction of carbon dioxide with hydrated paste. Other compounds identified in the mortars are scawtite ($Ca_7[(Si_6O_{18})(CO_3)] \cdot 2H_2O$) and nesquehonite ($MgCO_3 \cdot 2H_2O$) as well as calcium hydrosilicates (C-S-H) containing substantial amounts of aluminum and magnesium ions. The presence of calcium hydroxide was not observed.

The subject of present study were mortars cementing the boulders in the interior of Kurzyniec Lock wall, between 1.0 and 4.0 meter from wall face. The mortar binding the stones of the brickwork was a mixture of hydraulic cementitious material and fine quartz-sand with weight ratio not exceeding 1:1. At present, the mortars are characterized by relatively low strength. The mortar was placed into shafts in the walls as a suspension, basically for sealing purposes. The studied mortars are generally in good technical condition, with no signs of chemical corrosion except advanced carbonation.

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